

**BRIEF  
COMMUNICATIONS**

## Comment on the Paper “Determination of NO<sub>2</sub> Column Amounts from AERONET Data” by A.N. Rublev *et al.*¶

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It was with some concern that we read the communication by Rublev *et al.* (2003) on the possibility of measuring NO<sub>2</sub> abundance using broadband AERONET sunphotometry. While it has long been recognized that NO<sub>2</sub> presents a potential contamination problem in the derivation of aerosol parameters (Shaw, 1976; O’Neill and Miller, 1984; Tomasi *et al.*, 1985; Schroeder and Davies, 1987), it is decidedly a novel idea to suggest that the source of contamination could itself be extracted from the contaminated signal (Tomasi *et al.* actually did report on an algorithm similar in concept to that proposed by Rublev *et al.* but only as a means of providing a calibration correction for aerosol sunphotometry.). It has, in fact, been our more modest hope that secondary spectral measurements, short of those which could be obtained using a dedicated NO<sub>2</sub> spectrometer (see Brewer *et al.*, 1973, for example), could be employed to correct for the minor NO<sub>2</sub> contribution in aerosol measurements but certainly not as a primary monitoring technique as this article suggests. However, even auxiliary measurements would require, at the very least, a minimum of three bands which are spectrally and radiometrically optimized to exploit the high resolution UV/blue absorption structure of NO<sub>2</sub>. It is our contention that the broadband algorithm proposed by these authors cannot, in general, provide the quality of NO<sub>2</sub> columnar concentrations necessary for scientific

use, because one cannot satisfactorily discriminate the small NO<sub>2</sub> signal from the larger aerosol attenuation background.

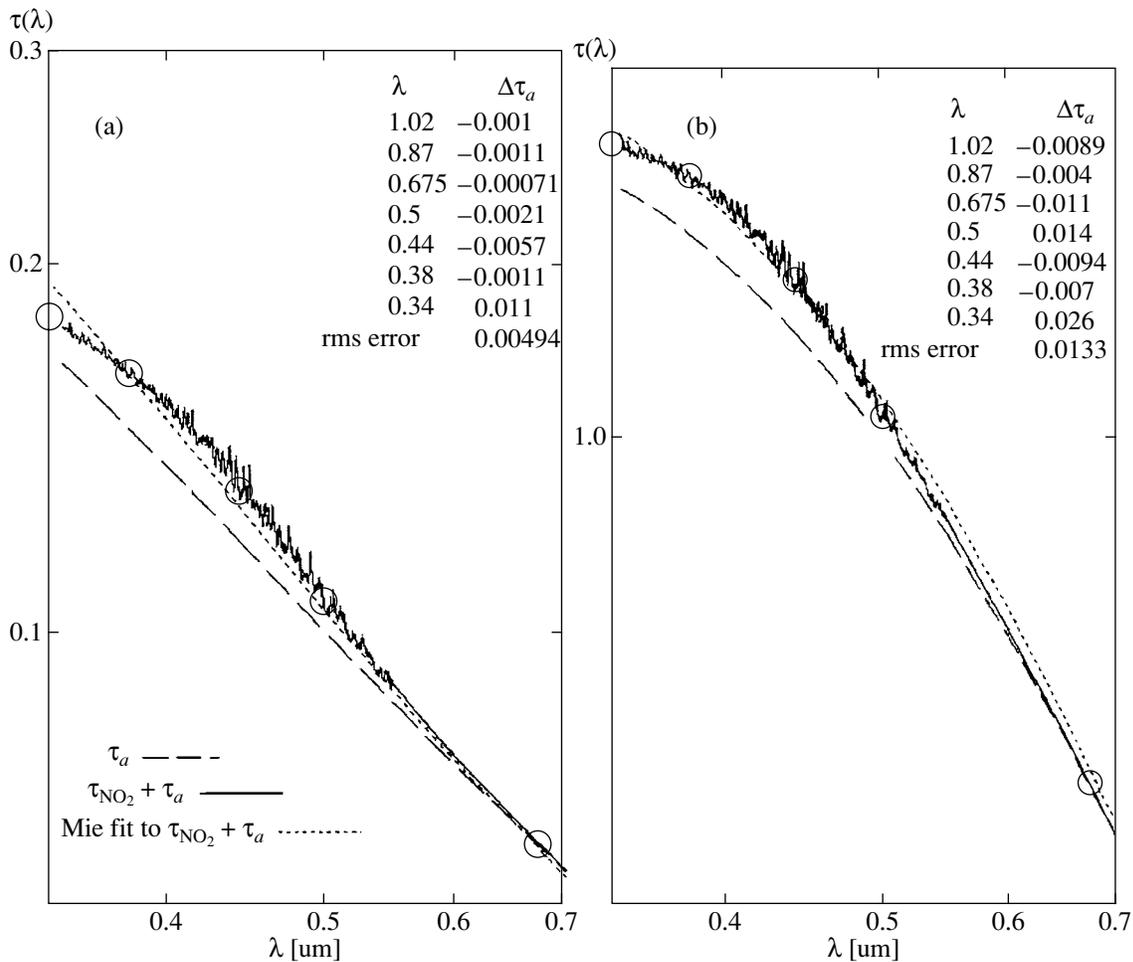
The main problem, which the authors do not address, is that broadband NO<sub>2</sub> absorption in the UV/blue spectral region mimics the presence of enhanced small particle attenuation (Shaw, 1976; Schroeder and Davies, 1987). Figure 1 illustrates this phenomenon for Mie calculations applied to two representative fine mode size distributions inspired by AERONET inversion archives (as well as a fixed coarse mode). The dashed curves represent a “true” aerosol spectrum while the solid curves represent the sum of the aerosol spectrum and the NO<sub>2</sub> absorption spectrum (given by Harder *et al.*, 1997; supplemented by Luther, 1976, for those weakly absorbing regions not covered by the Harder table). The NO<sub>2</sub> abundances in our examples were selected in order to reasonably represent extreme conditions (all greater, for example, than the monthly mean maximums reported by Velders *et al.*, 2001, in his global analysis of GOME data). The dotted curve is a manual informal attempt to find a slightly adjusted particle size distribution of smaller geometric mean and higher refractive index (real part) that approximately fits the aerosol + NO<sub>2</sub> spectrum. (Better fits could be obtained by fully exploiting all degrees of freedom, including the spectral dependence of the

Parameters employed to generate the Mie curves of Figure 1

Case	Fine mode “true”			Fine mode imitator			Coarse mode		
	$r_N$	$\sigma$	$m$	$r_N$	$\sigma$	$m$	$r_N$	$\sigma$	$m$
a	0.043	1.8	1.43–.0035i	0.035	1.8	1.43–0.0035i	0.5	2.5	1.5–0i
b	0.1326	1.5	1.5–0i* 1.8–0.6i	0.12	1.5	1.55–0i* 1.8–0.6i	0.5	2.5	1.5–0i

\* Inner shell of black carbon and an outer shell of non-absorptive dry aerosol (mass ratio of 6% black carbon).

¶ This article was submitted by the authors in English.



**Fig. 1.** Mie computations for two cases of  $\text{NO}_2$  contamination; (a) relatively clear small particle case with a 500 nm aerosol optical depth ( $\tau_a$ ) of 0.1 and a  $\text{NO}_2$  abundance of 1 DU (1 matm), (b) fairly thick large-particle smoke with a “true”  $\tau_a$  of 1.0 and a  $\text{NO}_2$  abundance of 5 DU. The dashed curve is the “true”  $\tau_a$  while the solid curve is the  $\tau_a + \tau_{\text{NO}_2}$  optical depth. The dotted (imitator) curve is the manual fit to the  $\tau_a + \tau_{\text{NO}_2}$  curve achieved by slightly decreasing the geometric mean and/or slightly increasing the real part of the refractive index relative to the original  $\tau_a$  curve (as well as a small change to the integrated number density of aerosols). The open circles simulate CIMEL measurements.  $\Delta\tau_a$  are the computed residuals between the “imitator” curve and the  $\tau_{\text{NO}_2} + \tau_a$  curve across the CIMEL passbands. Table 1 gives the physical and optical parameters employed to generate the curves of Fig. 1. (For simplicity we employed log-normal curves of geometric radius  $r_N$  and geometric standard deviation of  $\sigma$ .) The coarse mode optical depth was taken as 0.03 at 500 nm.

refractive index and the width of the distribution.) At the larger particle end of the fine mode spectrum (in the neighborhood of the anomalous diffraction peak of Mie scattering) one can even reproduce the downward trend of the  $\text{NO}_2$  absorption curve (cf the larger fine mode case of Fig. 1b). It is clear that the level of agreement achieved (with residuals all close to or within the nominal AERONET error of 0.01 to 0.02 for operational field instruments) renders any hope of extracting  $\text{NO}_2$  to be marginal at best.

While we cannot categorically exclude the optimistic predictions that “averaging over time intervals from one to several hours” will improve one’s ability to sys-

tematically detect variability in  $\text{NO}_2$  abundance (or the underlying general hypothesis that substantial improvements in field-instrument accuracy will follow on the heels of an increase in the number of measurements), we remain pessimistic that the fundamental problem discussed in this letter can be circumvented for operational broadband sunphotometry.

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