Anthropogenic NO_2 in the Atmosphere: Estimates of the Column Content and Radiative Forcing

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Introduction

The work summarizes the different methodical aspects, firstly, the use of atmosphere optical depths presented in Aerosol Robotic Network (AERONET) data for NO_2 column retrievals, and, secondly, its radiative forcing calculated as difference between integral solar fluxes absorbed in the atmosphere with and without NO_2 under given air mass or the sun zenith angle.

Our NO_2 retrieval assumes the simultaneous derivation of a few total NO_2 contents together with parameters of several aerosol models. Each model includes two or three fractions. In turn, the each fraction has own size distribution of particles and the spectral dependence of complex refraction coefficient. The estimated parameters are the numbers of fraction particles in the vertical column of atmosphere. The numbers are determined by least-squares method for each aerosol model together with NO_2 column. Selection of appropriate model and corresponding NO_2 column is performed by the minimum of root-mean-square discrepancy between calculated and measure optical depths determined for all seven solar photometer aerosol channels. In that way, we performed calculations of NO_2 column for a few months of measurements by means of several AERONET photometers situated from Alaska to the equator (including Moscow), and received good agreement with the aprioristic and parallel data.

The developed radiative transfer (RT) method assumes the calculation of solar fluxes vertical profiles integrated in the range of $0.2 \div 5.0$ μm for subsequent evaluation of solar absorption in atmosphere. In addition to the selective gaseous absorption, it also treats the NO_2 continuum absorption by 0.4 μm, aerosol scattering and absorption, Rayleigh scattering and spectral dependence on underlying surface albedo.

Total Content of NO_2 in the Atmosphere

From the review of the literary data over total content of NO_2 and its concentrations in the atmosphere, the preliminary regional types with different NO_2 column (Q_{NO2}) have been determined and presented in Table 1, 1 DU = 2.7×10^{16} molecules/cm^2. The NO_2 optical depths at 380 nm as well as NO_2 radiative forcing for summer (Sum.) and winter (Wint.) conditions by atmosphere air mass $m_A = 2$ are also shown in the table. The NO_2 forcing F_{NO2} was calculated using the online tool developed at KURCHATOV INSTITUTE and available for remote users from the site: www1.imp.kiae.ru/csif

Table 1. Types of Regions in Dependence on Column NO_2

#	Region type	Description and Examples	Q_{NO2}, DU	τ_{NO2} (380 nm)	F_{NO2}, W/m^2 Sum.	Wint.
1	Oceanic and Remote - continental	Without own sources, no any NO_2 advection due to transfer within troposphere (East Pacific; Northern Caucasia; Oklahoma, the US)	0.1 ÷ 0.4	0.002 ÷ 0.007	0.5 ÷ 1.9	0.7 ÷ 2.6
2	Continental	Without own anthropogenic sources, some NO_2 advection from remote industrial areas; (Northern Europe; some parts of Russia)	0.4 ÷ 0.8	0.007 ÷ 0.014	1.9 ÷ 3.8	2.6 ÷ 5.2
3	Suburban	Without own powerful anthropogenic sources of NO_2, but a site is nearby the air plume of city or big industrial area (Northern part of West Siberia, nearby Norilsk steel mill)	0.8 ÷ 3.0	0.014 ÷ 0.051	3.8 ÷ 13.4	5.2 ÷ 18.5
4	Urban	There are own powerful sources of NO_2 (Moscow; Hamilton)	1 ÷ 15	0.017 ÷ 0.253	4.7 ÷ 58.7	6.5 ÷ 78.6

Different Components of AERONET Data Errors

It is necessary to verify the possibility of detecting actual values of NO_2 column, measured with Cimel instrument, against the background of instrumental and methodical errors. There are different kinds of errors in Cimel measurements and their processing. The most of them were considered in well-known publications of AERONET group (e.g., Holben et al. 1998: Remote Sensing Environ. 66, 1, 1-16). Below we give their brief characteristics from the point of view of NO_2 retrieval:

The Cimel measurements errors $\Delta_m = 0.002 \div 0.009$ (corresponding root-mean-square error $\sigma_r \approx 0.001 \div 0.003$) due to the *instrumental noise* and the *atmospheric instability*.

Residual calibration errors $\Delta_{cal} = 0.01 \div 0.02$ after second calibration, strong correlation between channels; in fact, possible small residual constant errors for measurements during the day ÷ month intervals.

Additional calibration errors for 340 and 380 nm due to the difference between solar background for the conditions of calibration on Mauna Loa and measurements at the most of other sites: $0 \div 5 \times 10^{-3}$ in dependence on optical aerosol thickness and air masses.

The errors associated with the account of *Rayleigh scattering* and *O_3 absorption* linearly dependent in different Cimel channels. They are presented in Table 2.

Table 2. *Methodical* Errors (root mean square [rms]) in Optical Depths for Cimel Aerosol Channels

	λ, nm						
Type of Error	340	380	440	500	675	870	1020
Rayleigh × 103	7.1	4.6	2.0	1.4	0.4	0.1	0.0
Ozone × 103	1.5	0.0	1.4	1.9	1.6	0.0	0.0

Negative biases in optical depths caused by forward scattering in the Cimel field of View for standard aerosol models are presented in Table 3 for all aerosol channels.

Table 3. Underestimate of τ_a in Cimel Channels because of *Forward Scattering* (m_A = 2)

Aerosol Models[(a)]	**τa**				**λ, nm**			
		340	380	440	500	675	870	1020
	0.10	0.003	0.002	0.002	0.002	0.001	0.001	0.001
Maritime	0.15	0.004	0.004	0.003	0.003	0.002	0.001	0.001
	0.20	0.006	0.005	0.005	0.004	0.003	0.002	0.001
	0.1	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Continental	0.3	0.003	0.003	0.003	0.004	0.004	0.004	0.004
	0.5	0.007	0.007	0.007	0.007	0.008	0.008	0.008
	0.3	0.069	0.063	0.056	0.050	0.038	0.028	0.024
Dust	0.5	0.134	0.124	0.111	0.100	0.076	0.058	0.048
	0.7	0.218	0.203	0.183	0.165	0.127	0.099	0.083
	1.0	0.381	0.358	0.328	0.299	0.237	0.188	0.160

(a) A preliminary cloudless standard atmosphere for radiation computation, 1986: WCP-112, WMO/TD No. 24

The Description of NO_2 Retrieval Method

The derivation of a few total NO_2 contents Q_j is proposed to make together with parameters of several aerosol models. Each model includes two or three fractions. In turn, each fraction has own size distribution of particles and the spectral dependence of complex refraction coefficient. The estimated

parameters are the numbers w_k, where $k = 1 \div 3$, of fraction particles in the vertical column of atmosphere. The w_k are determined by least-squares method for each j-th model together with Q_j. The negative values are equated with zero.

Selection of appropriate model with number j_0 and corresponding Q_{j0} is fulfilled by the minimum of root-mean-square discrepancy σ_j calculated for all 7 Cimel aerosol channels and normalized to one freedom degree of the aerosol model.

The total extinction coefficient of each fraction together with other characteristics of scattering are calculated a priori by the Mie theory. For exception of negative biases due to forward scattered radiation the extinction coefficient are decreased by multiplication to the factor accounting the part of radiation scattered into FOV.

Accuracy of the Retrieval Algorithm

It is convenient to estimate the accuracy of the retrieval algorithm by mathematical modeling of its work using typical aerosol models and fixed Q_{NO2} contents. The above models of maritime and continental aerosol from WCP-112, 1986 have been taken as independent models. The correlation coefficient among the residual calibration errors has been taken $R_{cor} = 0.8$. The number of random realizations equals to $N_t = 500$. The results of modeling are shown in the Table 4, where m_Q- mean systematic bias; σ_Q-rms deviation relative to the given NO_2 content Q_{NO2}; σ - rms of the model from.

Additionally, for variants with $\sigma_r = 0.003$, $\Delta_{cal} = 0.01$, the possible rms errors of NO_2 retrieval because of residual calibration errors were calculated as $s_m = \sqrt{\sigma_Q^2 - \hat{\sigma}_Q^2}$, where $\hat{\sigma}_Q$ - rms of Q_{NO2} for corresponding variants with $\sigma_r = 0.003$, $\Delta = 0.0$.

Table 4. Modeling of NO_2 retrieval Under Different Conditions of Measurements

Aerosol Models	τa	Q_{NO2} DU	I σ_r =0.001; Δ_{cal} =0.00			II σ_r =0.003; Δ_{cal} =0.00			III σ_r =0.003; Δ_{cal} =0.01			
			m_Q DU	σ_Q DU	σ ×103	m_Q DU	σ_Q DU	σ ×103	m_Q DU	σ_Q DU	σ ×103	s_m DU
Maritime	0.05	0.0	0.03	0.07	1.7	0.14	0.22	4.7	0.21	0.34	7.2	0.26
		0.2	-0.04	0.13	1.0	0.05	0.29	3.8	0.11	0.41	6.2	0.29
		0.5	-0.05	0.14	0.9	-0.03	0.37	3.0	0.00	0.50	5.2	0.34
		1.0	-0.05	0.14	0.9	-0.06	0.42	2.8	0.00	0.59	4.6	0.41
	0.1	0.0	0.02	0.05	2.1	0.12	0.21	4.8	0.20	0.33	7.1	0.25
		0.2	-0.08	0.11	1.2	0.02	0.28	3.8	0.10	0.40	6.1	0.29
		0.5	-0.10	0.14	1.0	-0.07	0.36	3.0	-0.02	0.49	5.1	0.33
		1.0	-0.10	0.14	1.0	-0.11	0.42	2.8	-0.11	0.59	4.4	0.41
	0.2	0.0	0.01	0.03	3.0	0.09	0.18	5.4	0.16	0.30	7.5	0.24

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Aerosol Models	τa	Q_{NO2} DU	I σ_r =0.001; Δ_{cal} =0.00			II σ_r =0.003; Δ_{cal} =0.00			III σ_r =0.003; Δ_{cal} =0.01			
			m_Q DU	σ_Q DU	σ ×103	m_Q DU	σ_Q DU	σ ×103	m_Q DU	σ_Q DU	σ ×103	s_m DU
		0.2	-0.14	0.08	1.6	-0.03	0.25	4.4	0.05	0.37	6.4	0.27
		0.5	-0.20	0.14	1.2	-0.15	0.34	3.4	-0.08	0.47	5.3	0.32
		1.0	-0.20	0.15	1.2	-0.21	0.42	2.9	-0.19	0.58	4.4	0.40
	0.3	0.0	0.01	0.02	3.9	0.06	0.15	6.3	0.13	0.27	8.2	0.22
		0.2	-0.17	0.06	2.1	-0.08	0.21	5.1	0.00	0.34	7.1	0.27
		0.5	-0.29	0.14	1.5	-0.22	0.31	3.8	-0.15	0.44	5.8	0.31
		1.0	-0.30	0.15	1.5	-0.31	0.41	3.1	-0.29	0.57	4.7	0.40
Continental	0.1	0.2	-0.04	0.12	1.1	0.01	0.27	3.9	0.07	0.38	6.2	0.27
		0.5	-0.08	0.17	1.0	-0.08	0.36	3.1	-0.05	0.48	5.2	0.32
		1.0	-0.08	0.17	1.0	-0.14	0.43	2.9	-0.14	0.58	4.5	0.39
		2.0	-0.08	0.17	1.0	-0.14	0.43	2.9	-0.17	0.63	4.4	0.46
	0.2	0.2	-0.01	0.12	1.3	0.01	0.26	3.8	0.06	0.36	6.3	0.25
		0.5	-0.14	0.21	1.2	-0.11	0.35	3.2	-0.06	0.45	5.2	0.28
		1.0	-0.14	0.21	1.2	-0.19	0.44	3.0	-0.19	0.58	4.6	0.38
		2.0	-0.14	0.21	1.2	-0.20	0.45	2.9	-0.25	0.67	4.4	0.50
	0.3	0.2	0.06	0.13	1.6	-0.03	0.25	3.8	0.07	0.35	6.2	0.24
		0.5	-0.16	0.24	1.5	-0.10	0.34	3.2	-0.07	0.44	5.2	0.28
		1.0	-0.21	0.28	1.4	-0.23	0.46	3.1	-0.22	0.58	4.6	0.35
		2.0	-0.21	0.28	1.4	-0.25	0.50	3.0	-0.30	0.70	4.5	0.49
	0.5	0.2	0.17	0.14	2.2	0.10	0.28	4.0	0.09	0.35	6.2	0.21
		0.5	0.06	0.23	2.2	-0.05	0.34	3.6	-0.04	0.43	5.4	0.26
		1.0	-0.39	0.43	2.1	-0.28	0.48	3.4	-0.24	0.57	4.9	0.31
		2.0	-0.39	0.43	2.1	-0.37	0.59	3.4	-0.39	0.75	4.8	0.46

Retrieval of Total NO_2 Content at Different AERONET Sites

Determination of NO_2 was performed for 20 months at nine different AERONET sites (Table 5). The data of the second level of AERONET data were included in processing.

Table 5. Monthly Statistics of the NO_2 Retrieval at Different AERONET Sites

Site	Latitude Longitude	Year	Month	NT	$\sigma \times 10^3$	$\langle\tau a\rangle$	$\langle Q_{NO2}\rangle$, DU	$Max(Q_{NO2})$, DU	$R_{NO2,\tau}$
Barrow	71.31 -156.66	1999	July	241	5.3	0.088	0.85	1.8	0.4
GSFC	39.03	2001	March	560	3.3	0.113	1.37	3.0	0.3
	-76.88	2001	Sept.	569	3.0	0.138	0.44	2.1	0.4
Mauna	19.54 -155.58	1999	January	594	3.0	0.014	0.34	1.3	-0.1
		1999	May	933	3.0	0.029	0.26	1.1	-0.2
		2000	January	763	2.3	0.013	0.19	0.8	0.0
		2000	July	1039	3.5	0.017	0.13	0.7	0.0
Mexico	19.33	2001	May	293	6.4	0.414	1.48	5.9	0.5
	-99.18	2001	Sept.	157	12.0	0.367	0.94	7.2	0.7
Moscow	37.51 55.70	2001	Sept.	414	4.0	0.214	1.57	6.2	0.6
Nauru	-0.52	2000	January	398	5.8	0.080	0.16	0.7	0.1
	166.92	2000	March	362	5.0	0.088	0.10	0.5	-0.2
		2001	June	348	6.3	0.073	0.20	0.8	-0.3
Skukuza	-24.99 31.59	2000	August	587	6.8	0.264	0.50	2.2	0.6
Cart	36.61	1997	Sept.	294	5.0	0.105	0.28	1.5	0.3
Site	-97.41	1998	Sept.	389	6.9	0.296	0.70	2.6	0.7
		1999	Sept.	302	3.7	0.171	0.34	1.6	0.4
		2000	Sept.	779	4.3	0.184	0.32	1.8	0.4
		2001	Sept.	569	3.0	0.138	0.44	2.1	0.4
Tenerife	28.03 -16.63	1997	July	394	4.6	0.190	0.45	1.6	-0.4

where

N_T	=	the total number of measurements;
σ	=	rms discrepancy between the computational model and AERONET data;
Q_{NO2}	=	NO_2 total content (i.e., NO_2 column);
$<Q_{NO2}>$	=	mean of Q_{NO2}
σ_{NO2}	=	ms deviation of the estimate for single Q_{NO2} (including natural changeability + retrieval errors);
$Max(Q_{NO2})$,	=	maximal Q_{NO2} for the month;
$<\tau_a>$	=	the calculated aerosol depth for 500 nm by the used models;
$R_{NO2,\tau}$	=	the correlation coefficient between Q_{NO2} and τ_a.

As well as in the previous case of calculations with the fixed aerosol models, discrepancy σ in optical thickness with measurements is small. The discrepancy σ exceeds 0.01 only for Mexico (September 2001), where the reason was in four doubtful sequential readings on September 3 with $m_A \approx 3.0 \div 3.5$ and $\tau_a > 0.8$ when the useful optical signals in UV channels were very weak. After removal of the readings $\sigma=0.008$.

There are no contradictions with the literary data (see Table 1) by NO_2 content and its maximal values. Regularity has been clearly traced: if the point of measurements: the further from industrial areas, the smaller NO_2 content. Mexico and Moscow stand out against a background of other points, mainly, by the maximal values. The suburb of Washington (GSFC) takes an intermediate place.

Comparison of AERONET NO_2 Retrievals with Evaluated NO_2 Total Content from Surface Concentration Measurements in Moscow

Figure 1 shows daily mean NO_2 column from AERONET retrievals and NO_2 values from surface measurements (recalculated into total content) for Moscow conditions.

It can be clearly seen that the NO_2 column amounts recovered from the MSU MO measurements are close in shape and range to the column NO_2 estimated from the ecological monitoring data and do not go beyond the spatial variability of column NO_2 for a large city. It should be taken into account that the MO MSU is located 400 and 100 m away from Lomonosov and Michurin Avenues, respectively, which are highways with heavy traffic. Their weekly traffic-volume cycles, with the maxima (on September 14 and 21) corresponding to Fridays and with the minima (on September 16 and 23) corresponding to Sundays, can easily be seen in Curve 1. Similar pronounced temporal cycles are exhibited in the data from ecological monitoring sites located near other highways and the city center.

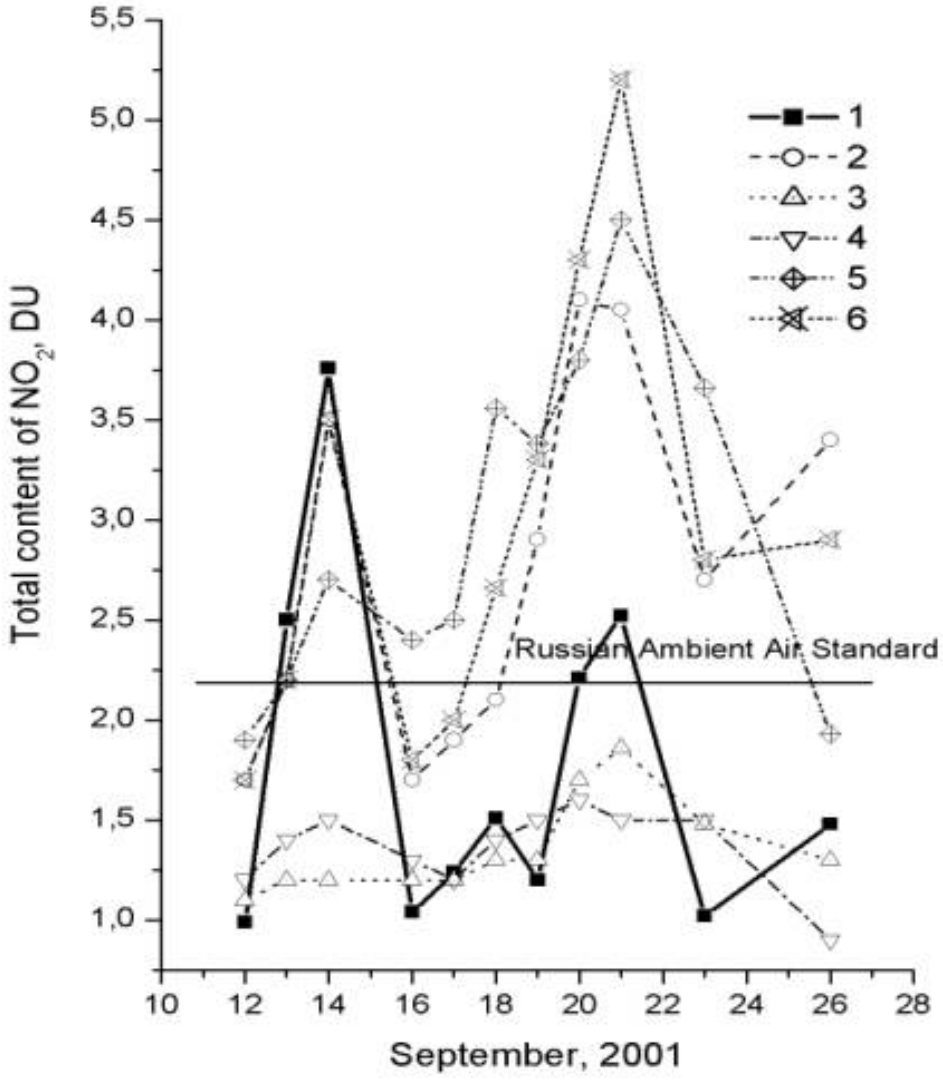

Figure 1. Comparison of AERONET NO_2 retrievals with data from ecological monitoring 1 – AERONET data from MO MSU site; 2÷6 – sites of ecological monitoring in different Moscow regions (horizontal line specifies the NO_2 content corresponding to NO_2 Russian Ambient Air Standard = 40μg/m^3).

Conclusion

Based on the obtained results one can see the possibility of AERONET direct Sun observations application for NO_2 retrievals in the atmosphere. The optical instability of the atmosphere directly at the moment of measurements causes the main error of the NO_2 evaluation. It contains random and systematic components. The root-mean square deviation of random component lies within 0.2÷0.6 DU in dependence on aerosol loading and NO_2 content itself in the atmosphere. With case number increasing this error is effectively averaged, and for most typical cases, its contribution to the average daily NO_2 estimates does not exceed 0.1 DU. The systematic component also depends on the level of

NO_2 and aerosol content in the atmosphere. In considered conditions, this bias does not exceed 0.4 DU, it may be taken into account by mean dependence.

It is fairly certain that potentially the greatest source of the errors in NO_2 estimations maybe the uncertainty of working devices calibrations. It results in variations of NO_2 estimates from 0 up to 0.5 DU depending on the time of measurements between calibrations and filters quality. For this reason, if it is necessary, one can choose the AERONET stations with small difference between data of level 1.5 (only one calibration) and level 2 (two calibrations). For example, for Moscow in September 2001, such difference in monthly averaged NO_2 column was less than 0.03 DU.

The proposed method allows taking tropospheric NO_2 into account. Using the developed software for computations of integral solar fluxes (www1.imp.kiae.ru/csif), we could estimate the NO_2 solar radiative forcing for the typical (1- 5 DU) diapason of NO_2 column in urban regions. For high sun positions, its values (5-25 W/m^2) are of similar magnitudes to the measurements performed by Solomon et al. 1999 (JGR, v.104, 12047-12058) during the storm in Colorado. These results in combination with the estimates presented in Table 1 allow believe that the impacts of anthropogenic NO_2 on regional climate changes will be significant and must be taken into account by modern forecast models.

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