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# Atmospheric peroxyacetyl nitrate (PAN): a global budget and source attribution

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## Abstract

Peroxyacetyl nitrate (PAN) formed in the atmospheric oxidation of non-methane volatile organic compounds (NMVOCs), is the principal tropospheric reservoir for nitrogen oxide radicals ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ). PAN enables the transport and release of  $\text{NO}_x$  to the remote troposphere with major implications for the global distributions of ozone and OH, the main tropospheric oxidants. Simulation of PAN is a challenge for global models because of the dependence of PAN on vertical transport as well as complex and uncertain NMVOC sources and chemistry. Here we use an improved representation of NMVOCs in a global 3-D chemical transport model (GEOS-Chem) and show that it can simulate PAN observations from aircraft campaigns worldwide. The immediate carbonyl precursors for PAN formation include acetaldehyde (44 % of the global source), methylglyoxal (30 %), acetone (7 %), and a suite of other isoprene and terpene oxidation products (19 %). A diversity of NMVOC emissions is responsible for PAN formation globally including isoprene (37 %) and alkanes (14 %). Anthropogenic sources are dominant in the extratropical Northern Hemisphere outside the growing season. Open fires appear to play little role except at high northern latitudes in spring, although results are very sensitive to plume chemistry and plume rise. Lightning  $\text{NO}_x$  is the dominant contributor to the observed PAN maximum in the free troposphere over the South Atlantic.

## 1 Introduction

Peroxyacetyl nitrate (PAN,  $\text{CH}_3\text{COO}_2\text{NO}_2$ ) is the principal tropospheric reservoir species for nitrogen oxide radicals ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ) with important implications for the production of tropospheric ozone ( $\text{O}_3$ ) and of the hydroxyl radical OH (the main atmospheric oxidant) (Singh and Hanst, 1981). PAN is formed by oxidation of non-methane volatile organic compounds (NMVOCs) in the presence of  $\text{NO}_x$ . NMVOCs and  $\text{NO}_x$  have both natural and anthropogenic sources. Fossil fuel combustion is the principal  $\text{NO}_x$  source with additional contributions from biomass burning, lightning and

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soils (van der A et al., 2008). The organic side of PAN formation involves many stages of NMVOC oxidation. Most NMVOCs can serve as PAN precursors but the yields vary widely (Roberts, 2007).

PAN enables the long-range transport of  $\text{NO}_x$  at cold temperatures, and PAN decomposition releases  $\text{NO}_x$  in the remote troposphere where it is most efficient at producing  $\text{O}_3$  and OH (Singh and Hanst, 1981; Hudman et al., 2004; Fischer et al., 2010; Singh, 1987).  $\text{NO}_x$  abundance controls the balance of  $\text{O}_3$  production and destruction. Without PAN formation the distributions of tropospheric  $\text{NO}_x$ ,  $\text{O}_3$  and OH would be very different, with higher values in  $\text{NO}_x$  source regions and lower values in the remote troposphere (Kasibhatla et al., 1993; Moxim et al., 1996; Wang et al., 1998a). PAN chemistry can also be important for oxidant formation on a regional scale. In polluted environments, PAN formation is a sink for both  $\text{NO}_x$  and hydrogen oxide radicals ( $\text{HO}_x$ ). Observations show that  $\text{O}_3$  concentrations increase when temperature increases, and this has been in part related to PAN thermal instability (Sillman and Samson, 1995). Observations also show that the production of PAN becomes more efficient relative to  $\text{O}_3$  in highly polluted air masses (Roberts et al., 1995). Thus a comprehensive understanding of PAN is needed to understand oxidant distributions on a spectrum of scales.

A large body of PAN observations worldwide has accumulated over the years, including in particular from aircraft platforms and mountaintop sites. There have also been recent retrievals of PAN concentrations in the upper troposphere from satellites (Glatthor et al., 2007; Tereszchuk et al., 2013). Concentrations vary from pptv levels in warm remote locations such as tropical oceans to ppbv levels in polluted source regions. Despite the relatively large database of measurements compared to other photochemical indicators, simulation of PAN in global chemical transport models (CTMs) has been a difficult challenge because of the complexity of PAN chemistry. Recent model inter-comparisons show very large difference among themselves and with observations in many regions of the atmosphere (Thakur et al., 1999; Singh et al., 2007; von Kuhlmann et al., 2003; Sudo et al., 2002), but confirm the very important role for PAN in sustaining  $\text{O}_3$  production in remote air (Zhang et al., 2008; Hudman et al., 2004).

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Here we exploit a worldwide collection of PAN observations to improve the PAN simulation in the GEOS-Chem CTM, which has been used extensively in global studies of tropospheric oxidants (Bey et al., 2001; Sauvage et al., 2007; Murray et al., 2012). The earliest global models that included PAN chemistry (Kasibhatla et al., 1993; Moxim et al., 1996) relied on highly simplified NMVOC budgets. Our improvements involve new treatments of NMVOC sources and chemistry, a well-known weakness even in current CTMs (Williams et al., 2013; Ito et al., 2007). Our new simulation, which captures the major features of the existing observations, affords a new opportunity to understand the factors driving the global PAN distribution and the essential chemistry that needs to be described. A detailed analysis of how PAN shapes the global distributions of the atmospheric oxidants and nitrogen deposition will be the focus of a subsequent paper.

## 2 Model description

We use the GEOS-Chem global 3-D CTM including detailed ozone-NO<sub>x</sub>-VOC-aerosol chemistry (version 9.01.01, www.geos-chem.org) with significant modifications as described below.

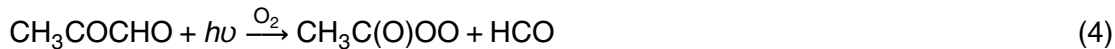
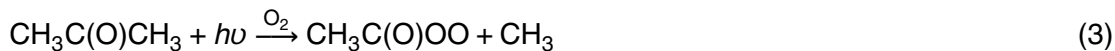
### 2.1 Chemistry

GEOS-Chem uses a chemical scheme originally described by Horowitz et al. (1998) and Bey et al. (2001), with recent updates outlined in Mao et al. (2010). Following Marais et al. (2012) we have updated the rate coefficients for the reactions of HO<sub>2</sub> with the >C<sub>2</sub> peroxy radicals to Eq. (iv) in Saunders et al. (2003). We also include nighttime reactions of organic peroxy radicals with NO<sub>3</sub> following Stone et al. (2013). We replaced the isoprene chemical mechanism with one based on Paulot et al. (2009a, b), as described by Mao et al. (2013b).

PAN is produced reversibly by reaction of the peroxyacetyl (PA) radical  $\text{CH}_3\text{C}(\text{O})\text{OO}$  with  $\text{NO}_2$ :



where  $M$  is a third body (typically  $\text{N}_2$  or  $\text{O}_2$ ). The dominant sources of  $\text{CH}_3\text{C}(\text{O})\text{OO}$  are the oxidation of acetaldehyde ( $\text{CH}_3\text{CHO}$ ) and the photolysis of acetone ( $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ ) and methylglyoxal ( $\text{CH}_3\text{COCHO}$ ):



PAN can also be produced at night via reaction of acetaldehyde with the nitrate radical. Acetaldehyde, acetone and methylglyoxal are both directly emitted (“primary” sources) and produced in the atmosphere from oxidation of primary emitted NMVOCs (“secondary” sources). These different sources will be discussed below. There are also other minor sources of the PA radical, again to be discussed below.

Higher acyl peroxy nitrates ( $\text{RC}(\text{O})\text{OONO}_2$ ) are similarly formed from the oxidation of NMVOCs, but their yields are much lower than that for PAN. We focus on PAN because observations show that it typically accounts for 75–90% of total acyl peroxy nitrates (Roberts, 2007; Roberts et al., 1998, 2002; Wolfe et al., 2007) and there are an abundance of measurements of PAN. Closure on measurements of total reactive nitrogen oxides ( $\text{NO}_y$ ) confirms the dominant role of PAN as an organic nitrate reservoir for  $\text{NO}_x$  (Roberts et al., 1995; Bertram et al., 2013).

The main sink of PAN is thermal decomposition (Reverse of Reaction 1), and the effective PAN lifetime depends on whether the released PA radical reacts with  $\text{NO}_2$  to return PAN, or with another species (mainly  $\text{NO}$  or  $\text{HO}_2$ ) leading to permanent loss. GEOS-Chem uses the equilibrium constant given in Tyndall et al. (2001) to describe

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the cycling between PAN and the PA radical, which is taken from Bridier et al. (1991) and Sehested et al. (1998). The parameters recommended by Bridier et al. (1991) are consistent with later studies of PAN decomposition by Roberts and Bertman (1992), Orlando et al. (1992), and Grosjean et al. (1994). The rate coefficient for the reaction of the PA radical with NO is also from Tyndall et al. (2001).

Primary NMVOCs in the standard GEOS-Chem mechanism that contribute to PAN formation include ethane, propane,  $>C_3$  alkanes (lumped),  $>C_2$  alkenes (lumped), isoprene, acetaldehyde, methylglyoxal, acetone, and  $>C_3$  ketones (lumped). Our extended mechanism adds several additional primary NMVOCs including ethanol, benzene, toluene and ethylbenzene (lumped), xylenes and trimethyl benzenes (lumped), and monoterpenes (lumped). The additions were partially motivated by the work of Ito et al. (2007) who extended the GEOS-Chem mechanism within the IMPACT CTM to include a broader suite of NMVOCs. One result of this exercise was a dramatic increase in PAN formation through methylglyoxal and hydroxyacetone. Liu et al. (2010) found aromatics to be a major source of PAN in urban China through the production of methylglyoxal. We calculate the associated yield of methylglyoxal using recommended values for the individual aromatic species (toluene, o-xylene, m-xylene, p-xylene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, and 1,3,5-trimethylbenzene) from Nishino et al. (2010) and the observed mean aromatic speciation for Chinese cities from Barletta et al. (2006).

We adopted the treatment of monoterpene oxidation from the RACM2 chemical mechanism (Goliff et al., 2013), lumping terpenes with one double bond (alpha-pinene, beta-pinene, sabinene and delta-3-carene) into one proxy. Unlike Ito et al. (2007), hydroxyacetone is not a product of terpene oxidation in the revised RACM2 mechanism used here.

In addition to thermal decomposition, we include minor sinks for PAN from dry deposition and photolysis. The dry deposition velocity for PAN is simulated using a standard resistance-in-series approach (Wesely, 1989) as implemented in GEOS-Chem by Wang et al. (1998b). We assume that the PAN reactivity with surfaces is as strong as

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that of O<sub>3</sub> (Shepson et al., 1992), but we explore the sensitivity to this choice. Photolysis and deposition account globally for 1.8 % and 1.2 % of the global PAN sink respectively. Photolysis of PAN is important in the upper troposphere where the lifetime against loss via photolysis is on the order of a month (Talukdar et al., 1995). We find that assuming PAN reactivity with surfaces is more similar to O<sub>3</sub> rather than NO<sub>2</sub>, decreases surface PAN concentrations over Northern Hemisphere continents by 15–20 % in spring. Reaction of PAN with both the OH radical and Cl atoms is slow, and these are both minor loss pathways, unnecessary to include in global models (Wallington et al., 1990; Talukdar et al., 1995). Uptake on ice particles in convective clouds (Marecal et al., 2010) and on organic aerosols (Roberts, 2005) are both thought to be negligible and are not included here. PAN is only sparingly soluble, but hydrolysis of the PA radical is thought to explain observed PAN loss in fog (Villalta et al., 1996; Roberts et al., 1996). We do not consider this to be a significant loss process for PAN on a global scale (Jacob, 2000).

## 2.2 Emissions

Production of PAN can be limited by either the supply of NO<sub>x</sub> or NMVOCs, as discussed below. Global fossil fuel emissions of NO<sub>x</sub> in GEOS-Chem are from the EDGAR inventory (Oliver and Berdowski, 2001) and are overwritten with regional inventories for Europe (EMEP) (Vestreng and Klein, 2002), Mexico (BRAVO) (Kuhns et al., 2003), East Asia (Zhang, Q. et al., 2009), Canada (NPRI, <http://www.ec.gc.ca/inrp-npri/>), and the United States (EPA/NEI2005, <http://www.epa.gov/ttnchie1/net/2005inventory.html>). All anthropogenic NO<sub>x</sub> emissions are scaled to 2008 based on energy statistics (van Donkelaar et al., 2008). Soil NO<sub>x</sub> emissions in GEOS-Chem are based on Yienger and Levy (1995) as implemented by Wang et al. (1998b). Lightning NO<sub>x</sub> emissions are described by Sauvage et al. (2007).

Table 1 lists the global emissions of all NMVOCs that contribute to PAN formation. We use the RETRO (REanalysis of the TROpospheric chemical composition) emission inventory (van het Bolscher et al., 2008) as global default for anthropogenic NMVOC



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emissions aside from ethane and propane. Ethane and propane emissions in RETRO were far too low compared to the GEOS-Chem inventories from Xiao et al. (2008), which are unbiased relative to observations. Emissions of both species appeared to be missing from the major natural gas production region in Russia. We used the ethane and propane emission inventories which were developed as in Xiao et al. (2008). The RETRO emission inventory is for 2000, and we scaled it to 2008 following van Donkelaar et al. (2008). RETRO includes anthropogenic emissions for benzene, xylene and toluene. Based on the observed CO to benzene ratio for TRACE-P, we increased benzene emissions over China by 25%. We then scaled xylene and toluene emissions to benzene based on measurements from 43 Chinese cities from Barletta et al. (2006). Thus RETRO emissions of toluene were increased by a factor of 4 over China to create our lumped toluene, and RETRO emissions of xylene were increased by a factor of 8 over China to create our lumped xylene species. Observations show large abundances of reactive aromatics over southern and eastern China (Ran et al., 2009; Wang et al., 2002, 2013; Zhang et al., 2007).

Terrestrial biogenic emissions of acetone, acetaldehyde, isoprene, ethanol, terpenes, and  $> C_2$  alkenes from metabolism and decay are calculated locally using the Model of Emissions of Gases and Aerosols from Nature (MEGAN v2.0) (Guenther et al., 2006). Specific other sources and sinks for acetone and acetaldehyde are described in Fischer et al. (2012) and Millet et al. (2010) respectively. The atmospheric budget of ethanol is also as described by Millet et al. (2010).

New estimates indicate that fires emit significantly more NMVOCs than previously thought (Wiedinmyer et al., 2011), and there is a large contribution from oxygenated species, many of which are unidentified (Warneke et al., 2011). Observations show rapid conversion of  $NO_x$  to PAN in fire plumes, seemingly due to the oxidation of very short-lived NMVOCs (Jacob et al., 1992). We use 2008 Global Fire Emissions Database (GFED3) monthly biomass burning emissions for  $NO_x$  and NMVOCs (van der Werf et al., 2010) with updated emission factors for NMVOCs and  $NO_x$  from extratropical forests, savannas and agricultural fires from Akagi et al. (2011). The updated  $NO_x$

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emission factor for extratropical fires is approximately a factor of three lower, and the emission factors for the NMVOCs are generally higher. Following Alvarado et al. (2010) we directly partition 40 % and 20 %  $\text{NO}_x$  emissions from fires directly to PAN and  $\text{HNO}_3$  respectively. The Alvarado et al. (2010) partitioning is based on an observation of fresh boreal fire plumes, but we apply it here to all fire types. To support PA radical formation on faster timescales we also added GFED3 emissions of several shorter lived hydrocarbons to the suite of species emitted from fires (terpenes, aromatics) along with additional oxygenated species (hydroxyacetone, methylglyoxal) as given in Table 1.

The standard version of GEOS-Chem releases all fire emissions in the boundary layer; however, previous studies have pointed out that a significant fraction of biomass burning emissions can be injected to the free troposphere because of buoyancy (Turquety et al., 2007; Val Martin et al., 2010). This is especially important for PAN because lower temperatures above the boundary layer enhance its stability. Val Martin et al. (2010) showed that a substantial fraction of plumes from North American fires are injected into the free troposphere. Smoke plumes over the boreal region reached the highest altitudes. Analysis of smoke clouds, which are a later stage of plume evolution, indicated that  $\sim 35\%$  were above the boundary layer. Here we distribute 35 % of biomass burning emissions by mass in the 10 sigma layers (4 km) above the boundary layer, and this improves our comparison with PAN observations at high latitudes.

Kaiser et al. (2012) and Yue et al. (personal communication, 2013) find that GFED3 underestimates fire emissions by not accounting for small fires, particularly at boreal latitudes. Following their work, we increased wild fire emissions by 60 % in North Asia ( $30\text{--}75^\circ\text{N}$ ,  $60\text{--}190^\circ\text{E}$ ), 25 % in Canada and 50 % in Alaska. Increasing fire emissions over Russian and North American boreal regions improves the PAN simulation over the Arctic, particularly above the surface.

## 2.3 Model configuration

In our work GEOS-Chem is driven by NASA GEOS-5 assimilated meteorological data with  $0.5^\circ \times 0.67^\circ$  horizontal resolution, 47 levels in the vertical, and 3–6 h temporal res-

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olution. We degrade the horizontal resolution to  $2^\circ \times 2.5^\circ$  for input into our GEOS-Chem simulation. We use a 1 yr simulation for 2008, preceded by a 1 yr spin-up to remove the effect of initial conditions. We also present a number of sensitivity simulations conducted at  $4^\circ \times 5^\circ$  horizontal resolution, which yields results very similar to the  $2^\circ \times 2.5^\circ$  resolution. The largest differences in the two resolutions occur over regions of biomass burning. Over these locations, the finer horizontal resolution produces 10–20 % more PAN.

Throughout the paper we present results using 2008 GEOS-5 assimilated meteorology. However we have compared results using both GEOS-4 and GEOS-5 for 2006, the last year of overlap for these two meteorological datasets. The lifetime of PAN doubles for every 4 K decrease in temperature. PAN is also sensitive to biogenic emissions, lightning  $\text{NO}_x$  emissions and vertical transport (Labrador et al., 2005), parameters that also depend on the underlying meteorological field. We found that differences in the monthly mean PAN produced using different assimilated meteorological grids are substantial in some locations ( $< 100$  pptv). Higher upper-tropospheric PAN mixing ratios over the tropical Pacific in GEOS-5 appear to be driven by slower convective overturning in GEOS-5 than GEOS-4. GEOS-4 agrees better with data from PEM-Tropics B (Maloney et al., 2001). The PEM-Tropics B dataset suggests very low ( $< 50$  pptv) PAN mixing ratios in the Pacific tropical UT. Differences between the simulated and observed  $\text{O}_3$  profiles for the PEM-Tropics B regions are consistent with the view that differences in vertical motion are driving the PAN differences. There are limited opportunities to chemically constrain convective overturning in data assimilation models. However, existing analyses suggest substantial differences between overturning rates derived from in situ measurements and those in GEOS-4 (Bertram et al., 2007). Mitrovski et al. (2012) assessed the impact of convection on  $\text{O}_3$  in GEOS-Chem and found tropical upper tropospheric  $\text{O}_3$  biases driven by the parameterized vertical transport in both GEOS-4 and GEOS-5.

### 3 Global PAN distribution

We used a large database of recent PAN observations from surface sites and airborne campaigns to evaluate the model, and these are presented in Table 2. For comparison to the model, we averaged the aircraft observations over the coherent regions in Fig. 1.

The measurements either relied on gas chromatography with electron capture detector (GC-ECD) (Flocke et al., 2005) or thermal decomposition chemical ionization mass spectrometry (TD-CIMS) (Zheng et al., 2011).

Figures 2 and 3 compare the observed global distribution of PAN to that simulated by GEOS-Chem. Mean observations from the studies compiled in Table 2 are shown as filled circles. Model fields are background contours. Full vertical profiles (median and mean) for the aircraft campaigns and seasonal cycles for several European mountain top datasets are in the Supplement. We compare model output from 2008 to observations collected over many years. Interannual variability in the model is smaller than other sources of error. There are relatively few in situ observations that can be used to assess interannual variability in PAN (Bottenheim et al., 1994). Observations at Mount Bachelor (Oregon, USA) indicate interannual variability of 20 % during the spring maximum (Fischer et al., 2011). Recent trends in PAN in many regions of the atmosphere are also hard to assess given a paucity of consistent data (Parrish et al., 2004). As shown later PAN is highly sensitive to  $\text{NO}_x$  and NMVOC emissions, both of which have changed considerably in some regions (Pollack et al., 2013).

Figure 2 indicates that spring and summer Northern Hemisphere average PAN abundances below 6 km are comparable over polluted continental regions. The Northern Hemisphere springtime maximum, previously attributed to photochemical production at a time when PAN has a long thermal lifetime (Penkett and Brice, 1986; Brice et al., 1988), is primarily a feature of remote air. Long term PAN measurements from the Hohenpeissenberg and Schauinsland European mountaintop observatories, both primarily within the atmospheric boundary layer, show either spring or summer maxima depending on the year (Supplement, Fig. 2). Pandey Deolal et al. (2013) found that the

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PAN spring maximum at the Jungfrauoch is mainly attributable to airmasses advected from the polluted European boundary layer, and PAN formation in the free troposphere does not play a dominant role. Both the model and surface observations indicate that the springtime maximum is pronounced over the Arctic, and this has previously been attributed to transport of northern mid-latitudes pollution (Moxim et al., 1996). We find that springtime fires in Russia and China also contribute to this feature, and this is discussed later in the context of our sensitivity simulations.

Successful simulation of PAN in Asian outflow is contingent on the inclusion of emissions of aromatic species. These account for 30 % of the PAN in that region in the model. Even with the addition of aromatics, the model is biased low for this region. This could suggest missing NMVOC emissions in China, as suggested by Fu et al. (2007) or unrealistically low PA radical yields from aromatics in the chemical scheme. The model largely reproduces the average vertical profiles observed during TRACE-P (see vertical profiles in the Supplement, Fig. 1, Panel 1), but these were collected in 2001 and the model output is for 2008. Chinese  $\text{NO}_x$  and NMVOCs emissions have increased by more than 55 % and 29 % over this period respectively (Zhang, Q. et al., 2007, 2009).

PAN is also sensitive to the parameterization of the uptake of the hydroperoxyl radical ( $\text{HO}_2$ ) by aerosols. Recent work (Mao et al., 2013a) suggests that the reactive uptake of  $\text{HO}_2$  is a much more efficient sink of  $\text{HO}_x$  than previously thought (Thornton et al., 2008) and implemented in the version of GEOS-Chem used here. We tested the impact of more efficient uptake of  $\text{HO}_2$  by aerosols on PAN by setting the reactive uptake coefficient of  $\text{HO}_2$  to 1 and eliminating conversion of  $\text{HO}_2$  to  $\text{H}_2\text{O}_2$  on aerosols. We found that the faster uptake of  $\text{HO}_2$  drastically reduced (50 %) springtime PAN over East Asia. The faster uptake produces springtime PAN outflow in the model that is inconsistent with observations in that region, and would imply a large missing source of PAN.

Though the differences are smaller, PAN observations from European mountain top sites also suggest missing PAN sources there. These PAN observations have not been used to justify emissions changes as observations from both Zugspitze (2658 m) and

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Jungfrauoch (3580 m) reflect terrain-induced injections of PAN rich boundary layer air (Zanis et al., 2003, 2007; Zellweger et al., 2000; Carpenter et al., 2000; Pandey Deolal et al., 2013), and this transport scale is not captured in the model. However, Fig. 3 indicates that the observations are also higher than the model output below the altitude  
5 of the measurements.

In Northern Hemisphere summer, both the model and observations show a strong contrast between high concentrations over source continents and adjacent oceans (Fig. 3), reflecting the short lifetime of PAN against thermal decomposition. PAN concentrations in the model are generally higher aloft, consistent with INTEX-A aircraft  
10 observations over the eastern US (90° W–45° W, Panel 3, Fig. 3) and measurements from the Azores (Val Martin et al., 2008), reflecting the longer PAN lifetime. As we see in Supplement, Fig. 1, Panels 26 and 27, the INTEX-A observations indicate that PAN mixing ratios begin to decrease with altitude above 8 km over the northeastern US and the western Atlantic, but not over the southeastern US where lightning and convection support PAN production aloft (Hudman et al., 2007).  
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The lowest three panels of Fig. 3 show that outside of winter months, there is a reservoir of 200–400 pptv PAN between 5–8 km over northern mid-latitudes. A similar PAN reservoir aloft has also been observed over the Arctic during aircraft campaigns in spring and summer (Singh et al., 1994). PAN can be 80–90 % of total NO<sub>y</sub> in the cold  
20 arctic atmosphere (Atlas et al., 2003; Jaffe et al., 1997; Bottenheim et al., 1986). Liang et al. (2011) note that the 2008 ARCTAS PAN observations are not notably different from either the 1988 ABLE or 2000 TOPSE observations, despite dramatic changes to NO<sub>x</sub> emissions in the major anthropogenic source regions. In the upper troposphere, Northern Hemisphere PAN mixing ratios peak in summer, with contributions from anthropogenic sources, biomass burning and lightning. This summertime upper tropospheric maximum is consistent with MIPAS retrievals for 300–150 hPa which indicate the highest Northern Hemisphere PAN concentrations in August and the lowest PAN  
25 from October to January (Moore and Remedios, 2010).

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The Polarstern Cruise data from Germany to South Africa in summer reveals a sharp meridional gradient with mixing ratios dropping below the detection limit (25 pptv) outside northern mid-latitudes (Fig. 2) (Jacobi et al., 1999). The meridional gradient is much less defined in the free troposphere, reflecting biogenic and fire contributions in the southern tropics with efficient convective lofting (Fig. 2).

We see from Fig. 2 that the Southern Hemisphere features a spring PAN maximum in the upper troposphere, similar to the remote northern extra-tropics. Moore and Remedios (2010) observed a spring PAN maximum in the upper troposphere at 0–35° S from MIPAS retrievals and attributed it to seasonal biomass burning over Central Africa. Moxim et al. (1999) also simulated the Southern Hemisphere springtime free tropospheric PAN maximum, but suggested that it is driven by convective transport rapidly mixing PAN upward from continental surface production regions. As discussed below, our model suggests that much of the PAN in the austral free troposphere is due to continental convective injection of biogenic NMVOCs together with the lightning NO<sub>x</sub> source.

#### 4 Contributions of different NMVOCs to PAN formation

PAN depends on NMVOCs and NO<sub>x</sub> in nonlinear ways. To diagnose this dependence and identify the most critical precursor, we conducted two sensitivity studies where NO<sub>x</sub> and NMVOC emissions were separately reduced by 20 % across all sectors. The results are presented in Fig. 4. We see that PAN concentration depends in general more strongly on NMVOC than NO<sub>x</sub> emissions. Exceptions are fire-dominated regions at northern high latitudes, reflecting the very low NO<sub>x</sub>/NMVOCs emission ratio from fires. This result is also partially an artifact of partitioning 40 % of GFED fire NO<sub>x</sub> emissions directly to PAN. A remarkable result is that PAN responds supra-linearly to NMVOC emissions in many locations, with the strongest effect over the North Pacific in spring and over the Arctic in summer. In both of these regions PAN is a principal source of NO<sub>x</sub> (Singh et al., 1992; Zhang et al., 2008), so that reducing PAN causes decreases

in O<sub>3</sub>, in turn decreasing the [NO<sub>2</sub>]/[NO] ratio and thus reducing the effective lifetime of PAN. This chemical feedback amplifies the sensitivity of PAN to NMVOC emission changes. Another chemical feedback in source regions is that reducing NMVOC emissions increases the concentration of OH and hence the conversion of NO<sub>x</sub> to nitric acid.

In order to understand the contributions of different NMVOC precursors to PAN formation, we conducted 14 sensitivity simulations where the emissions of each precursor in the leftmost column of Table 1 were turned off individually. The change in the total burden of PAN was compared to a standard simulation with all emissions switched on. In the case of isoprene where the effect is large, we reduced emissions by 20 % (and multiplied the change by 5) in order to minimize non-linear effects. Figure 5 presents a schematic of the relative contributions of individual NMVOCs to global PAN formation through the major carbonyl species (acetaldehyde, acetone, methylglyoxal) serving as precursors of PAN (Reactions R2–R4). The absolute contributions are in Table 1. Anthropogenic, biogenic and biomass burning emissions make significant contributions to all three of the most important immediate PAN precursors (acetaldehyde, acetone, and methylglyoxal). We track PA radical formation via four different chemical pathways, from acetaldehyde, acetone, methylglyoxal and via all other intermediate species. The bottom pie chart in Fig. 5 summarizes the relative importance of these four pathways for global annual total PA radical production.

Figure 6 summarizes the geographical distribution of annual total PA radical production for the lower, mid- and upper troposphere. PA production is strongest in NMVOC source regions, propagating to the free troposphere in the tropics through deep convection. The patterns in Fig. 6 reflect the dominant sources and lifetime for each PA radical precursor: mean lifetimes 1–2 h for methylglyoxal, 0.8 days for acetaldehyde and 14 days for acetone. The bottom row of Fig. 6 shows total PA radical production from other pathways, mainly via isoprene and monoterpene oxidation intermediates including methylvinyl ketone and methacrolein. These latter species contribute to PA rad-

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ical formation predominantly via photolysis. We traced PA radical formation via these species together with all other intermediates.

Figures 5 and 6 reveal that acetaldehyde is the most important PA radical precursor globally, responsible for ~ 40 % of total PA radical production at all altitudes. Photochemical production is the dominant source of acetaldehyde, with large contributions from both biogenic and anthropogenic primary emissions (Fig. 5). There is also PA production from acetaldehyde in the marine boundary layer, partially reflecting the ocean acetaldehyde source (Millet et al., 2010). The alkanes, > C<sub>2</sub> alkenes and ethanol all have high molar yields for acetaldehyde (Table 1). Though most originate over continents, the lifetimes of the primary precursors of acetaldehyde range from hours (isoprene) to months (ethane). Thus there is significant production of the PA radical from acetaldehyde at all altitudes over both continental regions and the downwind oceans (Millet et al., 2010).

Based on global simulations with and without acetone, Singh et al. (1995) estimated that up to 50 % of observed PAN in the mid-upper troposphere could be formed from acetone. However, they assumed a photolysis rate for acetone now known to be too high. Using a similar approach and the acetone budget from Fischer et al. (2012), we find that that the contribution of acetone to PAN is 25 % in the upper troposphere over the Northern Hemisphere during summer and less under other conditions. Acetone is the most important PA precursor only in the most remote regions of the upper troposphere.

Isoprene and monoterpenes are also important precursors for PAN formation through methylglyoxal and other intermediates. Due to relatively short lifetimes, their role is largest in continental boundary layers (Fig. 6). von Kuhlmann et al. (2004) showed that PAN formation in models is highly sensitive to the treatment of isoprene chemistry, and there have been a number of more recent advances regarding the oxidation chemistry of isoprene (Lelieveld et al., 2008; Paulot et al., 2009b; Peeters et al., 2009; Mao et al., 2012). There are also ongoing efforts to determine appropriate yields for methylglyoxal and other important intermediates under the high NO<sub>x</sub> conditions most relevant for PAN

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formation (Galloway et al., 2011). Implementation of the Paulot et al. (2009a, b) oxidation scheme in GEOS-Chem improves the simulation of summertime observations over the southeastern US (Mao et al., 2013b). It also substantially increases surface PAN mixing ratios over the Amazon and Central Africa, where there is very little observational data (Angelo, 2012). In these regions surface PAN increases by 100–300 pptv with the Paulot et al. (2009a, b) scheme, but the impact is more modest above the boundary layer, generally less than 50 pptv. In the model, most of the free tropospheric PAN in convective regions is produced above the boundary layer.

## 5 Contributions from different source types to PAN formation

Figure 7 presents the sensitivity of PAN concentrations to different emission types, as diagnosed by the relative decrease in a sensitivity simulation with that emission type shut off. Contributions do not add up to 100 % because of non-linearity.

During Northern Hemisphere spring, shutting off anthropogenic emissions decreases the integrated PAN burden by  $\sim 50\%$ . Alkanes are the most important class of anthropogenic NMVOC precursors for PAN in northern mid-latitudes. Their role is more important in spring when NMVOC emissions from the biosphere are smaller. In spring, the time of the surface PAN maximum, biogenic and anthropogenic NMVOCs species each support  $\sim 50\%$  of the PAN burden.

Though most biomass burning occurs primarily in the tropics, the effect of fires on PAN appears to be largest at northern latitudes. Shutting off emissions from springtime fires located in Russia and China decreases the hemispheric burden by  $\sim 25\%$ , but the decrease in PAN mixing ratios is 30–40 % at high latitudes. These springtime fires, which exhibit strong variability in magnitude and location, contribute to the observed spring PAN maximum. Russian fires likely accentuated this feature in April 2008, an unusually strong fire season (Vivchar, 2010; Warneke et al., 2009, 2010). PAN in fire plumes from the Russian Federation was shown to support efficient  $O_3$  production over the northeast Pacific during April 2008 (Fischer et al., 2010). Enhancements in  $O_3$  of

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up to 20 ppbv were observed during this time from Alaska to California (Oltmans et al., 2010). Spring 2008 was an extreme burning year, but Macdonald et al. (2011) also attribute elevated monthly mean O<sub>3</sub> concentrations at Whistler Mountain, BC in fall 2002 and spring 2003 to fires in the Russian Federation.

As stated earlier, the treatment of PAN formation in fires plays an important role in determining the global impact of this PAN source. Past model studies have found that reproducing observed free tropospheric CO and O<sub>3</sub> downwind from boreal fires requires injecting a fraction of the emissions above the boundary layer (Leung et al., 2007; Turquety et al., 2007; Generoso et al., 2007; Colarco et al., 2004). Tereszchuk et al. (2013) show that PAN in the upper troposphere at high latitudes is mainly from large boreal fires in summer. Emitting a fraction of the smoke above the boundary layer is an important model update that improves the simulation of the 2–6 km PAN reservoir at high latitudes. The fraction of NO<sub>x</sub> in the springtime Russian fires that is immediately partitioned to PAN also has a large impact on springtime PAN over high latitudes because PAN has a long lifetime during this season. The combination of model updates chosen here best reproduces the evolution of the springtime PAN profile as observed during TOPSE (Wang et al., 2003). Specifically, PAN remains relatively constant (150–200 pptv) with altitude in February and March, and the 2–6 km PAN reservoir forms in April. Springtime PAN in the model is acutely sensitive to the amount of NO<sub>x</sub> that is immediately partitioned to PAN in fires. Given that O<sub>3</sub> production in the Arctic lower troposphere is sensitive to the abundance of PAN (Walker et al., 2012; Beine et al., 1997), more work is warranted to determine the best way to incorporate the chemistry that rapidly produces PAN in fires.

We find that biogenic species drive PAN production in summer and fall. From June to October, shutting off biogenic emissions decreases the Northern Hemisphere integrated PAN burden by ~ 75%. In summer, the contribution to PAN from other biogenic NMVOCs (terpenes, acetone, acetaldehyde, ethanol and higher alkenes) is ~ 50 % that of isoprene. Consistent with our analysis, Roberts et al. (2006) estimated that the iso-

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prene contribution to PAN formation is 1.6 to 4 times larger than the anthropogenic NMVOC contribution in the northeastern US in summer.

The austral spring mid-to-upper tropospheric PAN maximum (> 400 pptv) spanning the Atlantic (Fig. 2) is also apparent in MIPAS PAN retrievals (Glatthor et al., 2007; Moore and Remedios, 2010; Wiegele et al., 2012). Figure 7 shows that this feature is more sensitive to emissions of  $\text{NO}_x$  from lightning than emissions from either biomass burning or anthropogenic sources. Biomass burning takes place from July to October in the part of Africa located in the Southern Hemisphere. Singh et al. (1996a) found that PAN correlated with tracers of biomass combustion in the eastern South Atlantic in the lower and middle troposphere, but not in the upper troposphere. To explain observed  $\text{NO}_x$  at higher altitudes, they had to invoke a large contribution from lightning (Smyth et al., 1996). Our simulation reproduces the TRACE-A vertical PAN profiles for the South Atlantic (This sentence refers to Supplement, Fig. 1, Panels 43–45.) and the correlation between PAN and CO (not shown). We find that fires are responsible for approximately 30 % of the PAN over the tropical Atlantic between 2 and 4 km. Above 6 km, the contribution from fires is small. In the upper troposphere, the oxidation of biogenic NMVOCs (lifted by convection; Murphy et al., 2010; Bechara et al., 2010; Warneke et al., 2001) in the presence of lightning  $\text{NO}_x$  is a large source of PAN (Tie et al., 2001; Labrador et al., 2005). Compared to the previous version of GEOS-Chem, the sensitivity of upper tropospheric PAN to lightning is reduced by 30 %. We attribute this change to increased OH in the boundary layer through the use of the Paulot et al. (2009a, b) isoprene scheme, that reduces the amount of NMVOC injected into the free troposphere (Paulot et al., 2012). Boundary layer and upper tropospheric chemistry in the tropics are tightly coupled (Paulot et al., 2012). Hence the simulation of upper tropospheric PAN is sensitive to the representation of boundary layer chemistry, which remains very uncertain (Hewitt et al., 2010).

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## 6 Conclusions

We utilized a worldwide collection of observations to improve a global simulation of PAN in the GEOS-Chem model. This new simulation, which includes an improved representation of numerous NMVOCs and a different treatment of biomass burning emissions, affords the opportunity to understand the factors driving the PAN distribution on the global scale.

1. We find that PAN is generally more sensitive to NMVOC emissions than  $\text{NO}_x$  emissions. In many regions of the atmosphere, changes to NMVOC emissions produce a supra-linear change in PAN through feedbacks to remote  $\text{NO}_x$  and  $\text{O}_3$  budgets. A different mixture of NMVOCs supports PAN formation in each region and season. Considerable improvement of the PAN simulation for the Asian outflow region is achieved by including aromatics. Our results stress the need for global CTMs, which can yield different results for PAN (Singh et al., 2007), to include and evaluate budgets for many NMVOCs that are routinely ignored.

2. In order to reproduce the observed PAN reservoir at 3–6 km over high northern latitudes, we have changed the way emissions from fires are incorporated into the model. We increased the simulated PAN reservoir over high latitudes by (1) adding biomass burning emissions of shorter lived NMVOCs (monoterpenes, aromatics), (2) emitting a fraction of the biomass burning  $\text{NO}_x$  directly as PAN (Alvarado et al., 2010), (3) emitting a portion of the smoke above the boundary layer, (4) updating the emission factors for NMVOCs and  $\text{NO}_x$  (Akagi et al., 2011), and increasing emissions to account for undetected small fires at high latitudes (Kaiser et al., 2012). We find that PAN over the Arctic is very sensitive to fires, and particularly sensitive to the amount of  $\text{NO}_x$  that is immediately partitioned to PAN in fires and to the altitude of the emissions. Given that  $\text{O}_3$  production in the Arctic lower troposphere is very sensitive to  $\text{NO}_x$  abundance (Stroud et al., 2004; Walker et al., 2012), more work is warranted to determine the best way to incorporate the plume chemistry that rapidly produces PAN into CTMs.

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3. The principal carbonyl precursors of PAN are acetaldehyde (44 % of the global source), methylglyoxal (30 %) and acetone (7 %). Acetaldehyde is produced by a large suite of NMVOCs and also directly emitted. Methylglyoxal is mostly from isoprene. Isoprene oxidation products, other than methylglyoxal, are also significant. With updated (lower) photolysis yields, acetone is a substantially less important pathway for PAN formation than previously thought (Singh et al., 1995).

4. Isoprene accounts for 37 % of the global PAN burden. Many other NMVOC emissions contribute to the balance, with no single species contributing more than 10 % (Table 1). At Northern Hemisphere mid-latitudes, alkanes contribute to a third of PAN formation during the springtime maximum.

5. A springtime upper troposphere PAN maximum across the tropical Atlantic is the major feature of the Southern Hemisphere PAN distribution. Lightning is the most important  $\text{NO}_x$  source for PAN formation in this region of the atmosphere. A cascade of isoprene oxidation products, delivered to the upper troposphere by deep convection, provides the PA radical source. This finding is sensitive to the description of boundary layer chemistry under low  $\text{NO}_x$  conditions.

The work presented here has increased confidence in our ability to simulate the observed distribution of PAN within the GEOS-Chem CTM. In a follow-up paper we will examine the importance of PAN in affecting global tropospheric  $\text{O}_3$  and OH, and the implications for intercontinental transport of pollution, the oxidizing power of the atmosphere, and climate forcing.

**Supplementary material related to this article is available online at <http://www.atmos-chem-phys-discuss.net/13/26841/2013/acpd-13-26841-2013-supplement.pdf>.**

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**Table 1.** Global contributions of primary NMVOCs to PAN formation<sup>a</sup>.

Primary NMVOC	Lifetime (days) <sup>b</sup>	Sources, TgCa <sup>-1</sup>			Molar yields of immediate PAN precursors			PAN Contribution (%) <sup>p</sup>
		Fuel and Industry <sup>c</sup>	Open Fires	Biogenic	Acetaldehyde <sup>d</sup>	Acetone	Methylglyoxal	
Isoprene	0.10	–	–	42 <sup>7</sup>	0.019	–	0.32	37 <sup>f</sup>
Terpenes	0.46	–	1.3	65 <sup>g</sup>	0.025 <sup>h</sup>	0.017 <sup>h</sup>	0.050 <sup>h</sup>	9
> C <sub>3</sub> alkanes <sup>i</sup>	5	24	0.67	–	1.07	0.30	–	9
Acetone	14	0.45	1.7	69 <sup>j</sup>	–	1	0.14 <sup>k</sup>	9
Acetaldehyde	0.8	1.1	1.6	44 <sup>l</sup>	1	–	–	8
Ethane	60	8.5	1.9	–	0.78	–	–	6
Propane	14	17	0.77	–	0.30	0.75	–	5
> C <sub>2</sub> alkenes <sup>l</sup>	0.38	3.9	2.7	12	0.85	–	–	4
Ethanol	2.8	1.0	0.04	12	0.95	–	–	4
Methylglyoxal	0.067	–	2.6	–	0.35 <sup>m</sup>	–	1	< 1
Xylenes <sup>n</sup>	0.58	11	0.73	–	–	–	0.21	< 1
Toluene <sup>o</sup>	2.2	14	0.26	–	–	–	0.46	< 1
Hydroxyacetone	2.1	–	0.65	–	–	–	0.82 <sup>p</sup>	< 1
Methylethylketone	4.3	0.34	0.99	–	0.002	–	–	< 1

<sup>a</sup> Global primary emitted NMVOC sources of PAN and their estimated yields for the three most important immediate carbonyl PAN precursors: acetaldehyde, acetone, and methylglyoxal. Details of sources can be found in Sect. 2.2.

<sup>b</sup> Global annual mean tropospheric lifetime. Lifetimes were calculated from global annual average burdens and loss rates.

<sup>c</sup> Includes biofuel use.

<sup>d</sup> Assumes 1 ppbv NO<sub>x</sub> from Millet et al. (2010) unless otherwise noted.

<sup>e</sup> The contribution to the global annual PAN burden from individual NMVOCs is calculated Contribution to global annual mean PAN calculated by simulations with corresponding emissions turned off. To avoid large nonlinear effect in the case of isoprene, emissions were reduced by 20 %, and the difference between that simulation and the standard simulation was multiplied by 5.

<sup>f</sup> PAN production from isoprene involves additional precursors other than acetaldehyde and methylglyoxal including methyl vinyl ketone, methacrolein and other short lived oxidation intermediates.

<sup>g</sup> 34 TgC as  $\alpha$ -pinene, 16 TgC as  $\beta$ -pinene, 7.3 TgC as sabinene, and 6.1 TgC as  $\delta$ -3-carene.

<sup>h</sup> Calculated using difference between global simulations with and without terpene chemistry.

<sup>i</sup> > C<sub>3</sub> alkanes are emitted as a mixed butane-pentane lumped species on a carbon-weighted basis (Lurmann et al., 1986).

<sup>j</sup> Includes primary terrestrial and ocean sources.

<sup>k</sup> From Fu et al. (2008).

<sup>l</sup> > C<sub>2</sub> alkenes are emitted as propene on a carbon-weighted basis.

<sup>m</sup> Photolysis of methylglyoxal produces acetaldehyde in GEOS-Chem. Calculation assumes each of two absorption bands is responsible for half of the photolysis.

<sup>n</sup> > Lumped species including, o-xylene, m-xylene, p-xylene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene and 1,2,5-trimethylbenzene with the reactivity of m-xylene.

<sup>o</sup> Also including ethylbenzene with the reactivity of toluene.

<sup>p</sup> Chemical yield from photolysis and reaction with OH of hydroxyacetone is unity, but 18 % of hydroxyacetone is removed by wet deposition.

**Table 2.** Global PAN measurements used for model evaluation listed in order of map regions labeled on Fig. 2.

Aircraft missions Experiment	Timeframe	Location	Fig. 1 map regions	Reference
TRACE-P	Mar–Apr 2001	W Pacific	1,2,5,6	Talbot et al. (2003)
PEM-West B	Feb–Mar 1994	W Pacific	3	Singh et al. (1998)
PEM-West A	Sep–Oct 1991	W Pacific	4,7,8	Singh et al. (1996b)
PEM-Tropics B	Mar–Apr 1999	Tropical Pacific	9–13	Maloney et al. (2001)
PEM-Tropics A	Aug–Oct 1996	S Pacific	14–17	Talbot et al. (2000)
INTEX-B	Mar–May 2006	E Pacific	18–20	Singh et al. (2009)
PHOBEA	Mar–Apr 1999	E Pacific	21	Kotchenruther et al. (2001)
ITCT-2K2	Apr–May 2002	E Pacific	22	Roberts et al. (2004)
MILAGRO	Mar–May 2006	Mexico	23	Singh et al. (2009)
CITE-2	Aug–Sep 1986	W US	24–25	Singh et al. (1990a)
INTEX-A	Jul–Aug 2004	Eastern N America	26–28	Singh et al. (2006)
SONEX	Oct–Nov 1997	N Atlantic	29, 42	Talbot et al. (1999)
ABLE-2B	Apr–May 1987	Amazon	30	Singh et al. (1990b)
TRACE-A	Sep–Oct 1992	S Atlantic	31–32, 43–45	Singh et al. (1996a)
ABLE-3A	Jul–Aug 1988	Alaska	33	Singh et al. (1992)
ABLE-3B	July–Aug 1990	E Canada	34–35	Singh et al. (1994)
ARCTAS	Apr–Jul 2008	N American Arctic	36–38	Alvarado et al. (2010)
ARCPAC	Mar–Apr 2008	Alaska	39	Slusher et al. (2004)
POLARCAT	Jul 2008	Greenland	40	Roiger et al. (2011)
TOPSE	Feb–Mar 2000	N American Arctic	41	Atlas et al. (2003)
AMMA	Aug 2006	West Africa	46	Stewart et al. (2008)

Surface measurements				
Site name	Timeframe	Location	Elevation	Reference
Mount Bachelor	Mar–May 2008–2010	44° N, 122° W	2.7 km	Fischer et al. (2010)
Jungfraujoch	1997–1998, 2005–2006, 2008	47° N, 9° E	3.6 km	Balzani Loov et al. (2008), Whalley et al. (2004), Zellweger et al. (2000), Pandey Deolal et al. (2013)
Hohenpeissenberg	2003–2008	48° N, 1° E	985 m	http://ds.data.jma.go.jp/gmd/wdcgg/
Schauinsland	1995–2010	48° N, 8° E	1.2 km	http://ds.data.jma.go.jp/gmd/wdcgg/
Zugspitze	2004–2008	47° N, 11° E	2.7 km	http://ds.data.jma.go.jp/gmd/wdcgg/
Waiguan	Jul–Aug 2006	36° N, 101° E	3.8 km	Xue et al. (2011)
Bush Estate	1994–1998	56° N, 3° W	200 m	McFayden et al. (2005)
Rishiri	1999	45° N, 141° E	35 m	Tanimoto et al. (2002)
Poker Flat	Mar–May 1993, 1995	65° N, 148° W	470 m	Beine et al. (1996)
Alert	Jan–Apr 1992, 1998, 2000	82° N, 62° W	200 m	Dassau et al. (2004), Worthly et al. (1994)
Zeppelin	1994–1998	78° N, 16° W	474 m	Beine et al. (1997), Beine and Krognes (2000)
Polarstern Cruise	May–Jun 1998	52° N–17° S, 7° E–19° W	Sea level	Jacobi et al. (1999)
Thompson Farm	2005–2007	43° N, 71° W	25 m	Robert Talbot, Ryan Chartier, unpublished data
Summit Greenland	Jun–Jul 1998, Jan 1999	47° N, 9° E	3.2 km	Ford et al. (2002)
Pico Mountain	Jul–Sep 2008, Mar–Jul 2009	38° N, 28° W	2.2 km	Katja Dzepina, Jim Roberts, unpublished data

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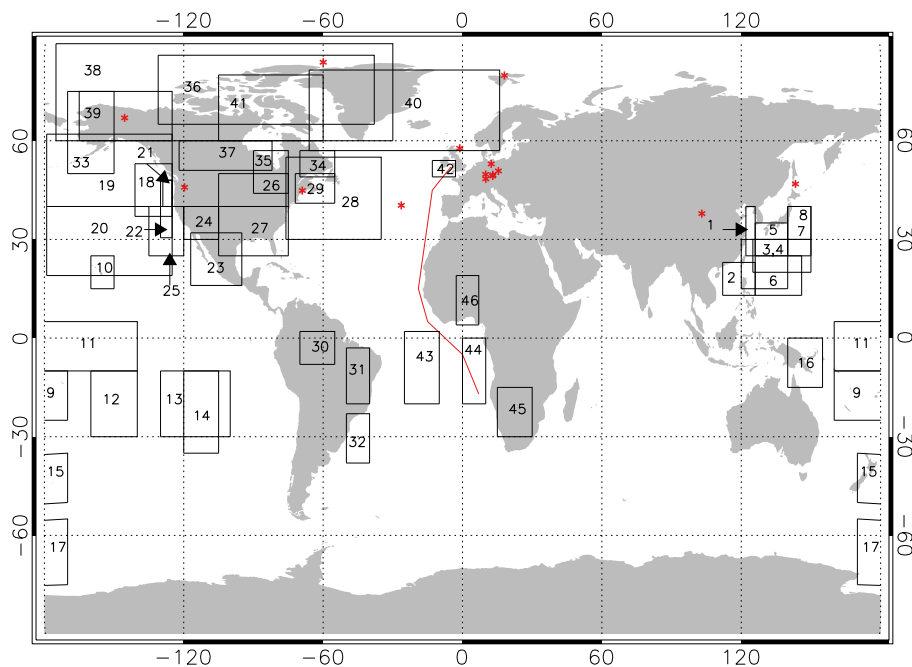
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**Fig. 1.** Locations of PAN observations used in our analysis (Table 2): surface sites (red \*); aircraft missions (black boxes) with region numbers indicated; and one cruise (red line).

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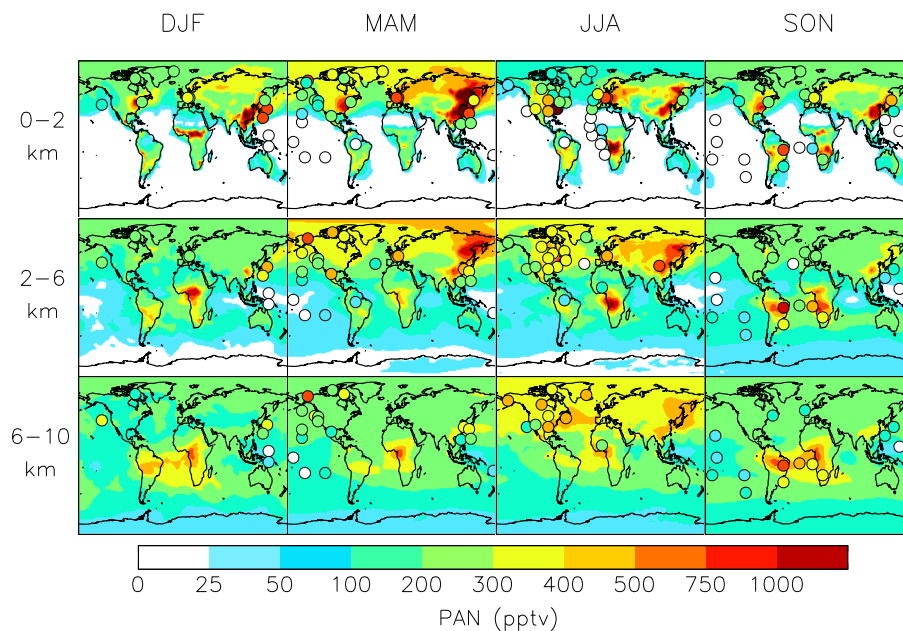
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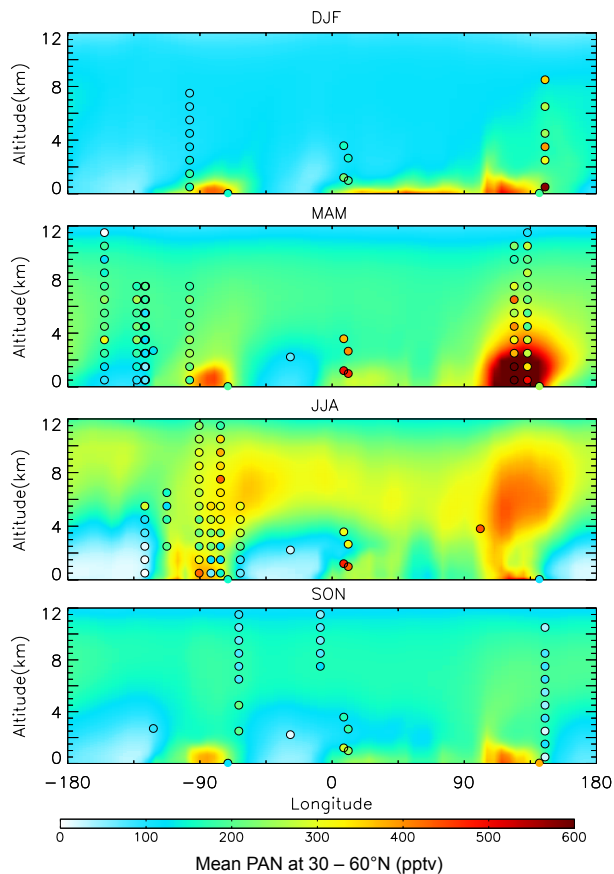


**Fig. 2.** Global mean distribution of PAN for different seasons and altitude ranges. Model results for 2008 (background solid contours) are compared to observations from Table 2 for all years (filled circles). Aircraft observations are averaged vertically and horizontally over the coherent regions of Fig. 2.

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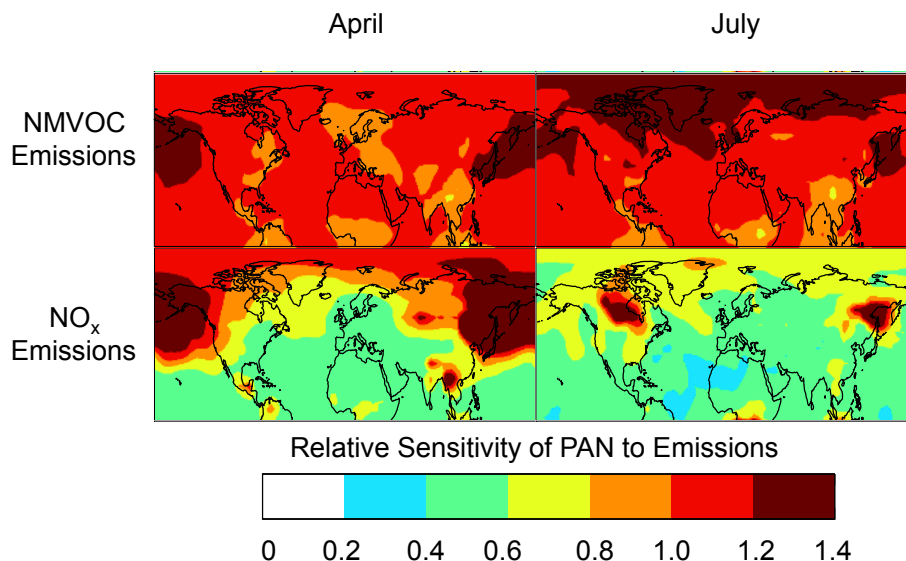


**Fig. 3.** Longitudinal cross-section of seasonal mean PAN concentrations at northern mid-latitudes ( $30\text{--}60^\circ\text{N}$ ) as a function of altitude. Model results for 2008 (background solid contours) are compared to observations from many years in Table 2 (filled circles). Circles are placed at the mean longitude of the coherent regions (Fig. 2) that fall between ( $30\text{--}60^\circ\text{N}$ ).

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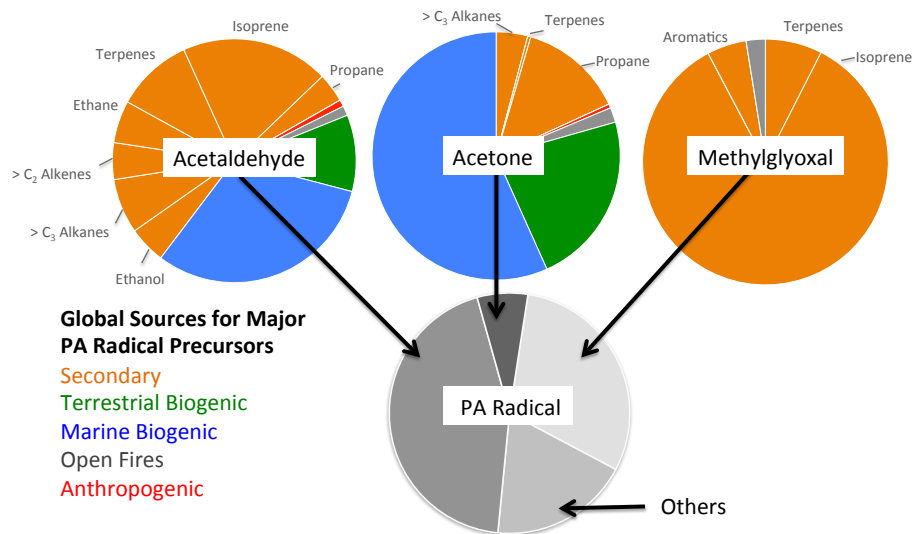
**Fig. 4.** Relative sensitivity of total column PAN concentrations to emissions of NO<sub>x</sub> and NMVOCs in April and July. The sensitivity is diagnosed as  $\Delta\text{PAN}/\Delta E$ , where  $\Delta\text{PAN}$  is the change in monthly mean PAN column concentrations resulting from a 20% decrease  $\Delta E$  in global emissions of either NMVOCs (top) or NO<sub>x</sub> (bottom), including all sources and sustained year-round. Zero indicates no sensitivity, while one indicates 1 : 1 sensitivity.

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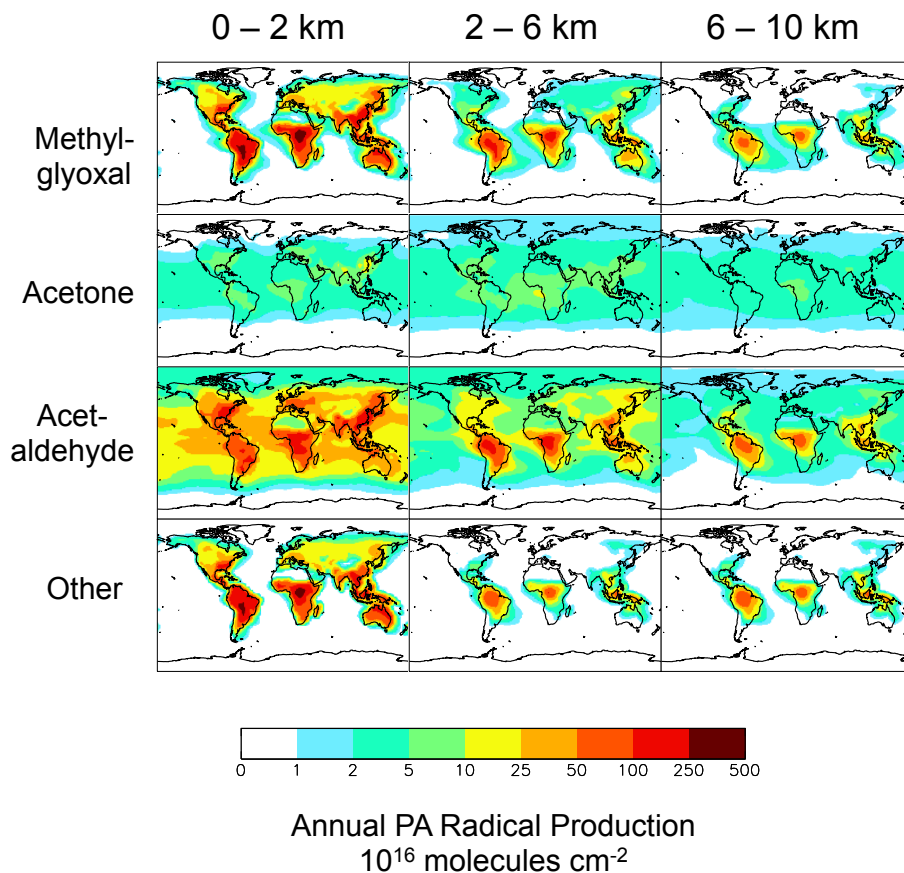


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**Fig. 5.** Global contributions of individual NMVOCs to PAN formation, expressed as the relative contributions to the major carbonyl species producing the peroxyacetyl radical (PA), and from there, the relative contributions of the carbonyl species to global PA production. Values are from Table 1. The geographical and vertical distribution of total PA radical production is given in Fig. 6.



**Fig. 6.** Annual total PA radical production for three altitude ranges contributed by the immediate precursors methylglyoxal, acetone, and acetaldehyde. The other precursors include a number of species produced in the oxidation of isoprene.

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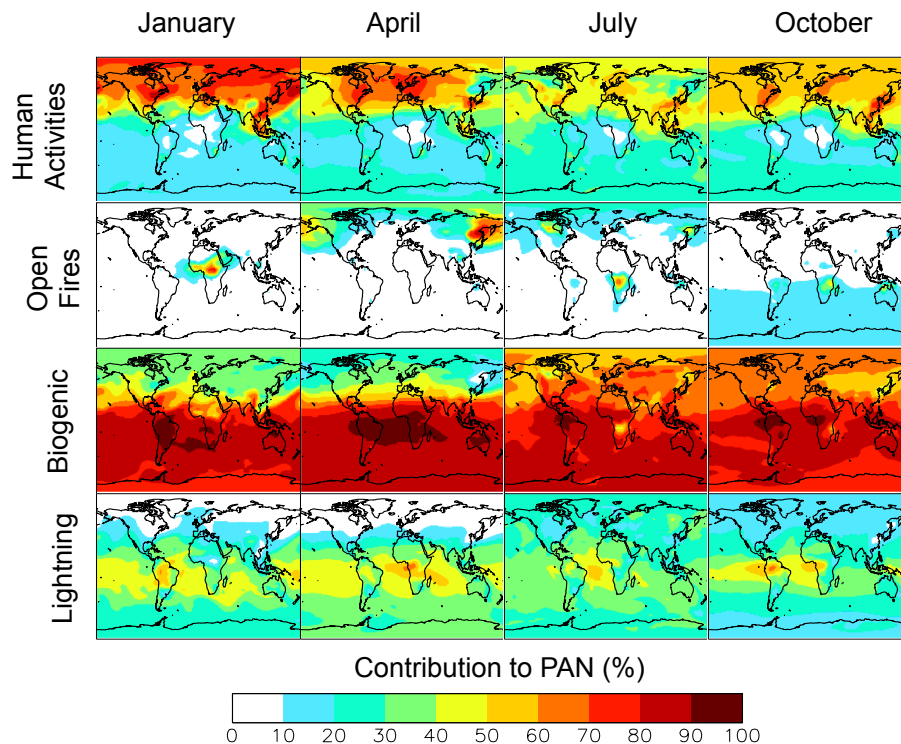
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**Fig. 7.** Sensitivity of PAN to different emission types. Results are shown as relative decreases of monthly mean total PAN columns in sensitivity simulations with individual emission types shut off. Biogenic signifies NMVOCs only.