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Comparison of weekly cycle of NO_2 satellite retrievals and NO_x emission inventories for the continental United States

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[1] Spatially resolved weekly NO_2 variations are obtained from 2003 to 2005 Scanning Imaging Absorption Spectrometer for Atmospheric Cartography (SCIAMACHY) tropospheric NO_2 columns for three different types of regions: urban, rural, and rural-point (rural with significant electricity generation unit (EGU) emissions). Regions are compared for magnitudes and weekly profiles. Rural regions do not show any weekly pattern, whereas urban areas show a distinct decrease on the weekends. Rural regions with EGUs show a slight decrease on Sundays. When compared with estimated mobile and stationary nitrogen oxides (NO_x) emissions from the year 2004 for seven cities, the satellite data have greater variation during weekdays (Monday–Friday). Overall comparisons show that SCIAMACHY-derived NO_2 correlate well with estimated NO_x emissions for urban and rural but less for rural-point regions.

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1. Introduction

[2] Nitrogen oxides ($NO_x = NO + NO_2$) play a key role in the chemistry of the troposphere and come mainly from fossil fuel combustion, biomass burning, soil release, oxidation of atmospheric ammonia, lightning, transport of NO_x from stratosphere and aircraft emissions. NO_x emission impacts include increasing tropospheric ozone, particulate matter, acid deposition and nutrient enrichment.

[3] U.S. anthropogenic NO_x emissions mainly come from transportation (55%), fuel combustion for electricity generation (22%) and industrial activities (14%) (http://www.epa.gov/ttn/chief/trends/). Recent control programs, including the 1998 NO_x State Implementation Plan (SIP) Call and the Clean Air Interstate Rule (CAIR) target power industry NO_x emissions to reduce ozone formation [*Environmental Protection Agency (EPA)*, 2005a] and estimated 2004 point source emissions in the United States decreased to 55% of 1990 levels even though total electricity production is increased [*EPA*, 2005b]. *Kim et al.* [2006] recently showed that space-based instruments also observed these declining regional NO_x levels between 1999 and 2005.

[4] The relationship between NO_x emissions and tropospheric NO_2 columns, which are closely related because of the short lifetime of NO_x, were investigated by several researchers. Most of the earlier studies have used models for this relationship [*Jaegle et al.*, 2005; *Kim et al.*, 2006; *Leue et al.*, 2001; *Martin et al.*, 2003; *Müller and Stavrakou*, 2005]. *Toenges-Schuller et al.* [2006] showed high correlations between tropospheric NO_2 columns and anthropogenic NO_x emissions. Observations from different satellite platforms were also compared (late morning SCIAMACHY and early afternoon OMI) to have more insight on the diurnal variation in different NO_x sources [*Boersma et al.*, 2008].

[5] In a previous study of the weekly cycle of NO_2 using a remote sensing instrument, *Beirle et al.* [2003] used the Global Ozone Monitoring Experiment (GOME) instrument and observed a distinct Sunday minimum for all countries with a Christian tradition. That study mainly focused the eastern United States and Los Angeles. The spatial resolution of GOME is 320×40 km^2, which is approximately 7 times larger than SCIAMACHY's spatial resolution.

[6] The aim of this study is to distinguish the relative effects of the urban NO_x sources which are dominantly mobile source-related (both on-road and off-road) and exhibit weekly variation from other sources like fuel combustion for electricity generation using satellite data and to compare these observed weekly and spatial variations with estimated emissions. Such comparison can help to assess the accuracy and consistency of current estimates. Comparing estimated emissions from relatively well-characterized areas with tropospheric columns obtained from satellites can also provide a better understanding of how to use satellite data in regions where emission estimates are unavailable or highly uncertain.

2. Methods

2.1. NO_2 Satellite Retrievals

[7] The Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) instrument

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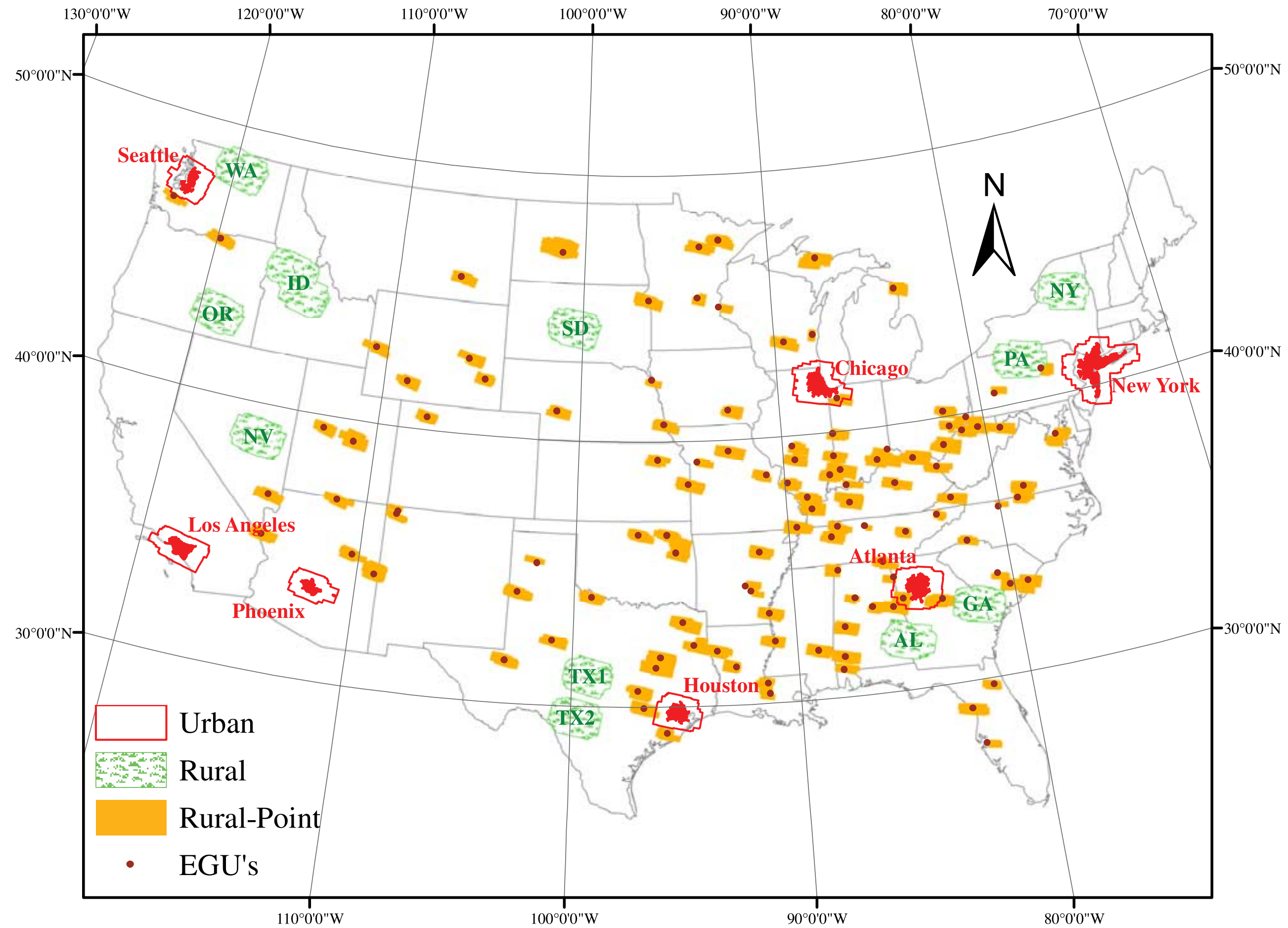

Figure 1. Urban, rural, and rural-point areas selected.

onboard the ENVISAT satellite measures atmospheric NO_2 columns through observation of global backscatter [*Bovensmann et al.*, 1999]. ENVISAT was launched in March 2002 into a Sun-synchronous orbit with an equator crossing time of 1000 local time (LT) and a typical U.S. observation time of 1030 LT. The SCIAMACHY instrument has a typical spatial resolution of 30 km along track by 60 km across track in the nadir view with a global coverage over 6 days. Algorithms used for retrieval of tropospheric NO_2 columns from SCIAMACHY data, along with uncertainty estimates used in this study (2003–2005), are obtained from *Martin et al.* [2002, 2003, 2006]. Satellite retrievals depend on normalized a priori NO_2 profiles which are usually obtained from chemical transport models. Several studies compared these profiles with aircraft measurements [*Bucsela et al.*, 2008; *Martin et al.*, 2004, 2006] and found minor differences.

[8] Three different region types (“urban,” “rural” and “rural-point”; that is, rural areas with a large-scale electricity generating unit (EGU)) are selected (Figure 1) in order to investigate how weekly patterns in NO_2 levels vary in different areas, and how they compare to emission estimates in urban and rural areas. Seven major cities in the United States (urban) are investigated (Atlanta, Chicago, Houston, Los Angeles, New York, Phoenix and Seattle). These cities are selected because of their large populations and related NO_x emissions. They also represent different topographical and meteorological conditions, both of which will affect ambient NO_2 concentrations and, possibly, satellite retrievals. All these cities, except Seattle, are in nonattainment of the 2008 U.S. EPA 8-h ozone standard of 0.075 ppmv. Eleven rural areas (rural) are selected close to these seven cities where there are neither significant point NO_x sources nor urbanized land (Figure 1). Additional rural areas (rural-point) were identified that contain no urbanized land but do contain one or more large EGUs emitting more than 0.1% of total NO_x emissions from all listed facilities. Urbanized area definitions used are from Census2000 (http://www.census.gov/geo/www/cob/ua2000.html) and NO_x emission information for major EGUs are obtained from Environmental Protection Agency (EPA) (http://www.epa.gov/air/data).

[9] SCIAMACHY pixels that intersect the selected areas at times with a cloud radiance fraction less than 0.5 are used for calculating the averaged weekly profiles of selected areas (Figure 1). SCIAMACHY maps the United States in the late mornings; therefore averaged pixels actually represent morning averages. Weekly profiles of these regions are obtained by averaging the pixels by day of the week. The averages are also normalized seasonally for areas in order to eliminate the effect of seasonal variation of NO_2 lifetime on weekly profiles. Normalization is performed by averaging intersected pixels for each season for each location and then dividing them with the seasonal average for that location,

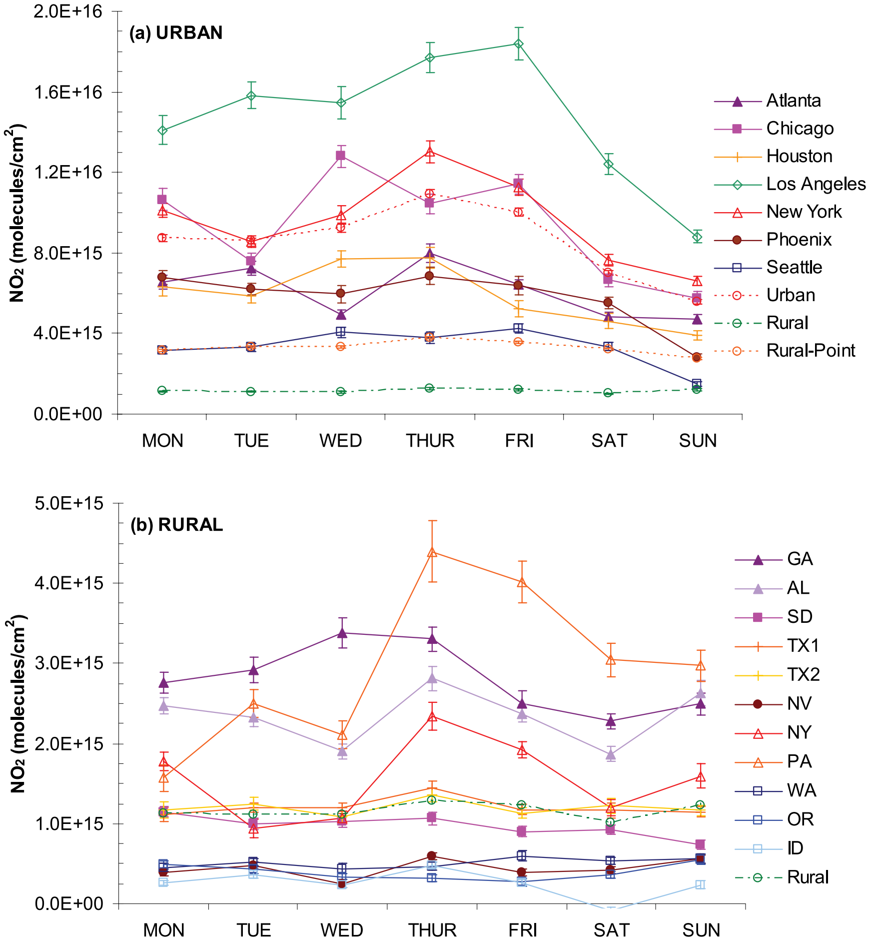

Figure 2. Averaged weekly profile of SCIAMACHY retrievals with uncertainties for (a) urban and (b) rural areas. Solid lines are the overall averages for indicated area types. (Rural areas are labeled by the abbreviation of the state they fall inside and color coded similarly with closest urban area for comparison.)

over all days of the week. Individual pixel uncertainties are propagated to calculate overall uncertainty.

[10] The SCIAMACHY nadir footprint is approximately 30 × 60 km^2, so when a pixel intersects an urban area, the pixel includes less urbanized land as well. However, as evidenced by emission estimates, urban emissions dominate over the extended region. One complication that could rise is the case where there is a large-scale EGU near an urban area, which could obscure the urban analyses. This is the case in Atlanta, and is further investigated in the results and discussion part.

2.2. NO_x Emissions

[11] The 2004 emission inventory (12 months) used in this study is estimated by applying growth and control factors to a 2002 base inventory (VISTAS) [*MACTEC*, 2005]. Growth factors are calculated using the Economic Growth Analysis System (EGAS) Version 4.0 and the control factors are obtained from EPA for the existing federal control strategies which were in place in 2004. In addition, hourly actual NO_x emissions in 2004 are obtained from the continuous emissions monitoring (CEM) database (EPA Clean Air Markets, http://camddataandmaps.epa.gov/gdm). Mobile emissions here are the sum of on-road and nonroad emissions; stationary emissions are the sum of area and point source emissions and total emissions are the sum of mobile, stationary and biogenic emissions. Gridded hourly emissions are prepared using the Sparse Matrix Operator Kernel for Emissions (SMOKE) [*Houyoux and Vukovich*, 1999].

[12] NO_x emissions are summed using the intersected area ratios (urban area inside the grid divided by total area of the grid) for each grid cell, 36 km × 36 km, that is part of the 7 cities (urban) and the 11 rural areas (rural). Daily totals for each city and rural area are averaged for each weekday to obtain weekly emission profiles for 2004. Emissions for grid cells that intersect with pixels for rural-point are also processed similarly.

[13] Although about 90% of the NO_x emissions are emitted as NO, in the presence of O_3 or other oxidants, NO quickly oxidizes to NO_2 in the atmosphere. Measurements show that in the lower troposphere, most of the NO_x is in the form of NO_2 during the day [*Bradshaw et al.*, 1999; *Martin et al.*, 2002], except near major NO_x sources, so NO_x emission estimates and SCIAMACHY NO_2 total tropospheric columns are comparable, recognizing that

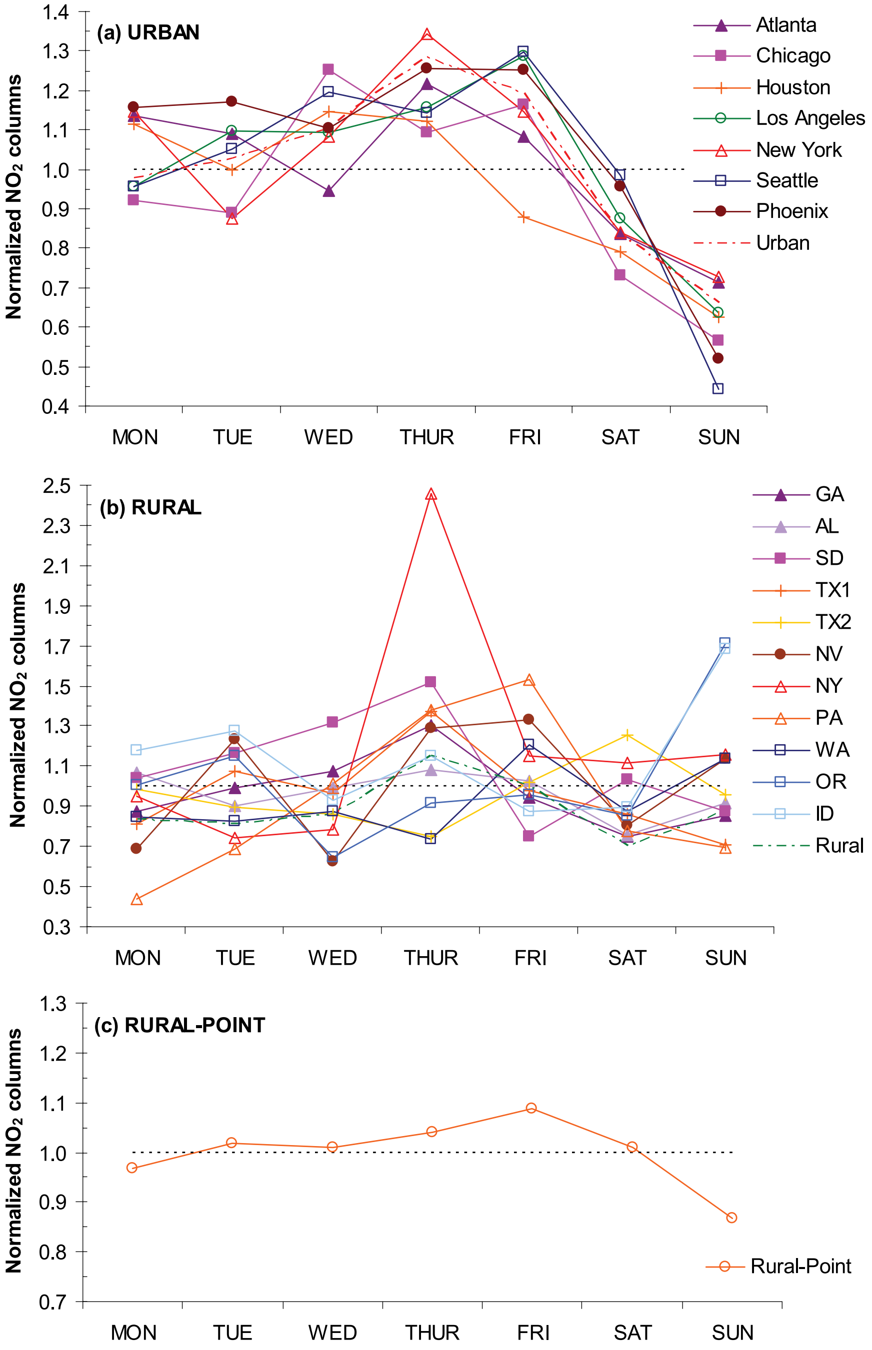

Figure 3. Seasonally normalized weekly profile of SCIAMACHY retrievals for (a) urban, (b) rural, and (c) rural-point areas. Dashed lines are the overall averages for all urban and rural areas. (High THUR value for rural area NY results from low number of scans with high columns available for fall season for that day.)

some NO_x will remain as NO, and a fraction will be oxidized to other products. Averaged NO_2 columns obtained from SCIAMACHY are multiplied by total pixel areas and converted to moles to obtain total NO_2 burden for each area to compare with NO_x emissions (moles/d). Total amounts calculated for each area by this method are directly related to the scanned urban area. The city with highest NO_2 columnar abundance is Los Angeles (molec/cm^2), while New York (moles) has the greatest total mass of NO_2 over the area investigated. This is consistent with the estimated total daily emissions.

3. Results and Discussion

[14] Averaged satellite observations of the individual cities clearly show a weekend decrease, whereas the rural areas without EGUs show no significant change during the weekends (Table 1 and Figure 2). The seasonally normalized weekly profiles for urban regions also show the Sunday

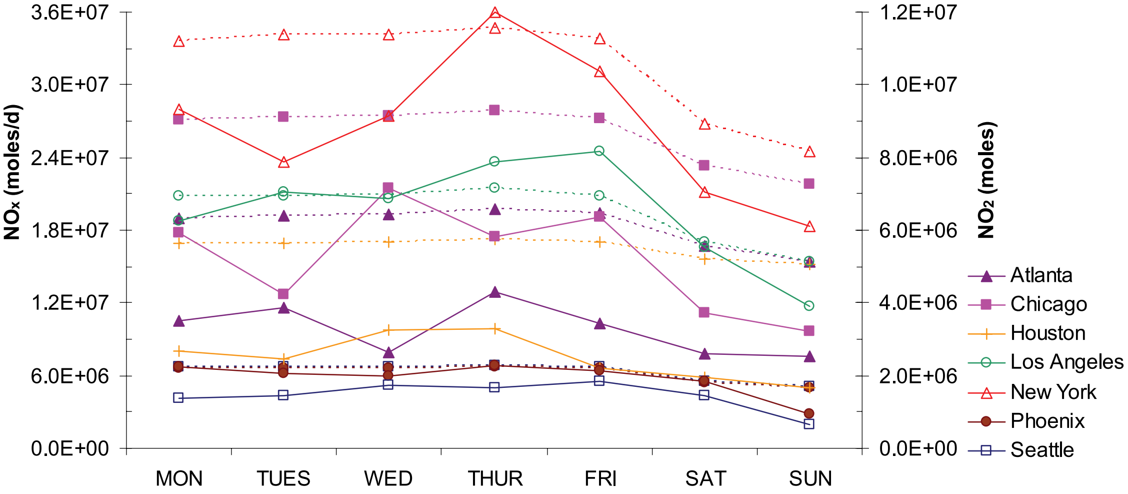

Figure 4. Comparison of SCIAMACHY-derived NO_2 with total NO_x emissions for selected cities (dashed lines, emission-derived NO_x; solid lines, SCIAMACHY-derived NO_2 burden).

minimum clearly (Figure 3). The minimum for rural-point is on Sunday as it is for cities, though the difference versus weekdays is small. New York has the highest and Seattle has the lowest net tropospheric NO_2 columns (area × NO_2 column density) among the seven cities (Figure 4). New York, Los Angeles, Chicago, Houston, Atlanta and Seattle show changes during the weekdays, whereas Phoenix does not show significant variation. All cities have minimums on Sunday. Atlanta, Chicago, Houston, Los Angeles, New York, Phoenix and Seattle, respectively show 28%, 47%, 42%, 46%, 37%, 56%, and 59% decreases on Sundays when compared with mean weekday values (Table 1). Rural regions with power plants show an average 20% decrease on Sunday. Days with maximum and minimum NO_2 for Los Angeles (Friday–Sunday), Chicago (Wednesday–Sunday) and New York (Thursday–Sunday) are consistent with previous work of *Beirle et al.* [2003] using GOME NO_2 retrievals. Normalized weekly profiles for Los Angeles and Chicago are very similar to those of *Beirle et al.* [2003], but weekly profiles obtained by GOME from New York lacks the day-to-day variation that SCIAMACHY observes in our study. Last, Chicago has a significantly lower normalized Sunday column, but Los Angeles and New York have slightly higher normalized Sunday columns than those of *Beirle et al.* [2003]. All cities except Seattle have significantly higher NO_2 columns than averaged rural and rural-point regions (Figure 2). All the urban regions have significantly higher tropospheric NO_2 columns than nearby rural regions, as expected.

[15] Even though lightning emissions are prepared for this episode [*Kaynak et al.*, 2008], they are not included in total emissions for this comparison. Unlike anthropogenic emissions which exist primarily as NO_2 in the lower troposphere, lightning NO_x in the free troposphere exists primarily as NO. Furthermore, lightning NO_x has a distinctive seasonal pattern with very intense activity in summer months. Including lightning emissions for one year may overestimate their effect on the emission inventory which would not be appropriate for comparison with 3-year averaged NO_2 retrievals. Further, lightning is associated with cloud cover, and one expects a decrease in the probability of capture its effects on clear days.

[16] A number of factors impact comparing SCIAMACHY retrievals and emission estimates: (1) uncertainty in the SCIAMACHY retrievals; (2) seasonal variation of NO_x lifetime, (3) 12-month averaging of the emissions, and (4) limited conversion of NO to NO_2 (or significant conversion of NO_2 to other species). Even if individual pixel uncertainties are high, as the number of pixels averaged increases, the uncertainty of the mean decreases for weekly variation. Averaging of the pixels over a year decreases scatter, but seasonal variation of NO_2 lifetime and partitioning of NO_2 in NO_x emissions, particularly near sources in winter and transport or conversion of NO_2 to HNO_3 and PAN is a concern. As such, the available 3-year data set is averaged to obtain statistically significant results for each area and normalized to remove seasonal variations. Emission inventories do not change significantly on a day-to-day basis (Table 2), except weekends and holidays, minimizing the need for long-term averaging.

[17] Another important issue is that in the areas studied, SCIAMACHY total tropospheric NO_2 columns are morning averages but NO_x sources continue to emit during the day, and atmospheric chemistry will deplete NO_x. This, and the limited NO_x lifetimes, would suggest that the amount of NO_x emitted daily in each airshed is likely to be more than that found by integrating SCIAMACHY pixels over the area. Total daily NO_x emissions in each city are always higher than column integrated NO_2 obtained from SCIAMACHY retrievals for urban areas (Figure 4). Observed NO_2 to estimated NO_x emissions ratios range between 0.11 (Houston Sunday) to 0.39 (Los Angeles Friday) for individual days and between 0.18 (Atlanta) to 0.33 (Los Angeles) on average. As discussed previously, a part of the reason for this can be due to transport out of the region used for comparison, conversion of NO_x to HNO_3 and PAN or a fraction of the emissions remaining as NO. Unlike SCIAMACHY retrievals, estimated total emissions for urban regions do not show significant differences between individual weekdays, but show decreases during the weekends (Table 2 and Figure 4). The decrease in each city reflects the contribution of different NO_x sources.

Table 1. Average, Standard Deviation, Uncertainty, and Count of Selected SCIAMACHY Retrievals in Each Region for 3 Years, 2003–2005[a]

Region		Mon	Tue	Wed	Thu	Fri	Sat	Sun	Total	Weekend	Weekdays
Atlanta	average	6.56	7.22	4.95	8.00	6.44	4.84	4.72	6.02	4.78	6.56
	std dev	4.01	5.51	3.24	5.89	4.06	3.04	3.73	4.39	3.42	4.64
	uncertainty	0.36	0.34	0.24	0.47	0.25	0.23	0.22	0.11	0.16	0.14
	count	74	113	98	71	157	103	118	734	221	513
Chicago	average	10.65	7.58	12.80	10.45	11.41	6.64	5.77	9.64	6.22	10.80
	std dev	7.61	5.75	8.31	8.45	9.73	4.89	5.00	7.97	4.95	8.45
	uncertainty	0.54	0.40	0.55	0.48	0.47	0.32	0.31	0.18	0.23	0.23
	count	93	91	125	124	162	105	97	797	202	595
Houston	average	6.29	5.86	7.70	7.77	5.23	4.62	3.91	6.11	4.16	6.76
	std dev	4.67	5.04	6.38	5.60	3.87	3.39	2.72	5.10	2.98	5.48
	uncertainty	0.44	0.37	0.39	0.50	0.38	0.37	0.23	0.15	0.20	0.19
	count	51	72	108	59	48	39	72	449	111	338
Los Angeles	average	14.10	15.83	15.45	17.70	18.41	12.41	8.82	14.34	10.27	16.45
	std dev	10.63	11.17	10.24	12.39	12.23	7.79	6.69	10.70	7.36	11.53
	uncertainty	0.73	0.64	0.79	0.75	0.81	0.54	0.33	0.24	0.29	0.33
	count	93	147	87	132	118	120	178	875	298	577
New York	average	10.14	8.55	9.91	13.02	11.26	7.64	6.61	9.48	7.11	10.47
	std dev	8.43	6.40	7.81	12.03	9.14	5.76	5.70	8.27	5.75	8.93
	uncertainty	0.35	0.29	0.41	0.55	0.42	0.27	0.25	0.14	0.18	0.18
	count	232	218	150	167	190	196	204	1357	400	957
Phoenix	average	6.78	6.21	5.96	6.85	6.39	5.52	2.83	5.71	4.20	6.48
	std dev	6.39	3.93	4.20	5.74	4.74	4.07	2.16	4.80	3.53	5.17
	uncertainty	0.36	0.29	0.41	0.43	0.45	0.28	0.15	0.13	0.16	0.17
	count	106	105	50	71	50	99	96	577	195	382
Seattle	average	3.15	3.32	4.05	3.82	4.26	3.35	1.51	3.31	2.37	3.71
	std dev	2.23	2.53	3.23	4.42	3.60	2.89	2.02	3.15	2.62	3.27
	uncertainty	0.17	0.21	0.26	0.28	0.25	0.21	0.12	0.08	0.12	0.10
	count	88	68	66	69	82	73	83	529	156	373
Urban	average	8.76	8.60	9.23	10.94	10.03	7.01	5.56	8.52	6.23	9.49
	std dev	7.94	7.71	7.93	10.30	9.28	5.87	5.36	8.06	5.65	8.71
	uncertainty	0.17	0.16	0.19	0.23	0.19	0.14	0.11	0.06	0.09	0.08
	count	737	814	684	693	807	735	848	5318	1583	3735
Rural-point	average	3.14	3.35	3.36	3.79	3.57	3.24	2.76	3.30	2.99	3.43
	std dev	2.65	2.80	2.62	3.36	2.89	2.76	2.16	2.76	2.48	2.87
	uncertainty	0.06	0.06	0.06	0.08	0.07	0.06	0.05	0.02	0.04	0.03
	count	846	796	840	699	789	795	871	5636	1666	3970
Rural	average	1.13	1.12	1.11	1.28	1.23	1.01	1.22	1.15	1.10	1.17
	std dev	1.42	1.54	1.74	1.83	1.84	1.64	1.85	1.70	1.74	1.69
	uncertainty	0.02	0.02	0.03	0.03	0.03	0.02	0.03	0.01	0.02	0.01
	count	1253	1274	1224	1294	1320	1376	1123	8864	2499	6365

[a] Unit is $\times 10^{15}$ molecules/cm^2; std dev is the standard deviation of the averaged pixels and is driven by seasonal variation and orbital changes in the location of the satellite footprint; uncertainty is the uncertainty of the mean calculated from individual uncertainties $((\Sigma u_i^2)^{0.5}/N)$. Random uncertainties are used here since major sources of systematic uncertainty, such as surface reflectivity and clouds, are unlikely to systematically affect day-of-week variation.

Table 2. Average and Standard Deviation of Daily Total NO_x Emissions Averaged for 2004[a]

Region		Mon	Tue	Wed	Thu	Fri	Sat	Sun	Total
Atlanta	average	19.01	19.22	19.30	19.73	19.42	16.70	15.37	18.40
	std dev	2.58	2.33	2.32	2.34	2.34	2.00	1.75	2.72
Chicago	average	27.11	27.31	27.39	27.85	27.22	23.33	21.77	26.01
	std dev	2.34	1.44	1.23	1.71	1.82	1.58	1.48	2.79
Houston	average	16.95	16.97	17.05	17.20	16.98	15.66	15.17	16.57
	std dev	0.76	0.69	0.30	0.54	0.81	0.25	0.48	0.94
Los Angeles	average	20.77	20.86	20.92	21.47	20.84	17.00	15.36	19.61
	std dev	1.80	1.16	0.46	1.25	1.66	0.40	0.64	2.51
New York	average	33.63	34.18	34.13	34.70	33.79	26.78	24.56	31.69
	std dev	3.91	2.67	2.47	3.10	3.30	2.89	2.62	4.89
Phoenix	average	6.57	6.64	6.65	6.72	6.59	5.43	5.03	6.24
	std dev	0.63	0.55	0.47	0.59	0.68	0.39	0.42	0.84
Seattle	average	6.68	6.71	6.73	6.87	6.71	5.54	5.13	6.34
	std dev	0.58	0.40	0.25	0.41	0.56	0.12	0.23	0.76
Urban	average	18.67	18.84	18.88	19.22	18.79	15.78	14.63	17.84
	std dev	9.46	9.48	9.45	9.67	9.44	7.64	7.04	9.09

[a] Unit is $\times 10^6$ moles/d.

Table 3. Sunday to Mean Weekday Percentage for Total, Stationary, and Mobile NO_x Emissions With SCIAMACHY-Derived NO_2 Columns

	NO_x Emissions			NO_2 Retrievals
City	TOTAL	STATIONARY	MOBILE	SCIAMACHY
Atlanta	80 ± 4	90 ± 9	71 ± 3	72 ± 4
Chicago	80 ± 4	94 ± 5	69 ± 3	53 ± 3
Houston	89 ± 3	98 ± 3	82 ± 3	58 ± 4
Los Angeles	73 ± 4	94 ± 4	69 ± 4	54 ± 2
New York	72 ± 5	87 ± 8	64 ± 4	63 ± 3
Phoenix	76 ± 4	89 ± 4	65 ± 4	44 ± 3
Seattle	76 ± 4	98 ± 5	70 ± 4	41 ± 3

[18] Given the observed daily NO_2 variations, it is clear that the dominant emission category is not stationary sources as they lack the weekly variation observed or that there is more variation in the stationary sources than is estimated. SCIAMACHY total NO_2 does not correlate to stationary emissions sources except Atlanta which has six EGUs inside its urban area. Additionally, all cities except Atlanta and New York have very low Sunday to mean weekday percentages in NO_2 retrievals which is not seen in NO_x emission estimates (Table 3 and Figure 3).

[19] Assuming weekly mobile emission profiles are representative, using Sunday to mean weekday percentages obtained from SCIAMACHY NO_2 retrievals and NO_x emission inventories (Table 3), one can approximate the contribution of mobile sources to total NO_x emissions for each city with the following formula:

$$R_{SCIAMACHY} = A_{STAT} \times R_{STAT} + A_{MOB} \times R_{MOB} + A_{NAT} \times 1.00, \quad (1)$$

where

$R_{SCIAMACHY}$	ratio of Sunday to mean weekday (Monday–Friday) NO_2 total columns;
A_{STAT}	fractional contribution to the mean weekday values by stationary NO_x emissions;
R_{STAT}	ratio of Sunday to mean weekday stationary NO_x emissions;
A_{MOB}	fractional contribution to the mean weekday values by mobile NO_x emissions;
R_{MOB}	ratio of Sunday to mean weekday mobile NO_x emissions;
A_{NAT}	fractional contribution to the mean weekday values by natural NO_x emissions.

Estimated emissions suggest that natural emissions are negligible in urban areas, which then can be removed from equation (1). Further, this means $A_{STAT} = 1 - A_{MOB}$, so equation (1) can be solved for A_{MOB} using observed $R_{SCIAMACHY}$ and R_{MOB} and R_{STAT} from the inventory. This leads to all A_{MOB} values being greater than 100% which indicates current mobile emission contributions and weekly profiles cannot explain the observed reductions on Sunday in SCIAMACHY NO_2 retrievals. Following are the possible reasons: (1) Mobile emissions contribute more than shown in the current inventories, (2) diurnal profiles are different than assumed in the inventories, and (3) Day-to-day variation is not correctly represented in emission inventories. *Harley et al.* [2005] observed the timing of gasoline engine emissions is shifted with a single broad peak in the afternoon on weekends. SCIAMACHY's typical U.S. observation time (1030 LT) combined with that shift may result in biased low satellite observations on Sundays compared to the rest of week. However, the Sunday to mean weekday ratios are significantly lower in satellite observations in all of the cities except New York and Atlanta. EGU NO_x data are actual hourly information. Mobile NO_x emissions, on the other hand, are ultimately based upon the Highway Performance Monitoring System (HPMS) traffic counts, though the data collected from HPMS is smoothed before being applied in estimating on-road emissions. The diurnal and daily changes (within a week) of mobile emissions in the inventory hence were obtained by averaging the sparse raw data first statewide and then across road types [*MACTEC*, 2005].

[20] SCIAMACHY total NO_2 correlates reasonably well with estimated NO_x emissions for urban areas (Figure 5a). One interesting result is how New York weekday (Monday–Friday) SCIAMACHY total NO_2 varies greatly while the estimated total or mobile emissions are almost constant. New York has the highest number of pixels available from SCIAMACHY (1357; Table 1), so representativeness should not be an issue in this case. This finding suggests that there is much more variation in New York NO_x emissions than captured in current emission inventories, though it is difficult to identify reasons. The lower value on Monday could be due to less NO_x carryover from Sunday. However, Tuesday is lower still. Nearby rural levels do not indicate regional transport is a reason. For all cities, the nearby rural pixels show much less NO_x.

[21] Estimated NO_x emissions and SCIAMACHY-derived total NO_2 for the eleven individual rural regions are also investigated and overall no significant decrease in the weekend is observed. ID and SD are the only rural areas showing around 30% decrease in total NO_2 on Sundays. Rural areas are usually dominated by natural emissions which do not have a weekly pattern, therefore it is expected that they could obscure any weekly cycle in anthropogenic emissions. Individual rural regions showed a similar correlation between total NO_2 and estimated NO_x emission as was found for urban regions (Figure 5b). Total observed NO_2 to total NO_x emissions ratios range between 0.30 (GA) to 2.87 (NV) on average. SCIAMACHY is actually seeing much more NO_2 compared to NO_x emissions in NV, WA and PA than in other rural regions (Figure 5b). Possible reasons could be (1) transport of NO_2 from another region (e.g., for PA, transport from the Ohio River Valley), (2) errors in retrieval of NO_2 and/or (3) missing emission sources in the inventory (e.g., for NV, underestimation of emissions coming from remote natural gas and oil pumps).

[22] For the 117 EGUs in the rural-point areas, the observed total NO_2 from SCIAMACHY is, on average, 5 times smaller than the estimated total NO_x emissions and the correlation is worse than urban and rural regions (Figure 6). On the other hand, this is surprising because emissions from EGUs are directly measured, so their emissions are known best. Additionally, there are some cases where the estimated NO_x emissions and SCIAMACHY-derived total NO_2 contradict each other (very high estimated NO_x emissions/very low SCIAMACHY total NO_2 column or vice versa). Given the large point source emissions, incomplete transformation

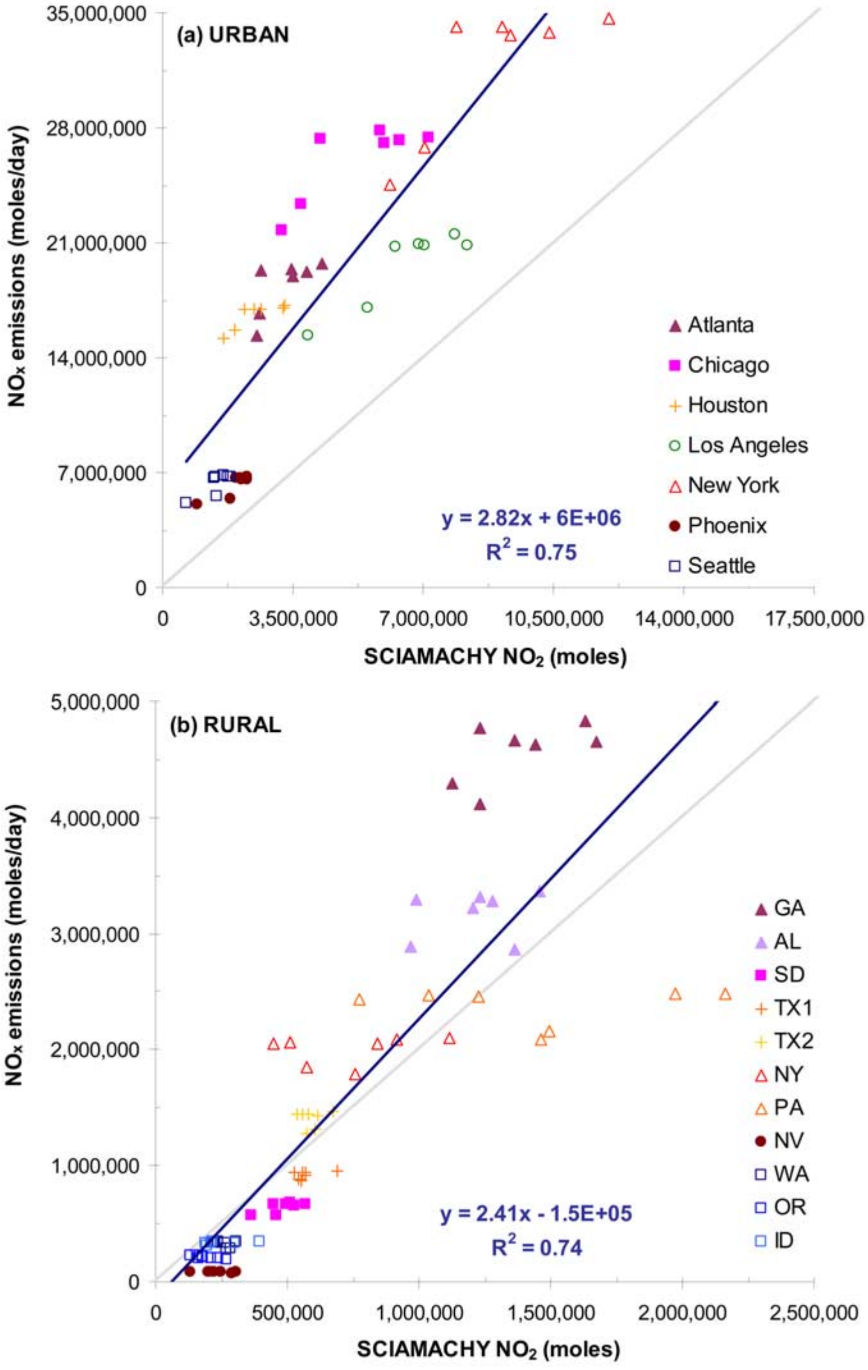

Figure 5. SCIAMACHY-derived NO_2 versus total NO_x emissions for (a) urban and (b) rural areas (each series contains seven data points, each one representing the average NO_2 for each day of the week; dashed line represents 2:1).

of NO to NO_2 and transport of NO_x from the chosen areas could be possible reasons. Removing the rural-point regions having less than 10 scans available did not significantly alter the findings. The total columns derived by a regional air quality model using these emissions resulted in a higher correlation ($R^2 = 0.52$), but still significantly lower than other region types (B. Kaynak et al., manuscript in preparation, 2009). This brings in the question how well SCIAMACHY retrievals can be used to quantify emissions from large, single sources, or if it is necessary to use a model of the plume transformation to conduct the comparison.

4. Conclusions

[23] NO_2 columns from SCIAMACHY during a 3-year period are analyzed for three different types of regions: urban, rural and rural-point. Total atmospheric burdens are compared to estimated NO_x emissions for the regions, both to identify how well the weekly variations agree as well as

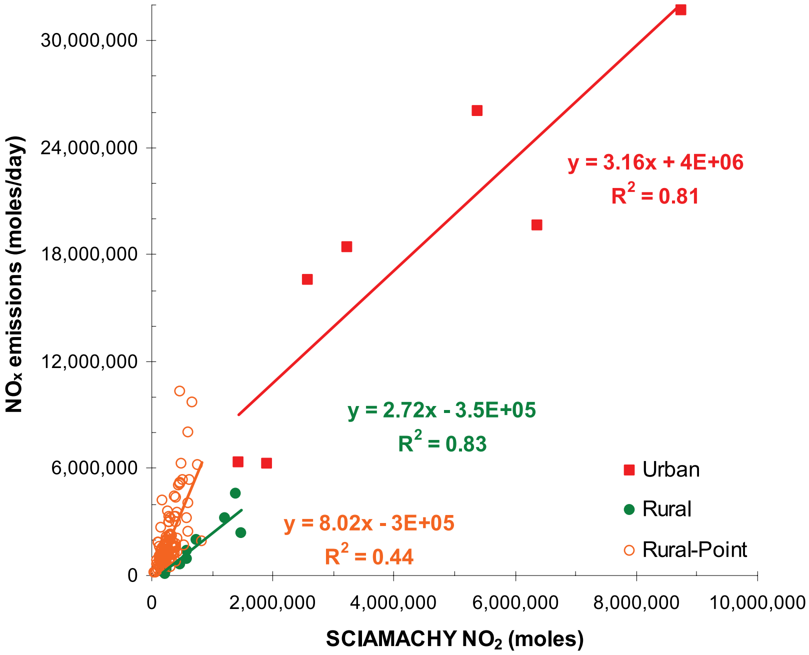

Figure 6. SCIAMACHY-derived NO_2 versus total NO_x emissions for individual urban, rural, and rural-point regions.

total mass. The existence of weekly patterns in urban areas (selected seven cities) is obvious, whereas rural regions do not show any weekly pattern. Rural-point regions show a minor decrease on Sundays (20% compared to mean weekday). Phoenix weekly profile does not show much variation during the week, in contrast with other urban areas. All cities have minimums on Sunday. Estimated total NO_x emissions are lower on the weekends, but do not show the day-to-day variation for weekdays as SCIAMACHY NO_2. This is particularly true for New York. Further, for all cities, there is a greater reduction in observed NO_2 on weekends than found in the inventory.

[24] Total NO_2 burden, which is the average NO_2 column multiplied by the area, over the cities derived from SCIAMACHY total tropospheric columns are always less than the total estimated NO_x emissions by a factor of 2.6 (Los Angeles) to 5.6 (Atlanta). A ratio greater than 1 is expected owing to SCIAMACHY scanning over the areas in the morning before a majority of the NO_x is emitted for the day, and not all the NO_x will be NO_2 due to chemical reactions. SCIAMACHY-derived total NO_2 for rural-point is on average 5 times smaller than estimated total NO_x emissions and correlation is lower than individual urban and rural regions (Figure 6). This goes against expectations as major point sources are viewed as having their emissions well characterized owing to the use of continuous emissions monitoring.

[25] Using Sunday to mean weekday percentages obtained from SCIAMACHY NO_2 retrievals and NO_x emission inventories, the contribution of mobile sources to total NO_x emissions for each city are also calculated. Results suggest that the fractions of emissions from mobile sources are greater than current estimates or that day-to-day variability in mobile sources is underestimated.

[26] This work suggests that current inventories lack day-to-day variability and satellites can provide information to improve the emission inventories. However, it also highlights the need for a model to relate satellite observations to estimate emissions.

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