LETTER

Evaluating current satellite capability to observe diurnal change in nitrogen oxides in preparation for geostationary satellite missions

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Keywords: air pollution, air quality, remote sensing

Abstract

This study characterizes the degree to which current polar-orbiting satellites can evaluate the daytime change in NO$_2$ vertical column density (VCD) in urban, suburban, and rural areas. We examine these issues by considering the diurnal cycle of NO$_2$ over the United States, using the large NO$_2$ monitoring network supported by states, tribes, and the US Environmental Protection Agency (EPA). Through this analysis, we identify the potential opportunities and limitations of current space-based NO$_2$ data in capturing diurnal change. Ground-based monitoring data from the US EPA are compared with satellite retrievals of NO$_2$ from the KNMI Tropospheric Emissions Monitoring Internet Service (TEMIS) for two instruments: GOME-2 with a mid-morning overpass, and OMI with an early afternoon overpass. Satellite data show evidence of higher morning NO$_2$ in the vicinity of large urban areas. Both satellites and ground monitors show $\sim$1.5–2x greater NO$_2$ abundance between morning and afternoon in urban areas. Despite differences in horizontal resolution and overpass time, the two satellite retrievals show similar agreement with ground-based NO$_2$ measurements. When analyzed on a pixel-by-pixel basis, we find evidence for spatial structure in the diurnal change in NO$_2$ between city center and surrounding areas in Southern California. Wider analysis of urban-suburban structure in diurnal NO$_2$ change is hindered by resolution differences in the two satellite instruments, which have the potential to create data artefacts. This study highlights the value of future geostationary instruments to provide comparable satellite retrievals for NO$_2$ over the course of a day, and research needs related to the effective utilization of NO$_2$ satellite data for air quality applications.

1. Introduction

Near-surface NO$_2$ impacts human health and ecosystems (Samet and Utell 1990, Jerrett et al 2009), plays an important role in atmospheric chemistry (Atkinson 2000, Elliott et al 2007, Pan et al 2016), and serves as a tracer of fossil fuel combustion (Streets et al 2013). In the United States, NO$_2$ is one of six criteria pollutants regulated under the National Ambient Air Quality Standard (NAAQS).

Because of its radiative properties, NO$_2$ is also one of a small group of gas-phase air pollutants that may be reliably detected from satellite instruments (Richter and Burrows 2002, Richter et al 2005, Martin 2008, Duncan et al 2014). Among satellite data products relevant to air quality, nitrogen dioxide (NO$_2$) has emerged as one of the most useful (Holloway et al 2018). Because of the relatively short atmospheric lifetime of NO$_2$, satellite-based observations of NO$_2$ have been found useful as an indicator of fossil fuel combustion (Streets et al 2013). Spatial and temporal patterns in atmospheric NO$_2$ columns have been shown to reflect spatial variability, day-to-day and year-to-year changes in emissions of NO$_X$ (e.g. Martin, 2003,
Lamsal et al 2011, Mijling and Van Der A 2012) and trends in economic development (e.g. Tong 2015, Montgomery and Holloway 2018).

Boundary layer mixing, photochemistry, emissions sources, and other processes affect near-surface NO₂, which varies strongly through the day. Some of these processes affect both the surface and column NO₂ abundance (e.g. dominant partitioning of NO₂ into NO₂ at night), while other processes controlling surface NO₂ may not affect the column (e.g. boundary layer height, Harkey et al 2015). Additionally, processes may affect the column with a delay from the surface (e.g. timing of NO₂ emissions, as discussed in Fishman et al (2008)).

We examine the degree to which current polar-orbiting satellites can quantify diurnal change in NO₂ vertical column density (VCD) in urban, suburban, and rural areas, and how this change compares with hourly cycles in surface NO₂ measured at the surface. Through this analysis, we identify the potential opportunities and limitations of current space-based NO₂ data in capturing near-surface air quality.

Currently, only polar orbiting instruments detect NO₂. Three of the most widely-used instruments are: the Global Ozone Monitoring Experiment 2, (GOME-2; resolution of 40 km × 80 km at nadir); the Ozone Monitoring Instrument (OMI; resolution of 13 km × 24 km at nadir); and the Tropospheric Ozone Monitoring Instrument (TROPOMI; resolution 7 km × 3.5 km at nadir). Each of these instruments offers near-daily global coverage. GOME-2 has a mid-morning overpass, where OMI and TROPOMI pass over in the early afternoon. For all three instruments, data are provided as ‘snapshots’ at the same time each day, except as limited by cloud cover, surface albedo, and instrument errors. Multiple retrievals have been calculated based on these satellite products, with different calculations of the air mass factor (AMF), determined by model calculations of surface albedo, clouds, a priori NO₂ profile, and other assumptions. In fact, AMF calculation is the leading source of uncertainty in satellite NO₂ products, with Lorente et al (2017) estimating that AMF calculations introduce structural uncertainty of 42% in polluted regions.

Here, we evaluate alternate methods to calculate diurnal change in NO₂ in the continental US, including evaluation of GOME-2 and OMI data on a common grid, and a case study over Los Angeles comparing GOME-2 and OMI pixels on a single day. We present a discussion of past work to reconcile temporal variability in column and surface NO₂ (section 2), an overview of methods used for this analysis (section 3), results on surface and satellite-derived NO₂ diurnal variability (section 4), and a discussion of relevance and research needs (section 5).

2. Reconciling surface and column NO₂ variability

The potential for satellite-derived NO₂ to serve as an indicator of near-surface air quality is a major strength of Earth observing satellites. The first comparison of satellite and ground-based NO₂ focused on data from the Global Ozone Monitoring Experiment (GOME) compared with NO₂ from an in situ chemiluminescent instrument in Northern Italy (Petritoli et al 2004). In that study, daily average NO₂ values were used for comparison, noting that the 10:30 am time of the GOME overpass typically aligns with the daily average NO₂ concentrations for the Po valley in northern Italy. Studies since then typically evaluate ground and satellite data at the satellite overpass time. Monitors for NO₂ often use chemiluminescence instruments with molybdenum oxide converters, which first convert NO₂ to NO, then measure the amount of NO. However, other compounds, including peroxyacetyl nitrate (PAN) and nitric acid (HNO₃), are also partly converted to NO by the molybdenum oxide converters, leading to overestimation of NO₂ under conditions of high PAN and/or high HNO₃ (Steinbacher et al 2007). In urban settings overestimation is greatest during the afternoon hours (Dunlea et al 2007), and in rural settings during the summer months (Steinbacher et al 2007). As a result, monitor bias is often corrected when evaluating afternoon overpass satellites like OMI (Lamsal et al 2008). Retrievals based on AMF calculations from higher resolution regional models show improved performance against surface observations (Russell et al 2011, Goldberg et al 2017, Laughner et al 2019).

An additional challenge in comparing OMI and TROPOMI with ground monitors is the potential lag-time between diurnal variability in the surface and column measurements. Fishman et al (2008) use a regional air quality model to show that magnitude of variability in NO₂ abundance is similar in surface and column values, but with a time lag of about three hours. This result suggests that comparing concurrent surface and column measurements may in fact underestimate the agreement between these two data sets.

The upward-looking Pandora instrument has emerged as a powerful tool to assess the diurnal variability of the NO₂ column, using a sun-tracking UV/Vis spectrometer to measure total column NO₂ from the surface. As we consider the ability of satellite data to detect hourly change in column NO₂, the gold standard for comparison is the Pandora instrument. Several papers have related Pandora measurements to in situ, surface measurements (Flynn et al 2014, Kneipp et al 2015, Kollonige et al 2018), and a few have explicitly examined diurnal variability. The most thorough examination of diurnal variability to date has been presented by Herman et al (2019), who find significant time-of-day structure in the NO₂ columns, with patterns differing by location, season, and individual days.

Understanding the diurnal variability in column NO₂ is essential to relate satellite data to ground-monitors, and prior studies suggest that diurnal changes in column NO₂ are detectable by polar-orbiting
satellites. Boersma et al. (2008) first used the difference of a morning and afternoon satellite overpass to estimate the diurnal change in NO$_2$, comparing SCIAMACHY, which has a mid-morning overpass similar to GOME-2, with data from OMI. Similarly, Lourens et al. (2012) compared SCIAMACHY and OMI, with a focus on South Africa. Lin et al. (2010) used GOME-2 and OMI together to increase temporal resolution for a top-down estimate of NO$_X$ emissions in China. A diurnal signal in formaldehyde (HCHO) has been observed by differenting GOME-2 and OMI (Smedt et al. 2015, Stavrakou et al. 2015). These previous studies find patterns in VCD attributable to known diurnal patterns in emissions and atmospheric processes.

Here we extend this line of inquiry to the regional scale, examining diurnal variability in urban, suburban, and rural environments. New issues arise when evaluating patterns at scales approaching or less than those of the instrument resolution. Large pixels over comparatively small plumes, such as those over cities and power plants, average the high concentrations of the plume with the lower surrounding concentrations. This results in a ‘smoothing effect’ for larger pixels. Because large pixels dilute major emission sources, they tend to underestimate city centers, and overestimate the edges of cities (Hilboll et al. 2013, Kim et al. 2016). Comparing OMI observations at mid-day with GOME-2 observations in the morning could erroneously suggest that mid-day NO$_2$ VCDs in urban areas are higher than morning NO$_2$ VCDs.

Different approaches have been used to mitigate the smoothing effect for NO$_2$ when comparing instruments of different resolution. Methods include the regridding of the finer resolution instrument to larger grids (Boersma et al. 2008, 2009), down-sampling finer pixels by averaging them into larger pixels (Hilboll et al. 2013), and ‘downscaling’ satellite data using a model (Kim et al. 2018). We explore the potential and limitations in deriving diurnal change from polar-orbiting satellites at smaller scales, using both a re-gridding approach as well as a down-sampling approach.

3. Study methods

We conduct our analysis for 2007, the first full year for which both GOME-2 and OMI data are available, when OMI had lower noise and minimal impacts from the ‘row anomaly.’ The ‘row anomaly’ refers to an internal blockage in the OMI instrument that obstructs certain rows in the sensor, producing data artefacts. The row anomaly first occurred on 25 June 2007, when it covered just two rows. The number of rows blocked has continued to increase erratically, and since 2009 about half of OMI rows are affected (Schenkeveld et al. 2017). The row anomaly blocks a maximum of two out of 60 rows in this study. Summer is selected as the study period for comparability with Boersma et al. (2008), and relevance to NO$_X$ emissions during the ozone season in many parts of the US. During summer months, increased photolysis leads to higher levels of O$_3$, which is important for its health effects, and OH, which reacts with NO$_X$ and removes it from the troposphere (Jacob 1999). The increase in OH leads to a NO$_X$ lifetime of approximately three hours in US cities, which is 30% shorter than in the spring or autumn (Liu et al. 2016). This shorter lifetime makes NO$_X$ less sensitive to transport processes, such that the observed spatial patterns are more closely associated with emissions.

Ground-based measurements are from the US EPA Air Quality System (AQS), taken by US states and tribes in compliance with EPA monitoring system protocols. These monitors report measured hourly NO$_2$, and most report NO as well. We have not applied an NO$_2$ bias correction factor because: (1) a goal of this study is to evaluate satellite data in a manner that is relevant to the US air quality management community, which does not apply a correction factor to AQS NO$_2$ measurements for regulatory purposes (consistent with the rational of Novotny et al. (2011)); and (2) Any such correction would necessitate the use of model-derived PAN and HNO$_3$ (which are rarely measured at the same sites as NO$_2$), thus introducing an additional layer of complexity, uncertainty, and limited reproducibility of our results. Future work quantifying the impact of the interference correction on monitor-satellite comparison would be helpful to support wider utilization of satellite data for research and applications.

We characterize the diurnal cycle of NO$_2$ during 92 summer days (1 June–31 August) in 2007, and consider spatial variability in this cycle. For the analysis of AQS NO$_2$ (e.g. figures 1, 2), we selected monitors data available for more than 70% of the hours in June, July, and August 2007. For figure 1, where NO and NO$_2$ are compared, we used only the 326 monitors which measured both compounds over the summer. For each monitor, we calculated the average NO$_2$ mixing ratio over the summer at each of the 24 h of the day. For figure 2, we required 70% data availability at both 09:00 and 13:00, which resulted in 314 available monitors.

We use satellite retrievals from the GOME-2 and OMI instruments, which are both ultraviolet–visible (UV–vis) spectrometers aboard polar orbiting synchronous satellites. The GOME-2 instrument on board MetOp-A has provided continuous data since late 2006, and has a resolution of 40 km x 80 km at the nadir. It passes over the equator at approximately 09:30 LST (local standard time) and produces a global coverage every 1.5 d (EUMETSAT 2014). The OMI instrument on board the NASA Aura satellite has provided continuous data from October 2004, with a resolution of 13 km x 24 km at the nadir and 68 km x 14 km at the edges of the swath (OMI team 2012). It passes over the equator at approximately 13:45 LST and achieved global coverage every day until June.
2007, when some of the pixels became blocked in the row anomaly (described above) (Schenkeveld et al 2017). We used daily level-2 satellite products from the Tropospheric Emission Monitoring Internet Service (TEMIS), which distributes satellite retrievals of NO2 from both GOME-2 (TM4NO2A product) (Boersma et al 2004) and OMI (DOMINO product) (Boersma et al 2011). These retrievals are calculated in a consistent manner, with TM4NO2A (for GOME-2) and DOMINO (for OMI) data products developed using the same algorithm based on the TM4 chemical transport model (Boersma et al 2004, Boersma et al 2008, 2011).

Our standard analysis approach allocates GOME-2 and OMI level-2 data products to 0.25° x 0.25° and 0.5° x 0.5° grids using the Wisconsin Horizontal Interpolation Program for Satellites (WHIPS) v2.1 (Harkey et al 2015), which utilizes the NASA OMN02d gridding algorithm (Buscera et al 2016). The WHIPS software allows users to apply a cloud filter, and we use only pixels with a cloud fraction less than 0.3. For each day, we selected only grid cells where data was available for both GOME-2 and OMI. We then averaged 92 d of gridded data in June, July, and August 2007 to create a summer average gridded data product (the number of days of data varies by grid cell, as shown in supplementary figure S1, which is available online at stacks.iop.org/ERL/15/034038/mmedia). For comparison between ground-based and satellite data (e.g. figure 2), daily values from each satellite grid cell were matched with AQS monitors located inside the grid boundaries. Only days for which both AQS and satellite are available are used to produce a temporally co-sampled average for each monitor and each coincident satellite pixel. As a result, different monitors have different numbers of observations. The median monitor has 28 observations which coincide with both GOME-2 and OMI over 92 d; figure S2 shows the distribution of number of observations. We selected AQS data where the sampling window overlapped with the

Figure 1. Average NO2 (a) and NO (b) mixing ratios at each hour of the day in 2007. Also shown is the ratio of NO2: NOx, where NOx = NO + NO2 (c). Only monitors that measured both compounds for more than 70% 2007 are compared. EPA AQS setting designations are used to determine urban, suburban, and rural monitors. 326 monitors across the US are considered here: 96 designated ‘urban,’ 132 designated ‘suburban,’ and 98 ‘rural.’ Arrows show approximate times of GOME-2 and OMI overpass.
approximate satellite overpass. Although GOME-2 and OMI pass over the United States slightly later than the equatorial overpass times given, they should still fall roughly within the ranges of 09:00–10:00 LST and 13:00–14:00 LST respectively.

In the discussion below, we refer to the difference between seasonal mean VCDs of each satellite instrument as the \( \Delta \text{NO}_2 \), where

\[
\Delta \text{NO}_2 = \text{GOME-2 NO}_2 \text{VCD} - \text{OMI NO}_2 \text{VCD} \text{ for summer 2007.}
\]

Where we present alternate methods to calculate \( \Delta \text{NO}_2 \), differences in methodology are described.

Interest in satellite data for atmospheric constituents has been expanding beyond the atmospheric science community to support applications and scholarship in related fields (Milford and Knight 2017, Holloway et al. 2018). To support a broader community of potential data users, we compared our results with a much easier analysis method using pre-processed, monthly-mean OMI and GOME-2 data. TEMIS distributes two monthly mean, level-3 products with OMI on a 0.125° x 0.125° grid and GOME-2 on a 0.25° x 0.25° grid. (we will refer to this as the ‘level-3 method,’ shown in figure S3). The level-3 method shown in figure S3 is comparable to figure 4(c) in the discussion below. However, because OMI and GOME-2 were evaluated on different grid resolutions in creating figure S3, these results likely reflect data artefacts. For example, in figure S3, some cities exhibit a structure where mid-day NO2 VCDs in urban areas are higher than morning NO2 VCDs. These patterns may be the result of the higher-resolution mid-day OMI retrieval compared with the lower-resolution morning GOME-2 retrieval. Differences between figure S3 and figure 4(c) highlight the strengths and limitations of comparing monthly average gridded Level-3 data to estimate diurnal change.

### 4. Results

We find NO2 abundance varies through the day in urban, suburban, and rural environments, as detected by both ground-based and satellite instruments.

#### 4.1. Diurnal cycle of NO2

Ambient measurements of near-surface NO2 have been shown to exhibit strong diurnal cycles, as a function of diurnal variability in emissions, photochemistry, and boundary layer height. Past studies (Bower et al. 1991,
Ketzel et al. (2003), Harley et al. (2005) attribute these patterns in part to NO\textsubscript{2} emissions from commuter traffic, which peak in the morning and evening. Both through the absence of photolysis and through a shallow nocturnal boundary layer height, chemical and physical processes favor higher levels of ambient NO\textsubscript{2} at night and lower levels during the day (Jacob 1999, Song et al. 2011).

Consistent with these factors, we find that the diurnal cycle of ambient NO\textsubscript{2} measured at the AQS monitoring sites is typically characterized by two peaks (~06:00 and ~21:00 LT), whereas NO has only one peak (~06:00 LT) (figure 1). The absence of a nighttime NO peak might be explained by rapid oxidation of NO to NO\textsubscript{2} by O\textsubscript{3}, which occurs in the absence of solar radiation (Song et al. 2011, Roberts–Semple et al. 2012). (The timing of morning and afternoon maxima in NO\textsubscript{2} varies by monitor, as shown in supplementary figure S4)

The amplitude of the diurnal cycles of both NO\textsubscript{X} components is greatest in urban areas (7–10 ppb for NO\textsubscript{2}; 9 ppb for NO) and suburban areas (5–8 ppb for NO\textsubscript{2}; 7 ppb for NO) and smaller in rural areas (2–3 ppb for NO\textsubscript{2}; 2 ppb for NO). In urban areas, peak morning NO\textsubscript{2} (16 ppb) is ~2x the value of afternoon minimum NO\textsubscript{2} (8 ppb), and the amplitude of diurnal NO\textsubscript{2} change in urban areas is ~3x larger in urban areas than in rural areas.

Given the suggestion of Fishman et al. (2008) that the VCD NO\textsubscript{2} diurnal cycle is shifted ~3 h later than the surface NO\textsubscript{2} cycle, we would expect the peak in the NO\textsubscript{2} column to occur ~09:00 LT (06:00 + 3:00) and the minimum to occur ~16:00 LT (13:00 + 3:00). This assumed time shift would suggest that GOME-2 overpass could capture morning maximum column NO\textsubscript{2} values.

Figure 1(c) considers the degree to which satellite NO\textsubscript{2} columns inform total NO\textsubscript{X} concentrations. We find that the surface NO\textsubscript{2}/NO\textsubscript{X} ratio varies through the day from 60%–70% to 90%–98%, consistent with ratios in prior work for NO\textsubscript{X} mixing ratios less than 50 ppb (Song et al. 2011). The rural and suburban monitors generally show higher NO\textsubscript{2}/NO\textsubscript{X} ratios than the urban monitors. NO is a primary pollutant from combustion, so it is present at higher concentrations in large urban centers. In contrast, NO\textsubscript{X} in rural areas may have been transported from an urban source, over which time the NO photolyses and reacts with O\textsubscript{3} and OH to form NO\textsubscript{2} (Bower et al. 1991). This would also cause a time lag in the peak for rural NO\textsubscript{2}, relative to urban NO\textsubscript{2}, which we observe in the morning, but not the afternoon (figure 1(a)). We find that NO\textsubscript{2} contributes less to surface NO\textsubscript{X} in the morning, and a greater contribution later in the day; this shift in NO\textsubscript{X} partitioning affects the relationship of NO\textsubscript{2} column values to total NO\textsubscript{X} at different times of the day.

4.2. Monitor versus satellite NO\textsubscript{2}

Figure 2 compares summer-average monitored NO\textsubscript{2} from AQS with NO\textsubscript{2} VCDs from OMI (3a), GOME-2 (3b), and the difference between GOME-2 and OMI (3c). We find similar levels of spatial agreement between AQS and the two satellite data sets, despite the difference in satellite horizontal resolution. For coincident surface and column measurements, GOME-2 has a coefficient of determination ($r^2$ value) of 0.61 compared to OMI at 0.59 and both instruments have slopes of 0.60 10\textsuperscript{15} molec. cm\textsuperscript{-2} ppb\textsuperscript{-1} (figure 2). We find that AQS measurements from earlier time windows show slightly better agreement with OMI ($r^2 = 0.64$ for 12:00 LST versus $r^2 = 0.59$ for 13:00 LST, see table S1), which may be due to the lag between surface and column diurnal cycles (Fishman et al. 2008). Our spatial correlation coefficients agree with prior work reporting spatial correlation of OMI with AQS monitors, including a comparison of 208 monitors averaged over 2005–2013 ($r^2 = 0.58$) (Lamsal et al. 2015), a comparison of 18 sites in the mid-Atlantic US averaged over June and July 2008–2012 ($r^2 = 0.58$) (Goldberg et al. 2017), and a comparison of 60 sites over Southern California ($r^2 = 0.58$) (Kim et al. 2018). Kim et al. (2018) also found a correlation coefficient of $r^2 = 0.67$ for GOME-2A.

Although both satellites were allocated to the same 0.25° x 0.25° grid and sampled only when measurements from both instruments were available, we would expect the coarser resolution of the GOME-2 instrument to exhibit a lower level of agreement with NO\textsubscript{2} monitors, because the GOME-2 pixels integrate over a larger area, and because each grid cell draws information from a smaller number of GOME-2 measurements (figure S5). Instead, we find that slopes and correlation coefficients are similar for both satellites.

The similar slopes and correlation coefficients between the two satellites suggest that the VCDs have similar sensitivity to surface concentrations, despite changes in boundary layer height from mid-morning to early afternoon. The intercept occurs at ~0.15 × 10\textsuperscript{15} molec. cm\textsuperscript{-2} for GOME-2 and 0.69 x 10\textsuperscript{15} molec. cm\textsuperscript{-2} for OMI, which might indicate a small high bias of OMI over GOME-2.

The simpler ‘level-3 method’ using TEMIS level-3 gridded data products at two different resolutions shows a similar level of spatial correlation between the surface- and satellite-based measurements gridded to the same scale, despite evidence of smoothing artefacts in figure S5, as discussed above. In the comparison against monthly average AQS data, GOME-2 has a coefficient of determination ($r^2$ value) of 0.72 compared to OMI at 0.74, and slopes of 0.52 and 0.50, respectively. That GOME-2 and OMI exhibit similar agreement with AQS, even when not on the same grid, suggests a similar skill in capturing surface NO\textsubscript{2}, may be due to the high contribution (~80%) of ‘urban background’ NO\textsubscript{2}, even at hotspots (Apte et al. 2017).

We also evaluate whether the difference between morning and mid-day NO\textsubscript{2} values are similar between AQS and satellites. Due to the time-lag in peak values between surface and column NO\textsubscript{2} discussed in
Fishman et al. (2008), and the role of boundary layer height in determining diurnal variability of NO2 discussed in Song et al. (2011) and Harkey et al. (2015), we would expect a lower level of agreement for temporal differences than we see for concurrent NO2 values. Indeed, figure 2(c) shows a relatively weak agreement between diurnal change from satellites and diurnal change at the surface, with summer mean $r^2 = 0.25$.

Although there is not a high level of spatial correlation between satellites and surface monitors in the difference of morning and mid-day NO2, large urban areas show a similar ratio between morning and afternoon NO2 values in the surface and column, with satellite measurements generally exhibiting a lower ratio than surface monitors. Figure 3 shows the morning-versus-afternoon NO2 ratios in metropolitan areas of New York (New York), Los Angeles (California), Chicago (Illinois), Dallas (Texas), Houston (Texas), and Philadelphia (Pennsylvania). Across these regions, morning surface NO2 measurements are 1.5 to 2.3 x higher than afternoon. Satellite derived ratios are somewhat lower, ranging from 1.2 to 1.8 x higher than afternoon. The agreement between surface and column ratio varies by city. Among the cities shown in figure 3, the greatest agreement is observed in Philadelphia (AQS = 1.55; satellite = 1.45), and the lowest in Chicago (AQS = 2.1; satellite = 1.2). (Ratios of morning to afternoon NO2 at all monitoring sites are shown in figure S6). Satellite measurements find a lower morning-to-afternoon ratio than that observed by surface monitors, likely due to the mediating effect of total column measurements. Venting NO2 to the upper troposphere in the afternoon would decrease NO2 abundance as measured by surface AQS monitors. However, this venting would not affect satellite-derived total column measurements in the same manner. Difference in the spatial resolution of GOME-2 versus OMI may also limit the ability of satellites to capture the morning-to-afternoon ratio, as the lower resolution GOME-2 pixels over urban sites may dilute morning maximum values.

4.3. Satellite-derived diurnal change in NO2 column

Figure 4 shows satellite values from the morning GOME-2 instrument (4a), mid-day OMI instrument (4b), and the difference $\Delta$NO2 of these two datasets (4c). Satellite-derived $\Delta$NO2 values exhibit a high level of spatial heterogeneity (figure 4(c)), where a positive $\Delta$NO2 value (red) indicates higher VCDs in the morning; a negative $\Delta$NO2 value (blue) indicates higher VCDs in the afternoon. The same patterns shown in figure 4 at 0.25° x 0.25° are also evident when both datasets are gridded to a coarser 0.5° x 0.5° (figure S7), ensuring that the patterns observed are not due to resolution artefacts.

Boersma et al. (2008) found similar spatial heterogeneity, including a decrease in VCDs from morning to afternoon in the Northeastern US, which they attribute in part to the morning peak in rush hour traffic, and an increase in VCDs from morning to afternoon in the rural Southeast US, which they attribute to soil NOX emissions. Our results show similar patterns in the Northeastern US, as well as other US cities in the Western US including Dallas, Denver, Phoenix, Salt Lake City Seattle, and most of California. We do not observe the signal of afternoon soil NOX emissions in the southeastern US observed in the Boersma et al. (2008) comparison of OMI and SCIAMACHY with the exception of southern Texas. The difference in the
Southeast patterns may be explained by the study years, where Boersma et al. (2008) focused on August 2006 versus our analysis of June, July, and August 2007. While both summers were exceptionally hot and dry, the severe drought through the summer of 2007 in the Southeast US likely limited biogenic emissions (NOAA National Centers for Environmental Information, 2008). Differences may also be introduced by our use of GOME-2 for morning values in lieu of SCIAMACHY in Boersma et al. (2008).

To examine NO₂ column variability in greater depth, we consider a case study of Los Angeles over a single day when the level-2 GOME-2 and OMI pixels align. For this analysis, OMI data are down-sampled onto level-2 GOME-2 pixels, as shown in figure 5 over Los Angeles. Here, we consider a single urban area and single day, selecting Southern California as the region where the diurnal change in NO₂ from satellites is most pronounced over a large area. 14 June 2007 was selected as a sample date for this technique because it is a weekday where full GOME-2 coverage of Southern California coincided with near-nadir OMI pixels.

We find a strong decrease in NO₂ VCDs from morning to afternoon (positive \( \Delta \text{NO}_2 \)) directly over Los Angeles and Orange County. In contrast, there is an increase in NO₂ VCDs from morning to afternoon (negative \( \Delta \text{NO}_2 \)) over the western Mojave Desert, where the primary source of pollution in the afternoon is transport of polluted air from Los Angeles through mountain passes (Lu and Turco 1995). Morning rush hour emissions of NO₂ in the Los Angeles Basin are lofted by afternoon convection over the San Gabriel mountains (VanCuren 2015). This causes higher NO₂ levels in the Mojave Desert to occur in the afternoon, which has also been observed by flight campaigns (Neuman et al. 2012).

The AQS monitors in figure 5 highlight the spatial heterogeneity of surface NO₂ mixing ratios within a city. Directly over Los Angeles basin, there are 21 monitors represented by only four GOME-2 pixels.

Figure 4. TEMIS satellite retrievals gridded to a common 0.25° x 0.25° grid using WHIPS. (a) Average vertical column density of NO₂ detected by the GOME-2 instrument at ~09:30 for summer 2007. (b) Average vertical column density of NO₂ detected by the OMI instrument at approximately ~13:45 for summer 2007. (c) Satellite difference GOME-2-OMI for summer 2007. Red colors indicate higher vertical column densities (VCDs) of NO₂ in the morning, and blue colors indicate higher VCDs of NO₂ in the afternoon.
Although most of these monitors detect decreased mixing ratios of NO\(_2\) from morning to afternoon, the amount of this decrease varies considerably, and some monitors even show higher levels of NO\(_2\) in the afternoon. Possible explanations for afternoon enhancements of NO\(_2\) at the surface and column include enhanced emissions from industrial emissions or heavy-duty trucking during mid-day. For example, the surface monitors showing the most pronounced increase in afternoon NO\(_2\) is located at the Port of Long Beach, the largest container port in the US. Freight transport from this port is a major source of NO\(_2\) emissions for Los Angeles, due to the high emissions associated with heavy-duty diesel trucks. Trucking activity peaks in mid-day (9:00 am–3:00 pm), with about 4x more traffic on nearby highways versus morning (6:00 am–9:00 am) (Fischer et al 2006).

This case study illustrates the impact of intra-urban variability over a single day, and the ability of satellite column measurements to capture known physical and chemical processes. Unfortunately these intra-urban structures are lost when satellite data are gridded in a method appropriate for comparison (figure 4(c)).

5. Discussion and conclusion

Understanding the relationship between surface and column NO\(_2\) supports the application of satellite data to air quality and public health analysis. We examine daytime changes in the NO\(_2\) column from two polar-orbiting satellites with a focus on urban, suburban, and rural patterns in NO\(_2\). In comparing OMI and GOME-2 over sub-regions of the US, our results are consistent with Boersma et al (2008) study of diurnal change in NO\(_2\) as detected by satellites, as well as model simulations showing variability in the NO\(_2\) column, especially Fishman et al (2008) and Harkey et al (2015).

The more pronounced NO\(_2\) diurnal cycle observed at the surface in urban areas is also detected by satellites. Satellite-derived change in column NO\(_2\) from morning to afternoon is consistent in pattern and sign as surface NO\(_2\), with both data sets showing higher NO\(_2\) abundance in the morning, and the strongest diurnal change in urban areas. Both data sets suggest a 1.5–2x greater NO\(_2\) abundance in large cities in the morning versus afternoon, although magnitude of change, and agreement between surface and column measurements, varies by city.

We examine higher resolution changes within a single urban area over Los Angeles, on a day when GOME-2 and OMI level-2 pixels align. Even within this single urban area, there is a high degree of spatial heterogeneity in the daytime trend. For the case study examined, both satellite columns and surface monitors showed some positive morning-to-afternoon ratios of NO\(_2\) and some negative ratios within a single urban area and single day. Morning maxima in NO\(_2\) are consistent with expected patterns due to nighttime chemistry, morning rush hour traffic, and boundary layer mixing. Afternoon maxima in NO\(_2\) are most likely explained by transport processes and/or higher afternoon NO\(_2\) emission sources (such has freight trucking near a port).

When comparing surface concentrations with satellite data, we find \(r^2\) of 0.61 and 0.59 for GOME-2 and OMI, respectively, and nearly identical slopes (0.60 \(10^{15}\) molec./cm\(^2\)/ppb). We had expected a higher level of agreement for OMI, given the higher resolution of the instrument. The similar performance of the two instruments may be due to the high contribution (~80%) of ‘urban background’ NO\(_2\), even at hotspots (Apte et al 2017). Although both surface and column data show a similar morning-to-afternoon shift in NO\(_2\) across most of the US, the spatial \(r^2\) of \(\Delta\text{NO}_2\) for monitors versus satellite detection of this shift was only 0.25, much lower than then \(r^2\) for absolute NO\(_2\) abundance (ppb versus VCD). This \(\Delta\text{NO}_2\) was calculated with monitor data at the time of the satellite overpass; a better understanding of the time lag in daytime cycles between surface measurements...
and column abundance may provide a basis for improved comparisons of column and surface data.

This work has also highlighted two areas of research, which will become even more important with the launch of geostationary satellites to detect NO2: (1) the characterization of urban to suburban variability in surface and column NO2; (2) the use of methods to characterize errors associated with once-a-day polar-orbiting data for comparison with surface measurements, emissions inventories, and future geostationary satellites.

With respect to urban and suburban NO2 column variability, we see clear intra-urban structure in both the NO2 column and surface abundances when comparing individual pixels (figure 5). However, this structure is mostly lost when data are aggregated to a grid to facilitate larger-scale and longer-term analysis (figure 4). The challenge of identifying intra-urban variability in satellite data has been addressed from multiple perspectives, including oversampling of satellite data to a finer resolution (e.g. Goldberg et al 2017), recalculating OMI NO2 retrievals with higher resolution regional models (e.g. Laughner et al 2019), and utilizing the newer TROPOMI satellite with higher resolution (Goldberg et al 2019, Griffin et al 2019). Clarifying how satellite-derived NO2 should be interpreted with respect to surface abundance and NOx emissions will be even more important with the advent of upcoming geostationary satellites. These will provide hourly, high-resolution coverage of NO2 VCDs over wide areas, and include Tropospheric Emissions: Monitoring Pollution (TEMPO) over North America, Geostationary Environment Monitoring Spectrometer (GEMS) over East Asia and Sentinel-4 over Europe. Reconciling temporal and spatial patterns across instruments is a challenge today, and it will remain a challenge as we leverage the capabilities of new geostationary instruments with the historic record of NO2 from polar-orbiting instruments. Further, the interpretation of hourly NO2 columns from geostationary satellites will require a clear understanding of surface-to-column relationships at relatively small spatial scales.

By understanding the physical and chemical processes that control diurnal variability at the surface and column, the next generation of NO2-observing instruments will have maximum value to air quality and public health around the world.

Acknowledgments

This work was supported by the NASA Air Quality Applied Sciences Team (AQAST), the NASA Health and Air Quality Applied Sciences Team (HAQAST), as well as the NOAA Earnest F Hollings Undergraduate Scholarship Program, the Mennes Foundation Scholarship, and the Society of Exploration Geophysicists. Additional thanks to public data sources including the Air Quality System (AQS) from the U.S. Environmental Protection Agency (EPA) and the Tropospheric Emissions Monitoring Internet Service (TEMIS) from the Royal Netherlands Meteorological Institute (KNMI). We would like to thank Monica Harkey for her technical guidance and WHIPS expertise, Brad Pierce for his comments on satellite resolution, and Jacob Oberman for his guidance with WHIPS. We would also like to acknowledge Paul Block and Hiram Levy II for helpful feedback on preliminary draft, and to thank Lok Lamsal, Steve Dutcher, and Erik Bucsel for answering questions about satellite data products. We appreciate the insights of members of the Holloway Lab Group at SAGE, especially David Abel, Matilyn Bindl, Anna Bottum, Monica Harkey, Alexandra Karambelas, and Peidong Wang. Additionally, we would like to thank the anonymous reviewers who have been generous in sharing their expertise as this paper has evolved.

Data Availability

The following files are available free of charge.

The supporting information include a map of maxima and minima for NO2, a replication of figure 2 on a 0.5° x 0.5° grid, the difference between the level-3 TEMIS products for GOME- and OMI at two different grid sizes, a histogram of the number of observations made by each monitor, relative decrease from 09:30–13:45 for satellite and surface monitors, a map of correlation coefficients for each monitor, and a table of RMA slope and correlation coefficient for various time windows. (supplementary material)

Tropospheric NO2 column data is publicly available from the OMI and GOME-2 sensors from www.temis.nl/airpollution/no2.html (Boersma et al 2004, Boersma et al 2011), EPA Air Quality System (AQS) ground-level emissions can be accessed through the AQS WebApp at www.epa.gov/aqs [US Environmental Protection Agency]. Code for this paper is available on GitHub at: https://github.com/pennelise/penn-holloway-2020

The Wisconsin Horizontal Interpolation Program for Satellites (WHIPS) is available for download at: https://nelson.wisc.edu/sage/data-and-models/software.php, or through the GitHub repository: https://github.com/WHIPS-team/WHIPS.

Sources of Funding

This work was supported by the NASA Air Quality Applied Sciences Team (AQAST), the NASA Health and Air Quality Applied Sciences Team (HAQAST).

Elise Penn was supported by the NOAA Ernest F Hollings Undergraduate Scholarship Program, the Mennes Foundation Scholarship, and the Society of Exploration Geophysicists.
Competing Financial Interests

The authors declare no competing financial interest.

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