Space-based diagnosis of surface ozone sensitivity to anthropogenic emissions

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1] We present a novel capability in satellite remote sensing with implications for air pollution control strategy. We show that the ratio of formaldehyde to tropospheric nitrogen dioxide columns is an indicator of the relative sensitivity of surface ozone to emissions of nitrogen oxides (NOx ≡ NO + NO2) and volatile organic compounds (VOCs). The diagnosis from these space-based observations is highly consistent with current understanding of surface ozone chemistry based on in situ observations. The satellite-derived ratios indicate that surface ozone is more sensitive to emissions of NOx than of VOCs throughout most continental regions of the Northern Hemisphere during summer. Exceptions include Los Angeles and industrial areas of Germany. A seasonal transition occurs in the fall when surface ozone becomes less sensitive to NO2 and more sensitive to VOCs. INDEX TERMS: 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 0394 Atmospheric Composition and Structure: Instruments and techniques. Citation: Martin, R. V., A. M. Fiore, and A. Van Donkelaar (2004), Space-based diagnosis of surface ozone sensitivity to anthropogenic emissions, Geophys. Res. Lett., 31, L06120, doi:10.1029/2004GL019416.

1. Introduction

2] Surface ozone is deleterious to human health, crops, and ecosystems [National Research Council, 1991]. Uncertainty in the relation between surface ozone and its two main precursors, nitrogen oxides (NOx ≡ NO + NO2) and volatile organic compounds (VOCs) remains a primary obstacle to improving surface air quality [Sillman, 1999]. Ozone is produced in both NOx-sensitive and NOx-saturated (also known as VOC-sensitive) regimes. The design of control strategies for surface ozone has been impeded by limited observations of ozone-NOx-VOC sensitivity [Sillman, 1999]. We develop a method to use space-based observations from the Global Ozone Monitoring Experiment (GOME) [European Space Agency, 1995; Burrows et al., 1999] to characterize ozone-NOx-VOC sensitivity in surface air and apply our method to determine the spatial and temporal variation in ozone-NOx-VOC sensitivity throughout the Northern Hemisphere.

3] Surface ozone is produced by a chain reaction involving the photochemical oxidation of VOCs in the presence of NOx. The chain reaction is propagated by cycling of HOx (≡ OH + peroxy) radicals. The pathway for HOx loss is determined by the relative abundance of HOx and NOx. Ozone production tends to be either NOx-sensitive if HOx-loss occurs primarily by self reaction of peroxy radicals, or NOx-saturated if the primary HOx-loss pathway is via reaction of nitrogen dioxide (NO2) and OH [Sillman et al., 1990]. Sillman [1995] first presented the concept of using ozone-NOx-VOC indicators to diagnose NOx-sensitive versus NOx-saturated conditions, and showed that the ratio of formaldehyde to total reactive nitrogen is such an indicator. A related ratio can be retrieved from the GOME satellite instrument, specifically the ratio of the HCHO to the tropospheric NO2 column.

2. Evaluation of the HCHO/NO2 Column Ratio as an Ozone-NOx-VOC Indicator

4] We use the GEOS-CHEM global 3-D model of ozone-NOx-VOC chemistry [Bey et al., 2001], version 4.16 [Martin et al., 2002a], to evaluate the quality of the HCHO/NO2 column ratio as an indicator of NOx-sensitive versus NOx-saturated conditions. We analyze results from three simulations previously described by Fiore et al. [2002]: a standard simulation, a simulation in which anthropogenic VOC emissions are reduced by 50%, and a simulation in which anthropogenic NOx emissions are reduced by 50%. The simulations use assimilated observations of meteorological fields from NASA GEOS-1 with 20 vertical levels and a 4° × 5° horizontal resolution. All simulations are spun up for 10 months to remove the effects of initial conditions. We present results for May–November.

5] Figure 1 shows the calculated response in monthly-mean afternoon surface ozone over polluted regions to a prescribed change in emissions as a function of the tropospheric HCHO/NO2 column ratio. The transition between NOx-sensitive and NOx-saturated regimes occurs for a HCHO/NO2 ratio of about 1. HCHO/NO2 ratios above 1 tend to be NOx-sensitive as indicated by the decrease in surface ozone for the simulation with reduced NOx emissions. HCHO/NO2 ratios below 1 reflect NOx-saturated conditions; reductions in NOx emissions increase surface ozone while reductions in VOC emissions decrease surface ozone.

6] Why does the HCHO/NO2 column ratio function effectively as an indicator of surface ozone-NOx-VOC sensitivity? First, the bulk of the tropospheric NO2 and
HCHO columns over polluted regions is within the mixed layer [Ladsta¨tter-Weißenmayer et al., 2003]. Second, the division between NOx-sensitive and NOx-saturated regimes generally follows a constant reactivity-weighted VOC/NOx ratio [Chameides et al., 1992], a ratio closely associated to the HCHO/NO2 ratio. Third, the HCHO/NO2 column ratio largely reflects the ratio of HOx to NOx sources near the surface. HCHO is positively correlated with the source of HOx in polluted environments [Martínez et al., 2003], and tropospheric NO2 is closely related to NOx emissions [Leue et al., 2001; Martin et al., 2003]. The ratio of the HOx source to the NOx source determines NOx-VOC sensitivity, and the transition from NOx-sensitive to NOx-saturated regimes occurs at a specific ratio over a range of conditions [Kleinman, 1991; Jacob et al., 1995].

3. Space-Based Observations of Tropospheric NO2 and HCHO

[7] The nadir-viewing GOME satellite instrument has provided the capability for continuous global monitoring of tropospheric NO2 and HCHO columns through observation of solar backscatter since 1995. Global coverage is achieved every 3 days after 43 orbits with a typical surface spatial resolution of 40 km by 320 km, sufficient to resolve the regional scale of ozone pollution episodes [Logan, 1989]. Observations at northern mid-latitudes occur between 10:30 AM–11:30 AM local solar time. Our numerical model calculations show that the HCHO/NO2 ratio exhibits little diurnal variation during daytime; the ratio at 11 AM is typically within 5% of the ratio in the afternoon, so the thresholds identified in Figure 1 are applicable to GOME observations.

[8] The GOME retrievals are described in Martin et al. [2002b, 2003] for tropospheric NO2 and in Chance et al. [2000] and Abbot et al. [2003] for HCHO. These retrievals include the air mass factor (AMF) formulation of Palmer et al. [2001] and radiative transfer calculations with the Linearized Discrete Ordinate Radiative Transfer (LIDORT) model developed by Spurr [2002]. Observation scenes are excluded when local cloud cover retrieved from GOME [Kurosu et al., 1999] exceeds 40%.

[9] Errors in the GOME HCHO/NO2 ratio are reduced by compensating effects. The largest source of error in individual trace gas retrievals is from the AMF calculation due to surface reflectivity, clouds, aerosols, and trace gas profile conditions due to a decline in isoprene and HOx that is expected from theory [Kleinman, 1991], in situ [Jacob et al., 1995], and models [Liang et al., 1998]. The seasonal decline in isoprene and HOx is also associated with a seasonal decline in the HCHO column to values below the GOME detection limit.

[10] Figure 2 shows the GOME HCHO/NO2 column ratio over North America, Europe, and East Asia during May to November 1997. Ratios greater than one, indicating NOx-sensitive conditions over most suburban and rural areas during summer, are consistent with analysis of in situ observations at rural sites of North America by Trainer et al. [1993]. The decrease in the HCHO/NO2 ratio to less than one over the eastern United States during fall shows the seasonal transition from NOx-sensitive to NOx-saturated conditions due to a decline in isoprene and HOx that is expected from theory [Kleinman, 1991], in situ [Jacob et al., 1995], and models [Liang et al., 1998]. The seasonal decline in isoprene and HOx is also associated with a seasonal decline in the HCHO column to values below the GOME detection limit.

[11] GOME shows that major urban and industrial centers such as Los Angeles tend to be NOx-saturated, but transition to a NOx-sensitive regime downwind, consistent with model calculations by Milford et al. [1989]. The initial NOx supply greatly exceeds the HOx supply in major urban areas, but a switch from NOx-saturated to NOx-sensitive conditions occurs from the combined effects of dilution and HOx production downwind, as the HOx supply surpasses the initial NOx source [Kleinman, 1991, 1994].

[12] Data over Europe are sparse due to HCHO columns below the GOME detection limit. London is near NOx-saturation, consistent with calculations of Derwent et al.
In situ measurements [Staffelbach et al., 1997] support GOME observations that southern Switzerland is NOx-sensitive during summer. GOME reveals that industrial Germany is NOx-saturated throughout the year, and that a transition from NOx-sensitive to NOx-saturated conditions occurs over the Po Valley from September to October.

[13] GOME HCHO/NO2 ratios greater than one during summer over eastern China, Korea, and Japan indicate NOx-sensitive conditions. However, there is a clear transition to NOx-saturated conditions in the northern regions during fall. The resulting gradient during October and November of NOx-sensitive conditions in rural southern China, but NOx-saturated conditions elsewhere, is consistent with photochemical model calculations of Luo et al. [2000]. This transition is of particular interest since episodes of enhanced ozone concentrations are frequent in the fall, and may be reducing crop yields [Chameides et al., 1999].

Figure 2. Monthly mean tropospheric HCHO/NO2 column ratio retrieved from the GOME satellite instrument for North America, Europe, and East Asia. Ratios greater than 1 tend to be NOx-sensitive. Ratios below 1 tend to be NOx-saturated. White areas indicate remote regions (observed tropospheric NO2 columns less than $2.5 \times 10^{15}$ molecules cm$^{-2}$) and regions below the HCHO detection limit of $4 \times 10^{15}$ molecules cm$^{-2}$.
Results presented here suggest that nascent capabilities in satellite remote sensing are of sufficient quality to contribute to air pollution management by providing guidance on the spatial and temporal sensitivity of surface ozone to reductions of NOx and VOC emissions. Such observations also provide a critical test of air quality models used to develop emission controls. These observational capabilities will be enhanced by the next generation of instruments, such as the SCIAMACHY and OMI satellite instruments, which feature higher spatial resolution that should resolve transitions between urban and suburban environments. Future work should systematically examine the relationship of these space-based column indicators with high-resolution simulations and in situ indicators.

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