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Improved satellite retrievals of NO₂ and SO₂ over the Canadian oil sands and comparisons with surface measurements

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Abstract

Satellite remote sensing is increasingly being used to monitor air quality over localized sources such as the Canadian oil sands. Following an initial study, significant low biases have been identified in current NO₂ and SO₂ retrieval products from the Ozone
Monitoring instrument (OMI) satellite sensor over this location resulting from a combination of its rapid development and small spatial scale. Air mass factors (AMFs) used to convert line-of-sight "slant" columns to vertical columns were re-calculated for this region based on updated and higher resolution input information including absorber profiles from a regional scale (15 km × 15 km resolution) air quality (AQ) model, higher spatial and temporal resolution surface reflectivity, and an improved treatment of snow. The overall impact of these new Environment Canada (EC) AMFs led to substantial increases in the peak NO₂ and SO₂ average vertical column density (VCD), occurring over an area of intensive surface mining, by factors of 2 and 1.4, respectively, relative to estimates made with previous AMFs. Comparisons are made with long-term aver-

- ages of NO₂ and SO₂ from in-situ surface monitors by using the AQ model to map the OMI VCDs to surface concentrations. This new OMI-EC product is able to capture the spatial distribution of the in-situ instruments (slopes of 0.7 to 1.0; correlation coefficients of 0.9). The concentration absolute values from surface network observations were in reasonable agreement, with OMI-EC NO₂ and SO₂ biased low by roughly
- 30 %. Several complications were addressed including correction for the interference effect in the surface NO₂ instruments and smoothing and clear-sky biases in the OMI measurements. Overall these results highlight the importance of using input information that accounts for the spatial and temporal variability of the location of interest when performing retrievals.





1 Introduction

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Space-based measurements of the near-surface atmospheric composition, or air quality (AQ), from near-UV-to-near-IR spectra have blossomed over the past two decades from relatively crude, research-grade products to refined, operational products suitable
 for monitoring and assimilation (e.g., Miyazaki et al., 2012). These products include tropospheric vertical column densities of NO₂, SO₂, CO, HCHO, and aerosol optical depth from nadir-viewing instruments that measure backscattered sunlight (e.g., Martin, 2008). Furthermore, through the fusion of satellite data and models, fundamental quantities crucial to air quality such as surface concentration (Lamsal et al., 2008) and
 emission rates (Streets et al., 2013) are now being derived from these less familiar vertically-integrated quantities.

This category of sensor began with the GOME (Global Ozone Monitoring Experiment) instrument (Burrows et al., 1999) and continued with SCIAMACHY (SCanning Imaging Absorption spectroMeter for Atmospheric CartograpHY, 2002–2012) (Bovens-

mann, 1999), OMI (Ozone Monitoring Instrument, 2004–present) (Levelt et al., 2006), and the operational GOME-2 (2006–present, 2012–present) instruments. Collectively these instruments have provided invaluable information on distributions and trends in NO₂ and SO₂ despite the complexities associated with the inversion of these spectra. Applications of these data to air quality issues are numerous and span wide spatial and temporal scales.

More recently these data have been applied to the analysis of localized sources whose spatial extent is comparable to that of a individual resolution element, or pixel (Beirle et al., 2011; Fioletov et al., 2011). One high-profile example is the Canadian oil sands (McLinden et al., 2012). This area in the northeast corner of the province of Alberta contains a vast deposit of hydrocarbons, including an equivalent of 170 billion barrels (roughly $2.7 \times 10^7 \text{ m}^3$) of oil in the form of bitumen, a viscous form of petroleum.

Production has increased rapidly from about 0.6 million barrels per day (mBPD) in 1998 to 2 mBPD in 2012 and with a further doubling expected over the next decade (ERCB,





2012). Another measure of the size of the industrial complex is capital expenditures which have fluctuated between Cdn10-20B since the mid-2000s, and are expected to remain in this range for at least the next decade. An initial study using these satellite instruments found distinct enhancements of NO₂ and SO₂ over the area of intensive

⁵ surface mining (an area of about 50 km × 30 km) and with the enhancement in NO₂ increasing at a rate of about 10 % yr⁻¹ (McLinden et al., 2012). A map of the area showing the oil sands boundary and the location of the surface mining is given in Fig. 1. The rapid expansion is evident from the Landsat images. Overlaid on the Landsat images are approximate boundaries of the active mining regions (for 2011) and are used for reference in later figures. A reference location (57.1° N, 111.6° W) is also identified.

Even among near-point sources the oil sands represents a particular challenge to satellite remote sensing due to a combination of the rapidly changing landscape and emissions, its higher latitude (57° N), frequent snow cover, and higher boundary layer winds that disperse the emitted compounds more rapidly. These factors conspire to make signals here more difficult to observe and, perhaps more importantly, the rapid industrial evolution of the region makes some of the assumptions in the current gener-

ation of retrieval algorithms suspect.

2 Satellite data products

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Of the nadir-viewing UV/visible satellite instruments listed above, OMI is the best suited to oil sands monitoring due to its finer spatial resolution and high density of measurements (Fioletov et al., 2013). It is also only one with sufficient signal-to-noise to detect SO₂ in this region. On this basis it will be the focus of this work.

2.1 The OMI instrument

OMI, a Dutch/Finnish instrument, was launched in July 2004 along with three other atmospheric sensors on the NASA Aura satellite (Levelt et al., 2006). OMI measures





spectra in the UV-visible (270–500 nm at 0.42 to 0.63 nm resolution) of sunlight reflected by the surface and scattered by the atmosphere back into space. It employs a two-dimensional detector that measures simultaneously at 60 across-track positions and thus does not require across-track scanning. This results in a spatial resolution that varies significantly with track position: those pixels nearer the track centre are roughly 30 km wide while those near the edge are > 100 km wide. A blockage beginning in 2007 – the so-called "row anomaly" – has meant some track positions are no longer reliable (see http://www.knmi.nl/omi/research/product/rowanomaly-background.php).

2.2 OMI data products

- Beginning with calibrated and geo-located nadir spectra, and with the exception of socalled direct inversions (e.g., Nowlan et al., 2011), UV-visible tropospheric NO₂ and SO₂ retrieval algorithms are composed of three distinct steps. The first step is a determination of the total absorption by that species (where the target species is hereafter referred to simply as the absorber) and this is quantified in terms of a slant column density (SCD), *S*. The SCD represents the absorber number density integrated along
- density (SCD), S. The SCD represents the absorber number density integrated along the path of the sunlight through the atmosphere. Since OMI measures back-scattered light the path is not a direct one and includes one or more scattering events and/or surface reflections. SCDs are derived through an analysis of the measured spectra by exploiting the difference in absorption at nearby wavelengths. The second step is the
- ²⁰ removal of the stratospheric component of the total SCD, relevant only for NO₂. This is generally done by either by a filtering or statistical approach, or by explicitly modelling or assimilating the stratospheric SCD and subtracting it. The final step is a conversion of the tropospheric SCD, S_t , into a tropospheric VCD, V, via an air mass factor (AMF), M, that accounts for the sensitivity of the instrument to the absorber. Owing to the
- ²⁵ complex path of the scattered and reflected sunlight, AMFs must be computed using a radiative transfer model. These tropospheric VCDs are the primary data product and generally serve as the starting point for science and monitoring applications.





Multiple OMI NO₂ VCD data products currently exist. The two global, primary products are the NASA standard product (SP) (Wenig et al., 2008; Bucsela et al., 2013; http: //disc.sci.gsfc.nasa.gov/Aura/data-holdings/OMI/omno2_v003.shtml) and the Dutch OMI NO₂ (DOMINO) (Boersma et., 2007, 2011; http://www.temis.nl/airpollution/no2. html) processed in near-real time. While there were some significant differences between their respective version 1 data products, their version 2 (v2) products are in much better agreement (Bucsela et al., 2013). The DOMINO v2 tropospheric VCD uncertainty is $(25\% + 10^{15} \text{ cm}^{-2})$. DOMINO and the SP use common SCDs derived using the technique of Differential Optical Absorption Spectroscopy (Platt, 1994) over the

- 405–465 nm wavelength range, but differ in how they remove the stratospheric SCD. The SP employs a complex high-pass filtering approach whereas DOMINO simulates the stratospheric NO₂ by assimilating OMI SCDs in a chemical data assimilation system (Dirksen et al., 2011). In addition there are other, offline products available such as the Empa OMI product for Europe (Zhou et al., 2009; http://temis.empa.ch/index.php)
 and the regional Berkley High-Resolution (BEHR) (Russell et al., 2011) which makes
- use of higher resolution input data but over a domain limited to the continental US. All of these products calculate an AMF specific to a given measurement based on a variety of factors.

In contrast, there is only one OMI SO₂ VCD planetary boundary layer (PBL) data product available. It is based on the NASA Band Residual Method (BRM; http://disc. sci.gsfc.nasa.gov/Aura/data-holdings/OMI/omso2_v003.shtml) which uses four wavelengths between 310 and 315 nm to quantify SO₂ absorption (Krotkov et al., 2006). Unlike the case of NO₂, the NASA SO₂ product uses a spatial and temporally invariant AMF, calculated for summertime conditions in the eastern US. Improved OMI SO₂

²⁵ AMFs have been calculated for portions of the OMI timeseries (Lee et al., 2009) but these have not yet been completely merged with the official NASA product.

In this work the DOMINO and SP NO_2 and the NASA SO_2 products are examined. They are collectively referred to as the "current" products.





2.3 Atmospheric chemistry models

This study also makes extensive use two atmospheric chemistry models. The first is the Global Environmental Multi-scale–Modelling Air quality and Chemistry (GEM-MACH). GEM-MACH is the Canadian regional air quality forecast model used operationally
to predict the concentrations of O₃, NO₂, PM_{2.5} over North America, and the Canadian Air Quality Health Index at cities wthin Canada (Moran et al., 2009; Anselmo et al., 2010). The model makes use of detailed tropospheric processes for gas and particle chemistry and microphysics originating in the off-line A Unified Regional Airquality Modelling System (AURAMS, Gong et al., 2006), but incorporated on-line into the Canadian weather forecast model (Global Environmental Multiscale model, Côté et al., 1998). A detailed description of the chemical processes found in AURAMS and GEM-MACH may also be found in Kelly et al. (2012). Both AURAMS and GEM-MACH share a sectional, speciated particle distribution – for the operational GEM-MACH forecasts used here, two bins are used, to represent particle fine and coarse modes, re-

- ¹⁵ spectively. These results used here are from archived forecasts from 2010 to 2011 for a domain covering North America at $15 \text{ km} \times 15 \text{ km}$ resolution. The emissions inventories for the model are from US EPA and Environment Canada data for the year 2006. Note that GEM-MACH at present does not include NO_x sources for biomass burning and lightning.
- ²⁰ The second is the GEOS-Chem chemical transport model (Bey et al., 2001) version v8-03-01 (www.geos-chem.org) driven by assimilated meteorological observations from the Goddard Earth Observing System (GEOS-5). These simulations were run at 1/2° (latitude) by 2/3° (longitude) resolution in a nested mode over a North-American grid (Chen et al., 2009; van Donkelaar et al., 2012). The model includes
- a detailed simulation of tropospheric ozone-NO_x-hydrocarbon chemistry as well as of aerosols and their precursors (Park et al., 2004). Canadian anthropogenic emissions are from the CAC inventory http://www.ec.gc.ca/inrp-npri) for 2005. Emissions from open fires for individual years are from the GFED2 inventory with monthly resolution





(van der Werf et al., 2009). Lightning NO_x emissions are computed as a function of cloud top height, and are scaled globally as described by Sauvage et al. (2007) to match OTD/LIS climatological observations of lightning flashes. The global source is imposed to be $6 \text{ Tg}(N) \text{ yr}^{-1}$ (Martin et al., 2007). Higher NO_x yields per flashes are used at mid-latitudes than in the tropics (Hudman et al., 2007).

Daily output from both models are sampled at the local time of the OMI overpass, roughly 13:30 LT, and from this monthly-means are calculated.

2.4 OMI measurements over the oil sands

The rapid development of the oil sands raises concern over the validity of some assumptions underlying current NO₂ and SO₂ data products. Space-based nadir UVsensors are generally less sensitive to an absorber located near the surface as opposed to one aloft, and thus a key parameter in the retrieval algorithm is the assumed vertical profile of the absorber. Both NO₂ algorithms, the SP and DOMINO, rely on model-calculated NO₂ profiles: the SP uses monthly-mean profiles from the Global
Modeling Initiative (GMI) (Bucsela et al., 2013) and DOMINO uses daily output from the TM4 (Tracer Model 4) chemical transport model (Boersma et al., 2007). Both models, however, make use of emission inventories appropriate for the late 1990s when oil sands NO_x emissions were significantly smaller than current values (Boersma et al., 2007; B. Swartz, personal communication, 2012). The impact of this can be seen in the NO

- ²⁰ the NO₂ profiles from these different sources of data in the vicinity of the oil sands. Figure 2a shows the annual-mean NO₂ profiles over the oil sands, sampled at the local time of the OMI overpass, from the GMI (horizontal resolution of 2° lat × 2.5° lon) and TM4 (2° × 3°) models. Also shown for comparison are profiles from the higher resolution models discussed in Sect. 2.3, GEOS-CHEM and GEM-MACH, smoothed to
- ²⁵ match the resolution of GMI. The profiles are presented as shape-factors, which are volume mixing ratio (vmr) profiles normalized by their column-averaged vmr. The GMI and TM4 profiles show values that are significantly smaller in the PBL, by a factor of 2–3, than GEOS-CHEM and GEM-MACH and generally resemble shape factors for





near-background profiles. In fact, their absolute value in the boundary is layer is only about 0.1–0.3 ppb, and so are representative of background levels. As is discussed below, the end result of this underestimate of NO_2 in the PBL is an underestimate of tropospheric VCDs.

- ⁵ Beyond the outdated emissions is the related issue of model resolution. With grid boxes in excess of 200 km (latitude) by 150 km (longitude), the GMI and TM4 models cannot resolve the surface mining region whose entirety spans 50 km by 30 km. This means the same model NO₂ profile may be used at both the center of emissions and 100 km away where the NO₂ would be at or near background levels. This issue of pro-
- file "representativeness" has been identified as a potential error source for near-point sources (Heckel et al., 2011). Figure 2b illustrates the steep horizontal gradients in the annual-mean NO₂ profiles from the GEM-MACH model by comparing vmr profiles at the maximum emissions with those at 10 and 50 km away.

Related concerns exist for SO₂ VCDs: the use of an invariant AMF, calculated for summertime conditions in the eastern US, will likely also lead to spatial and seasonal biases although in this case the sign of the bias is less apparent. On this basis it was concluded that there is a potential for significant systematic errors in these current (DOMINO and SP NO₂ and NASA SO₂) products over the oil sands region. Thus, any quantitative assessment of these gases requires AMFs to be re-evaluated in this region

accounting for both the rapidly changing emissions and their small spatial scale. Furthermore, calculating NO₂ and SO₂ AMFs in a consistent manner should increase their compatibility, possibly allowing for their ratio or differences in their spatial distributions to be used to infer additional information about the nature of sources.





3 Air mass factors

3.1 General concept

The general AMF framework used herein follows that of Palmer et al. (2001), Martin et al. (2002), and others. The AMF (*M*), defined as the ratio of the SCD (*S*) to the VCD (V), or M = S/V, describes the enhancement in absorption when light traverses a slant path through a layer and represents a cornerstone of retrievals in the UV-visible portion of the spectrum. From this definition, the steps in the retrieval algorithm described in Sect. 2.2 can be expressed as,

$$V_{\rm t} = \frac{S_{\rm t}}{M} = \frac{S - S_{\rm s}}{M}$$

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- ¹⁰ where $S = S_t + S_s$, and subscripts "s" and "t" refer to stratosphere and troposphere, respectively, and *M* is the tropospheric AMF. Here *S*, determined from the spectral analysis, is the only quantity measured directly by OMI; S_s and *M* must be determined from a combination of statistical considerations, modelling, or assimilation. For SO₂ it is assumed there is no appreciable stratospheric component ($S_s = 0$).
- ¹⁵ When direct sunlight is measured, as may be the case for a ground-based spectrometer, it is straightforward to determine the path of the sunlight through the atmosphere, and hence the AMF may be deduced from purely geometrical considerations. However, when scattered sunlight is the source of information, the path is much more complex involving, in general, multiple scattering and surface reflection events. More-
- over, the measured radiance will be a combination of many different paths. Resolving this requires radiative transfer models capable of simulating the multiple-scattering and absorption processes.

The distribution of scattered light, including nadir radiances (and thus AMFs), is controlled by many factors including solar and instrument viewing geometry, surface reflectivity, aerosols and clouds, and the vertical distribution of the absorber (e.g., Martin et al., 2003). It is most convenient to account for the dependence on vertical distribution



(1)



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where w is the radiative cloud fraction and the subscripts "c" and "a" represent

cloudy and clear-sky, respectively. The radiative cloud fraction represents the frac-

tion of the nadir radiance that is due to the cloudy portion of the pixel. It differs

from the effective (geometric) cloud fraction, f, as clouds tend to be more reflective and thus contribute disproportionately to the overall radiance. They are related by

 $w = f \cdot I_c / [f \cdot I_c + (1 - f) \cdot I_a]$, where *I* is the nadir radiance.

by using a vertically-resolved AMF, m(z), such that M represents the absorber number density weighted-average of m(z),

$$M = \frac{S}{V} = \frac{\int_{z}^{z} n(z) \cdot m(z) \cdot \alpha[T(z)] \cdot dz}{\int_{z}^{z} n(z) \cdot dz}$$

where n(z) is the absorber number density vertical profile and $\alpha[T(z)]$ is a correction factor that accounts for the change in the absorption cross-section with temperature. For both species a correction of $\alpha = 1 - 0.003[T(z) - T_0]$ was used where $T_0 = 220$ K for NO₂ (Boersma et al., 2004) and $T_0 = 273$ K for SO₂ correspond to the temperatures of the cross-sections used in the spectral analysis. Values of m(z) are also referred to a box-AMFs and are analogous to the scattering weights used in other studies (e.g., Martin et al., 2002) but without a normalization by a geometric AMF.

Another of the key factors in determining AMFs are clouds. Clouds behave as bright surfaces reflecting more light than that of the underlying surface. They also act to shield the sensor from any absorbers located below the cloud. The treatment of clouds used here follows the general approach used in other studies (Boersma et al., 2004; Martin ¹⁵ et al., 2006) in which they are modelled as Lambertian reflectors located at the cloud altitude, and with an albedo of 0.8. In the case of a partially cloudy pixel, the AMF is taken as a linear combination of the cloudy and clear-sky AMF as follows,

 $M = w \cdot M_{\rm c} + (1 - w) \cdot M_{\rm a}$

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(2)

(3)



3.2 Air mass factor input information

AMFs are calculated using radiative transfer models that simulate nadir radiances while accounting for all relevant physical processes, including multiple scattering by molecules and aerosols, absorption by trace gases, and reflection from the surface.

⁵ Their accuracy is governed to a large extent by the accuracy of the input information with the most important being the shape of the absorber vertical profile, the surface reflectivity, cloud and aerosol information, surface pressure, and, in the case of SO₂, the stratospheric ozone column. These are discussed below and summarized in Table 1.

3.2.1 Absorber profiles

- ¹⁰ Knowledge of the NO₂ and SO₂ vertical distribution is required to correctly determine the instrument sensitivity. Absorption by these species is sufficiently small that they do not impact the bulk properties of the radiation field and thus it is only the shape of the vertical profile that is relevant. In order to better capture the large spatial gradients these species display in the immediate vicinity of the surface mines, the GEM-MACH
- ¹⁵ regional, air quality forecast model is used as a source of profile information. The 2010– 2011 monthly means are used for all years as GEM-MACH output is not available prior to mid-2009. The 15 km grid size is well suited for OMI retrievals as it is comparable in size to that of the median OMI pixel size (consider only the smaller pixels) and so no additional smoothing was applied.
- The lack of biomass-burning and lightning NO_x sources in GEM-MACH can be seen in Fig. 2a as NO₂ profiles in the free troposphere are smaller than those of the other three models. To remedy this, the GEM-MACH profiles above the boundary layer are transitioned to monthly mean profiles from the GEOS-CHEM model. When GEM-MACH profiles are smoothed to the GEOS-CHEM resolution, there is good general agreement between the two in the boundary layer and thus this transitioning does not generally introduce significant discontinuities. A linear weighting is used between -0.5 km and +1.5 km, relative to the GEM-MACH boundary layer height, to ensure





a smooth hybrid profile. For PBL heights below 0.5 km, the transition begins at the surface. The coarser resolution of GEOS-CHEM (by roughly a factor of 10 as compared with GEM-MACH) is not an issue in the free troposphere where horizontal gradients tend to be smaller. For consistency, hybrid SO₂ profiles are constructed in a similar manner. The use of pure GEM-MACH and GEOS-CHEM profiles are discussed as part of the sensitivity study, below. A comparison of the annual mean GEOS-CHEM and the hybrid vmr profiles (smoothed to GEOS-CHEM resolution) over the surface mining region is shown in Fig. 2c.

3.2.2 Surface reflectivity

- For simplicity, most AMF algorithms incorporate surface reflection using a Lambertian Equivalent Reflectance (LER) which is independent of geometry. Monthly-mean LER climatologies derived from the GOME or OMI instruments (e.g., Kleipool et al., 2008) which are, at best, available on a 0.5° × 0.5° grid are common used. While in some respects the use of an OMI-derived LER database is advantageous for OMI trace gas
- retrievals (same viewing conditions and wavelengths), compared with the spatial scale of interest in this work and the resolution of other input information, 0.5° remains somewhat coarse. Furthermore, its lack of inter-annual variability is problematic in that the rapidly changing land cover of the oil sands may introduce a bias in any trend from an unaccounted for change in reflectivity.
- ²⁰ An alternative source of albedo is available from the Moderate-Resolution Imaging Spectroradiometer (MODIS) satellite instrument (Schaaf et al., 2002), used previously for OMI NO₂ retrievals (Zhou et al., 2009, 2010; Russel et al., 2011). MODIS provides white-sky albedo (WSA) and black-sky albedo (BSA), based on 16 day averages available every 8 days, at a resolution of 0.05° × 0.05° (MOD43C3, collection 5). The
- improved spatial resolution of this product is a significant advantage when targeting near-point sources, and the inter-annual variability accounts for the evolution of land cover changes. A limitation of this data product however is the spectral range – the shortest wavelength is 477 nm, similar to that required for NO₂ (~ 440 nm) but long of



the SO₂ spectral region (~ 315 nm). The errors introduced in OMI NO₂ AMFs using this MODIS product over the more rigourous bidirectional reflection distribution function (BRDF) has been examined by Zhou et al. (2010). In the summer errors are < 5 % while for lower sun angles errors of 10–20 % are possible depending on the shape of the absorbing profile.

The spatial patterns in the OMI albedos (Kleipool et al., 2008) at 342 nm and 477 nm reveals were found to be general consistent, thereby suggesting it is reasonable to simply scale the MODIS albedo by an OMI-derived ratio to arrive at a better representation of reflectivity at near-SO₂ wavelengths. As MODIS provides both BSA and WSA, where BSA is more appropriate for direct sunlight incident on the surface and WSA for diffuse light, a weighted average is used with the weighting determined by the model calculated fraction of downwelling irradiance that is diffuse. In this work, albedo was calculated using,

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$$\alpha(\lambda; t; x, y) = \left[(1 - f_{dif}) \cdot \alpha_{bs}(\lambda_M; t, x, y) + f_{dif} \cdot \alpha_{ws}(\lambda_M; t, x, y) \right] \cdot \left[\frac{\alpha(\lambda)}{\alpha(\lambda_M)} \right]_{OMI}$$
(4)

¹⁵ where $\alpha_{\rm bs}$ and $\alpha_{\rm ws}$ are the MODIS monthly-mean BSA and WSA at a wavelength of $\lambda_M = 477$ nm and $f_{\rm dif}$ is the model-calculated (see Sect. 3.3) fraction of the total downwelling irradiance at the surface that is diffuse. The averages are calculated using 100 % snow-free scenes and were smoothed to approximate the resolution of a representative OMI pixel (15 km × 30 km). The final factor in Eq. (3) adjusts the MODIS albedo to that a wavelength more representative of the spectral region used in the analyses, $\lambda = 440$ nm for NO₂ or $\lambda = 342$ nm for SO₂, using the updated Kleipool et al. (2008) OMI monthly climatology.

Examples of the MODIS-derived surface albedo (via Eq. 4) for NO₂ and SO₂ are shown in Fig. 3, along with that from the OMI-climatology, averaged over the summer (JJA). The MODIS maps for NO₂ albedo are for 2005 and 2011 and for SO₂ for 2005. The general magnitudes of the OMI reflectivity and the MODIS are similar, but the higher resolution of the MODIS clearly show the footprint of the surface mines. They



also reveal that there is an evolution with time. Also of note are the slightly larger values of albedo for SO_2 relative to NO_2 resulting from the wavelength adjustment.

3.2.3 Identication and treatment of snow

Owing to the large fraction of OMI observations that are made over snow in the oil sands region, roughly 40 %, it is important to address this aspect as well. Problems with UV/visible measurements over snow have been discussed in previous work (O'Byrne et al., 2010). In principle snow represents an ideal surface in that its higher reflectivity means the instrument is more sensitive to the near-surface and thus less sensitive to the shape of the absorber profile. In practice, however, complications arise due to is-

- sues with correctly identifying the presence of snow (either false positives or false negatives) and the subsequent choice of an appropriate surface albedo (snow or snow-free) for the determination of the cloud fraction and AMFs. The end result is often large errors in the cloud fraction and the use of an inappropriate surface reflectivity. The intent here is not to remedy the entirety of the problem as this requires an improved cloud fraction
- ¹⁵ data product which is beyond the scope of this study. Nonetheless, two elements can be readily addressed: identification of snow and the choice of snow albedo.

The presence of snow in an OMI scene is currently determined using the Near-realtime Ice and Snow Extent (NISE; http://nsidc.org/data/nise1.html), an operational, daily, global product derived from the Special Sensor Microwave Imager/Sounder (SSMIS)

- ²⁰ passive microwave sensor (Nolin et al., 1998) on a 24km × 24km grid. When using an independent, ground-based determination of snow cover O'Byrne et al. (2010) found this product often missed thin snow cover, a common feature among snow products derived from passive microwave instruments. A similar evaluation was conducted here. Figure 4 shows comparisons (2000–2011) between daily snow cover from NISE com-
- ²⁵ pared with measurements made at two meteorological stations: Fort McMurray (30 km south of the surface mining) and Mildred Lake (in the middle of surface mining). When taking the surface-observed conditions as the truth, NISE misses snow cover roughly 30 % of the time in an annual average. Breaking this down by month (Fig. 4b) reveals





the largest discrepancies generally appear in the autumn months where NISE missed snow more than half the time. Other snow products were examined to determine their potential suitability including the Canadian Meteorological Centre (CMC) Daily Snow Depth Analysis Data (Brown et al., 2003) and the Interactive Multisensor Snow and Ice

- ⁵ Mapping System (IMS) (Helfrich et al., 2007; http://www.natice.noaa.gov/ims/). Both the CMC and the IMS are Northern Hemisphere products on a 24 km × 24 km grid and have been evaluated for their accuracy in northern Canada (Frei and Lee, 2010). IMS is an operational daily, Northern Hemispheric product also on a 4 km grid. Comparisons of these products with the same surface data are also shown in Fig. 4. Annually, CMC
- and IMS misidentified the conditions at the meteorological station 6% of the time, in comparison with NISE that was incorrect 17% of the time. As seen in Fig. 4b CMC tended to over-predict snow in the spring whereas IMS under-predicted snow in the fall. Delving deeper into these instances reveals that when IMS does miss snow, the snow depth is usually very thin, 1–2 cm.
- ¹⁵ When present, snow tends to increase the reflectivity of the scene. The DOMINO retrieval assumed a constant snow albedo of 0.6 and while this value may be reasonable for a global average, snow albedo depends significantly on the underying surface type with values varying between 0.2 for forests to 0.8 for open plains (Moody et al., 2007). Here, MODIS reflectivity was again used to determine snow albedo. Average
- ²⁰ BSA and WSA maps were derived from MODIS (2005–2012) for December, January, and February, limited to 100 % snow covered scenes, and smoothed to 15 km × 30 km. The resultant albedo map is shown in Fig. 5 along with a snow-albedo product from OMI on a $0.5^{\circ} \times 0.5^{\circ}$ grid (O'Byrne et al., 2010). Both are generally consistent with snow albedo values in the 0.2 to 0.4 range. However, due to its coarser resolution the
- ²⁵ OMI product misses the oil sands entirely, which, according to MODIS, is enhanced by as much as 0.2 relative to its surroundings.

The approach adopted in this work was to use the IMS product to identify snowcovered scenes. The IMS product was selected over the CMC as it is operational whereas there is a delay before the CMC reanalysis product is available. As discussed





below, snow-covered scenes are not considered in the OMI data analysis and thus the mention of snow albedo, above, may seem somewhat superfluous. However, future studies will address the issue of cloud fraction determination over snow where an improved estimate of snow albedo becomes important.

5 3.2.4 Topography, surface pressure, and temperature profiles

Elevation, surface pressure, and temperature profiles are all taken from the GEM-MACH model with surface pressure and temperature profiles sampled at the local time of the OMI overpass and averaged monthly.

3.2.5 Ozone

¹⁰ At SO₂ wavelengths, overhead ozone impacts AMFs as it alters the depth to which the UV light can penetrate. Each OMI observation was assigned an OMI-derived total column ozone value appropriate for that day. If a value was not-available for that day, the mean for that month was used instead.

3.2.6 Aerosols

- A robust implementation of aerosol in UV-visible retrievals remains a challenge. Some algorithms do not explicitly include aerosols and argue that, as the OMI cloud fraction algorithm is somewhat sensitive to them, there is some cancelation of errors (Boersma et al., 2011). The degree to which, or even if, this applies will depend on where in the vertical the aerosols are located relative to the absorber. Other algorithms use an aerosol correction factor that can be applied to an aerosol-free AMF (Lee et al., 2009). MODIS observations of average aerosol optical depth over the oil sands suggests values are typically small, 0.1 to 0.2, and are consistent with sunphotometer measurements from Fort McMurray, roughly 30 km south of surface mining area. Previous studies, Martin et al. (2003) for NO₂ and Lee et al. (2009) for SO₂, show aerosol
- $_{\rm 25}$ $\,$ correction factors suggest aerosols would impact SO_2 AMFs in this region by a few





percent at most and so, on this basis, aerosols are neglected. An assessment of the uncertainty introduced from this assumption is provided in Sect. 4.1, below.

3.3 Calculation of AMFs

AMFs were calculated using the VECTOR (VECTor Orders-of-scattering Radiative transfer model) (McLinden et al., 2002, 2006; Wagner et al., 2007). As an initial step to verify the consistency between the AMFs computed using VECTOR to those provided in the DOMINO (v2.0) product, AMFs were calculated by VECTOR using the same input information as used by DOMINO, including the NO₂ profile, albedo, surface pressure, and geometry. For cloud-free pixels within 100 km of the reference location VECTOR AMFs were found to differ from the DOMINO AMFs on average by less than 3%. This agreement is acceptable given that not all input parameters were identical. Using the input information described in Sect. 3.2, vertically-resolved AMFs, *m*(*z*),

were computed on a 0.5 km altitude grid between 0 and 16 km by successively perturbing the absorber over the 0.5 km layers and computing,

¹⁵
$$m(z) = -\frac{1}{l} \cdot \frac{\Delta l}{\Delta \tau(z)}$$

where ΔI is the change in radiance for a change in the optical depth of $\Delta \tau$ due to the perturbation. It is impractical to calculate m(z) for each OMI observation. Instead, a pair of multi-dimensional look-up tables for m(z), I, and f_{dir} , were generated, one for cloud-free conditions and one for cloudy conditions. Recall f_{dir} is used in the calculation of albedo in Eq. (3) and so is not relevant for cloud AMFs since the albedo is set to 0.8. The dependencies of the cloud-free table are surface albedo, solar zenith angle, viewing zenith angle, change in azimuthal angle, surface pressure, and column ozone. The dependencies of the cloud table are cloud-top pressure, solar zenith angle, viewing zenith angle, change in azimuthal angle, and column ozone. These are summarized in 25 Table 2.



(5)



3.4 Environment Canada AMFs over the oil sands

AMFs were computed as described above for each OMI NO₂ and SO₂ measurement recorded within 500 km of the reference location (57.1° N, 111.6° W – see Fig. 1). These AMFs are referred to hereafter as Environment Canada (EC) AMFs. A scatterplot com-

- ⁵ paring these with the DOMINO v2 AMFs is shown in Fig. 6a. The highest density of points occurs in two locations on or just below the 1 : 1 line: at an AMF of 1.5 for snow-free conditions, and around 2.5–3 for snow covered surfaces. The points corresponding to the surface mining area, which represents a small fraction overall, lie well below the 1 : 1 as indicated. This is a result primarily of a larger fraction of the NO₂ being present
- ¹⁰ in the PBL. The cluster of points representing snow-covered surfaces is generally below the 1 : 1 line as a result of the smaller values snow albedo used for the EC-AMFs, typically 0.2–0.35 as compared to 0.6 in the DOMINO product. The purpose of this scatterplot is to explore how the input information outlined in Sect. 3.2 directly impacts AMFs. As such, both TEMIS and EC AMFs use the same cloud fraction. Assessing
- ¹⁵ how a cloud fraction, based on improved snow identification and snow albedo, might also impact AMFs is beyond the scope of this study. Figure 6b shows a histogram of SO₂ AMFs. Recall the NASA algorithm uses a constant AMF of 0.36. The EC snow-free average SO₂ AMF is 0.41 with considerable variability including minimum values of 0.25 which occurs over the surface mining area. For snow scenes the average EC
 ²⁰ SO₂ AMF is 0.79.

The spatial distribution of these AMFs is shown in Fig. 7 where average summer (June-July-August) NO₂ and SO₂ AMFs are shown. These maps are calculated using the pixel averaging method of Fioletov et al. (2011) on a 1 km × 1 km grid and with an averaging radius of 8 km. The DOMINO v2 NO₂ AMFs (panel a) display no dif-

ference between the surface mining area and the surroundings, consistent with the background-like TM4 profiles from Fig. 2. In contrast the EC NO₂ AMFs show a distinct minimum over the surface mines but are otherwise appear similar to the DOMINO AMFs if slightly smaller. Note all AMFs display a banding due to sampling geometry.





The DOMINO: EC AMF ratio, a quantity that reflects the expected impact of VCDs, is also shown. It has a maximum of about 1.9 over the mines, but decreases rapidly with distance to about one. The SO₂ EC-AMFs are also shown. The minimum over the mines is about 0.2–0.25 and they increase to about 0.4 in the surrounding. The ⁵ minimum SO₂ AMF covers a larger area than seen for NO₂ as a result of a larger area of enhancement predicted by GEM-MACH due to its longer lifetime and/or more rapid dispersion (see Sect. 4.2, below).

4 Vertical column densities over the oil sands

The OMI SO₂ SCDs are known to suffer from a variable offset or bias (Lee et al.,
 2009; Fioletov et al., 2011, 2013) resulting in part from an imperfect removal of the stratospheric ozone absorption signal. This bias is treated as a correction that must be made to the SCD in much the same way as the stratospheric SCD must be removed. Thus, the general expression for the tropospheric NO₂ or SO₂ VCD, Eq. (1), becomes,

$$V_{\rm t} = \frac{S - S_{\rm s} - S_{\rm b}}{M}$$

¹⁵ where S_b is the local bias (where $S_b = 0$ for NO₂). It is calculated by averaging *S* over all OMI pixels located between 100 and 150 km from the reference location where SO₂ is assumed to be zero (Fioletov et al., 2011, 2013). There is some time-dependence to this correction and so it is calculated monthly. While Eq. (6) represents the methodology conceptually, it is most convenient to simply apply the calculated quantities directly to the current VCDs using,

$$V_{\rm EC} = \frac{V \cdot M - S_{\rm b}}{M_{\rm EC}}$$

Where *M* is the AMF for the current product (e.g., M = 0.36 for SO₂) and V_{EC} and M_{EC} are the EC VCDs and AMFs, respectively.

(6)

(7)



4.1 Error budget and sensitivity study

Beginning with Eq. (6), the total random uncertainty in VCD, ε , can be expressed as,

$$\varepsilon = \sqrt{\left(\frac{\varepsilon_{\rm s}}{M}\right)^2 + \left(\frac{\varepsilon_{\rm ss}}{M}\right)^2 + \left(\frac{\varepsilon_{\rm b}}{M}\right)^2 + \left(V \cdot \frac{\varepsilon_{\rm M}}{M}\right)^2} \tag{8}$$

where ε_i are uncertainties in the individual terms: ε_s is the uncertainty in the SCD, ε_{ss} in the stratospheric SCD, ε_b the SCD bias, and ε_M the AMF. Values for ε_s and ε_{ss} for NO₂ are taken directly from Boersma et al. (2007) and ε_s for SO₂ from Krokov et al. (2008). The uncertainty in the SO₂ bias correction is based on the standard error of the mean of the bias, averaged over all months. These values are given in Table 3.

- The uncertainty in AMF arises from several different sources, including uncertainties
 in cloud fraction, cloud pressure, surface albedo, profile shape, terrain height/surface pressure, aerosol, and stratospheric ozone. The impact of these on the AMF is assessed by varying each by an amount indicative of its own uncertainty and recalculating the AMF. For example, the surface albedo is varied by ±0.02 and the extent to which this changes the AMF is taken as its uncertainty to this parameter. This is
 assessed using all OMI observations within 200 km of the reference location for the year 2005. Perturbing an input parameter in this way yields a distribution in the relative change in AMF. The standard deviation of the distribution is taken as the uncertainty to a given parameter and it is computed separately for polluted, within 50 km of the reference location, and background, between 50 and 200 km, areas. Only observations
- with radiative cloud fractions of 0.2 or smaller were considered. The results of this are also given in Table 3. The uncertainty due to profile shape was evaluated by recalculating AMFs but using profiles from GEOS-CHEM. Uncertainties in these parameters were assumed to be independent and so the total uncertainty in AMF was calculated by adding the individual terms in quadrature.
- 25

From Table 3 it can be seen that uncertainties in AMFs are about 20–25% for NO₂ and 25–35% for SO₂, with the larger values for the polluted areas. In the case





of NO₂, the contributions from cloud fraction, albedo and profile shape are all comparable at 10+%. For SO₂ the profile shape is the largest contributor. Considering cloud fractions larger than 0.2 leads to much larger uncertainties in AMF, consistent with Lee et al. (2009). The total NO₂ VCD random error is about 0.5×10^{15} cm⁻² for background and 0.8×10^{15} cm⁻² for polluted, with the largest contributor to this being the uncertainty in SCD. The total SO₂ VCD random error is about 0.6 DU (1 DU = 2.69×10^{16} molecules cm⁻²) for background and 0.8 DU for polluted areas, again with the largest contributor being the SCD. For locations with larger VCDs the uncertainty in AMF can become the largest contributor.

- ¹⁰ Note that these uncertainties represent an estimate of the precision of an individual measurement and do not account for systematic errors. It was the primary goal of this work to address systematic errors in the current data products and it is believed that the approach outlined above goes a long way towards achieving this. However, it is likely some systematic errors remain and three potential AMF effects are discussed
- ¹⁵ below. One is the use of a LER as opposed to a BRDF in the treatment of surface reflection, as discussed above. Based on Zhou et al. (2010) this is estimated to be on average less than +10%, and +5% or smaller in the summer. It is appropriate here to discuss the impact of using either the GEOS-CHEM or the GEM-MACH profile shapes, as opposed to the hybrid. GEOS-CHEM NO₂ profiles led to change in AMFs,
- $_{20}$ -7±14% (mean±1- σ). While the average change is modest, the coarser resolution of GEOS-CHEM nevertheless means changes are more significant directly over the mines. GEM-MACH profiles, which are weighted more towards the BL, had a largest impact, -31±25%.

EC-AMFs take into account the evolution of the surface albedo but have thus far neglected the change in absorber profiles as would result from increasing emissions. EC-AMFs were based on model calculations from a 2006 inventory and so are representative of the beginning of the OMI timeseries. The impact of a continuing increase of oil sands NO_x emissions on the VCDs was estimated by recalculating AMFs using profiles shapes in which the values in the PBL have been doubled, crudely representa-



tive of what might be expected from a doubling of emissions. Close to the source this led to an average reduction in AMF of 6%. Further away where there are no sources there should be little to no change. The relatively small impact suggests that a type of saturation effect is occurring: AMFs were already sufficiently weighted towards the PBL that adding additional NO₂ there had only a modest impact. Nonetheless, a 6% effect

that adding additional NO₂ there had only a modest impact. Nonetheless, a 6% effect may still be an important when evaluating trends.

As discussed in Sect. 3.2.6, aerosols were not explicitly included in the AMF calculations. While difficult to uncouple from the aerosol-biased cloud fraction effect, this is a potential source of systematic error that needs to be explored. Similar to clouds,

- ¹⁰ aerosols can either enhance the AMF due to increased scattering or decrease it by shielding an absorbing layer below. To assess this, AMFs were recalculated using single aerosol profile shape that decreases with altitude between 0 and 3 km, purely scattering, and scaled to give an optical depth of 0.1. The inclusion of aerosols acted to either increase or decrease AMF and is linked to the relative profile shapes and height
- ¹⁵ of the PBL. On average aerosols decreased NO₂ AMF within the polluted area by 6 %, with almost no impact over the background locations. Its average effect on SO₂ was about zero. A more comprehensive treatment would consider profiles shape what vary in space and time, and also take into account a correction for aerosols in the cloud retrieval.

20 4.2 VCD climatologies

Long-term (2005–2011) annual average NO₂ and SO₂ VCDs were calculated to examine their spatial distribution. Only small pixels (track positions 11–50), unaffected by the row-anomaly, snow-free, and observations with a radiative cloud fraction of 0.2 or less were considered here. In addition, SZAs were limited to 75° for NO₂ and 60° for SO₂.

Finally, SO₂ VCDs were restricted to values between -5 and +15 DU with the upper limit imposed to avoid spikes from volcanic eruptions. Averages were calculated using the oversampling, pixel averaging method of Fioletov et al. (2011) on a 1 km × 1 km grid





and with an averaging radius of 8 km for NO_2 and 24 km for SO_2 . The larger averaging radius for SO_2 is required due to its higher noise.

Averages are shown in Fig. 8 for the DOMINO and SP NO₂ and NASA SO₂ products. In each case, the corresponding maps based on EC-VCDs are also shown. The difference between the NO₂ EC-VCDs derived from the DOMINO and SP products lay mainly in how the stratosphere is removed. All maps show a clear enhancement over the region of surface mining consistent with the location of the largest emissions and in

- agreement with results from McLinden et al. (2012). The enhancement in NO₂ is largest over the southern mines but displays a secondary maximum over the northern cluster of mines whereas SO₂ is enhanced primarily only over the southern mines. This is also consistent with current information on source locations: SO₂ is emitted principally from upgrading facilities (which convert bitumen to synthetic crude) in the south whereas NO₂ also has area sources from transportation (e.g., the heavy-hauler trucks) in both the north and south. Despite the more diffuse source of NO₂, the SO₂ enhancement is
- ¹⁵ seen to cover a larger area. This is suggestive of a longer lifetime. Also worth noting is the difference in the height of the release: much of the NO_x is emitted at the surface (transportation) whereas SO_2 is emitted primarily from stacks some 200–300 m above the surface where winds are generally faster.

The DOMINO (Fig. 8a) and NASA SP (Fig. 8c) NO₂ are generally consistent with SP

- ²⁰ being 30 % larger over the mines. The difference between DOMINO and EC (Fig. 8b) NO₂ are consistent with what might have been expected from the AMFs: comparable spatial distributions with similar background values but over the surface mines the EC VCDs are larger by a factor of up to 1.9. The same is true when comparing the NASA (Fig. 8e) and EC (Fig. 8f) SO₂, with the EC larger by up to a factor of 1.3. Note that the
- EC-VCDs derived from the DOMINO (Fig. 8b) and SP (Fig. 8d) products are in very good agreement, differences are less than 10 % over the mines and about 2×10¹⁴ cm⁻² in the background.

The mass of these enhancements, where the enhancement is defined as the NO_2 or SO_2 above the background (presumably from oil sands operations), was determined by





performing a non-linear fit of a two dimensional Gaussian with a constant offset to the VCDs (Fioletov et al., 2011; McLinden et al., 2012). The mass of the enhancement is relevant as it is proportional to the local emissions. In the case of SO₂, the background is zero (as a result of the bias correction) and no offset term is used. The mass was
 ⁵ calculated by integrating the Gaussian over all space. Note the fit is performed using the individual VCDs and not the maps from Fig. 8, although the two approaches yield nearly identical results. The mass of the NO₂ enhancements are 4.5 t[NO₂] (DOMINO)

and 9.8 t[NO₂] (EC) and the mass of the SO₂ enhancements are 60 t[SO₂] (NASA) and 80 t[SO₂] (EC). Thus, the EC products gives masses that are 120 % (NO₂) and 34 % (SO₂) larger than the current products.

5 Comparison with surface concentrations

15

It is difficult to validate these results directly. Ideally, coincident measurements of VCD from ground-based spectrometers or vertically-integrated aircraft profiles would be used, but over the oil sands neither of these is available. The general consistency of GEM-MACH with GEOS-CHEM, a well established model often used for AMF calculations (e.g., Lee et al., 2009) provides some confidence in the ability of GEM-MACH to simulate NO₂ and SO₂ in the PBL. Likewise, the ability of the VECTOR RT model to generally reproduce the DOMINO AMFs is also important, but these do not directly address the issue of VCD validation.

The only NO₂ and SO₂ measurements currently available in the oil sands region are from in-situ ground-based (GB) instruments as part of observing network operated by the Wood Buffalo Environment Association (WBEA; http://www.wbea.org/) (Percy et al., 2012). Their locations are shown in Fig. 9, and additional information on the sites and their instrumentation are provided in the Supplement. Note that not all of the stations measure NO₂.

The correlation between these GB measurements of concentration and OMI VCDs can be assessed as has been done by several others studies (e.g., Geddes et al.,



2012), yet this approach only provides information on the ability of the satellite to capture variability. A more direct method of comparison is to transform the surface vmr into a VCD, or vice-versa, with either approach requiring knowledge of the vertical profile. Here the method described in Lamsal et al. (2008) is used in which VCD is mapped to vmr using a modelled profile,

$$\chi = V \cdot \left(\frac{\chi}{V}\right)_{\text{mode}}$$

where *χ* is the surface vmr. This assumes the model can adequately capture the spatial and temporal behaviour of this ratio. Eq. (9) was applied to the EC-VCDs using the same monthly-mean profiles used in the calculation of their AMFs and the resultant
vmrs are referred to as EC-vmr for simplicity. The 2005–2011 average surface NO₂ and SO₂ EC-vmr maps are shown in Fig. 10, calculated using the same pixel-averaging parameters as the VCDs from Fig. 8. In this example the EC-vmr NO₂ is based on the DOMINO v2 product. The spatial distributions generally mimic that of their VCDs with a maximum NO₂ vmr of 2.3 ppbv and a maximum SO₂ vmr of 4.0 ppbv. Also shown
here are the corresponding surface vmr maps obtained using AMFs and VCD-to-vmr mapping based on GEOS-CHEM model profiles. The GEOS-CHEM maps show similar spatial patterns as the EC maps but GEOS-CHEM NO₂ values are typically 30 % smaller and the SO₂ are about 10 % smaller through the enhancement, with contribu-

tions to this difference from both the AMF and the column-to-surface ratio. The location of the WBEA stations are also shown in Fig. 10 and it is clear that in the case of NO₂ the existing stations "miss" the maximum of the OMI distribution.

Comparisons between average GB and EC-vmrs are shown in Fig. 11 for NO₂ and Fig. 12 for SO₂ as a function of the latitude of the WBEA station. Inset in each is the corresponding scatter-plot. The EC-vmr values are calculated by averaging over measurements within 6 km for NO₂ and 12 km for SO₂ of the WBEA station. Again, the larger SO₂ radius is necessary due to its higher noise level. The GB average for a given station was computed by first determining its average as a function of wind direction (using 20°-wide bins), and then taking this average, thereby giving an equal weighting



(9)



to all wind directions. This approach is favoured as satellites measure over a large area (~ 500 km² for OMI) and weight the upwind and downwind directions equally. Averaging in this way, as opposed to a "simple" average that preferentially weights the prevailing wind direction, impacts the mean NO₂ values by between -15% to +15%. For SO₂ the effect is larger, -30% to +30%, which reflects its more localized sources.

One additional effect was considered in advance of the GB-satellite comparisons. The GB NO₂ measurements are made by commercial, chemiluminescence analyzers that rely on molybdenum converters. These instruments alternate between measuring NO_x and NO, with NO₂ inferred as the difference. However, it is well known that these instruments are also sensitive to nitric acid, peroxyacetyl nitrate (PAN), and other oxidized nitrogen-containing species (Winer et al., 1974; Lamsal et al., 2008) which are mistakenly interpreted as NO₂. A simple factor, CF, for this "interference" effect was used herein, following Lamsal et al. (2008, 2010),

$$CF = \frac{NO_2}{NO_2 + \sum AN + 0.15 \cdot HNO_3 + 0.95 \cdot PAN}$$

5

10

- and based on model calculated concentrations (ΣAN is the sum of all alkyl nitrates and PAN is peroxyacetyl nitrate). The multipliers preceding PAN and HNO₃ account for the reduced conversion efficiency of these species by the instrument. Equation (4) was evaluated separately for monthly-mean GEM-MACH and GEOS-CHEM concentrations and their average CF was used to correct the GB measurements. At the relatively low NO₂ levels over the oil sands (average values of < 5 ppb) this correction factor can be considerably smaller than one due to the larger contribution of non-NO_x oxygenated nitrogen species (Lamsal et al., 2008). The station-specific correction factors are given in Table S1. Values range from 0.35 to 0.7, with the smaller factors corresponding
- to smaller mean NO₂ levels. It is difficult to determine the accuracy of these correction factors and errors due to both the modelled species concentration ratios and the conversion efficiencies (which can vary from instrument-to-instrument) may be appre-



(10)



ciable. For simplicity, in this work the difference between the two model evaluations of CF was used as a measure of its uncertainty.

From Figs. 11 and 12, the EC-vmrs are able to capture the spatial variation and gradients of the NO_2 and SO_2 displayed by the GB stations through the mining region.

- For NO₂ (Fig. 11), the EC-vmrs are typically smaller than the GB values (with the CF applied) by a factor of two (roughly 1 ppb) with the exception of the Millennium station (#3), where the differences are larger (3 ppb, a factor of 5). There is no obvious explanation for the larger differences in NO₂ at Millennium and the measurements are roughly constant with wind direction. Excluding Millenium, the slope of the scatterplot
- is 0.54 and the correlation coefficient is 0.80. The SO₂ comparison (Fig. 12) shows much better agreement including the Millennium station (slope of 0.88; correlation coefficient of 0.91). A summary of the linear correlation coefficients and slopes are given in Table 4.
- Given its spatial resolution, OMI is only able to provide a smoothed version of the true surface vmr distribution. Indeed, this may be the origin of some of the GB-satellite differences seen in Figs. 11 and 12. To better understand this, idealized estimates of the true NO₂ and SO₂ surface vmr distributions were constructed assuming the distribution resulting from a source "region" is reasonably represented by a 2-D gaussian. Parameters for the gaussians were selected so that (i) their vmrs were comparable
- to the average measured values at the GB stations and (ii) after smoothing the distributions generally resembled those from Fig. 8 (although not necessarily the absolute values). For NO₂, the sum of three Gaussians was used: one each for the north and south grouping of mines, and a smaller one for the Fort McMurray area. For SO₂ only one Gaussian was used, reflecting the lack of a significant source of SO₂ in the north
- or Fort McMurray. GB measurements from Fort Chipewyan (station 12) were used to define background values. These idealized distributions were then smoothed using a 15 km × 30 km 2-D boxcar to simulate the OMI pixel size, and both original and smoothed distributions (shown in the Supplement) were sampled at the location of the WBEA stations using values with 6 km for NO₂ or 12 km for SO₂. As expected, stations





near the peaks became smaller and those in the wings became larger as a result of the smoothing: NO₂ was impacted by -35% to +15%, SO₂ by -10 to +30%. Of particular note is NO₂ is near stations 8 and 9 which suggest that there is a local minimum between the two mining regions (see also Fig. 11).

- ⁵ Ignored to this point is the clear-sky bias in the OMI measurements resulting from the requirement that only (near) cloud-free measurements be used, with no such restriction on the GB measurements. Averaging over clear-sky data only may introduce a bias from the direct effect of generally faster photochemistry due to higher levels of sunlight, including the photolysis rate of NO₂ which is important in the NO-NO₂ partitioning.
- There may also be an indirect effect if cloudiness is correlated with wind direction, and hence air mass origin. The most obvious way of avoiding this bias is to sample the GB data in the same way as OMI. However, this is complicated by the method used here to compute GB station averages: first calculating averages as a function of wind direction, and then averaging over these. Another method of removing clear-sky bias is to use
- ¹⁵ a measure of cloud cover at each of surface stations to screen GB measurements, analogous to the satellite measurements, with the source of cloud information being a either a surface monitor or the OMI or MODIS-Aqua cloud fraction products (e.g., Geddes et al., 2012). A third alternative, and the approach used here, is to compare NO₂ and SO₂ from GEM-MACH with and without cloud-screening. Limiting NO₂ to
- clear-skies leads to a low bias, relative to all-sky conditions, in an amount varying from 5–50%. This is similar to the clear-sky bias observed over the greater Toronto area (Geddes et al., 2012) and consistent with a shift in the NO_x partitioning to favour NO as a result of increased photolysis. For SO₂ the opposite effect was observed: cloud screening led to a high bias between 5 and 25%. Scavenging of SO₂ by clouds is an efficient loss mechanism, thus higher SO₂ concentrations when considering only cloud-

free conditions are expected. Average clear-sky biases are given in the Supplement.

The impact of smoothing and clear-sky bias on the GB-satellite comparison was assessed by applying the scaling factors for each to the EC-vmrs. These are also shown in Figs. 11 and 12, and the linear corrections and slopes are given in Table 4.





The EC-VMR NO₂ increased at all stations and substantially improved the agreement. Excluding Millennium, which showed almost no change, now gives a scatter-plot slope of 0.65 and a correlation coefficient of 0.91. Also of note is the ability of the EC-vmrs to capture the minimum in NO₂ between the northern and southern mining regions. In ⁵ contrast, there was a smaller impact on SO₂ as the two effects somewhat cancelled (slope 1.01; correlation coefficient 0.91). The combined effect of the smoothing and clear-sky bias corrections explains (with the exception of Millennium) a large portion of the GB-satellite difference in NO₂ and highlights its importance.

To conclude this section, it is noted that the stringent SZA threshold of 60° (combined with the snow filter) means > 99% of OMI SO₂ measurements considered are from April to September. For NO₂, with a SZA threshold of 75°, the breakdown is about 75% (April–September): 25% (October–March) which allows for some seasonal analysis. The comparison above was repeated but for limited to these two 6 month "seasons". For April–September, the agreement between GB and EC-vmrs improved (slope 1.00,

- ¹⁵ correlation coefficient 0.94) and October–March the agreement decreased (slope 0.47, correlation coefficient 0.68). The relative poor agreement in winter could simply be due to larger SZAs or a result of the shallower BL heights in the winter. Part of the underestimate by the EC-vmrs could be related to the simplified treatment of surface reflection. Zhou et al. (2010) predict a 10–20 % underestimate in the winter when using the surface is medalled as a Lambartian reflector instead of the mare rigarous BDDE.
- the surface is modelled as a Lambertian reflector instead of the more rigorous BRDF. A more detailed investigation into these differences is beyond the scope of this study.

6 Summary and conclusions

25

Significant low biases have been identified in current NO₂ and SO₂ retrieval products from the Ozone Monitoring instrument (OMI) over the Canadian oil sands arising from a combination of its rapid development and small spatial scale. Air mass factors (AMFs) were re-calculated for this region based on updated and higher resolution input information. These include: gas absorber profiles from the high-resolution (15 km × 15 km)



GEM-MACH air quality forecast model, higher spatial and temporal resolution surface reflectivity from the MODIS satellite instruments, and an improved treatment of snow via a more precise determination of snow cover and more appropriate surface albedo when snow is present.

- ⁵ The overall impact of these new Environment Canada AMFs led to increases in the peak NO₂ and SO₂ average vertical column density (VCD), occurring over the area of intensive surface mining, by factors of roughly 2 and 1.5, respectively. Due to a lack of validation profile or VCD data in this region, comparisons were made with long-term averages of NO₂ and SO₂ from in-situ surface monitors at several WBEA stations. This
- ¹⁰ was achieved by using the AQ model to map the EC-VMR VCDs to surface concentrations. The OMI-EC surface concentrations were able to capture the NO₂ and SO₂ spatial distribution of the in-situ instruments. The absolute values were in reasonable agreement with OMI-EC surface NO₂ and SO₂ biased low by roughly 30 %. The exception to this is the NO₂ comparison at the Millenium monitoring station which showed ¹⁵ much larger values. This level of agreement was improved by addressing complications
- in these comparisons. The first was the NO_2 high bias in the molybdenum-based surface instruments. The other two were the effects of smoothing by OMI and the clear-sky bias.

This work is the first attempt to homogenize the OMI NO₂ and SO₂ data products through a consistent treatment of AMFs. It also examines the impact of inter-annual variability in a number of AMF-dependent parameters including profile shape, surface albedo, and ozone column. The use of output from the high-resolution air quality model GEM-MACH was valuable in several regards: input into the AMF calculations, for performing the column to surface mapping, and also in assessing the sources of bias.

²⁵ Overall these results highlight the importance of using input information that accounts for the spatial and temporal variability at the location of interest when performing retrievals.





Supplementary material related to this article is available online at http://www.atmos-chem-phys-discuss.net/13/21609/2013/ acpd-13-21609-2013-supplement.pdf.

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Table 1. Summary of air mass factor input parameters.

Parameter	Source	Horizontal resolution	Intra- annual variability	Interannual variability
Absorber profiles (NO ₂ , SO ₂)	GEM-MACH + GEOS- CHEM	15 km × 15 km	Monthly	No ^a
Temperature profiles	GEM-MACH	15 km × 15 km	Monthly	No
Surface reflectivity (snow-free)	MODIS + OMI	0.05° × 0.05°; smoothed to 15 km × 30 km	Monthly	Yes
Surface reflectivity (snow)	MODIS	0.05° × 0.05°; smoothed to 15 km × 30 km	None	No
Ozone column	OMI (TOMS algorithm)	Single-value	Daily	Yes
Surface pressure	GEM-MACH	15 km × 15 km	Monthly	No

 $^{\rm a}$ As a sensitivity study, NO_2 profiles in the planetary boundary layer were doubled to account to approximate the effect of increasing emissions (see Sect. 4.1).





Table 2. Air mass factor look-up table nodes.

Parameter	Number of nodes	Table type	Node values
Altitude	30	Both	0 to 16 km in 0.5 km in layers
Surface Albedo	10	Clear-sky	0, 0.03, 0.06, 0.09, 0.12, 0.20, 0.30, 0.50, 0.75, 1.00
Column ozone	5	Both	275, 325, 375, 425, 475 DU
Surface Pressure	4	Clear-sky	600, 800, 900, 1000 hPa
Cloud top pressure	5	Cloudy	200, 400, 600, 800, 900 hPa
Solar Zenith Angle	10	Both	0, 30°, 50°, 60°, 65°, 70°, 73°, 76°, 78°, 80°
Viewing Zenith Angles	7	Both	0, 30°, 50°, 60°, 65°, 70°, 72°
Change in azimuthal angle	7	Both	0 to 180° in 30° increments





Table 3. Error budget for EC-VCDs considering cloud-free observations (w < 0.2). Polluted refers to observations make within 50 km of the reference location; background (bg) from 50 to 200 km.

Error source	Parameter	Parameter uncertainty	NO ₂ uncertainty (polluted/bg)	SO ₂ Uncertainty (polluted/bg)
Precision				
SCD, S			7.0 × 10 ¹⁴ cm ⁻²	0.22 DU ²
Strat SCD, S _s			1.5 × 10 ¹⁴ cm ⁻²	0
Bias correction, <i>S</i> _b			0	0.03 DU ³
Air Mass Factor, <i>M</i>	Cloud fraction	0.05	17 %/13 %	14 %/10 %
	Cloud pressure	60 hPa	3%/3%	8 %/6 %
	Albedo	0.02	11%/9%	5%/4%
	pressure	50 nPa	7%/7%	6%/7%
	Profile shape	See text	11 %/10 %	29%/18%
	Column ozone	20 DU	-	4 %/3 %
	AMF total		24 %/20 %	34 %/23 %
Total			$7.7/5.7 \times 10^{14} \mathrm{cm}^{-2}$	0.78/0.51 DU
		Accura	су	
Air Mass Factor, <i>M</i>	Surface	BRDF	+5–10 % 4	unknown
	Aerosol	0.1	-6%/-2%	0%/+1%
	Changing emissions	Double profile in PBL	-6%/-8%	-

¹ From Boersma et al. (2007).

² From Krotkov et al. (2008).

³ Average over monthly standard-error of the means.

⁴ Annual average estimated from Zhou et al. (2010), Fig. 9b.

Discussion Pa	AC 13, 21609–4	ACPD 13, 21609–21664, 2013		
iper Discussion	Improved retrievals of SO ₂ or Canadian C. A. McLi	Improved satellite retrievals of NO ₂ and SO ₂ over the Canadian oil sands C. A. McLinden et al.		
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Table 4. Summary of comparisons between WBEA and OMI-EC-derived long-term (2005–2011) average volume mixing ratios. The slope and correlation coefficient are based on a sample of 12 SO_2 stations and 8 NO_2 stations.

Species		Slope	Correlation coefficient
NO ₂		0.20	0.45
	 Millenium station 	0.54	0.80
	+ smoothing correction	0.56	0.90
	+ clear-sky bias correction	0.65	0.91
	Apr–Sep ¹	1.00	0.94
	Oct–Mar ¹	0.47	0.68
SO ₂		0.88	0.91
	 + smoothing correction 	1.15	0.91
	+ clear-sky bias correction	1.01	0.91

¹ Includes corrections for smoothing and clear-sky bias; excludes Millenium station.









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Fig. 1. (a) Map of the Canada showing the oil sands area (tan) and the location of the surface mining (red) which also corresponds to the area shown in panels **(b)** and **(c)**. Panels **(b)** and **(c)** show Landsat images from 2005 and 2011 of the surface mining area (http://earthobservatory.nasa.gov/Features/WorldOfChange/athabasca.php?all=y). The white outlines denote the approximate boundaries of the main mining operations (as of 2011). The communities of Fort McMurray and Fort McKay are also indicated. The red dot denotes the reference location (57.1° N, 111.6° W). These panels cover approximately 90 km in both NS and EW directions.







Fig. 2. Comparison of annual-mean model NO₂ profiles over the oil sands (sampled at the local time of the OMI overpass, ~ 13:30 LT): **(a)** TM4, GMI, GEOS-CHEM, and GEM-MACH shape factors each at a resolution of roughly 200 km (N–S) × 150 km (E–W), **(b)** GEM-MACH number density profiles (at its native 15 km × 15 km resolution) at distances of 0, 10, and 50 km from the reference location, and **(c)** GEOS-CHEM and the GEOS-CHEM+GEM-MACH hybrid (see text) profiles over the surface mines at a resolution of 0.5° × 0.67°.







Fig. 3. Comparison of mean summer (JJA) surface albedos: **(a)** OMI climatological albedo at 442 nm (Kleipool et al., 2007), **(b)** MODIS albedo for 2005 from Eq. (3) for NO₂ (477 nm but scaled to 442 nm), **(c)** MODIS albedo for 2005 from Eq. (3) for SO₂ (477 nm but scaled to 354 nm), and **(d)** MODIS albedo for 2011 from Eq. (3) for NO₂ (477 nm but scaled to 442 nm). Each map shows the approximate outline of the surface mining region.







Fig. 4. Left: Fraction of days in which the snow cover product misidentified the presence of snow on the ground, relative to the determination from the meteorological station. Right: Monthlymean fraction of days with snow as determined to be on the ground according to four source of data. These results are averaged over 2000–2011 and combined results from the Fort McMurray and Mildred Lake meteorological stations.







Fig. 5. Snow albedo over the oil sands surface mining region from: **(a)** OMI at at 354 nm and on a $0.5^{\circ} \times 0.5^{\circ}$ grid (O'Byrne et al., 2010) and **(b)** MODIS at 477 nm smoothed to $30 \text{ km} \times 15 \text{ km}$.







Fig. 6. (a) Scatterplot of DOMINOv2 vs. EC NO₂ AMFs for all OMI observations within 200 km of the reference location and radiative cloud fraction of 0.2 or smaller. Note the non-linear scale. The white ellipse shows the AMFs over the surface mines (a small overall fraction of the points considered here). **(b)** Histogram of SO₂ AMFs within 200 km of the reference location, separated according to snow covered surface, and snow-free. The black line indicates the constant AMF of 0.36 used in the NASA SO₂ product.







Fig. 7. Summertime air mass factors (AMFs) averaged over 2005–2011: (a) from the DOMI-NOv2 data files, (b) EC-AMF, (c) the ratio of DOMINOv2:EC which also represents the scaling that would be applied to the VCDs (the maximum is 1.4), and (d) EC SO₂ AMFs. These data have been averaged in the. The stripes arise due to sampling differences by the OMI sampling.







Fig. 8. Average (2005–2011) tropospheric VCDs: (a) DOMINO v2 NO₂, (b) EC NO₂ (from DOMINO) (c) SP v2 NO₂, (d) EC NO₂ (from SP), (e) NASA SO₂, (f) EC SO₂.



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Fig. 9. Map of Wood Buffalo Environment Association (WBEA) monitoring stations and the parameters measured (http://earthobservatory.nasa.gov/Features/WorldOfChange/athabasca. php?all=y). A 12th site (Fort Chippewyan), measuring SO₂ and NO₂, is located approximately 160 km north of site 10. Additional information on these sites can be found in the Supplement.



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Fig. 10. Average (2005–2011) EC-OMI distributions of NO_2 and SO_2 vmr: (a) EC-OMI NO_2 , (b) as (a) but using GEOS-CHEM profiles to calculate AMFs and the column to surface mapping, (c) EC-OMI SO2, (d) as (c) but using GEOS-CHEM profiles to calculate AMFs and the column to surface mapping. The points indicate the location of the NO_2 and SO_2 in-situ instruments.





Fig. 11. Average (2005–2011) ground-based in-situ and EC-OMI-derived NO_2 surface mixing ratio measurements as a function of WBEA station latitude. Inset is the scatter-plot comparing ground-based with EC-vmrs. The red represents original OMI-vmrs while the green is after accounting for smoothing and clear-sky bias. Errors bars denote twice the standard error of the mean. The ground-based measurements have been corrected for the interference effect and include this uncertainty in their error bars (see Table S1). The lines in the inset represent the linear fits with (solid) and without (dashed) including the Millennium station (#3).









