Changes to Peroxyacyl Nitrates (PANs) over Megacities in Response to COVID-19 Tropospheric NO2 Reductions Observed by the Cross-track Infrared Sounder (CrIS)

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Abstract

The COVID-19 pandemic perturbed air pollutant emissions as cities shutdown worldwide. Peroxyacyl nitrates (PANs) are important tracers of photochemistry that are formed through the oxidation of non-methane volatile organic compounds (NMVOCs) in the presence of nitrogen oxide radicals (NOx = NO + NO2). We use satellite measurements of free tropospheric PANs from the S-NPP Cross-Track Infrared Sounder (CrIS) over eight of the world's megacities: Mexico City, Beijing, Los Angeles, Tokyo, São Paulo, Delhi, Lagos, and Karachi. We quantify the seasonal cycle of PANs over these megacities and find seasonal maxima in PANs correspond to seasonal peaks in local photochemistry. CrIS is used to explore changes in PANs in response to the COVID-19 lockdowns. Statistically significant changes to PANs occurred over two megacities: Los Angeles (PAN decreased) and Beijing (PAN increased). Our analysis suggests that large perturbations in NOx may not result in significant declines in NOx export potential of megacities.

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Key Points:

- There are pronounced seasonal cycles of PANs over each megacity that align with seasonal maximums in photochemistry.
- Observed free tropospheric mixing ratios of PANs during COVID-19 were significantly different over two out of eight surveyed megacities.
- Sensitivity of free tropospheric PANs to the abundance of precursors is seasonally dependent in some locations.

Abstract

The COVID-19 pandemic perturbed air pollutant emissions as cities shutdown worldwide. Peroxyacyl nitrates (PANs) are important tracers of photochemistry that are formed through the oxidation of non-methane volatile organic compounds (NMVOCs) in the presence of nitrogen oxide radicals (NO_x = NO + NO_2). We use satellite measurements of free tropospheric PANs from the S-NPP Cross-Track Infrared Sounder (CrIS) over eight of the world's megacities: Mexico City, Beijing, Los Angeles, Tokyo, São Paulo, Delhi, Lagos, and Karachi. We quantify the seasonal cycle of PANs over these megacities and find seasonal maxima in PANs correspond to seasonal peaks in local photochemistry. CrIS is used to explore changes in PANs in response to the COVID-19 lockdowns. Statistically significant changes to PANs occurred over two megacities: Los Angeles (PAN decreased) and Beijing (PAN increased). Our analysis suggests that large perturbations in NO_x may not result in significant declines in NO_x export potential of megacities.

Plain Language Summary

The COVID-19 pandemic led to the lockdown of urban centers worldwide, drastically perturbing the concentrations of global air pollutants. Peroxyacyl nitrates (PANs) are important photochemical pollutants formed from reactions between NO_x and volatile organic compounds (VOCs), which were substantially reduced during the pandemic. We use satellite measurements of PANs from the Suomi-National Polar-orbiting Partnership (S-NPP) Cross-Track Infrared Sounder (CrIS) in the free troposphere over and surrounding eight of the world's megacities: Mexico City, Beijing, Los Angeles, Tokyo, São Paulo, Delhi, Lagos, and Karachi. Seasonal cycles of PANs are pronounced and the seasonal maxima correspond to seasonal peaks in local photochemistry. Significant changes to PANs in response to COVID-19 occurred over two out of the eight cities: Los Angeles (PANs decreased) and Beijing (PANs increased). Our results indicate that large changes in NO_x may not result in equally significant changes to PANs and the NO_x export potential of megacities.

1 Introduction

To slow the spread of the 2019 novel coronavirus (COVID-19), urban centers across the globe partially shut down for various amounts of time (Chinazzi et al., 2020; WHO, 2020). While the timing differed for each urban region, a consequence of these bursts of reduced economic activity was a radical decrease in the emissions of many primary air pollutants. Reductions in global and regional particulate matter, nitrogen oxides (NO_x = NO + NO_2), carbon dioxide (CO_2), and other trace gasses associated with the COVID-19 pandemic have been documented (Bauwens et al., 2020; Z. Liu et al., n.d.; Miyazaki, Bowman, Sekiya, Jiang, et al., 2020; Miyazaki et al., 2021; Odekanle et al., 2022; Sharma et al., 2020; Shi & Brasseur, 2020; Venter et al., 2020; J. Zhang et al., 2022) Less is understood about changes to secondary pollutants as they respond non-linearly to changes in precursor emissions, and their production and lifetime also depend on environmental conditions (*e.g.*, Stavrakou et al., 2021). For example, both increases and decreases in surface ozone (O_3) have been documented in urban areas during the COVID-19 pandemic despite decreases in precursor emissions (*e.g.,* Le et al., 2020; Miyazaki et al., 2021; Qiu et al., 2020; Shi & Brasseur, 2020; Sicard et al., 2020).

Peroxyacyl nitrates (PANs) are important photochemically-produced species that are formed alongside O_3 in polluted environments by the oxidation of non-methane volatile organic compounds (NMVOCs) in the presence of NO_x (Fischer et al., 2014; Gaffney et al., 1989; Roberts, 2007; Singh et al., 1986; Singh & Hanst, 1981). PANs are considered to be a sensitive tracer of photochemistry (e.g., Coggon et al., 2021; Rappenglück et al., 2003). Formation and decomposition of PANs can impact the production of O_3 (e.g. Steiner et al., 2010), the production of PANs acts as an indicator of regional photochemistry (Sillman & West, 2009), and the concentration of PANs can be used to gauge effectiveness of O_3-control strategies (Gaffney et al., 1989). PANs respond to precursor emissions non-linearly and have been shown to be more sensitive to changes in NMVOCs versus changes in NO_x for many regions of the global atmosphere (Fischer et al., 2014) and in some urban regions (T. Liu et al., 2022).

The lifetime of PANs against thermal decomposition is strongly dependent on temperature, where PANs are thermally unstable in the lower troposphere (lifetime on the order of hours at 20°C), but have a lifetime >1 month at temperatures characteristic of the mid-troposphere (Honrath et al., 1996). When transported from polluted continental regions to the remote troposphere, PANs serve as the principal reservoir species for NO_x and can contribute to efficient production of downwind O_3 in NO_x limited conditions (Fischer et al., 2014; Mena-Carrasco et al., 2009). The distribution of O_3 in the remote atmosphere would be substantially different without PAN chemistry (e.g., Jiang et al., 2016). There have been major changes in NO_x and VOC emissions in urban areas in recent decades, elevating the need for continued and extended observations of photochemically-relevant species in urban regions. In situ measurements of PANs have been collected for select urban areas for select seasons (Gaffney et al., 1989; Qiu et al., 2019; G. Zhang et al., 2015a), though observations are generally sparse.

Here we present new satellite observations of PANs over eight megacities. We utilize measurements from the Suomi-National Polar-orbiting Partnership (S-NPP) Cross-Track Infrared Sounder (CrIS) and other complimentary satellite and reanalysis datasets to document the seasonal cycles of PANs over select megacities and the response of PANs to COVID-19 induced reductions of precursor concentrations in these locations.

2 Materials and Methods

2.1 CrIS Observations

We use observations of free tropospheric PANs and CO from the CrIS instrument, a nadir viewing Fourier transform spectroradiometer currently flying on the S-NPP satellite. The datasets used here were produced under the NASA Tropospheric Ozone and Precursors from Earth System Sounding (TROPESS) project (Bowman, 2021c, 2021k, 2021o, 2021a, 2021e, 2021i, 2021l, 2021p, 2021d, 2021j, 2021b, 2021f, 2021c; Shogrin, 2023). Information on the CrIS PANs retrieval algorithm and validation against aircraft observations can be found in Payne et al. (2022). The validation efforts for the CrIS PANs product suggest a single sounding uncertainty of around 0.08 ppbv that reduces with averaging to an approximate floor of 0.05 ppbv and demonstrates the ability of CrIS to capture variation in the "background" PANs over remote regions (Payne et al., 2022). The CrIS CO algorithm is described in Fu et al. (2016) and validation is presented in Worden et al. (2022). A single sounding uncertainty for CrIS CO retrievals is on the order of 6-10% (Worden et al., 2022) and this is expected to reduce with averaging. Our analysis uses the column average PANs volume mixing ratio (VMR) between 825 and 215 hPa. CrIS PANs retrievals have peak sensitivity in the free troposphere (~680 hPa) and the sensitivity decreases rapidly near the surface. At most, CrIS PANs retrievals have 1 degree of freedom for signal (DOF), meaning this product does not include information about the vertical distribution of PANs in the atmosphere. The spectral feature utilized by CrIS for retrieval of PANs is centered at 790 cm^{-1}. This infrared spectral feature appears in the spectra of all PANs at essentially the same frequency, so CrIS measurements include all PAN species (i.e., they include propionyl peroxy nitrate (PPN; $CH_3CH_2C(O)OONO_2$), methacryloyl peroxy nitrate (MPAN; $CH_2C(CH_3)C(O)OONO_2$), etc.) in addition to peroxyacetyl nitrate (PAN; $CH_3C(O)O_2NO_2$). We also use a tropospheric average of CrIS CO between 825 hPa and 215 hPa. Our analysis focuses on CrIS PANs over and around 9 megacities utilizing CrIS CO to contextualize seasonal enhancements in PANs.

PAN observations from nadir-viewing satellites include those from the Tropospheric Emission Spectrometer (TES) (Payne et al., 2014) as well as meteorological sounders namely the Infrared Atmospheric Sounding Interferometer (IASI) (Franco et al., 2018) and CrIS (Payne et al., 2022). Studies observing PAN from space thus far have focused on PAN enhancements associated with fires (Alvarado et al., 2011; Clarisse et al., 2011; Juncosa Calahorrano et al., 2021) and the global distribution of PAN and its role in the long range transport of O_3 (Fischer et al., 2018; Jiang et al., 2016; Payne et al., 2017; Zhu et al., 2015; 2017). Although TES had provided a set of special observations over select megacities (Cady-Pereira et al., 2017; Shogrin et al., 2023), the spatial and temporal coverage of this dataset is somewhat limited. Here, we utilize the more comprehensive spatial and temporal coverage of CrIS to explore the spatiotemporal distribution of PANs over and around megacities.

2.2 Ozone Monitoring Instrument (OMI) Observations

We use Level 3 NO_2 tropospheric column measurements from NASA Aura-OMI to identify months with anomalously low NO_2 columns associated with COVID in 2020. We use the Quality Assurance for Essential Climate Variables (QA4ECV) NO_2 Level 3 product described in Boersma et al. (2018) as this is the most recently updated data product. OMI NO_2 L3 monthly mean data used in this study is provided on a global 0.125° x 0.125° grid and can be found on the TEMIS database (Boersma et al., 2017b).

We use Level 3 (L3) HCHO tropospheric column measurements, also from OMI, to contextualize changes in monthly VOC concentrations in megacities during the period of anomalously low tropospheric NO_2. Space-based observations of HCHO are used as an indicator of VOC emissions (De Smedt et al., 2008; Shen et al., 2019). HCHO is also processed using the QA4ECV algorithm consistently with the NO_2 data used in this study. HCHO L3 monthly mean data is also provided on a global 0.125° x 0.125° grid and can also be found on the TEMIS database (De Smedt et al., 2017).

2.3 Chemical Reanalysis Product

We use NO_x emission reanalysis data to also place changes to PANs in the context of NO_x emission flux reductions in megacities associated with COVID-19. NO_x emissions are from an assimilation of multi-species satellite observations (O_3, CO, NO_2, HNO_3, and SO_2) in the Tropospheric Chemistry Reanalysis version 2 (TCR-2) framework (Miyazaki et al., 2020; https://doi.org/10.25966/9qgv-fe81). NO_x emissions are constrained by tropospheric column NO_2 retrievals from the QA4ECV version 1.1 Level 2 products from OMI and Global Ozone Monitoring Experiment 2 (GOME-2) (Boersma et al., 2017a, 2017b). A priori emissions are from HTAP version 2 for 2010 (Janssens-Maenhout et al., 2015), Global Fire Emissions Database (GFED) version 4 (Randerson et al., 2018), and the Global Emissions Inventory Activity (GEIA) (Graedel et al., 1993). The reanalysis fields have been evaluated against independent observations on regional and global scales (Miyazaki et al., 2020). NO_x emissions for 2020 used in our analysis are estimated using business as usual (BAU) emissions added to the estimated COVID-19 emissions anomaly described in Miyazaki et al. (2021). While the observed NO_2 concentrations are affected by meteorological concentrations, their effect is already taken into account when estimating the NO_x emissions (Miyazaki et al., 2017; 2020)

3 Results and discussion

3.1 Seasonal Cycles of PANs, CO, and HCHO in megacities

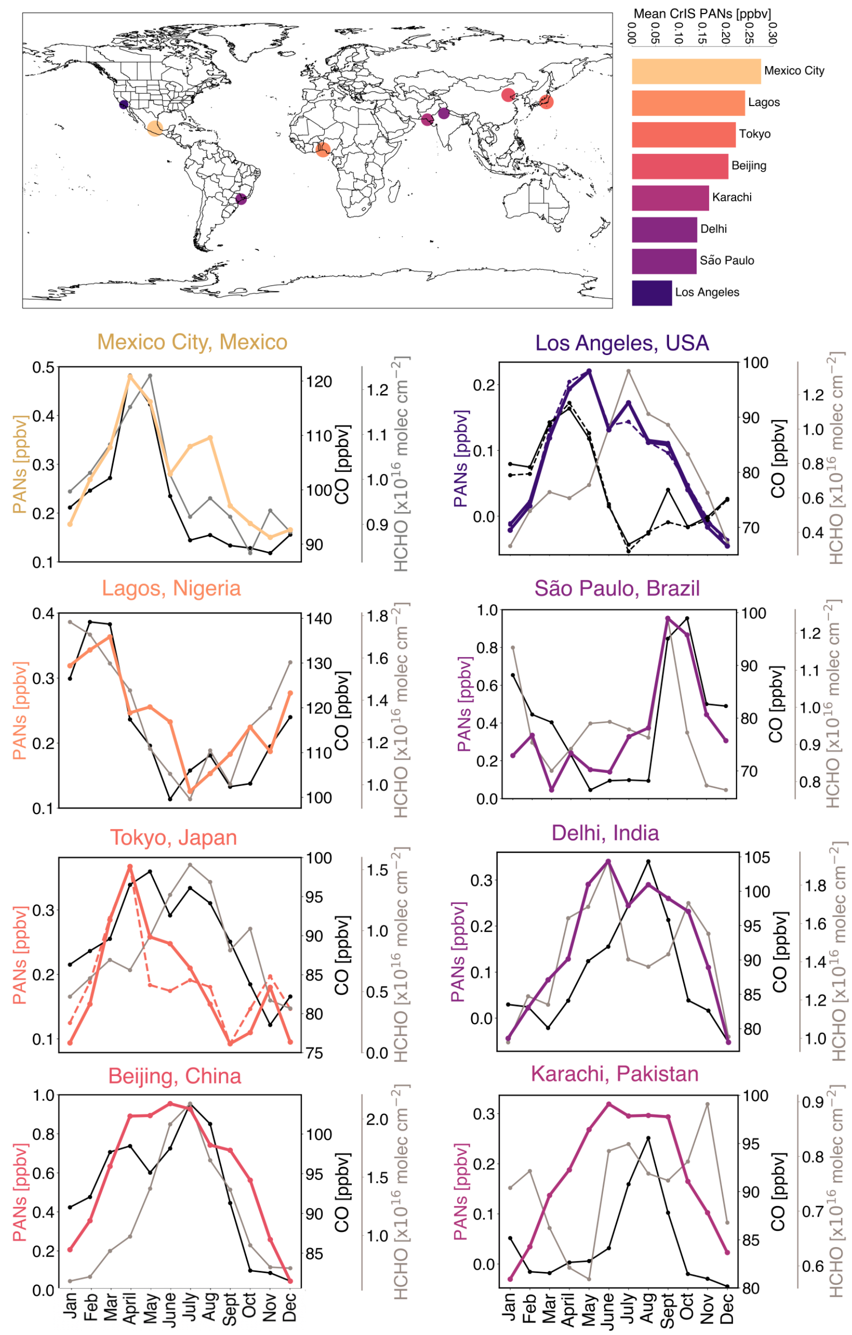

Figure 1. Top: Map shows mean detected CrIS PANs for the entire study period. The scale to the right of the map ranks the cities using the mean PANs. Dot sizing is indicative of abundance of mean PANs. Seasonal cycles of CrIS PANs [ppbv] (color denoted in color bar, dashed denotes median values), CrIS tropospheric CO [ppbv] (dark grey), and OMI HCHO tropospheric column average [x10^{16} molecules cm^{-2}]

(lighter grey) for eight megacities. Note: scales vary for each plot. Monthly means include data from January 2016 to May 2021.

Figure 1 displays the mean seasonal cycles for CrIS PANs, CrIS CO, and OMI HCHO for eight different global megacities from 2016-2021. Figure 1 helps identify periods in the annual cycle with production of PANs and values of PANs above a threshold where CrIS is able to provide quantitative information. For most cities, NO_2 changes from COVID-19 coincide with periods where PANs are above the CrIS detection limit (Section 2.1) and conditions support photochemical production.

All but two selected megacities experience a springtime maxima in PANs. The seasonal springtime maximum in PANs is attributed to an increase in photochemical activity at a time when PANs have a relatively long lifetime against thermal decomposition (Brice et al., 1988; Fischer et al., 2014; Penkett & Brice, 1986). Seasonal maxima occur in March, April, and/or May for northern hemisphere megacities (Mexico City, Los Angeles (LA), Tokyo, Delhi, and Lagos), and in September for São Paulo (23.56°S), the beginning of austral spring. Over Lagos (6.52°N) PANs begin increasing towards the end of the calendar year and maximize in March or April. In addition to a springtime maxima, PANs over Beijing (39.92°N) and Karachi (24.86°N) remain elevated through the summer (April-September). Though it has a springtime maxima, Delhi (28.71°N) has a comparably wide seasonal cycle in PANs. Mexico City, LA, and Tokyo also show an additional period of elevated PANs later in the year.

PANs over each megacity reflect a combination of sources and meteorological conditions, but the extent of the published literature on air pollutants in each megacity differs widely. Here we focus our discussion on LA, Beijing, and to a more limited extent, Tokyo, Delhi, and Lagos.

There is a longstanding effort to attribute and control O_3 and other photochemical pollutants in LA (Langford et al., 2010; Nussbaumer & Cohen, 2020; Pollack et al., 2013; Warneke et al., 2013). CrIS data indicate that the seasonal cycle in PANs over LA is distinct from both HCHO and surface O_3 (not shown); tropospheric column HCHO and surface O_3 have broad maxima extending from April through October and June through October, respectively. Increasing temperatures during the summer decrease the lifetime of PANs due to thermal decomposition and decrease the ratio of free tropospheric PANs to surface O_3. The secondary and tertiary peaks in monthly mean PANs over LA in July and September are driven by wildfire smoke transported into the LA Basin in 2018 and 2020, respectively (Liang et al., 2021). Wildfire impacts in September 2020 also drive the peak in September CO; note the difference between the mean and median as these peaks are not evident in the median (dashed) CO and PANs for these months.

Information on PANs within and around Beijing is growing rapidly (e.g., Z. Liu et al., 2010; B. Zhang et al., 2017, 2019). In Beijing, surface O_3 and tropospheric column HCHO have seasonal maxima in summer months (JJA), corresponding to the seasonal maximum in CrIS PANs (Figure 1) and recorded surface observations of PAN and PPN (B. Zhang et al., 2017; G. Zhang et al., 2015b). Ground-level PAN is also elevated during winter haze events in Beijing (Li et al., 2021; Qiu et al., 2019; B. Zhang et al., 2019; G. Zhang et al., 2020). CrIS observes elevated CO over Beijing in March and April, consistent with a seasonal peak in local fire activity in northeast China (Feng et al., 2015; L. Wang et al., 2020; Yin et al., 2019; Zhao et al., 2022).

Tokyo has a seasonal spring maximum in photochemical species from both local and distant (*i.e.,* China and Korea) sources of precursors (Lee et al., 2021; Yoshitomi et al., 2011). Delhi has a humid subtropical/semi-arid climate and air pollution is strongly influenced by the Indian monsoon (Gurjar et al., 2016). The monsoon season lasts from July-September and the dry season is considered to be September-June. CrIS observes elevated PANs over Delhi from April to October; on average PANs remain elevated through the monsoon season. Crop residue burning in April-May and October-November can deteriorate air quality in the Delhi metropolitan area (Saxena et al., 2021). These periods correspond with periods of elevated PANs and tropospheric column HCHO. Lagos surface O_3 increases seasonally during the dry season (Abdul Raheem et al., 2009). This is consistent with CrIS observations of PANs and CO, which increase and decrease with the respective dry and wet seasons.

3.2 2020 NO_2 Anomalies

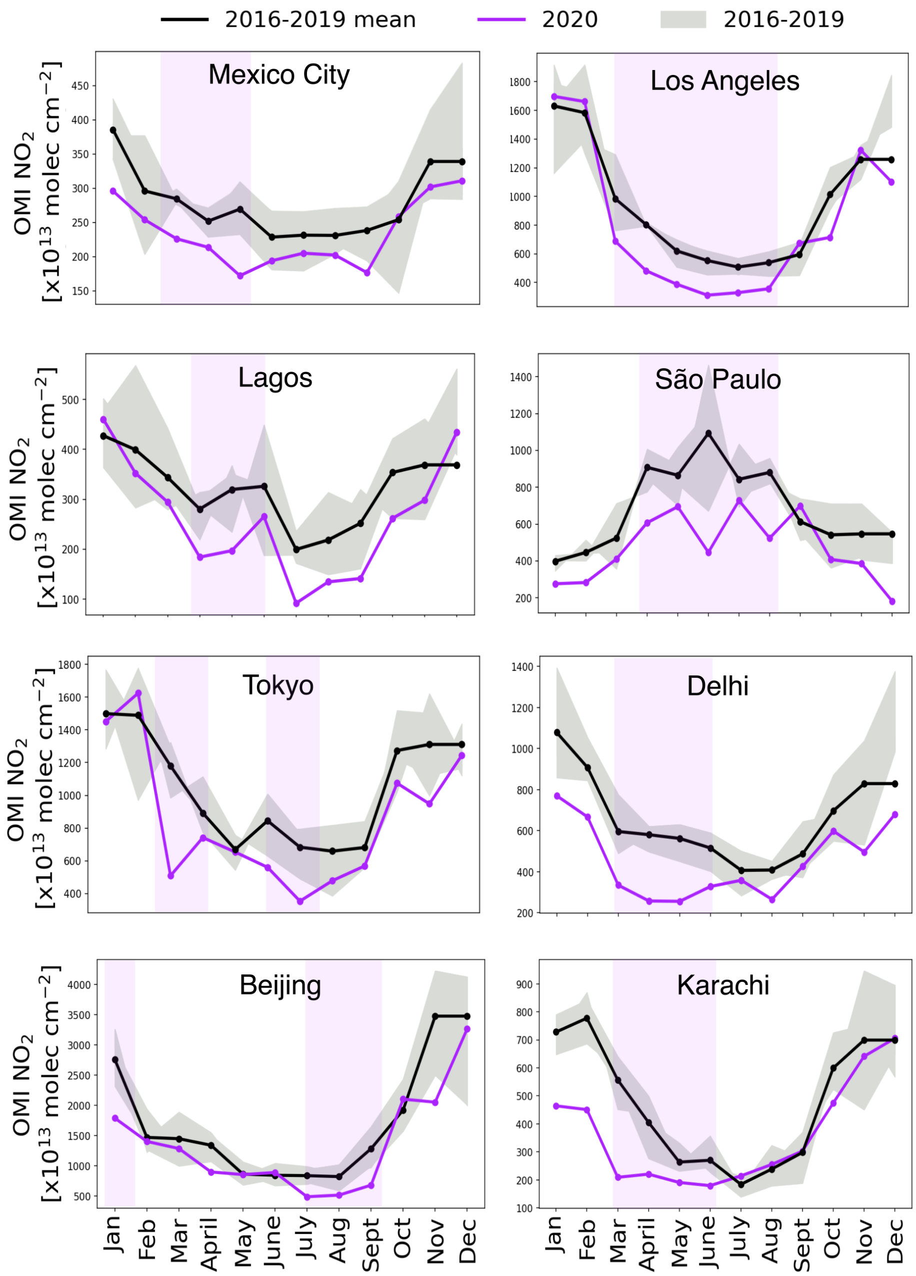

Figure 2. OMI NO_2 tropospheric column monthly means for 9 megacities. The area used for each city is the same area around the urban area of each city used for CrIS selection and this information is provided in Table 1. 2020 is shown in purple. The mean of 2016-2019 is shown in bold black. Months with substantial NO_2 declines in 2020 have been highlighted in purple shading and these time frames are used in the subsequent analysis presented in Figure 3.

Major changes in NO_x emissions and tropospheric NO_2 column abundances have been documented worldwide for different periods of the COVID-19 pandemic (Bauwens et al., 2020; Berman & Ebisu, 2020; J. Zhang et al., 2022). For the analysis presented here, we identify periods where 1) the monthly mean NO_2 column during 2020 was at least 15% below the corresponding monthly mean for 2016-2019 (black line in Figure 2), and 2) the monthly mean PANs mixing ratio are at least 0.05 ppbv (Figure 1). We only consider times in the seasonal cycle where mixing ratios of PANs are at least 0.05 ppbv because this corresponds with the uncertainty discussed in Section 2.1 and Payne et al. (2022). The months that meet these criteria are highlighted by the light purple shading in Figure 2. The 2020 monthly mean NO_2 column density associated with these shaded periods is at least 15% less than the mean of the corresponding months for the period 2016-2019. Periods of lower observed NO_2 often do not exactly coincide with the COVID-19 government-enforced lockdowns, as reduced traffic was often observed prior to government-imposed stay-at-home orders.

Table 1. Changes to Chemical Species during Respective Time Periods.

City	**Monthly mean time period**	**NO2 change (%)**	**NOx change (%)**	**HCHO change (%)**	**PANs change (%)**	**P-value**
Mexico City	February-May	-22%	-14%	5.6%	1.8%	0.45
Beijing	January	-35%	-19%	59%	80%	0.03
Beijing	July-September	-40%	-16%	-7.6%	-1.9%	0.31
Tokyo	March-April	-40%	-23%	-26%	6.9%	0.11
Tokyo	June-July	-40%	-15%	-43%	-0.9%	0.44
Los Angeles	March-August	-36%	-17%	-10%	-11%	0.06
São Paulo	April-August	-35%	-11%	-1.7%	3.7%	0.33
Delhi	March-June	-48%	-28%	-9.6%	-20%	0.33
Lagos	April-June	-35%	-16%	-0.08%	11%	0.33
Karachi	March-June	-52%	-5%	3.6%	12%	0.14

Table 1. Periods of significant NO_2 decline based on tropospheric column OMI NO_2 monthly means shown in Figure 2. Percent change represents the change in 2020 values relative to the mean of 2016-2019 for the respective time periods. Percent change in PANs were calculated using daily means during the months of NO_2 anomaly. P-values are from Mann-Whitney u test. A negative percent change signifies a decline in 2020 relative to the same months in prior years; likewise, positive percent changes signify an increase.

3.3 Impacts of COVID-19 NO_x reductions on PANs over megacities

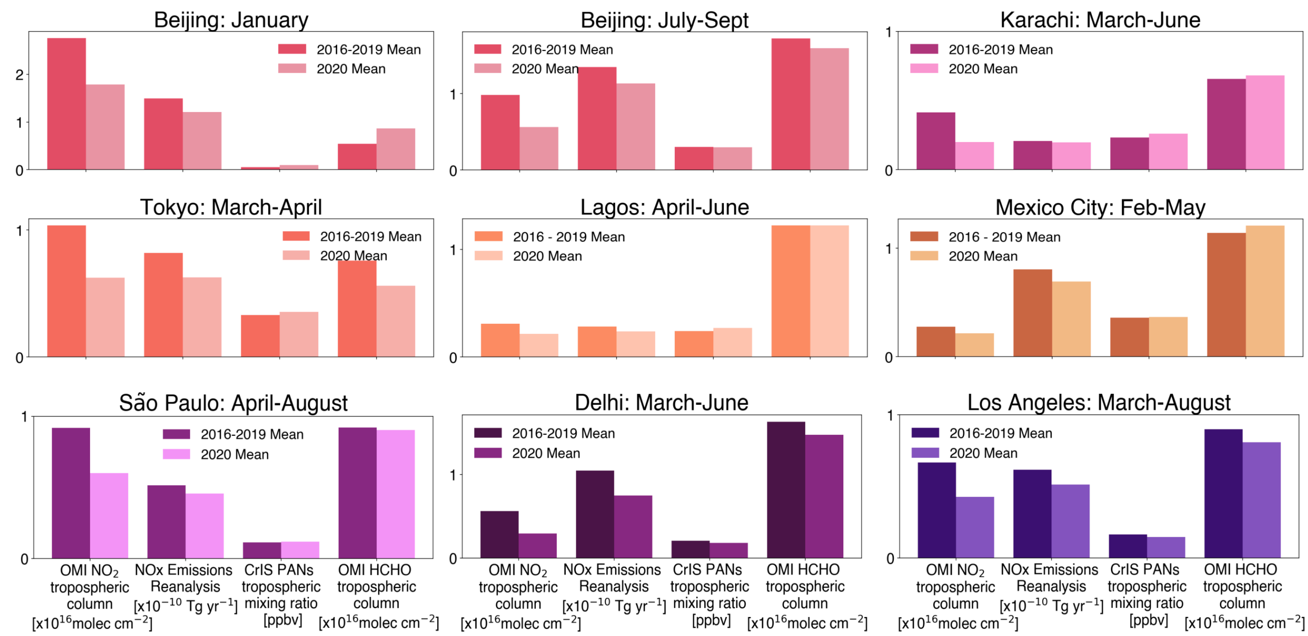

Figure 3. Bar charts comparing monthly means for specified months of OMI NO_2 tropospheric columns [x10^{16} molecules cm^{-2}], NO_x emissions from the Tropospheric Chemical Reanalysis [x10^{-10} Tg yr^{-1}], CrIS free troposphere PANs [ppbv], and OMI HCHO tropospheric columns [x10^{16} molecules cm^{-2}] for each megacity. Means of monthly means for specified periods in 2020 (shown in Figure 2 and listed in Table 1) are plotted in the lighter colors and means of 2016-2019 are plotted in the darker colors. We performed a Mann-Whitney u-test to test the significance of changes to PANs during the respective time periods of COVID-19 NO_2 perturbations listed in Table 1; 2020 was compared to the same time period from 2016-2019. We set our alpha at 0.1, so p values < 0.1 are considered significant and receive more discussion.

Figure 3 shows that while there were large decreases in NO_2 declines at some point in 2020, this did not yield a similarly large change in free tropospheric PANs for each region. Most megacities surveyed did not experience significant change in PANs at the 90% confidence level, except for LA, which experienced a significant decline, and Beijing in winter, which experienced a significant increase. We expect that PANs (and the sensitivity of CrIS) would also respond to other environmental factors including temperature; we analyze two possible environmental indicators: 2 meter air temperature and 500 hPa air temperature changes between the two respective periods over each of the megacities using MERRA-2 Reanalysis monthly mean product (Global Modeling and Assimilation Office (GMAO), 2015; DOI:10.5067/AP1B0BA5PD2K). We find no significant change in mean temperature at either pressure level between 2020 and corresponding months during the prior 4 years. Thus temperature was likely not a significant factor driving anomalies in PANs during the extended periods of NO_x perturbations highlighted in Figure 2. PANs have been used to gauge effectiveness of O_3-control strategies (*e.g.*, Gaffney et al., 1989). The tropospheric column ratios of HCHO to NO_2 have been used as a qualitative indicator of NO_x sensitive versus NO_x saturated (VOC-limited) regimes (*e.g.,* Jin et al., 2017; Martin et al., 2004; Souri et al., 2023). Threshold values vary by location (Souri et al., 2020), but higher (lower) ratios indicate NO_x-sensitive (saturated) conditions. Reductions in NO_x during the pandemic were substantial enough to shift the photochemical regime in some areas, *i.e.,* from NO_x-saturated to a transition zone or from a transition zone to NO_x-sensitive conditions (Peralta et al., 2021). The SI contains a version of Table 1 that also includes tropospheric column HCHO:NO_2 ratios over each city. We did not identify a consistent relationship between this ratio and the sensitivity of PAN to COVID induced-changes to NO_x.

PANs decreased significantly over LA during COVID-19 NO_x emission reductions, and this coincided with decreases in surface O_3 (Connerton et al., 2020; Schroeder et al., 2022). The underlying photochemical environment of LA has been transitioning from a VOC-limited regime to a NO_x-limited regime (Lee et al., 2021; Schroeder et al., 2022); spring 2020 was the first NO_x-limited year (Schroeder et al., 2022). PAN abundances at the ground have decreased much more rapidly than O_3 in response to emission controls in the LA Basin (Pollack et al., 2013). The CrIS data suggest that PAN would continue to respond to NO_x emission reductions in this city.

PANs did not show marked changes over Mexico City, São Paulo or Tokyo despite major NO_x perturbations. O_3 over Tokyo also did not significantly change with COVID-19 lockdown measures; this has been attributed to a shift in the underlying photochemical regime from VOC-limited towards the transition zone where O_3 production is expected to be equally sensitive to changes in both NO_x and VOCs (Damiani et al., 2022; Ito et al., 2021; Q. Wang & Li, 2021). O_3 in Mexico City was also statistically indistinguishable during periods of substantial precursor reduction in 2020 from that of other years (Peralta et al., 2021). São Paulo experienced an increase in O_3 in April and May, but largely in areas most seriously impacted by vehicle emissions (Alvim et al., 2023).

The largest and only significant increase in free tropospheric PANs on a monthly mean scale in our analysis occurred over Beijing in January (80%, $p = 0.03$), coincident with the lowest average HCHO: NO_2 ratio of all cities included here. Qiu et al. (2020) reported a threefold increase in ground-level PAN in urban Beijing during this first lockdown period, connected to enhanced local photochemistry and abnormal meteorological conditions, including anomalous wind convergence under higher temperatures. We find a similar change in free tropospheric PANs over Beijing, where mean CrIS PANs are 2.4 times higher during the same lockdown period. Beijing had a second period of NO_2 decline in July and August 2020, which was associated with an insignificant change in PANs (-1.96%, $p = 0.31$). Stavrakou et al. (2021) also investigated the impact of COVID-19 on PAN over China.

5 Conclusions

We use CrIS data from 2016-2021 to identify the seasonality of PANs over 8 megacities, and identify time periods with elevated PANs. This is the first detailed analysis of satellite observations of PANs over multiple megacities. We use this to inform our analysis in diagnosing the impact of NO_2 declines related to the COVID-19 pandemic on PANs in these locations.

1. There are pronounced seasonal cycles in PANs over each megacity. Monthly mean PANs peak in the spring or summer (Beijing and Karachi), aligning with respective seasonal maximums in photochemical activity. Wildfire smoke can occasionally enhance monthly mean PANs.

2. Despite large changes in tropospheric NO_2 columns associated with the COVID-19 pandemic, we only identify two megacities over which PANs changed significantly: Beijing and LA. The relative response of PANs in these locations was smaller than the changes in NO_2. The response of PANs to a major change in precursor emissions is highly non-linear.

3. Sensitivity of free tropospheric PANs to the abundance of precursors appears to be seasonally dependent in Beijing and Tokyo. PANs over Beijing and Tokyo are likely more sensitive to NO_x reductions in winter and spring respectively.

4. Based on this survey of megacities, relatively large perturbations in NO_x may not result in significant declines in NO_x export potential of megacities in all seasons. Thus satellite observations of PANs may be an additional useful diagnostic in predicting the complex response of O_3 to NO_x reductions in downwind regions. Next steps should focus on identifying the response of PAN downwind of megacities to COVID-19 NO_x reductions.

Acknowledgments

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Open Research

The Summary and Standard Product of CrIS PANs megacity Special Collection data for each megacity used in this study are available online through the Goddard Earch Sciences Data and Information services Center (NASA GES DISC) (Bowman, 2021c, 2021k, 2021g, 2021o, 2021a, 2021e, 2021m, 2021i, 2021l, 2021h, 2021p, 2021d, 2021n, 2021j, 2021b, 2021f, 2021c). Megacity datasets for Lagos and São Paulo can be found at https://doi.org/10.5061/dryad.wpzgmsbtk and eventually on the NASA GES DISC. OMI NO_2 and HCHO data were obtained from https://www.temis.nl/airpollution/no2.php and https://h2co.aeronomie.be/ (last access: August 2021), (Boersma et al., 2017b; De Smedt et al., 2017).

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Changes to Peroxyacyl Nitrates (PANs) over Megacities in Response to COVID-19 Tropospheric NO_2 Reductions Observed by the Cross-track Infrared Sounder (CrIS)

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Key Points:

- There are pronounced seasonal cycles of PANs over each megacity that align with seasonal maximums in photochemistry.
- Observed free tropospheric mixing ratios of PANs during COVID-19 were significantly different over two out of eight surveyed megacities.
- Sensitivity of free tropospheric PANs to the abundance of precursors is seasonally dependent in some locations.

Abstract

The COVID-19 pandemic perturbed air pollutant emissions as cities shutdown worldwide. Peroxyacyl nitrates (PANs) are important tracers of photochemistry that are formed through the oxidation of non-methane volatile organic compounds (NMVOCs) in the presence of nitrogen oxide radicals ($NO_x = NO + NO_2$). We use satellite measurements of free tropospheric PANs from the S-NPP Cross-Track Infrared Sounder (CrIS) over eight of the world's megacities: Mexico City, Beijing, Los Angeles, Tokyo, São Paulo, Delhi, Lagos, and Karachi. We quantify the seasonal cycle of PANs over these megacities and find seasonal maxima in PANs correspond to seasonal peaks in local photochemistry. CrIS is used to explore changes in PANs in response to the COVID-19 lockdowns. Statistically significant changes to PANs occurred over two megacities: Los Angeles (PAN decreased) and Beijing (PAN increased). Our analysis suggests that large perturbations in NO_x may not result in significant declines in NO_x export potential of megacities.

Plain Language Summary

The COVID-19 pandemic led to the lockdown of urban centers worldwide, drastically perturbing the concentrations of global air pollutants. Peroxyacyl nitrates (PANs) are important photochemical pollutants formed from reactions between NO_x and volatile organic compounds (VOCs), which were substantially reduced during the pandemic. We use satellite measurements of PANs from the Suomi-National Polar-orbiting Partnership (S-NPP) Cross-Track Infrared Sounder (CrIS) in the free troposphere over and surrounding eight of the world's megacities: Mexico City, Beijing, Los Angeles, Tokyo, São Paulo, Delhi, Lagos, and Karachi. Seasonal cycles of PANs are pronounced and the seasonal maxima correspond to seasonal peaks in local photochemistry. Significant changes to PANs in response to COVID-19 occurred over two out of the eight cities: Los Angeles (PANs decreased) and Beijing (PANs increased). Our results indicate that large changes in NO_x may not result in equally significant changes to PANs and the NO_x export potential of megacities.

1 Introduction

To slow the spread of the 2019 novel coronavirus (COVID-19), urban centers across the globe partially shut down for various amounts of time (Chinazzi et al., 2020; WHO, 2020). While the timing differed for each urban region, a consequence of these bursts of reduced economic activity was a radical decrease in the emissions of many primary air pollutants. Reductions in global and regional particulate matter, nitrogen oxides ($NO_x = NO + NO_2$), carbon dioxide (CO_2), and other trace gasses associated with the COVID-19 pandemic have been documented (Bauwens et al., 2020; Z. Liu et al., n.d.; Miyazaki, Bowman, Sekiya, Jiang, et al., 2020; Miyazaki et al., 2021; Odekanle et al., 2022; Sharma et al., 2020; Shi & Brasseur, 2020; Venter et al., 2020; J. Zhang et al., 2022) Less is understood about changes to secondary pollutants as they respond non-linearly to changes in precursor emissions, and their production and lifetime also depend on environmental conditions (*e.g.*, Stavrakou et al., 2021). For example, both increases and decreases in surface ozone (O_3) have been documented in urban areas during the COVID-19 pandemic despite decreases in precursor emissions (*e.g.,* Le et al., 2020; Miyazaki et al., 2021; Qiu et al., 2020; Shi & Brasseur, 2020; Sicard et al., 2020).

Peroxyacyl nitrates (PANs) are important photochemically-produced species that are formed alongside O_3 in polluted environments by the oxidation of non-methane volatile organic compounds (NMVOCs) in the presence of NO_x (Fischer et al., 2014; Gaffney et al., 1989; Roberts, 2007; Singh et al., 1986; Singh & Hanst, 1981). PANs are considered to be a sensitive tracer of photochemistry (e.g., Coggon et al., 2021; Rappenglück et al., 2003). Formation and decomposition of PANs can impact the production of O_3 (e.g. Steiner et al., 2010), the production of PANs acts as an indicator of regional photochemistry (Sillman & West, 2009), and the concentration of PANs can be used to gauge effectiveness of O_3-control strategies (Gaffney et al., 1989). PANs respond to precursor emissions non-linearly and have been shown to be more sensitive to changes in NMVOCs versus changes in NO_x for many regions of the global atmosphere (Fischer et al., 2014) and in some urban regions (T. Liu et al., 2022).

The lifetime of PANs against thermal decomposition is strongly dependent on temperature, where PANs are thermally unstable in the lower troposphere (lifetime on the order of hours at 20°C), but have a lifetime >1 month at temperatures characteristic of the mid-troposphere (Honrath et al., 1996). When transported from polluted continental regions to the remote troposphere, PANs serve as the principal reservoir species for NO_x and can contribute to efficient production of downwind O_3 in NO_x limited conditions (Fischer et al., 2014; Mena-Carrasco et al., 2009). The distribution of O_3 in the remote atmosphere would be substantially different without PAN chemistry (e.g., Jiang et al., 2016). There have been major changes in NO_x and VOC emissions in urban areas in recent decades, elevating the need for continued and extended observations of photochemically-relevant species in urban regions. In situ measurements of PANs have been collected for select urban areas for select seasons (Gaffney et al., 1989; Qiu et al., 2019; G. Zhang et al., 2015a), though observations are generally sparse.

Here we present new satellite observations of PANs over eight megacities. We utilize measurements from the Suomi-National Polar-orbiting Partnership (S-NPP) Cross-Track Infrared Sounder (CrIS) and other complimentary satellite and reanalysis datasets to document the seasonal cycles of PANs over select megacities and the response of PANs to COVID-19 induced reductions of precursor concentrations in these locations.

2 Materials and Methods

2.1 CrIS Observations

We use observations of free tropospheric PANs and CO from the CrIS instrument, a nadir viewing Fourier transform spectroradiometer currently flying on the S-NPP satellite. The datasets used here were produced under the NASA Tropospheric Ozone and Precursors from Earth System Sounding (TROPESS) project (Bowman, 2021c, 2021k, 2021o, 2021a, 2021e, 2021i, 2021l, 2021p, 2021d, 2021j, 2021b, 2021f, 2021c; Shogrin, 2023). Information on the CrIS PANs retrieval algorithm and validation against aircraft observations can be found in Payne et al. (2022). The validation efforts for the CrIS PANs product suggest a single sounding uncertainty of around 0.08 ppbv that reduces with averaging to an approximate floor of 0.05 ppbv and demonstrates the ability of CrIS to capture variation in the "background" PANs over remote regions (Payne et al., 2022). The CrIS CO algorithm is described in Fu et al. (2016) and validation is presented in Worden et al. (2022). A single sounding uncertainty for CrIS CO retrievals is on the order of 6-10% (Worden et al., 2022) and this is expected to reduce with averaging. Our analysis uses the column average PANs volume mixing ratio (VMR) between 825 and 215 hPa. CrIS PANs retrievals have peak sensitivity in the free troposphere (~680 hPa) and the sensitivity decreases rapidly near the surface. At most, CrIS PANs retrievals have 1 degree of freedom for signal (DOF), meaning this product does not include information about the vertical distribution of PANs in the atmosphere. The spectral feature utilized by CrIS for retrieval of PANs is centered at 790 cm^{-1}. This infrared spectral feature appears in the spectra of all PANs at essentially the same frequency, so CrIS measurements include all PAN species (i.e., they include propionyl peroxy nitrate (PPN; $CH_3CH_2C(O)OONO_2$), methacryloyl peroxy nitrate (MPAN; $CH_2C(CH_3)C(O)OONO_2$), etc.) in addition to peroxyacetyl nitrate (PAN; $CH_3C(O)O_2NO_2$). We also use a tropospheric average of CrIS CO between 825 hPa and 215 hPa. Our analysis focuses on CrIS PANs over and around 9 megacities utilizing CrIS CO to contextualize seasonal enhancements in PANs.

PAN observations from nadir-viewing satellites include those from the Tropospheric Emission Spectrometer (TES) (Payne et al., 2014) as well as meteorological sounders namely the Infrared Atmospheric Sounding Interferometer (IASI) (Franco et al., 2018) and CrIS (Payne et al., 2022). Studies observing PAN from space thus far have focused on PAN enhancements associated with fires (Alvarado et al., 2011; Clarisse et al., 2011; Juncosa Calahorrano et al., 2021) and the global distribution of PAN and its role in the long range transport of O_3 (Fischer et al., 2018; Jiang et al., 2016; Payne et al., 2017; Zhu et al., 2015; 2017). Although TES had provided a set of special observations over select megacities (Cady-Pereira et al., 2017; Shogrin et al., 2023), the spatial and temporal coverage of this dataset is somewhat limited. Here, we utilize the more comprehensive spatial and temporal coverage of CrIS to explore the spatiotemporal distribution of PANs over and around megacities.

2.2 Ozone Monitoring Instrument (OMI) Observations

We use Level 3 NO_2 tropospheric column measurements from NASA Aura-OMI to identify months with anomalously low NO_2 columns associated with COVID in 2020. We use the Quality Assurance for Essential Climate Variables (QA4ECV) NO_2 Level 3 product described in Boersma et al. (2018) as this is the most recently updated data product. OMI NO_2 L3 monthly mean data used in this study is provided on a global 0.125° x 0.125° grid and can be found on the TEMIS database (Boersma et al., 2017b).

We use Level 3 (L3) HCHO tropospheric column measurements, also from OMI, to contextualize changes in monthly VOC concentrations in megacities during the period of anomalously low tropospheric NO_2. Space-based observations of HCHO are used as an indicator of VOC emissions (De Smedt et al., 2008; Shen et al., 2019). HCHO is also processed using the QA4ECV algorithm consistently with the NO_2 data used in this study. HCHO L3 monthly mean data is also provided on a global 0.125° x 0.125° grid and can also be found on the TEMIS database (De Smedt et al., 2017).

2.3 Chemical Reanalysis Product

We use NO_x emission reanalysis data to also place changes to PANs in the context of NO_x emission flux reductions in megacities associated with COVID-19. NO_x emissions are from an assimilation of multi-species satellite observations (O_3, CO, NO_2, HNO_3, and SO_2) in the Tropospheric Chemistry Reanalysis version 2 (TCR-2) framework (Miyazaki et al., 2020; https://doi.org/10.25966/9qgv-fe81). NO_x emissions are constrained by tropospheric column NO_2 retrievals from the QA4ECV version 1.1 Level 2 products from OMI and Global Ozone Monitoring Experiment 2 (GOME-2) (Boersma et al., 2017a, 2017b). A priori emissions are from HTAP version 2 for 2010 (Janssens-Maenhout et al., 2015), Global Fire Emissions Database (GFED) version 4 (Randerson et al., 2018), and the Global Emissions Inventory Activity (GEIA) (Graedel et al., 1993). The reanalysis fields have been evaluated against independent observations on regional and global scales (Miyazaki et al., 2020). NO_x emissions for 2020 used in our analysis are estimated using business as usual (BAU) emissions added to the estimated COVID-19 emissions anomaly described in Miyazaki et al. (2021). While the observed NO_2 concentrations are affected by meteorological concentrations, their effect is already taken into account when estimating the NO_x emissions (Miyazaki et al., 2017; 2020)

3 Results and discussion

3.1 Seasonal Cycles of PANs, CO, and HCHO in megacities

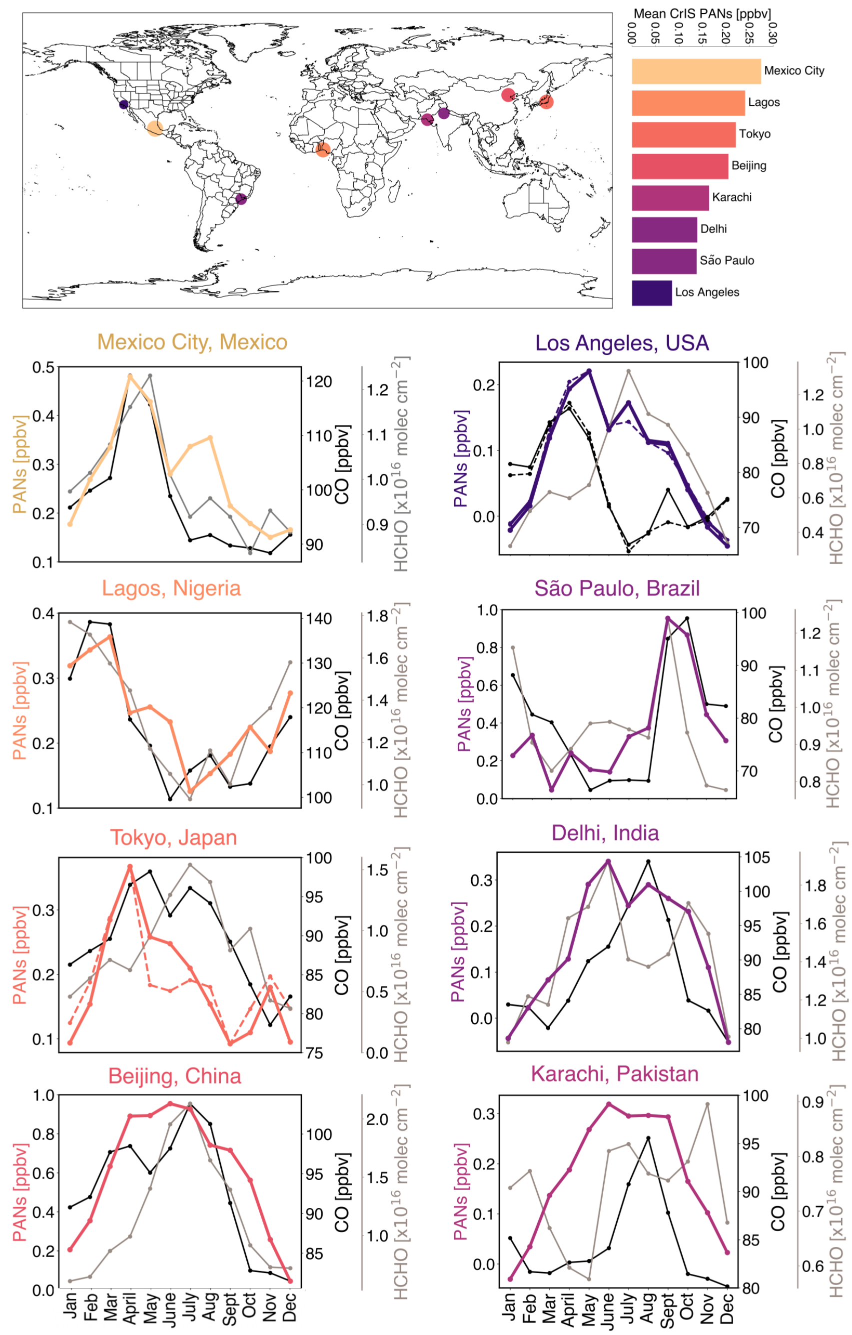

Figure 1. Top: Map shows mean detected CrIS PANs for the entire study period. The scale to the right of the map ranks the cities using the mean PANs. Dot sizing is indicative of abundance of mean PANs. Seasonal cycles of CrIS PANs [ppbv] (color denoted in color bar, dashed denotes median values), CrIS tropospheric CO [ppbv] (dark grey), and OMI HCHO tropospheric column average [x10^{16} molecules cm^{-2}]

(lighter grey) for eight megacities. Note: scales vary for each plot. Monthly means include data from January 2016 to May 2021.

Figure 1 displays the mean seasonal cycles for CrIS PANs, CrIS CO, and OMI HCHO for eight different global megacities from 2016-2021. Figure 1 helps identify periods in the annual cycle with production of PANs and values of PANs above a threshold where CrIS is able to provide quantitative information. For most cities, NO_2 changes from COVID-19 coincide with periods where PANs are above the CrIS detection limit (Section 2.1) and conditions support photochemical production.

All but two selected megacities experience a springtime maxima in PANs. The seasonal springtime maximum in PANs is attributed to an increase in photochemical activity at a time when PANs have a relatively long lifetime against thermal decomposition (Brice et al., 1988; Fischer et al., 2014; Penkett & Brice, 1986). Seasonal maxima occur in March, April, and/or May for northern hemisphere megacities (Mexico City, Los Angeles (LA), Tokyo, Delhi, and Lagos), and in September for São Paulo (23.56°S), the beginning of austral spring. Over Lagos (6.52°N) PANs begin increasing towards the end of the calendar year and maximize in March or April. In addition to a springtime maxima, PANs over Beijing (39.92°N) and Karachi (24.86°N) remain elevated through the summer (April-September). Though it has a springtime maxima, Delhi (28.71°N) has a comparably wide seasonal cycle in PANs. Mexico City, LA, and Tokyo also show an additional period of elevated PANs later in the year.

PANs over each megacity reflect a combination of sources and meteorological conditions, but the extent of the published literature on air pollutants in each megacity differs widely. Here we focus our discussion on LA, Beijing, and to a more limited extent, Tokyo, Delhi, and Lagos.

There is a longstanding effort to attribute and control O_3 and other photochemical pollutants in LA (Langford et al., 2010; Nussbaumer & Cohen, 2020; Pollack et al., 2013; Warneke et al., 2013). CrIS data indicate that the seasonal cycle in PANs over LA is distinct from both HCHO and surface O_3 (not shown); tropospheric column HCHO and surface O_3 have broad maxima extending from April through October and June through October, respectively. Increasing temperatures during the summer decrease the lifetime of PANs due to thermal decomposition and decrease the ratio of free tropospheric PANs to surface O_3. The secondary and tertiary peaks in monthly mean PANs over LA in July and September are driven by wildfire smoke transported into the LA Basin in 2018 and 2020, respectively (Liang et al., 2021). Wildfire impacts in September 2020 also drive the peak in September CO; note the difference between the mean and median as these peaks are not evident in the median (dashed) CO and PANs for these months.

Information on PANs within and around Beijing is growing rapidly (e.g., Z. Liu et al., 2010; B. Zhang et al., 2017, 2019). In Beijing, surface O_3 and tropospheric column HCHO have seasonal maxima in summer months (JJA), corresponding to the seasonal maximum in CrIS PANs (Figure 1) and recorded surface observations of PAN and PPN (B. Zhang et al., 2017; G. Zhang et al., 2015b). Ground-level PAN is also elevated during winter haze events in Beijing (Li et al., 2021; Qiu et al., 2019; B. Zhang et al., 2019; G. Zhang et al., 2020). CrIS observes elevated CO over Beijing in March and April, consistent with a seasonal peak in local fire activity in northeast China (Feng et al., 2015; L. Wang et al., 2020; Yin et al., 2019; Zhao et al., 2022).

Tokyo has a seasonal spring maximum in photochemical species from both local and distant (*i.e.,* China and Korea) sources of precursors (Lee et al., 2021; Yoshitomi et al., 2011). Delhi has a humid subtropical/semi-arid climate and air pollution is strongly influenced by the Indian monsoon (Gurjar et al., 2016). The monsoon season lasts from July-September and the dry season is considered to be September-June. CrIS observes elevated PANs over Delhi from April to October; on average PANs remain elevated through the monsoon season. Crop residue burning in April-May and October-November can deteriorate air quality in the Delhi metropolitan area (Saxena et al., 2021). These periods correspond with periods of elevated PANs and tropospheric column HCHO. Lagos surface O_3 increases seasonally during the dry season (Abdul Raheem et al., 2009). This is consistent with CrIS observations of PANs and CO, which increase and decrease with the respective dry and wet seasons.

3.2 2020 NO_2 Anomalies

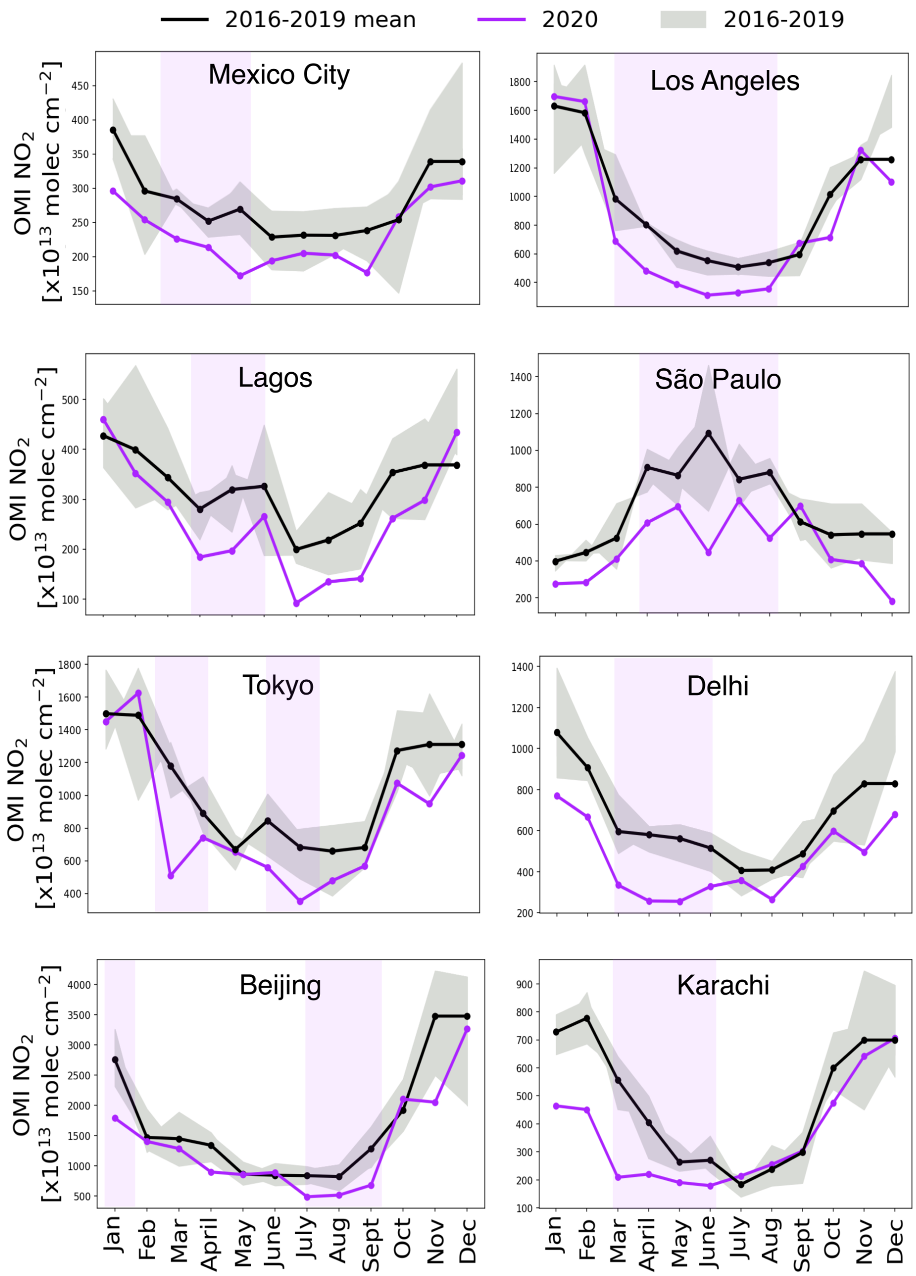

Figure 2. OMI NO_2 tropospheric column monthly means for 9 megacities. The area used for each city is the same area around the urban area of each city used for CrIS selection and this information is provided in Table 1. 2020 is shown in purple. The mean of 2016-2019 is shown in bold black. Months with substantial NO_2 declines in 2020 have been highlighted in purple shading and these time frames are used in the subsequent analysis presented in Figure 3.

Major changes in NO_x emissions and tropospheric NO_2 column abundances have been documented worldwide for different periods of the COVID-19 pandemic (Bauwens et al., 2020; Berman & Ebisu, 2020; J. Zhang et al., 2022). For the analysis presented here, we identify periods where 1) the monthly mean NO_2 column during 2020 was at least 15% below the corresponding monthly mean for 2016-2019 (black line in Figure 2), and 2) the monthly mean PANs mixing ratio are at least 0.05 ppbv (Figure 1). We only consider times in the seasonal cycle where mixing ratios of PANs are at least 0.05 ppbv because this corresponds with the uncertainty discussed in Section 2.1 and Payne et al. (2022). The months that meet these criteria are highlighted by the light purple shading in Figure 2. The 2020 monthly mean NO_2 column density associated with these shaded periods is at least 15% less than the mean of the corresponding months for the period 2016-2019. Periods of lower observed NO_2 often do not exactly coincide with the COVID-19 government-enforced lockdowns, as reduced traffic was often observed prior to government-imposed stay-at-home orders.

Table 1. Changes to Chemical Species during Respective Time Periods.

City	Monthly mean time period	NO2 change (%)	NOx change (%)	HCHO change (%)	PANs change (%)	P-value
Mexico City	February-May	-22%	-14%	5.6%	1.8%	0.45
Beijing	January	-35%	-19%	59%	80%	0.03
Beijing	July-September	-40%	-16%	-7.6%	-1.9%	0.31
Tokyo	March-April	-40%	-23%	-26%	6.9%	0.11
Tokyo	June-July	-40%	-15%	-43%	-0.9%	0.44
Los Angeles	March-August	-36%	-17%	-10%	-11%	0.06
São Paulo	April-August	-35%	-11%	-1.7%	3.7%	0.33
Delhi	March-June	-48%	-28%	-9.6%	-20%	0.33
Lagos	April-June	-35%	-16%	-0.08%	11%	0.33
Karachi	March-June	-52%	-5%	3.6%	12%	0.14

Table 1. Periods of significant NO_2 decline based on tropospheric column OMI NO_2 monthly means shown in Figure 2. Percent change represents the change in 2020 values relative to the mean of 2016-2019 for the respective time periods. Percent change in PANs were calculated using daily means during the months of NO_2 anomaly. P-values are from Mann-Whitney u test. A negative percent change signifies a decline in 2020 relative to the same months in prior years; likewise, positive percent changes signify an increase.

3.3 Impacts of COVID-19 NO_x reductions on PANs over megacities

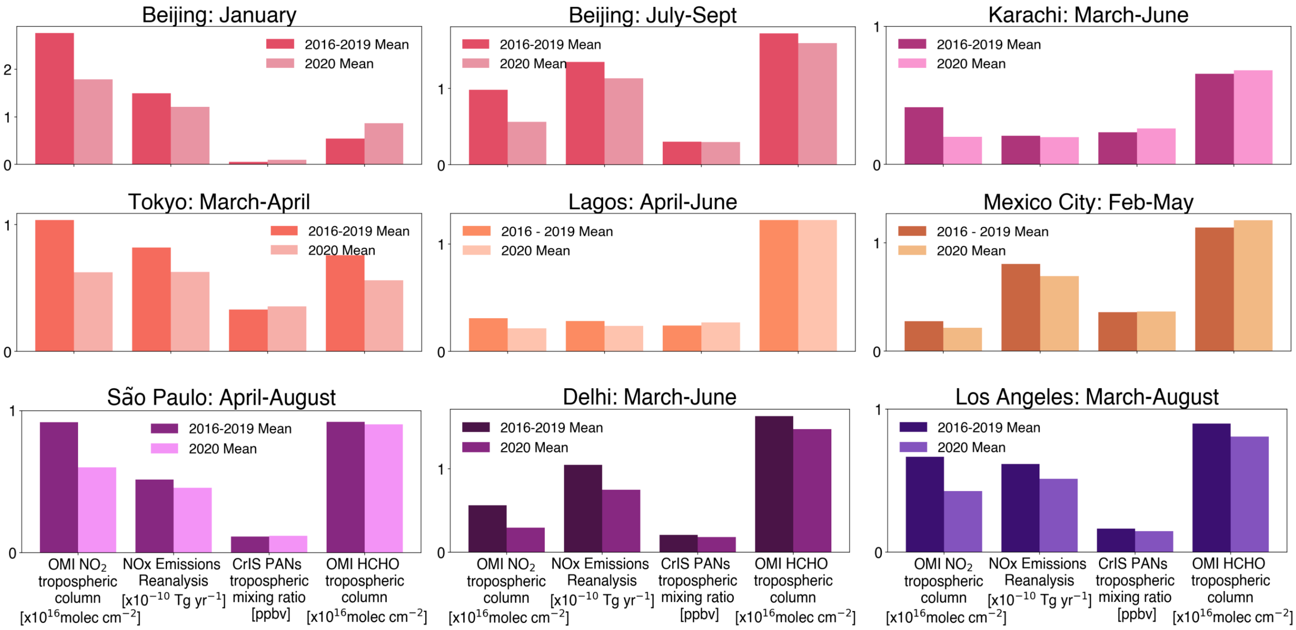

Figure 3. Bar charts comparing monthly means for specified months of OMI NO_2 tropospheric columns [x10^{16} molecules cm^{-2}], NO_x emissions from the Tropospheric Chemical Reanalysis [x10^{-10} Tg yr^{-1}], CrIS free troposphere PANs [ppbv], and OMI HCHO tropospheric columns [x10^{16} molecules cm^{-2}] for each megacity. Means of monthly means for specified periods in 2020 (shown in Figure 2 and listed in Table 1) are plotted in the lighter colors and means of 2016-2019 are plotted in the darker colors. We performed a Mann-Whitney u-test to test the significance of changes to PANs during the respective time periods of COVID-19 NO_2 perturbations listed in Table 1; 2020 was compared to the same time period from 2016-2019. We set our alpha at 0.1, so p values < 0.1 are considered significant and receive more discussion.

Figure 3 shows that while there were large decreases in NO_2 declines at some point in 2020, this did not yield a similarly large change in free tropospheric PANs for each region. Most megacities surveyed did not experience significant change in PANs at the 90% confidence level, except for LA, which experienced a significant decline, and Beijing in winter, which experienced a significant increase. We expect that PANs (and the sensitivity of CrIS) would also respond to other environmental factors including temperature; we analyze two possible environmental indicators: 2 meter air temperature and 500 hPa air temperature changes between the two respective periods over each of the megacities using MERRA-2 Reanalysis monthly mean product (Global Modeling and Assimilation Office (GMAO), 2015; DOI:10.5067/AP1B0BA5PD2K). We find no significant change in mean temperature at either pressure level between 2020 and corresponding months during the prior 4 years. Thus temperature was likely not a significant factor driving anomalies in PANs during the extended periods of NO_x perturbations highlighted in Figure 2. PANs have been used to gauge effectiveness of O_3-control strategies (*e.g.*, Gaffney et al., 1989). The tropospheric column ratios of HCHO to NO_2 have been used as a qualitative indicator of NO_x sensitive versus NO_x saturated (VOC-limited) regimes (*e.g.,* Jin et al., 2017; Martin et al., 2004; Souri et al., 2023). Threshold values vary by location (Souri et al., 2020), but higher (lower) ratios indicate NO_x-sensitive (saturated) conditions. Reductions in NO_x during the pandemic were substantial enough to shift the photochemical regime in some areas, *i.e.,* from NO_x-saturated to a transition zone or from a transition zone to NO_x-sensitive conditions (Peralta et al., 2021). The SI contains a version of Table 1 that also includes tropospheric column HCHO:NO_2 ratios over each city. We did not identify a consistent relationship between this ratio and the sensitivity of PAN to COVID induced-changes to NO_x.

PANs decreased significantly over LA during COVID-19 NO_x emission reductions, and this coincided with decreases in surface O_3 (Connerton et al., 2020; Schroeder et al., 2022). The underlying photochemical environment of LA has been transitioning from a VOC-limited regime to a NO_x-limited regime (Lee et al., 2021; Schroeder et al., 2022); spring 2020 was the first NO_x-limited year (Schroeder et al., 2022). PAN abundances at the ground have decreased much more rapidly than O_3 in response to emission controls in the LA Basin (Pollack et al., 2013). The CrIS data suggest that PAN would continue to respond to NO_x emission reductions in this city.

PANs did not show marked changes over Mexico City, São Paulo or Tokyo despite major NO_x perturbations. O_3 over Tokyo also did not significantly change with COVID-19 lockdown measures; this has been attributed to a shift in the underlying photochemical regime from VOC-limited towards the transition zone where O_3 production is expected to be equally sensitive to changes in both NO_x and VOCs (Damiani et al., 2022; Ito et al., 2021; Q. Wang & Li, 2021). O_3 in Mexico City was also statistically indistinguishable during periods of substantial precursor reduction in 2020 from that of other years (Peralta et al., 2021). São Paulo experienced an increase in O_3 in April and May, but largely in areas most seriously impacted by vehicle emissions (Alvim et al., 2023).

The largest and only significant increase in free tropospheric PANs on a monthly mean scale in our analysis occurred over Beijing in January (80%, p = 0.03), coincident with the lowest average HCHO: NO_2 ratio of all cities included here. Qiu et al. (2020) reported a threefold increase in ground-level PAN in urban Beijing during this first lockdown period, connected to enhanced local photochemistry and abnormal meteorological conditions, including anomalous wind convergence under higher temperatures. We find a similar change in free tropospheric PANs over Beijing, where mean CrIS PANs are 2.4 times higher during the same lockdown period. Beijing had a second period of NO_2 decline in July and August 2020, which was associated with an insignificant change in PANs (-1.96%, p = 0.31). Stavrakou et al. (2021) also investigated the impact of COVID-19 on PAN over China.

5 Conclusions

We use CrIS data from 2016-2021 to identify the seasonality of PANs over 8 megacities, and identify time periods with elevated PANs. This is the first detailed analysis of satellite observations of PANs over multiple megacities. We use this to inform our analysis in diagnosing the impact of NO_2 declines related to the COVID-19 pandemic on PANs in these locations.

1. There are pronounced seasonal cycles in PANs over each megacity. Monthly mean PANs peak in the spring or summer (Beijing and Karachi), aligning with respective seasonal maximums in photochemical activity. Wildfire smoke can occasionally enhance monthly mean PANs.

2. Despite large changes in tropospheric NO_2 columns associated with the COVID-19 pandemic, we only identify two megacities over which PANs changed significantly: Beijing and LA. The relative response of PANs in these locations was smaller than the changes in NO_2. The response of PANs to a major change in precursor emissions is highly non-linear.

3. Sensitivity of free tropospheric PANs to the abundance of precursors appears to be seasonally dependent in Beijing and Tokyo. PANs over Beijing and Tokyo are likely more sensitive to NO_x reductions in winter and spring respectively.

4. Based on this survey of megacities, relatively large perturbations in NO_x may not result in significant declines in NO_x export potential of megacities in all seasons. Thus satellite observations of PANs may be an additional useful diagnostic in predicting the complex response of O_3 to NO_x reductions in downwind regions. Next steps should focus on identifying the response of PAN downwind of megacities to COVID-19 NO_x reductions.

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Open Research

The Summary and Standard Product of CrIS PANs megacity Special Collection data for each megacity used in this study are available online through the Goddard Earch Sciences Data and Information services Center (NASA GES DISC) (Bowman, 2021c, 2021k, 2021g, 2021o, 2021a, 2021e, 2021m, 2021i, 2021l, 2021h, 2021p, 2021d, 2021n, 2021j, 2021b, 2021f, 2021c). Megacity datasets for Lagos and São Paulo can be found at https://doi.org/10.5061/dryad.wpzgmsbtk and eventually on the NASA GES DISC. OMI NO_2 and HCHO data were obtained from https://www.temis.nl/airpollution/no2.php and https://h2co.aeronomie.be/ (last access: August 2021), (Boersma et al., 2017b; De Smedt et al., 2017).

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