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Jerome Vidot, Olivier Jourdan, Alexander Kokhanosvky, Frédéric Szczap, Vincent Giraud, et al.. Retrieval of tropospheric NO₂ columns from satellite measurements in presence of cirrus: A theoretical sensitivity study using SCIATRAN and prospect application for the A-Train. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 2010, 111 (4), pp.586-601. 10.1016/j.jqsrt.2009.10.015 . hal-01971909

HAL Id: hal-01971909

<https://hal.science/hal-01971909>

Submitted on 20 Mar 2022

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1 **Retrieval of tropospheric NO₂ columns from satellite**
2 **measurements in presence of cirrus: a theoretical sensitivity study**
3 **using SCIATRAN and prospect application for the A-Train**

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20

21**Abstract**

22A theoretical sensitivity study of the influence of cirrus cloud properties on tropospheric NO₂

23columns retrieved from the spaceborne Ozone Monitoring Instrument (OMI) measurements is

24performed. It is conducted within the framework of the synergetic use of A-Train sensors to

1 derive more representative trace gas products. We aim to study the potential effects of cirrus
2 clouds on tropospheric NO₂ retrievals using a retrieval algorithm that, unlike the OMI
3 Standard and DOMINO algorithms, does not correct for the effects of clouds. The sensitivity
4 study is based on the radiative transfer code SCIATRAN that performs both simulations of
5 top of atmosphere (TOA) reflectances as measured by an OMI-like band and tropospheric
6 NO₂ column retrievals based on the Differential Optical Absorption Spectroscopy (DOAS)
7 method. The results of the sensitivity study show that if a correction for cirrus clouds is not
8 included in our simple retrieval that does not account for clouds in the first place, the
9 tropospheric column can be underestimated by 55%. This underestimation depends strongly
10 on cirrus parameters as, in order of importance, cloud fraction, cloud optical depth,
11 asymmetry factor of cirrus cloud phase function and cloud top height. The perspective of the
12 synergy between OMI and cloud information obtained from cloud-derived products of the A-
13 Train is evaluated in two parts by applying a simple cloud correction scheme based on the
14 independent pixel approximation (IPA). Firstly, we evaluated the tropospheric NO₂ column
15 retrievals error caused by uncertainties in cirrus cloud properties. Secondly we studied the
16 influence of subpixel cloud optical depth variability on NO₂ retrievals. From our simulations,
17 it is demonstrated that the error will be reduced significantly if the cloud fraction is lower or
18 equal to 0.5. In this case, the cloud fraction and the cloud optical depth must be known within
19 accuracy less than 0.05 and 50 %, respectively. The cloud top height and the asymmetry
20 factor must be known within uncertainty of at least 1 km and less than 0.05, respectively. The
21 latter result shows that the uncertainty of the asymmetry factor is a major source of error in
22 the cloud correction for tropospheric NO₂ retrieval in the presence of cirrus.

23

24 **Keywords:** Cirrus properties; OMI; Tropospheric NO₂ vertical column; SCIATRAN; A-
25 Train.

11. Introduction

2

3 Nitrogen dioxide (NO₂) plays an important role in the tropospheric chemistry [1]. NO₂ is
4 known to be one of the key species in the formation of photochemical smog during pollution
5 episodes. In the troposphere, the concentration of NO₂ takes part in the chemical budget of
6 ozone. It also contributes to acid rain and locally, to radiative forcing over industrial regions
7 and urban areas [2]. To assess accurately our current knowledge of tropospheric chemistry
8 and its interaction with climate, global information about the amounts and distribution of NO₂
9 is required. By their high spatial and temporal coverage, satellite measurements of NO₂ are
10 essential for air quality monitoring (for health regulation) and regional scale modelling
11 (improvement of emission estimates).

12 The measurement of tropospheric NO₂ from space began with the precursor satellite
13 Global Ozone Monitoring Experiment (GOME) [3] followed by the Scanning Imaging
14 Absorption Spectrometer for Atmospheric Cartography (SCIAMACHY) [4] and the Ozone
15 Monitoring Instrument (OMI) [5]. The retrieval algorithms of the NO₂ vertical columns are
16 based on the Differential Optical Absorption Spectroscopy (DOAS) approach [6]. This
17 technique is based on the analysis of differential structure of backscattered signal using non
18 linear least squares fitting in a specific wavelength window. The spectral fit determines a slant
19 column density of NO₂ which is converted into a vertical column by application of an air mass
20 factor (AMF). Retrievals of tropospheric NO₂ columns from GOME, SCIAMACHY and OMI
21 have demonstrated the weekly cycle of NO₂ [7], its relationship with NO_x emission, the
22 annual trend over industrial countries [8], the global cartography of tropospheric NO₂ [9] and
23 the diurnal evolution of NO₂ driven by emissions and photochemistry [10]. Space-based
24 measurements of NO₂ have been validated against ground-based measurements [11,12],
25 atmospheric models [13,14] and aircraft measurements [9,15].

1 Nevertheless, the retrieval of NO₂ from space measurements can be subject to significant
2 errors. Boersma et al. [16] showed that NO₂ tropospheric vertical column can only be
3 retrieved with an accuracy of 35-60%. The retrieval errors are dominated by uncertainties in
4 the tropospheric AMF. The *a priori* NO₂ profile shape, the surface albedo and the cloud
5 properties (especially cloud fraction) are the leading sources of errors associated with AMF
6 computation. Moreover, clouds cover approximately 60% of the earth's surface. Hence,
7 considering the weak spatial resolutions of trace gas monitoring sensors (for GOME: 320×40
8 km², SCIAMACHY: 60×30 km² and OMI: 13×24 km² at nadir), more than 90% of their
9 measurements are contaminated by clouds [17].

10 The effects of clouds on trace gas retrieval from space measurements can be separated
11 into three parts [18-22]. The first effect, called shielding effect, reduces the interaction
12 between photons and trace gas underneath the cloud leading to an “apparent” decrease of
13 depths of absorption lines. The second effect, called albedo effect, increases the depth of
14 absorption lines of the gas layer above the cloud as compared to the clear sky. This is due to
15 enhanced single and multiple scattering light paths from Sun to cloud to satellite. The third
16 effect, called in-cloud absorption, increases the depth of absorption lines of gas layer inside
17 the cloud. Here, light scattering process due to the cloud is responsible for the light path
18 enhancement as compared to a nonscattering layer. These three effects are competing together
19 and the final effect depends on the cloud properties as well as on the profile of the trace gas.
20 Therefore, accurate space-based retrievals of trace gas column in presence of clouds
21 necessarily imply a precise assessment of the cloud radiative and macrophysical properties
22 which are, in turn, determined by their microphysical, optical and geometrical characteristics.

23 The most important point to perform a cloud correction for the retrievals of tropospheric
24 NO₂ column is to identify the cloud parameters that significantly modify the depth of
25 absorption lines of NO₂. Studies of Boersma et al. [16] and Wang et al. [23] showed that the

1cloud fraction, cloud albedo and cloud pressure were important quantities for cloud
2correction. Errors in these cloud properties will directly end up in errors in NO₂ columns.
3However the quantitative estimate of the retrieval errors depends on the chosen cloud model.
4For OMI, the cloud correction scheme of the current algorithm is based on the simplified
5Lambertian cloud model that assumes a homogeneous cloud with an albedo of 0.8 [24]. This
6method corrects the cloud contribution of the total reflectance at the top of atmosphere (TOA)
7measured for an OMI pixel using only two cloud parameters: the effective cloud fraction and
8cloud pressure. The use of this Lambertian cloud model compared to a scattering cloud model
9has been estimated to lead to AMF differences between -10% and 10% [23] and mean AMF
10differences of -12% with a standard deviation of 10% [25], depending on cloud properties,
11cloud fraction and NO₂ pollution. However, the assumption of a Lambertian cloud model is
12only valid if the bi-directional properties of light reflectance from clouds can be neglected.

13 In order to overcome these limitations, the cloud correction algorithm can be improved on
14the basis of collocated data from cloud sensors and gas sensors onboard different satellites.
15The A-train satellite constellation allows for near simultaneous measurements of cloud and
16trace gas properties at different spatial scales. For instance, high spatial resolution (typically
17(1×1 km²) cloud properties can be assessed from the Moderate Resolution Imaging
18Spectroradiometer (MODIS) [26] and from the 5-km resolution cloud product provided by the
19Cloud-Aerosol Lidar with Orthogonal Polarization (CALIOP) (Level 2 Algorithm Theoretical
20Basis Document, available at [http://www-calipso.larc.nasa.gov/resources/pdfs/PC-SCI-](http://www-calipso.larc.nasa.gov/resources/pdfs/PC-SCI-21202_Part4_v1.0.pdf)
21202_Part4_v1.0.pdf). This subpixel cloud information (cloud cover, optical thickness, cloud
22top height...) can then be used to constrain a cloud correction algorithm applied to OMI
23measurements. Nevertheless, the use of CALIOP information is limited by the fact that
24CALIOP only overlaps with the nadir pixel of OMI.

1 This paper lies within the framework of using the synergy of A-Train instruments to
2 improve trace gas retrievals in presence of cirrus clouds. Due to their low optical thickness,
3 cirrus clouds are more difficult to detect compared to cumulus, particularly over land and ice
4 surfaces. Additionally, infrared measurements have shown that thin cirrus clouds (with optical
5 depths between 0.1 and 1.0) have a global frequency of about 20 to 40% [27]. More recently,
6 a cirrus occurrence up to 70% near the tropics over the 100°-180°E longitude band has been
7 derived from active measurements by CALIOP [28]. From these observations, this paper aims
8 at studying into the potential effects of cirrus clouds on the tropospheric NO₂ column
9 retrievals from OMI space-based measurements and the impact of uncertainties in cirrus cloud
10 properties in a cloud correction scheme based on the IPA. It is important to point out that this
11 study is focusing on the effect of cirrus clouds properties in the NO₂ absorption band and that
12 the results presented here are not compared with the operational cloud correction scheme of
13 OMI that is based on the O₂-O₂ absorption band [24]. Even if we can assume that the O₂-O₂
14 band is sensitive to cirrus, the OMI O₂-O₂ algorithm will retrieve, in presence of cirrus, a
15 small value for effective cloud fraction and high cloud height. For small cloud fractions, the
16 assumption on the surface albedo plays an important role and will impact the retrieval of
17 tropospheric NO₂ column. This effect is beyond the scope of the paper, but the new surface
18 albedo database made from OMI itself (Kleipool et al., 2008) will certainly change the
19 tropospheric NO₂ retrievals, because the previous albedo database was from GOME with a
20 coarser pixel resolution than OMI.

21 Theoretical sensitivity study of the inversion of the tropospheric NO₂ column to
22 undetected or retrieved (with errors) cirrus cloud properties is discussed in this paper. The
23 sensitivity study is based on radiative transfer model (RTM) simulations of TOA reflectances
24 as measured in an OMI-like band. The first part of the paper will describe the atmospheric
25 model, the retrieval algorithm and the cirrus cloud model. In the second part of the paper, the

1 results of the sensitivity study that highlight the cirrus parameters that influence tropospheric
2 NO₂ column retrievals are presented. The last part is devoted to the perspective on application
3 of A-Train cloud-derived products by estimating tropospheric NO₂ column error caused by
4 uncertainties in cirrus cloud parameter or caused by subpixel cloud optical depth
5 inhomogeneity within an OMI pixel at nadir.

6

7

82. NO₂ retrieval algorithm and model setups

9

102.1 Atmospheric model

11 In our study, the atmosphere is treated as plane-parallel. In the spectral band used by OMI
12 for NO₂ retrieval (between 405 and 465 nm), the two other trace gases, namely O₃ and H₂O
13 are included with fixed standard atmospheric profiles. The collision complex of oxygen
14 molecules O₂-O₂ is included as well by assuming a fixed standard atmospheric profile of O₂.
15 The influence of cirrus clouds is evaluated in different tropospheric NO₂ situations
16 characterized by the three atmospheric profiles of NO₂ Volume Mixing Ratio (VMR in ppbv)
17 shown in Fig. 1. The NO₂ VMR profile represented by the full line corresponds to the lowest
18 NO₂ contribution in the troposphere whereas the NO₂ VMR profile represented by the dotted-
19 dashed line corresponds to the largest NO₂ contribution. The tropospheric part of the total
20 atmospheric NO₂ vertical column is commonly retrieved by assuming that the longitudinal
21 variation of the stratospheric NO₂ vertical column is small. Therefore, tropospheric NO₂
22 vertical column (V_r) over a polluted location (e.g., over a city) can be retrieved from the total
23 NO₂ vertical column by removing the total NO₂ vertical column over a clean site (e.g., Pacific
24 ocean) at a given location with the same latitude. Here, we simply removed a constant
25 stratospheric NO₂ vertical column from the total vertical column. The stratospheric NO₂

1vertical column was calculated as the integral of the NO₂ profile from 12 km to the top of
2atmosphere (TOA). Accordingly, the three profiles displayed in Fig. 1 correspond to three
3tropospheric NO₂ conditions defined as: (1) low polluted with $V_{tr} = 0.43 \cdot 10^{15}$ molec/cm² (full
4line), (2) moderately polluted with $V_{tr} = 2.81 \cdot 10^{15}$ molec/cm² (dotted line) and, (3) heavily
5polluted with $V_{tr} = 9.36 \cdot 10^{15}$ molec/cm² (dotted-dashed line).

6 The modelling results presented in this paper are performed for single values of the
7surface albedo $A = 0.05$, the solar zenith angle $\theta_s = 30^\circ$ and the viewing zenith angle $\theta_v = 0^\circ$
8(according to OMI nadir viewing geometry). The influence of the solar angle and the surface
9albedo are discussed in section 3. We note in passing that aerosols were chosen to be not
10included in the atmospheric model.

11

122.2 DOAS retrieval

13 The tropospheric NO₂ vertical column (V_{tr}) retrieval algorithm has been developed in the
14framework of SCIATRAN [29]. SCIATRAN is both a radiative transfer code and a retrieval
15algorithm for many atmospheric gases (see <http://www.iup.uni-bremen.de/sciatran/> for full
16description of SCIATRAN). For the retrievals of V_{tr} , the DOAS technique is applied to
17simulated TOA reflectance in the OMI-like band with a spectral sampling of 0.21 nm [30] and
18with a signal to noise ratio (SNR) of 1400 [10]. Retrievals of V_{tr} are performed by converting
19the simulated TOA reflectances R_{TOA} to so-called differential optical densities D , which are
20calculated as

21

$$22 \quad D(\lambda) = \ln(R_{TOA}(\lambda)) - P_3(\lambda), \quad (1)$$

23

24where $P_3(\lambda)$ is a 3rd degree least squares polynomial fit of the logarithm of R_{TOA} with respect to
25the wavelength λ , that removes slowly varying functions. The conversion of R_{TOA} into D

1 ensures the better contrast of the NO₂ absorption line depths to improve the accuracy of the
2 fitting procedure. Then, in the retrieval algorithm the quadratic form

3

$$4 \quad F(\lambda, V_{tr,ret}) = \|D_{true}(\lambda, V_{tr,true}) - D_{ret}(\lambda, V_{tr,ret})\|^2, \quad (2)$$

5

6 is minimized with respect to unknown parameter $V_{tr,ret}$. D_{true} is the differential optical density
7 spectrum simulated with SCIATRAN for the true tropospheric NO₂ column $V_{tr,true}$. D_{ret} is the
8 retrieved differential optical density spectrum for the retrieved tropospheric NO₂ column $V_{tr,ret}$.

9

10 2.3 Cirrus cloud model

11 Cirrus clouds are treated as single layer homogeneous clouds. The most important cirrus
12 cloud parameters that potentially influence the trace gas retrieval are those which determine
13 the photon paths in the atmosphere. In the visible spectral range, these parameters are
14 expected to be the cloud optical depth τ , the cloud phase function P , the cloud top height z and
15 the cloud geometrical depth h [31]. These parameters are used as inputs in SCIATRAN.
16 Because of the quite large spatial resolution of OMI measurement (13×24 km²), one more
17 important parameter is the geometric cloud fraction c . In most retrieval, c is accounted for
18 considering the independent pixel approximation (IPA). IPA consists in the hypothesis that
19 R_{TOA} is the sum of the reflectance of a cloudy part (R_{cloudy}) and the reflectance of a clear-sky
20 part (R_{clear}) as

21

$$22 \quad R_{TOA} = cR_{cloudy} + (1 - c)R_{clear} \quad (3)$$

23

24 The ice crystals phase function used for SCIATRAN simulations has been retrieved from in
25 situ aircraft measurements during the Cirrus Cloud Experiment (CIRCLE2) campaign. The

1phase function (Fig. 2) was inferred from the Polar Nephelometer (PN) measurements. The
2best fit of the PN measurements was achieved using a combination of spherical ice particles
3with diameters ranging from 1 to 100 μm and rough droxtal shaped particules with maximum
4dimension between 2 and 200 μm . Accordingly, two particle size distributions were retrieved
5using the iterative inversion method developed by Oshchepkov et al. [32] and upgraded by
6Jourdan et al. [33]. Then, the scattering patterns of the retrieved particle size distribution were
7computed with the Lorenz-Mie theory (for spherical particles) and with an improved
8geometric-optics model (for droxtal particles) at a wavelength of 420 nm [34]. The retrieved
9phase function exhibits a featureless behaviour and is flat at side scattering angles which is in
10accordance with most of the observations [32-33,35-37] or scientific recommendations in ice
11cloud remote sensing application [38-41] . The corresponding asymmetry factor g is 0.75.

12 To illustrate the influence of cirrus clouds on the retrieval of V_{tr} , Fig. 3 shows simulated
13differential optical densities (calculated with Eqs. 1 and 3) with and without cirrus clouds.
14 R_{clear} is calculated using SCIATRAN with standard profiles of O_3 , H_2O and O_2 , surface albedo
15and geometries described in section 2.1. Clouds properties ($\tau = 1$, CIRCLE2 phase function, z
16= 10 km and $h = 1$ km) are added in the calculation of R_{cloudy} . The heavily polluted NO_2 profile
17is considered. The clear-sky differential optical density ($c = 0$ in Eq. 3) is represented by the
18green line. Blue and red lines represent differential optical densities when a cirrus cloud is
19included and cover the full pixel ($c = 1$) and half of the pixel ($c = 0.5$), respectively. When a
20cirrus cloud is included, the depths of NO_2 absorption lines are reduced. This stems from the
21cloud shielding effect discussed in the introduction, which is greater to both cloud albedo and
22in-cloud absorption effects. Because V_{tr} varies with the NO_2 absorption lines depths, the
23presence of undetected cirrus would lead to a lower apparent V_{tr} , that depends on the cloud
24fraction. Nevertheless, these results are valid for algorithms that do not make any attempt to
25correct for clouds in the first place. In the current available OMI NO_2 algorithms such as the

1 OMI standard retrieval (bucsela et al, 2006) and the Dutch OMI NO₂ (DOMINO) retrieval
2 (Boersma et al. 2008b), the missing tropospheric NO₂ column due to clouds is compensated
3 by adding a ghost column obtained from chemical transport model. In situations of cirrus, the
4 OMI O₂-O₂ algorithm will retrieve a small value for effective cloud fraction and high cloud
5 height. Because of the small effective cloud fraction, the ghost column effect will also be
6 small.

7

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113. **Influence of undetected cirrus clouds on NO₂ retrieval**

12

13 The differential optical densities simulated previously are used to introduce the following
14 discussion that focuses on the influence of undetected cirrus cloud on the tropospheric NO₂
15 column retrieval. The influence of undetected cirrus clouds is evaluated as an error on the
16 retrieved tropospheric NO₂ column $V_{tr,ret}$ compared to a true tropospheric NO₂ column $V_{tr,true}$:

17

$$18 \quad Error = \frac{V_{tr,ret} - V_{tr,true}}{V_{tr,true}} \times 100, \quad (4)$$

19

20 $V_{tr,ret}$ is retrieved according to the following methodology: A true TOA reflectance spectrum is
21 calculated following Eq. 3, for an atmosphere characterized by both a cirrus cloud with
22 prescribed properties and a true tropospheric NO₂ column $V_{tr,true}$. Then, this TOA reflectance is
23 used as the input spectrum for the DOAS-based SCIATRAN retrieval algorithm. The
24 retrieved quantity is, in that case, called $V_{tr,ret}$. It is important to point out that the inversion

1 procedure is performed with the hypothesis of a non cloudy atmosphere. By this mean, errors
2 caused by a specific cirrus parameter (optical depth, cloud top height, etc...) can be quantified
3 and used to determine the relative importance of the impact of a given cloud parameter on the
4 retrieval of tropospheric NO₂ columns for retrievals that do not correct for clouds in the first
5 place.

6

7 3.1 Cloud fraction and cloud optical depth

8 The panel of Fig. 4 displays errors of the retrieved $V_{tr,ret}$ as a function of cloud optical
9 depth and cloud fraction for low polluted condition (Fig. 4a), for moderately polluted
10 condition (Fig. 4b) and for heavily polluted condition (Fig. 4c). For these cases, $z = 10$ km, h
11 = 1 km and $g = 0.75$ (i.e., with the CIRCLE2 ice crystal phase function). The overall negative
12 error (underestimation) highlights the predominance of the shielding effect. This is explained
13 by the fact that the tropospheric NO₂ is mainly situated under the cirrus cloud. Even for the
14 highest value of the cloud optical depth considered in this study ($\tau = 3$), the albedo effect still
15 remains negligible compared to the shielding effect. The underestimation of $V_{tr,ret}$ increases
16 rapidly with both τ and c and can reach, for $\tau = 3$ and $c = 1$, an underestimation of ~35% in
17 low polluted conditions (Fig. 4a), ~45% in moderately polluted conditions (Fig. 4b) and
18 ~55% in heavily polluted condition (Fig. 4c). It is interesting to notice that the
19 underestimation remains less than 5% for optical depth less than 0.2 whatever the cloud
20 fraction and the polluted conditions are. This implies, from our simulations, that optically thin
21 cirrus or subvisible cirrus do not significantly influence the NO₂ tropospheric column retrieval
22 which is not the case for example, in atmospheric CO₂ retrieval [42,43]. This might be
23 explained by the fact that, in the NO₂ absorption band, the signal is predominantly due to
24 Rayleigh scattering as compared to CO₂ absorption band that is in the near infrared spectral
25 band and where the Rayleigh scattering is very low.

1

23.2 Cloud top height and cloud geometrical depth

3 The influence of cloud top height (z) and cloud geometrical depth (h) is evaluated in term
4of error difference between the maximum and the minimum NO_2 tropospheric column errors
5over the different values of z and h considered. Fig. 5 displays the error caused by undetected
6cirrus clouds versus cloud top height z . In these simulations, $g = 0.75$ and $h = 1$ km. Colour
7lines and symbols differ with pollution conditions, cloud fraction and cloud optical depth. For
8 $c = 1$ and $\tau = 3$ in low polluted condition (represented by the green line with triangles), the
9error is -29% at $z = 8$ km and -37% at $z = 15$ km leading to an error difference of 8% between
10 $z = 8$ km and $z = 15$ km. As comparison, the error difference is ~6% for moderately polluted
11condition (represented by the blue line with triangles) and ~4% for heavily polluted condition
12(represented by the red line with triangles). The underestimation increase with cloud top
13height mostly between $z = 8$ to $z = 12$ km. This is explained by the increase of shielding effect
14with the altitude of the cirrus cloud. For $c = 0.5$ and $\tau = 1$ (represented by lines with
15diamonds), error differences are almost constant with z . Table 1 provides a summary of error
16differences for different values of c and τ . Errors remain less than 1% for low optical depth (τ
17= 0.05) or for low cloud fraction ($c = 0.05$). We noticed also that, for fixed c and τ , error
18differences decrease with polluted conditions, which can be explained by an increase of the
19in-cloud absorption effect when the cloud is lower due to higher tropospheric NO_2 (see Fig.
201). The error caused by undetected cirrus clouds versus cloud geometrical depth h is
21represented in Fig. 6 for the same cases as Fig. 5. Underestimation of V_r decrease slowly with
22 h due to increase of in-cloud absorption leading to error difference of few percents between h
23= 0.1 km and $h = 2$ km. Table 2 provides a summary of error differences for different values
24of c and τ which, overall, remain less than 3%.

25

13.3 Asymmetry factor of ice crystal phase function

2 The influence of ice crystal phase function is evaluated by comparing the retrieval errors
3 versus the asymmetry factor g . g is used to parameterize the general behaviour of the ice
4 crystal phase function because it is an integrated optical parameter (scalar) taking into account
5 both ice crystals shape and size variability. The different values of asymmetry factor tested
6 here are obtained on the basis of nine pre-calculated phase functions for different ice crystal
7 shape (aggregate, plate, column, bullet and dendrite) and effective diameters comprise
8 between 4.5 and 150 μm that are used for cirrus clouds modelling [44]. The CIRCLE-2 phase
9 function is included as well. The asymmetry factor values obtained are between 0.70 and
10 0.85. Errors caused by undetected cirrus clouds versus asymmetry factors are displayed in
11 Fig. 7. It appears that the underestimation decreases with the asymmetry factor. This is
12 explained by the fact that cirrus cloud particles with a large value of g reflect less solar
13 radiation than ice crystals with smaller asymmetry factor. Then, for a large value of g , more
14 solar radiation exhibited by the cirrus cloud will interact with tropospheric NO_2 located below
15 the cloud. From the summary given in Table 3, error differences between $g = 0.70$ and $g =$
16 0.85 are comprise between 0.07 % (for $c = 0.05$, $\tau = 0.05$ and low polluted condition) and
17 21.3 % (for $c = 1$, $\tau = 3$ and heavily polluted condition). These results imply that, for fixed c
18 and τ , the error difference caused by undetected cirrus clouds with g lying between 0.70 and
19 0.85 (Table 3) is more important than the one caused by undetected cirrus clouds with z
20 comprise between 8 and 15 km (Table 1) or h comprise between 0.1 km and 3 km (Table 2).
21 The asymmetry factor appears to be a major source of error in tropospheric NO_2 retrieval in
22 the presence of cirrus.

23

24 This sensitivity study showed that four cirrus parameters influence the retrieval of
25 tropospheric NO_2 columns. These parameters are, in descending order, the cloud fraction c ,

1the cloud optical depth τ , the asymmetry factor g and the cloud top height z . Since the error
2difference caused by cloud geometrical depth variability remains less than 3%, we have
3considered that cloud geometrical depth does not influence significantly the retrieval of
4tropospheric NO_2 columns. The $V_{tr,ret}$ errors have also been estimated for other solar zenith
5angles (15° , 45° and 60°) and other surface albedos (0.03 and 0.1) but they do not show large
6discrepancies with the results obtained for a solar zenith angle of 30° and a surface albedo of
70.05.

8

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11

12

134. **Error on NO_2 retrieval caused by uncertainties in cirrus clouds** 14**properties**

15

16 The next step of our study is to look at the $V_{tr,ret}$ error induced by uncertainties of the cirrus
17parameters that were identified previously as critical. The objective here is to evaluate the
18precision needed for these parameters in order to constrain the retrievals. To this respect, we
19simulated a true R_{TOA} using Eq. (3) with a set of cirrus properties (τ , g , z , h), a cloud fraction c
20and a true tropospheric NO_2 vertical column $V_{tr,true}$. Then, $V_{tr,ret}$ is obtained by using as the
21input reflectance spectrum for the inversion algorithm, the clear-sky part of the TOA
22reflectance R_{clear} . R_{clear} is a function of $R_{TOA}(p)$ and $R_{cloud}(p+\delta p)$ where p is τ , g , z , h or c . The
23formulation of R_{clear} is presented for each cloud parameters in the following subsections.

1 Results are presented for moderately polluted condition as results found for the three polluted
2 conditions did not differ significantly.

3

44.1 Cloud fraction

5 The error on tropospheric NO₂ column retrievals caused by uncertainty in cloud fraction is
6 calculated as Eq. (4). The input reflectance spectrum of the inversion scheme is defined as:

7

$$8 \quad R_{clear} = \frac{R_{TOA}(\tau, g, z, h, c) - (c + \delta c)R_{cloud}(\tau, g, z, h)}{1 - (c + \delta c)}, \quad (5)$$

9

10 where δc is the uncertainty on cloud fraction. The simulations were performed for a cirrus
11 cloud characterized by an asymmetry factor of 0.75, a cloud top height of 10 km and a
12 geometrical thickness of 1 km. The surface albedo, solar zenith angle and the viewing angle
13 are the same as in Section 3. Fig. 8 displays errors on $V_{tr,ret}$ versus cloud optical depth for $\delta c =$
14 0.01 (Fig. 8a), $\delta c = 0.05$ (Fig. 8b) and $\delta c = 0.09$ (Fig. 8c) and for three values of c (0.1, 0.5
15 and 0.8) representing low, medium and high cloud fractions. Overall, the overestimation of
16 cloud fraction results in an overestimation of tropospheric NO₂ columns (i.e., positive errors).
17 If $c \leq 0.5$ (represented by lines with triangles or diamonds), overestimations are expected to
18 be less than 10 % if $\delta c \leq 0.05$ (Figs. 8a and Fig. 8b) and less than 20 % if $\delta c = 0.09$ (Fig. 8c).
19 If $c \geq 0.8$, overestimations are expected to be higher, ranging from 10% to more than 100%, if
20 $\delta c \geq 0.05$ (Figs. 8b and 8c) for large cloud optical depth ($\tau > 1$).

21 Within the framework of combining measurements performed by A-train sensors to
22 improve OMI NO₂ products, cloud fraction can be derived from independent measurements.
23 For example, MODIS can provide a subpixel cloud fraction information with a 1×1 km²
24 resolution. Accordingly, the cloud fraction estimation from MODIS within an OMI pixel is
25 expected to be achieved with lower uncertainty than the value of 0.05 reported by

1 Koelemeijer et al. [45]. However, the estimation of the uncertainty on MODIS cloud fraction
 2 is a difficult task because it depends on the cloud type. Koren et al. [46] reported that for
 3 small cumulus cloud, MODIS cloud fraction is almost twice as the cloud fraction obtained
 4 from a finer spatial resolution (30 m) instrument. Fortunately, cirrus clouds have larger spatial
 5 extension than small cumulus clouds and would be less influenced by the scale dependence.
 6 Finally, these results highlight that cloud fraction within an OMI pixel should be determined
 7 with uncertainty lower than 0.05 in order to reduce the tropospheric NO₂ vertical columns
 8 errors, especially if the cloud optical depth is greater than 1.

9

10 4.2 Cloud optical depth

11 The error on tropospheric NO₂ columns retrieval caused by uncertainties in the cloud
 12 optical depth is calculated as Eq. (4) where the retrieval is applied on the clear-sky part of the
 13 reflectance given by

14

$$15 \quad R_{clear} = \frac{R_{TOA}(\tau, g, z, h, c) - cR_{cloud}(\tau + \delta\tau, g, z, h)}{1 - c}, \quad (6)$$

16

17 where $\delta\tau$ is the uncertainty in cloud optical depth. The simulations were performed for a cirrus
 18 cloud characterized by $g = 0.75$, $z = 10$ km and $h = 1$ km. The panel of Fig. 9 displays errors
 19 on V_r versus cloud optical depth for $\delta\tau/\tau = 10$ % (Fig. 9a), $\delta\tau/\tau = 20$ % (Fig. 9b) and $\delta\tau/\tau = 50$
 20 % (Fig. 9c) and for three values of c (0.1, 0.5 and 0.8, differentiated by symbols). Here again,
 21 the overestimation of cloud optical depth results in an overestimation of tropospheric NO₂
 22 columns. This is explained by the fact that an overestimation of τ will increase the cloud
 23 reflectance. The numerator of Eq. (6) will then decrease leading to an overestimation of
 24 tropospheric NO₂ columns. For $c \leq 0.5$, overestimations are expected to be less than 15 % if

1 $\delta\tau/\tau \leq 20\%$ (Figs. 9a and 9b). The same result is seen if $\delta\tau/\tau = 50\%$ and $\tau < 1$ (Fig. 9c). If $c =$
2 20.8, overestimations are expected to increase quickly, especially if $\delta\tau/\tau = 50\%$ (Fig. 9c).

3 By comparison, cirrus optical depth from MODIS and ground-based measurement has
4 shown that MODIS overestimates the optical depth by 30% [47]. However, clouds with low
5 optical depth (less than 0.4) are not retrieved from MODIS [48]. The use of CALIOP data will
6 be helpful for a better characterisation of the optical depth since CALIOP is able to detect
7 clouds with $\tau < 0.05$ [49]. Nevertheless, the use of CALIOP information is limited by the fact
8 that CALIOP only overlaps with the nadir pixel of OMI. If no CALIOP data is available and
9 the cirrus cloud is undetected by MODIS (ie, $\tau < 0.4$), tropospheric NO_2 vertical column
10 errors are expected to be less than 10% (Fig. 4).

11

12

13

14 4.3 Asymmetry factor

15 The error on tropospheric NO_2 columns retrieval caused by uncertainties in asymmetry factor
16 is retrieved from the clear-sky part of the reflectance given by Eq. (6) and where the
17 uncertainty is applied to g instead of τ . Here again, g was chosen instead of the phase
18 function because it is a convenient integrated parameter function of the ice particle shape and
19 effective size. So it is a first guess indicator of the general scattering behaviour of the cirrus
20 cloud. Fig. 10 displays errors versus cloud optical depth. R_{TOA} is simulated with $g = 0.75$, $z =$
21 110 km and $h = 1$ km. Here, the overestimation of asymmetry factor results in an
22 underestimation of tropospheric NO_2 columns (i.e., negative errors). Underestimations up to
23 40% are expected if $c = 0.5$ (full lines) and up to 60% if $c = 0.8$ (dashed lines), but do not
24 change that much whether $\delta g = 0.05$ (diamonds) or $\delta g = 0.1$ (triangles). These results show
25 that the uncertainty of the asymmetry factor is a major source of error in tropospheric NO_2

1retrieval in the presence of cirrus. However, although modelling studies show that for ice
2crystals values of g could vary from 0.7 to 0.9 (see for instance the review paper of Baran
3[2009]), measurements do not show such variability in ice clouds. An uncertainty less than
40.05 can be expected since the asymmetry factor ranges more likely from 0.75 to 0.80 for ice
5clouds and from 0.80 to 0.85 for mixed phase clouds depending on the liquid water fraction
6[50,51]. However, the operational algorithms of MODIS retrieve the ice crystals effective
7radius (R_{eff}) and not g . Both information on R_{eff} and shape are needed to model the scattering
8properties of ice crystals. Usually, a combination of particles with different shapes and sizes is
9used as an equivalent microphysical model in MODIS retrieval process of the effective radius.
10The retrieved R_{eff} from MODIS corresponding to a specific microphysical shape model could
11be used to assess appropriate phase function and asymmetry parameter on the basis of
12MODIS Look-Up-Tables (LUT) [52,53]. However, MODIS R_{eff} seems to be overestimated by
13comparison with Lidar retrievals [54].

144.4 Cloud top height

15 The error on tropospheric NO₂ column retrievals caused by uncertainties in the cloud top
16height is assumed from the clear-sky part of the reflectance given by Eq. (6) and where the
17uncertainty is applied on z instead of τ . The panel of Fig. 11 displays errors on V_{tr} versus
18cloud optical depth for $\delta z = 0.5$ km (Fig. 11a), $\delta z = 1$ km (Fig. 11b) and $\delta z = 3$ km (Fig. 11c)
19and for two values of c (0.5 and 0.8) and three values of z (8, 10 and 12 km). If $\delta z \leq 1$ km
20(Figs. 11a and 11b), errors are expected to be less than 20 %. If $\delta z = 3$ km (Fig. 11c), errors
21are expected to be less than 20 % if $c \leq 0.5$. Uncertainty of z retrieved from MODIS is
22currently under investigation but preliminary results by comparison with Lidar measurements
23show difference on the order of 1 km [54]. However, this comparison remains limited due to
24the high occurrence of multi-layers ice clouds where MODIS only retrieves an effective cloud

1top height. The use of CALIOP retrieval will allow constraining the cloud top height input in
2order to retrieve the tropospheric NO₂ column in presence of cirrus cloud.

3

4

55. Contribution of subpixel cloud optical depth

6

7 The IPA formulation of the TOA reflectance in presence of clouds given by Eq. (3) does
8not consider the subpixel inhomogeneity of cloud properties. To this respect, we can consider
9that the optical thickness can be derived more accurately from high spatial resolution
10measurements (1×1 km²) of MODIS. This information will be used to describe the variability
11of the optical thickness within an OMI pixel (13×24 km²). Therefore, two ways of
12determining the contribution of the cloud to the total reflectance measured by OMI can be
13considered: (1) by calculating R_{cloud} from the mean cloud optical depth $\langle \tau \rangle$ or (2) by
14calculating the mean cirrus cloud reflectance $\langle R_{cloud} \rangle$ corresponding to a distribution of
15optical depth within an OMI pixel. These two ways of calculating the contribution of the
16cloud would have an important impact on the computing time of the retrieval because in the
17first way, there is only one calculation for the mean cloud optical depth whereas in the second
18way there are several calculations for each value of the subpixel cloud optical depth
19distributions. To compare these two ways, we have simulated different distribution of cloud
20optical depth considering a gamma distribution. Nine distributions have been selected
21randomly with three mean cloud optical depths ($\langle \tau \rangle = 0.5, 1$ or 2) and three variances ($\nu_\tau =$
220.1, 1 or 2). In these distributions, 312 values have been considered representing the
23maximum total number of MODIS subpixels within an OMI pixel at nadir. Cloud fractions
24have been included in the study by considering 31 subpixels for $c = 0.1$, 62 subpixels for $c =$
250.2, etc... to 281 subpixels for $c = 0.9$. For the cloud simulations we have used $z = 10$ km, $h =$

11 km and $g = 0.75$. The influence of the solar zenith angle has been tested by considering two values, $\theta_s = 30^\circ$ and $\theta_s = 60^\circ$. Figure 12 illustrates the tropospheric NO_2 column error retrieved from the clear-sky part of the reflectance given by

4

$$5 \quad R_{clear} = \frac{\langle R_{TOA} \rangle - c R_{cloud}(\langle \tau \rangle, g, z, h)}{1 - c}, \quad (7)$$

6

7 where $\langle R_{TOA} \rangle$ is the mean TOA reflectance calculated as the average of TOA reflectances
8 calculated using Eq. (3) for the different values of the cloud optical depth distribution. The
9 tropospheric NO_2 column error resulting from the use of a mean cloud optical depth is either
10 positive or negative. The error remains negative for $\langle \tau \rangle = 0.5$ (dotted-dashed lines) and
11 remains positive for $\langle \tau \rangle = 2$ (dashed lines). Interestingly, the error is negative for $\langle \tau \rangle = 1$
12 (full lines) if $\theta_s = 30^\circ$ and positive if $\theta_s = 60^\circ$ showing the importance of the solar zenith angle
13 in the subpixel inhomogeneity consideration. If $\theta_s = 30^\circ$ or 60° , errors caused by the use of a
14 mean cloud optical depth are expected to be less than $\pm 15\%$ for $c \leq 0.5$. For cloud fractions
15 greater than 0.5, errors increase quickly with cloud fraction and strongly with variances and
16 cloud optical depth. The increase of errors with cloud fraction is explained by the
17 denominator $1-c$ in Eq. (7). The blow-up of errors at $\text{SZA}=60^\circ$ is explained by the bias
18 between R_{cloud} calculated with the distribution of subpixels cloud optical depth and calculated
19 with the mean cloud optical depth. This bias increases with the variability of cloud optical
20 depths and solar zenith angle [55].

21 Finally, when the cloud fraction is lower than 0.5, the subpixel variability of the cloud optical
22 depth does not need to be included in the cloud correction scheme. Otherwise, the subpixel
23 variability of the cloud optical depth is significant and should be considered in the cloud
24 correction scheme. Such information can be deduced from MODIS observations.

25

1

26. Conclusion

3

4 In this study, we have theoretically demonstrated the sensitivity of tropospheric NO₂
5column (V_{tr}) retrieval to the presence of cirrus clouds. In order of importance, we concluded
6that c (cloud fraction), τ (cloud optical depth), g (asymmetry factor of ice crystal phase
7function) and z (cloud top height) influence the retrieval of V_{tr} . It appears from our
8simulations that V_{tr} is less influenced by h (cloud geometrical depth). The error on the
9retrieved tropospheric NO₂ column depends also on the NO₂ profile. Because tropospheric
10NO₂ is generally situated underneath the cirrus cloud, the shielding effect leads to
11underestimating the tropospheric NO₂ columns for retrievals that do not correct for clouds in
12the first place. The underestimation depends strongly on c and τ ranging from few percents
13for low cloud fraction to 55 % for $c = 1$ in heavily polluted conditions (i.e. for $V_{tr} = 9.36 \cdot 10^{15}$
14molec/cm²). In the context of the A-Train constellation, the tropospheric NO₂ column in
15presence of cirrus clouds can be retrieved by using the independent pixel approximation. The
16MODIS sensor coupled with CALIOP should be able to describe the optical and physical
17properties of the clouds in such way to reduce the error on the tropospheric NO₂ column. The
18use of CALIOP information is however limited by the fact that CALIOP only overlaps with
19the nadir pixel of OMI. Nevertheless, errors on cloud properties will end up by errors on
20tropospheric NO₂ column retrieval. From our simulations, we have demonstrated that the error
21will be reduced significantly if $c \leq 0.5$ as opposed to a retrieval that does not correct for
22cirrus. In the case of a cirrus cloud correction based on IPA, c and τ would have to be known
23within accuracy better than 0.05 and 50 %, respectively. z would have to be known within
24accuracy of at least 1 km and g would have to be known within accuracy better than 0.05.
25The latter result shows that the uncertainty of the asymmetry factor is a major source of error

1in tropospheric NO_2 retrieval in the presence of cirrus. Using the subpixel information from
2MODIS cloud flag for c , from MODIS and CALIOP cloud products for τ and z and from
3MODIS R_{eff} for the phase function should be sufficient to reduce the error on tropospheric
4 NO_2 column retrieval. Under this circumstance, the use of a mean value of the cloud optical
5depth from subpixel information as provided by MODIS should be enough to take into
6account the cirrus cloud and speed up the retrieval significantly. If the cloud fraction is greater
7than 0.5, the subpixel variability of the cloud optical depth has to be included in the cloud
8correction scheme and can be obtained from MODIS. Moreover, differences between
9radiative transfer models used for cloud retrievals and sensor's calibration issues would
10introduce some discrepancies in the cloud correction scheme. The results in this study hold
11for retrievals that do not attempt to correct for cirrus clouds. Current state-of-science
12retrievals do correct for clouds that include a range of situations including cirrus clouds.
13Nevertheless, the current NO_2 algorithm have not be evaluated in presence of cirrus. To
14interpret our results in the context of current retrieval algorithms, the sensitivity for cirrus
15clouds in the $\text{O}_2\text{-O}_2$ (OMI) and $\text{O}_2\text{-A}$ (GOME(-2), SCIAMACHY) band based cloud retrievals
16needs to be studied. Such studies could point out whether a correction for cirrus based on
17concurrent A-Train cloud information would be useful

18

19

20**Acknowledgments**

21 The authors are grateful to Céline Cornet, Philippe Dubuisson and Nicolas Ferlay from
22the Laboratoire d'Optique Atmosphérique (LOA) for fruitful discussions. Authors are also
23grateful to Christophe Gourbeyre, Guillaume Mioche and Jean-François Gayet from the
24Laboratoire de Météorologie Physique (LaMP) for providing data from the CIRCLE-2

1campaign. This research was supported by the Centre National d'Etudes Spatiales (CNES)
2and the Institut National des Sciences de l'Univers (INSU/PNTS).

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2Figure 1. Atmospheric profiles of NO₂ Volume Mixing Ratio in ppbv used in the study.

3Figure 2. Cirrus cloud phase function inferred from aircraft measurement during the
4CIRCLE2 campaign.

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7Figure 4. NO₂ tropospheric error caused by undetected cirrus cloud as function of cloud
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14Figure 7. Same as Fig. 5 versus asymmetry factor. Here, $z = 10$ km and $h = 1$ km.

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19Figure 9. Same as Fig. 8 for $\delta\tau/\tau = 10\%$ (a), $\delta\tau/\tau = 20\%$ (b) and $\delta\tau/\tau = 50\%$ (c).

20Figure 10. NO₂ tropospheric column error caused by an uncertainty in the asymmetry factor
21 $\delta g = 0.05$ (diamonds) and $\delta g = 0.1$ (triangles) versus cloud optical depth for $c = 0.5$ (full lines)
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24Figure 11. NO₂ tropospheric column error caused by an uncertainty in the cloud top height δz
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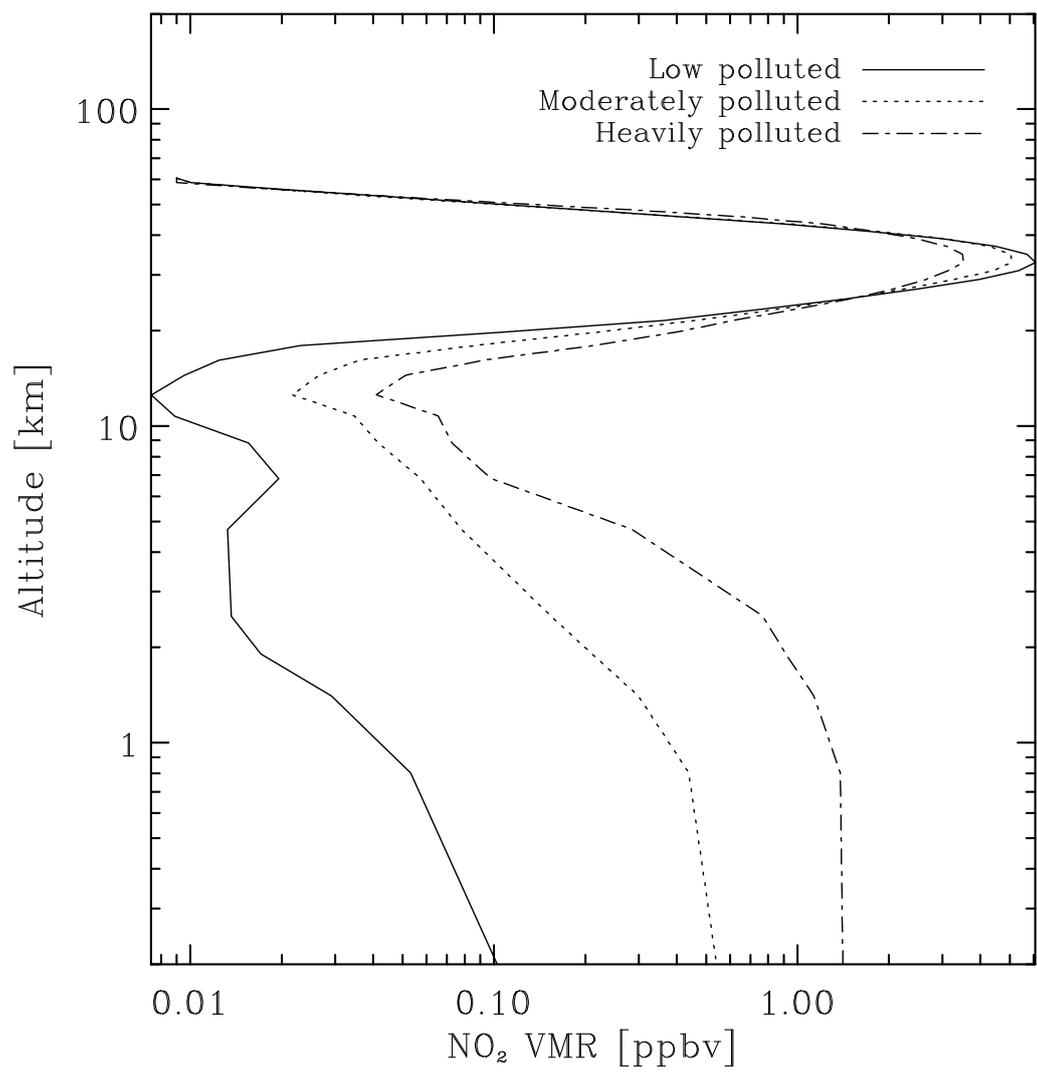
3Figure 12. NO_2 tropospheric column error caused by the use of a mean cloud optical depth
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3 each box of fixed c and τ correspond to low, moderately and heavily polluted conditions,
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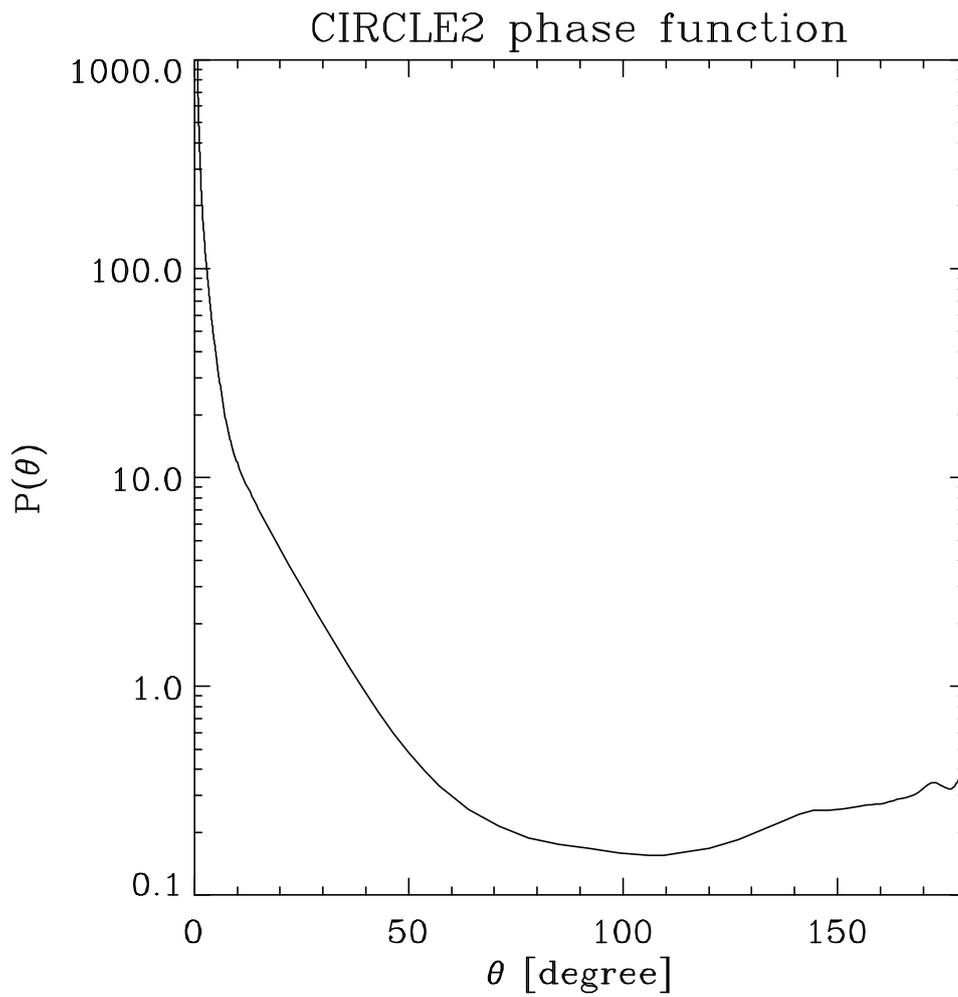
6 Table 3. Same as Table 1 for asymmetry factor g .



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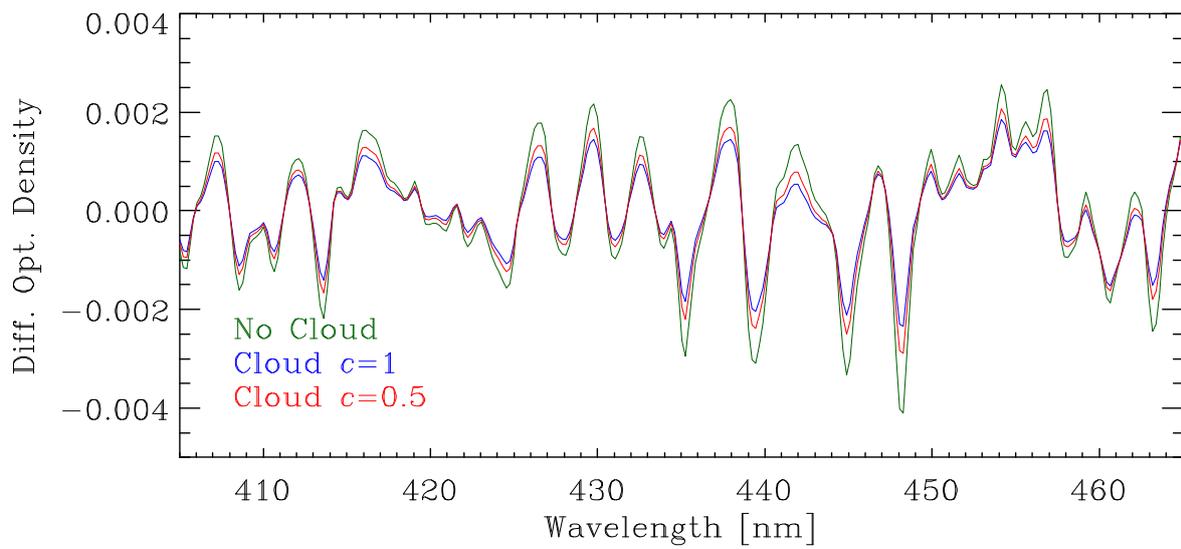
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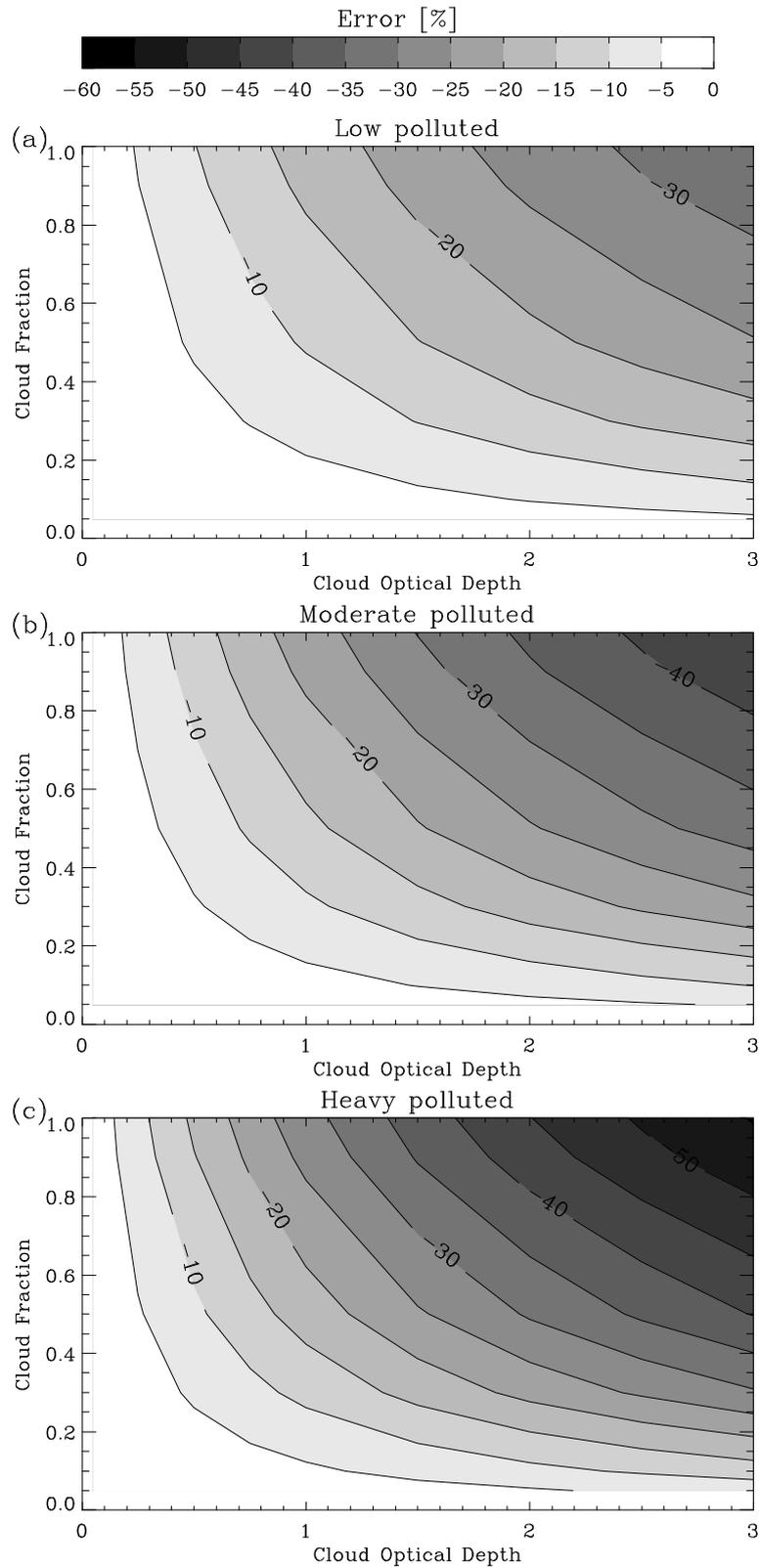
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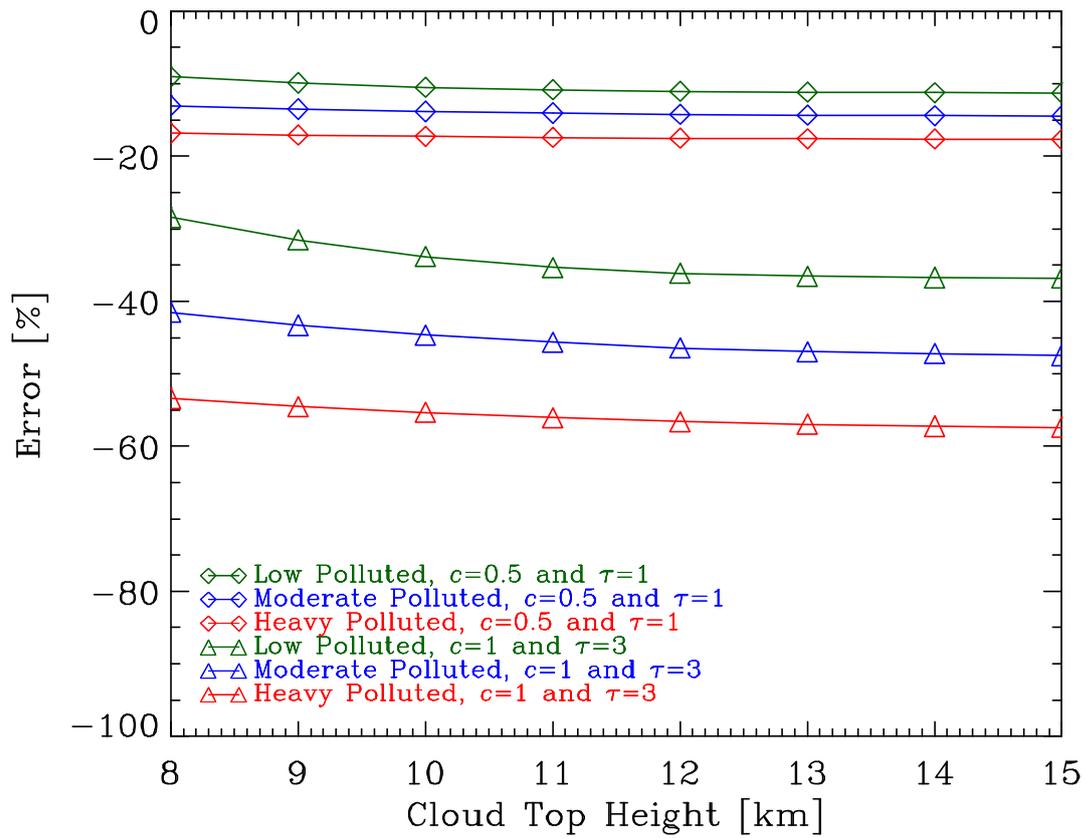
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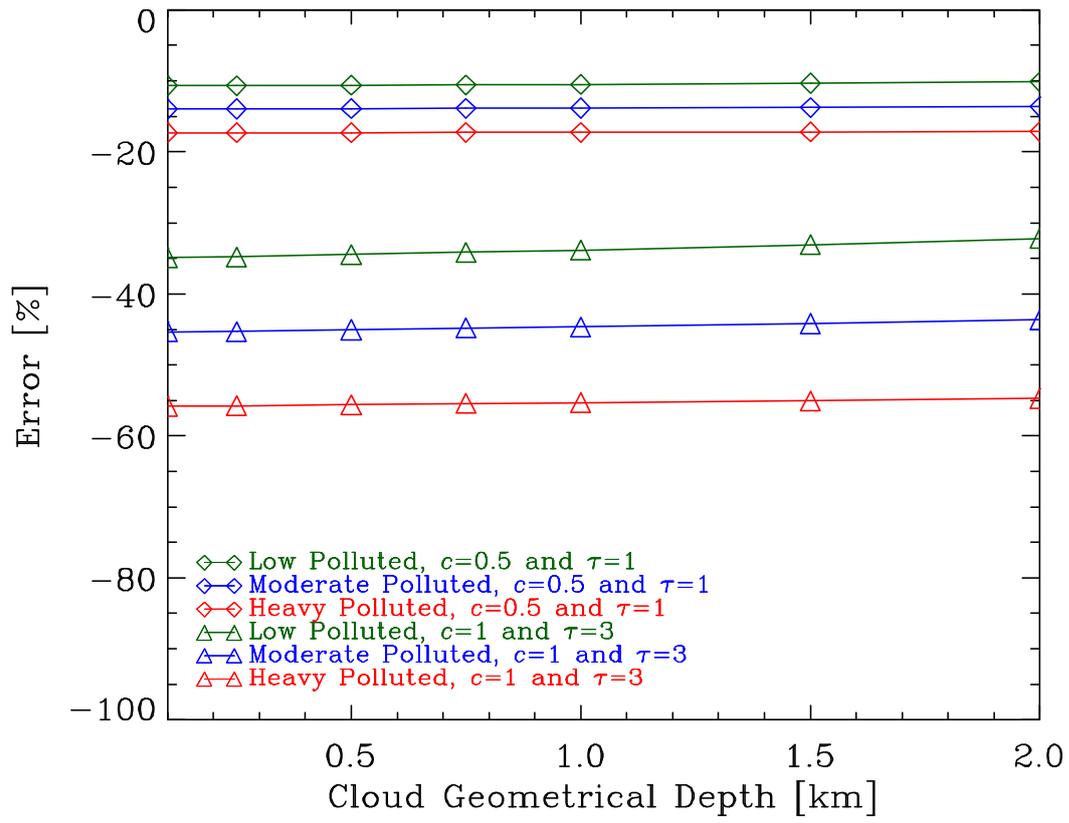
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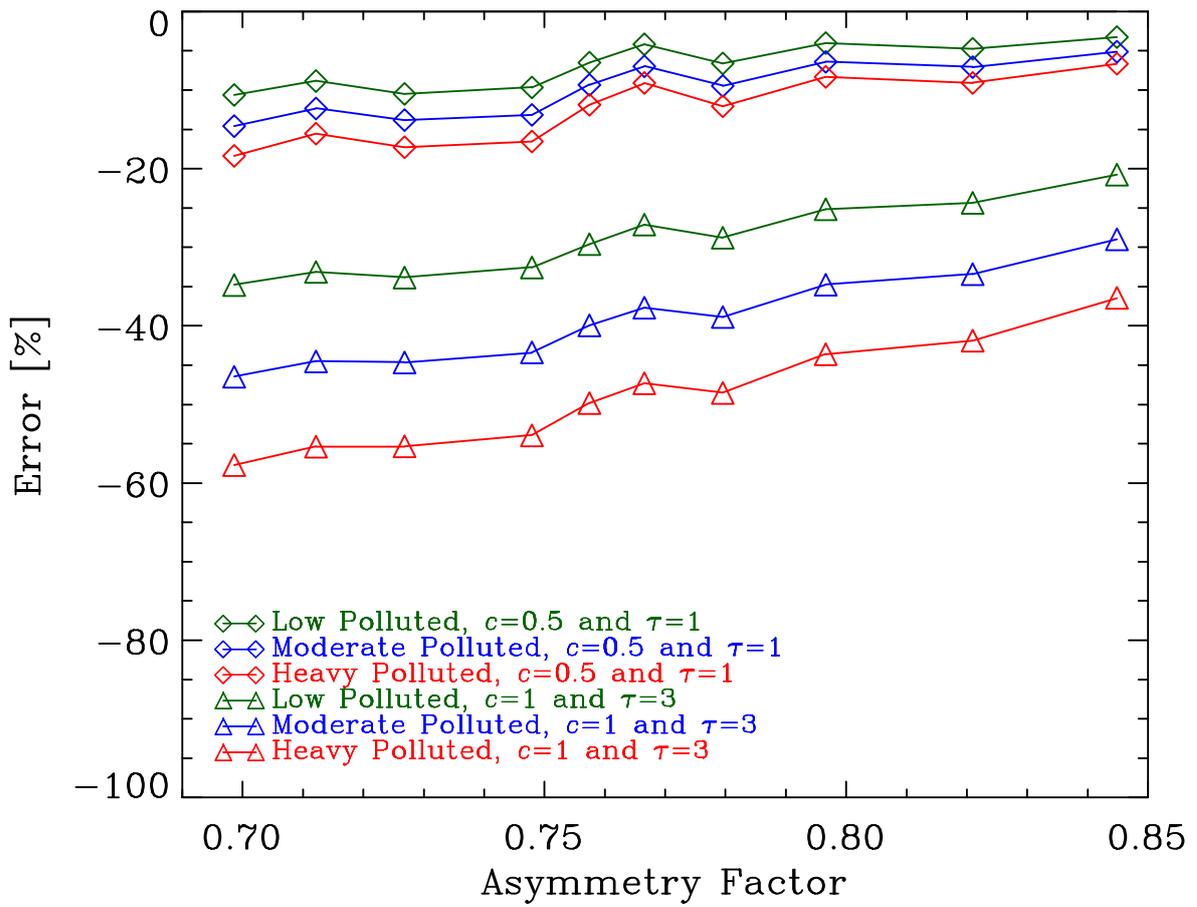
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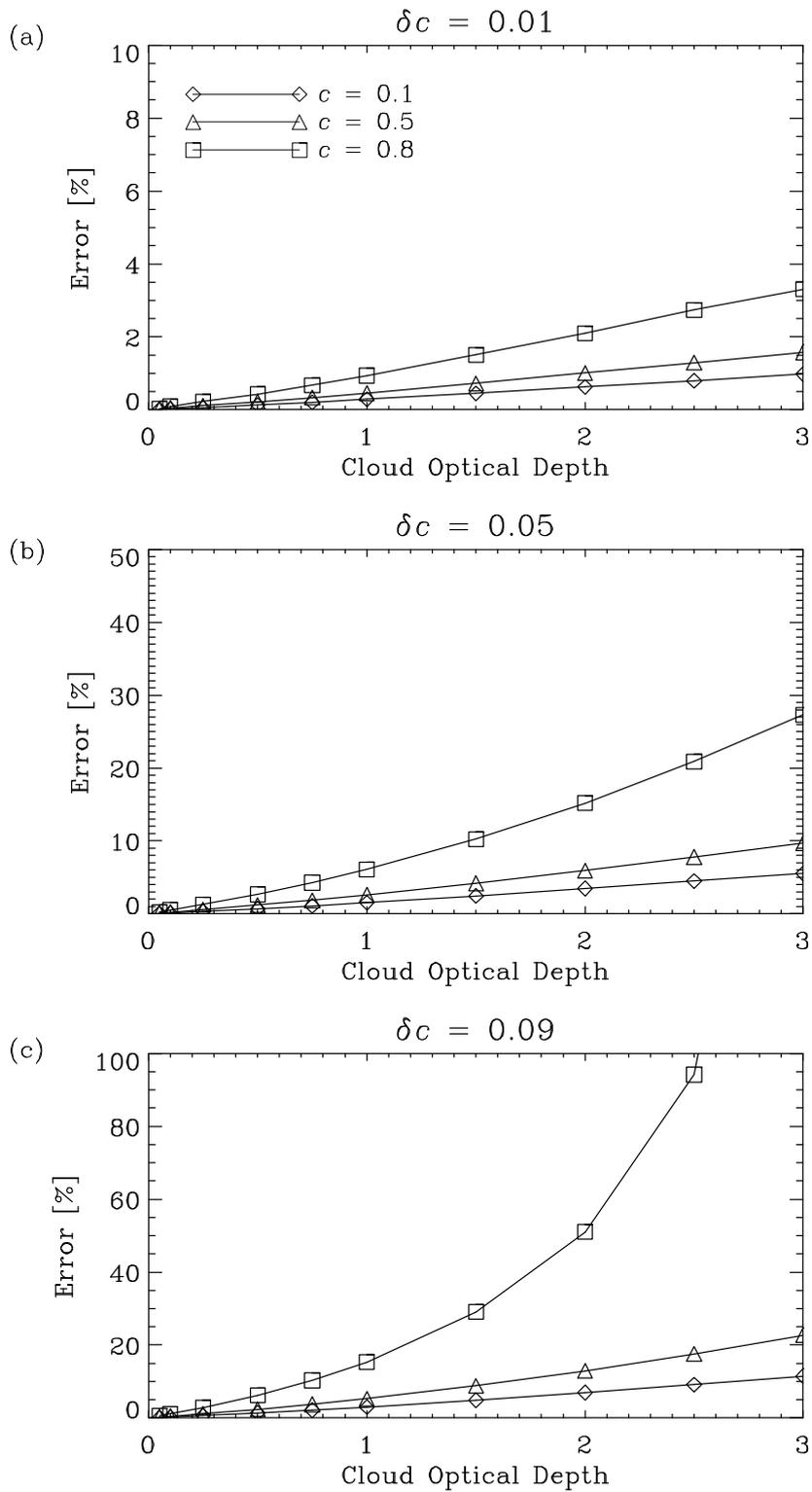
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2Figure 7. Same as Fig. 5 versus asymmetry factor. Here, $z = 10$ km and $h = 1$ km.

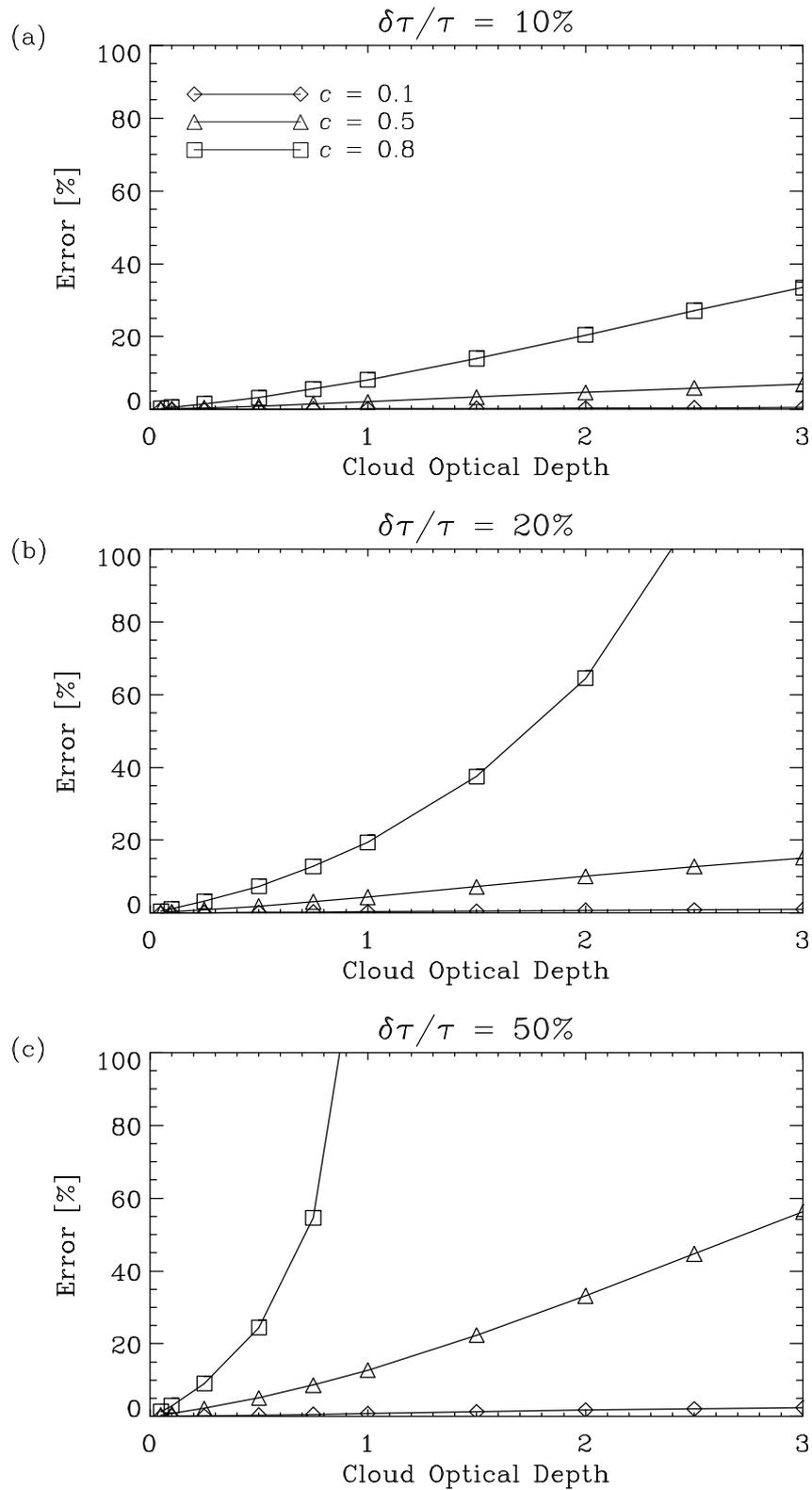
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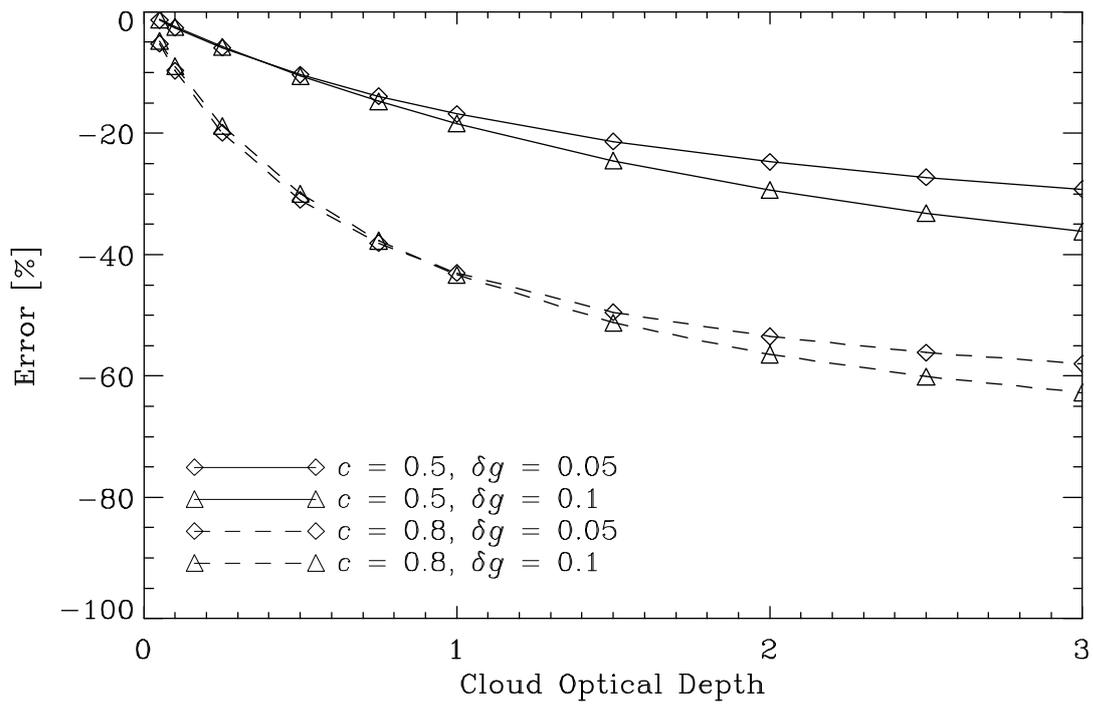
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 50.75 and moderately polluted condition is assumed.

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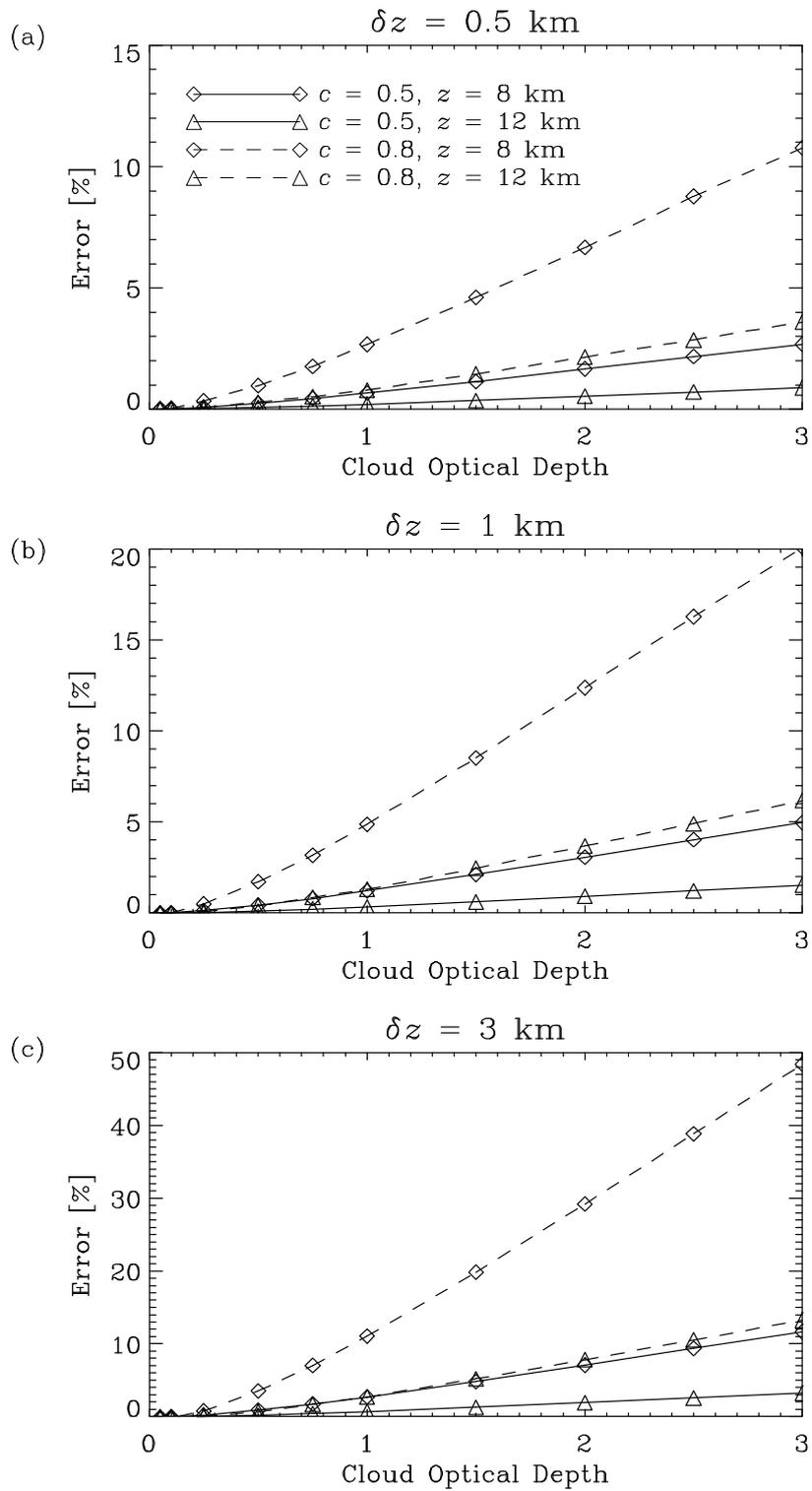
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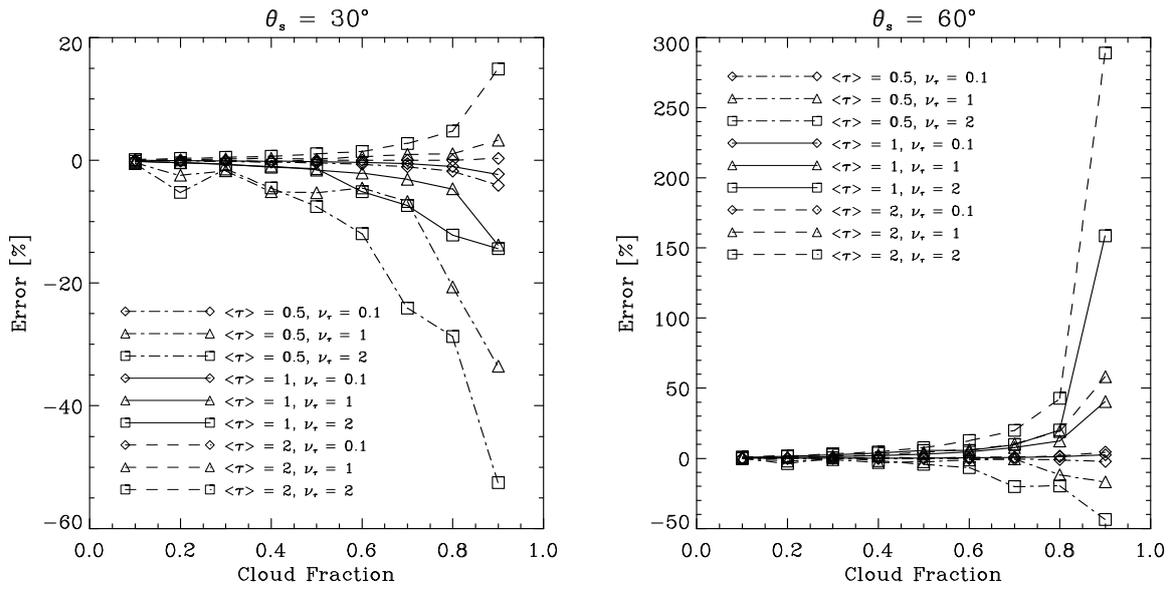
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1

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2Figure 12. NO₂ tropospheric column error caused by the use of a mean cloud optical depth
3instead of subpixels information versus cloud fraction if $\theta_s = 30^\circ$ (left) and if $\theta_s = 60^\circ$ (right).

1

Error difference [%] between $z = 8$ km and $z = 15$ km	$\tau = 0.05$	$\tau = 1$	$\tau = 3$
$c = 0.05$	0.01	0.29	1.07
	0.01	0.18	0.78
	0.01	0.12	0.56
$c = 0.5$	0.10	2.26	6.15
	0.06	1.40	4.39
	0.09	0.90	3.03
$c = 1$	0.19	3.63	8.35
	0.12	2.20	5.93
	0.17	1.35	4.02

2Table 1. NO₂ tropospheric error difference caused by cloud top height z variability. Values in

3each box of fixed c and τ correspond to low, moderately and heavily polluted conditions,

4respectively.

1

Error difference [%] between $h = 0.1$ km and $h = 2$ km	$\tau = 0.05$	$\tau = 1$	$\tau = 3$
$c = 0.05$	0.01	0.08	0.34
	<0.01	0.04	0.21
	<0.01	0.02	0.14
$c = 0.5$	0.03	0.54	1.96
	0.02	0.31	1.23
	0.02	0.17	0.81
$c = 1$	0.05	0.88	2.69
	0.04	0.49	1.69
	0.04	0.27	1.10

2Table 2. Same as Table 1 for cloud geometrical depth h .

3

1 Error difference [%] between $g = 0.65$ and $g = 0.85$	$\tau = 0.05$	$\tau = 1$	$\tau = 3$
$c = 0.05$	0.07	1.00	2.66
	0.07	1.29	3.40
	0.09	1.61	4.21
$c = 0.5$	0.66	7.37	12.25
	0.77	9.44	15.40
	0.89	11.69	18.85
$c = 1$	1.27	11.30	14.04
	1.52	14.24	17.50
	1.76	17.58	21.27

2Table 3. Same as Table 1 for asymmetry factor g .

3