

Point-by-point clarification to Referee #1

5 In the present response letter, we summarize our modifications in the revised version of the manuscript and we provide point-by-point clarifications (in blue color) to the referee's comments and suggestions (in black color). We found the referee's comments very useful and in the right direction in order to improve the scientific quality of the paper. All of the referee's comments were taken into account in the revised version and we believe that it is now much better.

10 The authors present a trend analyses of ground-level SO₂ concentrations from OMI measurements over the US. This paper is interesting and has high potential, but, in my opinion, currently lacks sufficient contest and motivation. The flow of the paper is good and logical, although some sections are a bit too compact to my liking. I therefore suggest the paper to be accepted after major revisions, considering the text below.

15 We thank the referee for recommending the manuscript for publication. We have incorporated all the comments/suggestion in the revised manuscript as suggested by referee.

Introduction.

20 The introduction clearly states the benefits of studying SO₂ from satellite, mentioning its role in the formation of sulfate aerosol and the effect of the latter on climate and environmental and health issues. Related previous work is adequately cited. However, the cited paper of Krotkov et al. [2016] already gives a trend analyses of OMI total column, over the same time period as the current paper, and furthermore indicates (for polluted areas) the close relationship between derived total columns and emissions. Although the current paper studies surface concentration rather than total column, I would
25 like to see a more elaborate text, motivating why studying total column is not sufficient a proxy for emission trend analysis and the connected assessment of health risks. Only one short sentence is currently dedicated to the novel aspects of the paper and at first glance the overlap with previous work seems high. Please expand.

30 We agree with referee's view point and included more detail on novel aspects of the paper in the revised manuscript. The total column SO₂ is a sufficient proxy for emission trend analysis but is of low utility for the assessment of health risks. We include the sentence "In contrast to total column SO₂, long-term records of ground-level SO₂ concentrations from satellite observations will be directly useful to assess air quality and associated health risks." in the revised manuscript at Page number 2, Line number 18-20.

35 Section 2. 2.1 OMI: Concise paragraph. Line 3: 'Also, SO₂ variability...' I presume background SO₂ is meant here? Line 6: Please explain the use of the respective thresholds of 0.2 and 65 degree or give an reference.

40 We have modified the sentence as "Also, SO₂ retrieval variability is reduced by a factor of two in the PCA algorithm relative to the BRD algorithm (Li et al., 2013)" at Page number 3, Line number 8-9, and

provided reference for respective thresholds at Page number 3, Line number 18 in the revised manuscript.

2.3: Model information Line 24: It would be good to have a quantitative indication of the thickness of the lowest model layer, so reader not familiar with GEM-MACH can develop a feeling for what is assumed as 'surface concentration'. Along the same line, an indication of the partial column of the lowest layer with respect to the total boundary layer column is missing. The reader is referred to McLinden et al papers for AMF related information, but I think it should be discussed to some extent in the text (here or in the next paragraph).

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We have modified the sentence as “The lowest model layer, which is 20 m thick, is taken as ground-level concentration.” in the revised manuscript at Page number 4, Line number 11-12.

We have included the following paragraph on AMF related information in section 2.1 at Page number 3, Line number 9-16:-

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“Even though the PCA algorithm directly estimates SO₂ vertical column density in one step using SO₂ Jacobians, the air mass factor (AMF) is effectively fixed at 0.36 (representing summertime conditions in the eastern USA), similar to the BRD algorithm. A better estimation of AMFs is needed for different regions to reduce these systematic errors that result from conditions that do not match these. For this, we re-calculated the AMFs using SO₂ profile information from the high resolution (15 km x 15 km) GEM-MACH air quality forecast model (discussed in section 2.3), monthly-varying surface reflectivity from the MODIS satellite instruments, and an improved identification of snow. More details on Environment Canada Air Mass Factors calculation for SO₂ are discussed in McLinden et al., 2014; 2016b.”

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2.4 Estimation of ground-level SO₂ from OMI. I have the same problem with this paragraph as with the previous. A simple connection between observed and model concentration and column properties is given, adopted from literature, but no discussion is given. This would be ok in the case of an extended section 2.3 Line 2: The cited Lamsal [2008] paper on NO₂ is missing from the list of references.

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We have included Lamsal [2008] reference and more detail on AMF calculation in section 2.1 in the revised manuscript.

“Lamsal, L. N., Martin, R. V., van Donkelaar, A., Steinbacher, M., Celarier, E. A., Bucsela, E., Dunlea, E. J., and Pinto, J. P.: Ground-level nitrogen dioxide concentrations inferred from the satellite-borne Ozone Monitoring Instrument, *J. Geophys. Res.*, 113, D16308, doi:10.1029/2007JD009235, 2008.”

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3 Results and Discussion. The actual results look sound and well described. Line 26/27: Lee et al [2011] paper is missing from the list of references. Also, this paper already derived SO₂ surface mixing ratios from OMI and compared them to in-site measurements, be it only for 2006. Also this motivates a clearer description of the novel aspects of your paper in the introduction.

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We have included Lee et al [2011] reference in the revised manuscript.

5 “Lee, C., Martin, R. V., van Donkelaar, A., Lee, H., Dickerson, R. R., Hains, J. C., Krotkov, N.,
Richter, A., Vinnikov, K., and Schwab, J. J.: SO₂ emissions and lifetimes: Estimates from inverse
modeling using in situ and global, space-based (SCIAMACHY and OMI) observations, J. Geophys.
Res., 116, D06304, doi:10.1029/2010JD014758, 2011.”

We have included the following sentence in the introduction at Page number 2, Line number 16-17.

10 “In previous studies (Lee et al., 2011; Nowlan et al., 2011), ground-level SO₂ concentrations were
estimated for only a one year period using satellite observations over North America.”

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Point-by-point clarification to Referee #2

5 We thank the referee for his valuable comments/suggestions. We found the referee's comments very useful and in the right direction in order to improve the scientific quality of the paper. The point-by-point clarifications (in blue color) to the referee's comments and suggestions (in black color) are given below.

10 In this paper, Shailesh K. Kharol et al. presented an estimation of ground-level sulfur dioxide concentrations from the Ozone Monitoring Instrument (OMI) using SO₂ profiles from the Global Environmental Multi-scale – Modelling Air quality and Chemistry (GEM-MACH) model over North America for the period of 2005–2015. Also comparisons and trend analysis using OMI, GEM-MACH and in-situ SO₂ observations are presented.

15 General observations: The paper is quite interesting but need more details. The authors should highlight their work and the novelty of this paper. SO₂ from space and comparisons with ground or model observations is not a new subject, I suggest a more detailed presentation of Section 2 Data sets & methodology. The authors should show that this paper is more than just a database manipulation.

20 We have incorporated all the comments/suggestion in the revised manuscript as suggested by the referee. The point-by-point clarifications to the referee's comments are as follows:

1 Introduction

25 In this section the authors should connect their work with other studies, e.g. China, etc. Also, in this section, the authors should highlight the novelty of their work.

We agree with referee's view point and included the sentence "In contrast to total column SO₂, long-term records of ground-level SO₂ concentrations from satellite observations will be directly useful to assess air quality and associated health risks" in revised manuscript at Page number 2, Line number 18-20 to highlight the novel aspects of the paper.

30 The cited Fioletov et al., (2013) and Krotkov et al., (2016) papers are examples of related studies over China and other regions.

2 Data sets & methodology

35 In this section they should introduce more details.

We have included more details in data sets & methodology section in the revised manuscript.

40 The following paragraph on AMF related information is included in section 2.1 at Page number 3, Line number 9-16:-

“Even though the PCA algorithm directly estimates SO₂ vertical column density in one step using SO₂ Jacobians, the air mass factor (AMF) is effectively fixed at 0.36 (representing summertime conditions in the eastern USA), similar to the BRD algorithm. A better estimation of AMFs is needed for different regions to reduce these systematic errors that result from conditions that do not match these. For this, we re-calculated the AMFs using SO₂ profile information from the high resolution (15 km x 15 km) GEM-MACH air quality forecast model (discussed in section 2.3), monthly-varying surface reflectivity from the MODIS satellite instruments, and an improved identification of snow. More details on Environment Canada Air Mass Factors calculation for SO₂ are discussed in McLinden et al., 2014; 2016b.”

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3 Results & Discussion

page 5/L1:5 you should give some coordinates and to specify if Flin Flon, Snow Lake, Sudbury, Thompson, Montreal are power plants (?)

15 We have modified the sentence as “There are far fewer sources in the western US and Canada, with a few notable exceptions such as Flin Flon (54.77° N, 101.88° W; copper smelter), Sudbury (46.52° N, 80.95° W; copper and nickel smelter), Thompson (55.74° N, 97.85° W; metal ore mining), Montreal (45.50° N, 73.56° W), the oil sands region in northern Alberta and power plants nearby Edmonton.” in the revised manuscript at Page number 5, Line number 14-17.

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page 5/L5:10 where is apparent the closure of Flin Flon copper smelter?

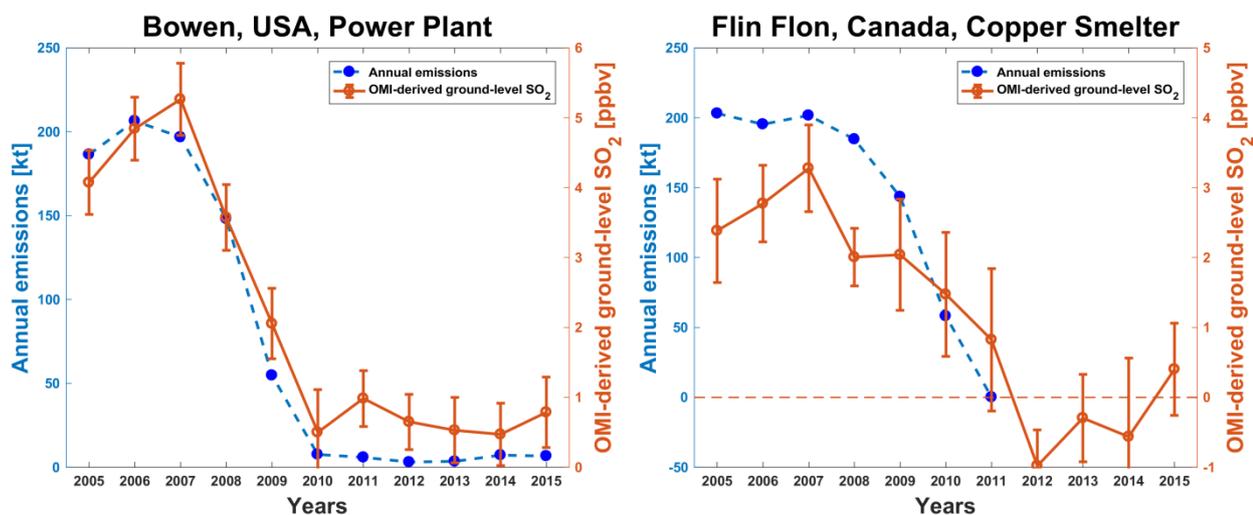
We have modified the sentence as “The closure of Flin Flon (54.77° N, 101.88° W) copper smelter in June 2010 is also apparent in OMI-derived ground-level SO₂ during 2011-2015 in Figure 1.” in the revised manuscript at Page number 5, Line number 21-22.

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Other observations: I suggest to introduce a study case using one (or more) power plants for the SO₂ sources mentioned in this work.

30 We have included following time series figure for Bowen power plant (34.13° N, 84.92° W), USA, and Flin Flon copper smelter (54.77° N, 101.88° W), Canada in the revised manuscript.

The following figure description is included at Page number 7, Line number 6-9 for the figure below in the revised manuscript.



20 Figure 6 shows that bottom-up SO₂ emissions and OMI-derived ground-level SO₂ concentrations are temporally correlated even for larger individual point sources, namely the Bowen power plant (34.13° N, 84.92° W), USA, and Flin Flon copper smelter (54.77° N, 101.88° W), Canada. The bottom-up emission data for these sites are obtained from the US EPA (2016), and National Pollutant Release Inventory (NPRI, 2017), respectively.

OMI Satellite Observations of decadal changes in Ground-Level Sulfur Dioxide over North America

Shailesh K. Kharol¹, Chris A. McLinden¹, Christopher E. Sioris¹, Mark W. Shephard¹, Vitali Fioletov¹, Aaron van Donkelaar², Sajeev Philip², Randall V. Martin²

5 ¹Air Quality Research Division, Environment and Climate Change Canada, Toronto, Ontario M3H 5T4, Canada

²Department of Physics and Atmospheric Science, Dalhousie University, Halifax, Nova Scotia, Canada

Correspondence to: S. K. Kharol (shailesh.kharol@canada.ca)

Abstract. Sulfur dioxide (SO₂) has a significant impact on the environment and human health. We estimated ground-level sulfur dioxide (SO₂) concentrations from the Ozone Monitoring Instrument (OMI) using SO₂ profiles from the Global Environmental Multi-scale – Modelling Air quality and CHEMistry (GEM-MACH) model over North America for the period of 2005-2015. OMI-derived ground-level SO₂ concentrations ($r = 0.61$) and trends ($r=0.74$) correlated well with coincident in-situ measurements from air quality networks over North America. We found a strong decreasing trend in coincidentally sampled ground-level SO₂ from OMI ($-81\pm 19\%$) and in-situ measurements ($-86\pm 13\%$) over Eastern US for the period of 2005-2015, which reflects the implementation of stricter pollution control laws including flue-gas desulfurization (FGD) devices in power plants. The spatially and temporally contiguous OMI-derived ground-level SO₂ concentrations can be used to assess the impact of long-term exposure to SO₂ on the health of humans and the environment.

1 Introduction

Sulfur dioxide (SO₂) is a short-lived atmospheric trace gas emitted into the atmosphere from natural (e.g. volcanic eruption, oxidation of dimethylsulphate (DMS) over oceans) and anthropogenic sources (e.g. combustion of fossil fuels and smelting of sulfur-containing metal ores), and plays a pivotal role in the global sulfur cycle. SO₂ has a short lifetime of hours to days, and it oxidizes quickly in the atmosphere to produce sulfate aerosols that affect the climate (Intergovernmental Panel on Climate Change, 2013) and the environment from local to regional and global scales. Sulfate aerosols are major contributor to PM_{2.5} (particulate matter with aerodynamic diameter < 2.5 μm) chemical composition and accounts for 17% and ~30% of the annual mean PM_{2.5} mass globally and over eastern United States (Philip et al., 2014). Sulfate aerosol formation leads to degradation in visibility and air quality (van Donkelaar et al., 2008), deposition of sulfuric acid (Dentener, et al., 2006; Vet et al., 2014), and poses a serious health hazard to the general population (Lee et al., 2015). The increased risk of premature mortality associated with SO₂ alone or its secondary pollutants has been emphasized in several epidemiological studies (Chinn et al., 1981; Derriennic et al., 1989; Hatzakis et al., 1986; Krzyzanowski & Wojtymiak, 1982). Furthermore, it has been recently reported by Lelieveld et al., (2015) using the EMAC (ECHAM5/MESSy Atmospheric Chemistry) general circulation model that in the U. S., in addition to agricultural emissions (an important source of ammonia (NH₃)), emission from coal fired power plants (an important source of SO₂ and nitrogen oxides (NO_x)) is the largest contributor to premature

mortality in 2010. Due to the adverse impact on the environment and human health, SO₂ and its oxidation products (i.e. fine particulate matter (PM_{2.5})) are considered as designated criteria pollutants in European Union (European Commission, <http://ec.europa.eu/environment/air/quality/standards.htm>), United States of America (US Environmental Protection Agency (EPA), <https://www.epa.gov/criteria-air-pollutants>) and Canada (5 <https://www.ec.gc.ca/Air/default.asp?lang=En&n=7C43740B-1>).

Globally, atmospheric SO₂ is monitored regularly through a relatively small number of measurement networks, that produce accurate measurements, but over a limited spatial area. Satellite measurements have the advantage of providing complete daily global coverage of SO₂. Satellite observations of SO₂ vertical column density (VCD) began in the 1980s but -the 10 launch of the Ozone Monitoring Instrument (OMI) (Krotkov et al., 2006, Yang et al., 2007) on the Aura satellite in 2004 has enabled large point sources to be resolved with its higher spatial resolution (13 x 24 km² at nadir) (Fioletov et al., 2013). Satellite measurements of SO₂ have been used to identify and analyze emissions (Fioletov et al., 2011, 2013, 2015, 2016; Lee et al., 2011; McLinden et al., 2016a), track changes in total column density in various regions including Canadian oil sands, eastern US, eastern Europe, eastern China, India and Middle East (McLinden et al., 2016b; Krotkov et al., 2016), and 15 estimate dry deposition flux (Nowlan et al., 2014). In previous studies (Lee et al., 2011; Nowlan et al., 2011), ground-level SO₂ concentrations were estimated for only a one year period using satellite observations over North America. However multi-year spatialotemporal variations in ground-level SO₂ have not yet been assessed from the satellite observations. In contrast to total column SO₂, long-term records of ground-level SO₂ concentrations from satellite observations will be directly useful to assess air quality and associated health risks. Recently, a decreasing trend in SO₂ emissions and particulate 20 sulfate has been reported by Hand et al. (2012) over the United States from the early 1990s through 2010.

In this paper we first describe the OMI SO₂ product, in-situ measurement network, the GEM-MACH (Global Environmental Multi-scale – Modelling Air quality and Chemistry) air quality model, ground-based SO₂ estimation from OMI and trend analysis. We then use these data and methodology to estimate ground-level SO₂ from OMI and evaluate it with coincident 25 in-situ measurements over North America for the period of 2005-2015. These results are then used to determine the trend in ground-level SO₂ from both OMI and collocated in-situ measurements.

2 Data sets & methodology

2.1 OMI

OMI is a nadir-viewing UV-visible spectrometer boarded on the Aura satellite that was launched in July 2004, and is part of 30 the NASA A-train constellation (Levelt et al., 2006). The Aura satellite overpasses the equator at early afternoon (1300-1430 local time) in sun-synchronous ascending polar orbit. OMI provides daily global coverage of aerosols and trace gases, including SO₂, with a variable ground spatial resolution of 13 km × 24 km at nadir to 140 km × 26 km at swath edge. We use

the OMI operational Principal Component Analysis (PCA) SO₂ product (OMSO2 v1.2.0), which is publically available from NASA Goddard Earth Sciences (GES) Data and Information Services Center (DISC) (http://disc.sci.gsfc.nasa.gov/Aura/data-holdings/OMI/omso2_v003.shtml). The details of PCA algorithm can be found elsewhere (Li et al., 2013). In brief, this algorithm applies the PCA technique to OMI-measured radiances between 310.5 and 340 nm to extract principal components from each row [of data](#) on an orbital basis. The PCA algorithm replaced the Band Residual Difference ([BRD](#)) algorithm (Krotkov et al., 2006) as the operational algorithm for the standard OMI SO₂ data because only the latter algorithm was biased (Fioletov et al., 2013; Krotkov et al., 2016). Also, SO₂ [retrieval](#) variability is reduced by a factor of two in the PCA algorithm ([Li et al., 2013](#))[relative to the BRD algorithm \(Li et al., 2013\)](#). [Even though the PCA algorithm directly estimates SO₂ vertical column density in one step using SO₂ Jacobians, the air mass factor \(AMF\) is effectively fixed at 0.36 \(representing summertime conditions in the eastern USA\), similar to the BRD algorithm. A better estimation of AMFs is needed for different regions to reduce these systematic errors that result from conditions that do not match these. For this, we re-calculated the AMFs using SO₂ profile information from the high resolution \(15 km x 15 km\) GEM-MACH air quality forecast model \(discussed in section 2.3\), monthly-varying surface reflectivity from the MODIS satellite instruments, and an improved identification of snow. More details on Environment Canada Air Mass Factors calculation for SO₂ are discussed in McLinden et al., 2014; 2016b.](#) Here, we exclude the cross-track pixels affected by the row anomaly (<http://www.knmi.nl/omi/research/product/rowanomaly-background.php>), which was first noticed in the data in June 2007. We use OMI SO₂ columns with cloud radiance fraction <0.2, and solar zenith angles <65° [following Nowlan et al. \(2014\)](#). We exclude from the analysis the OMI SO₂ data affected by the largest northern mid-latitude volcanic eruptions in the OMI time frame namely Kasatochi (Aleutian Islands, Alaska, August 2008, 52°N) and Sarychev (Kuril Islands, Eastern Russia, June 2009, 48°N). Here, we used the mean OMI values over a 32 km averaging-radius (Fioletov et al., 2011) that is oversampled onto a 0.1° x 0.1° latitude/longitude grid.

2.2 SO₂ monitoring networks

To evaluate the OMI-derived ground-level SO₂ we use hourly in-situ SO₂ measurements from the Air Quality System (AQS) network of the US EPA (<http://www.epa.gov/ttn/airs/airsaqs/detaildata/downloadaqsdta.htm>) and Environment and Climate Change Canada's National Air Pollution Surveillance (NAPS) network (<http://maps-cartes.ec.gc.ca/rnsps-naps/data.aspx>) over the US and Canada for the period of 2005 to 2015. US-EPA AQS site locations vary from regional background to urban and industrial locations, and measures SO₂ using continuous gas monitors. The Canadian NAPS sites are generally located in populated areas. The hourly in-situ measurements are averaged over a 2 h period (1300-1500 Local Time) to correspond with the satellite observation times over North America.

2.3 Model information

We use the Global Environmental Multi-scale – Modelling Air quality and CHemistry (GEM-MACH) model for the tropospheric SO₂ profile to relate the OMI SO₂ column to ground-level concentrations. GEM-MACH is the Canadian

regional air quality forecast model used operationally to predict the concentrations of O₃, NO₂, and PM_{2.5} over North America (Moran et al., 2010, Gong et al., 2015). GEM-MACH model utilizes emissions inventories from US EPA and Environment Canada data for the year 2006. It uses detailed tropospheric processes for gas and particle chemistry and microphysics originating in the offline AURAMS model (A Unified Regional Air-quality Modelling System; Gong et al., 2006), and incorporates them 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 is provided elsewhere (Kelly et al., 2012). The results used here are from archived forecasts from 2010 to 2011 for a domain covering North America at 15 km×15 km resolution. The lowest model layer, which is 20 m thick, is taken as ground-level concentration. ~~More details on Environment Canada Air Mass Factors calculation for SO₂ are discussed in McLinden et al., 2014; 2016b.~~

2.4 Estimation of ground-level SO₂ from OMI

The ground-level SO₂ mixing ratio from OMI is estimated using the approach described by Lamsal et al. (2008) over North America for the period of 2005-2015. The ground-level SO₂ mixing ratio S is estimated from the local OMI tropospheric SO₂ column Ω as:

$$S_{OMI} = \Omega_{OMI} \times \frac{S_{model}}{\Omega_{model}} \quad (1)$$

The subscript *model* represents GEM-MACH model. More details on the procedure are discussed in McLinden et al. (2014).

2.5 Trend Analysis

We analyzed the trends in monthly ground-level SO₂ over North America from OMI and in-situ measurements for the period of January 2005 - December 2015. We applied a general least squares regression following Boys et al. (2014) and Kharol et al. (2015) using the basic model:

$$x = z\beta + e, \quad e \sim N(0, \sigma^2 V) \quad (2)$$

where, for a time series of n months, x is a time series vector ($n \times 1$) containing SO₂ surface mixing ratio values; z is a design matrix ($n \times 2$) for the linear model; β is a vector (2×1) containing the intercept and slope of the linear model; e is an error vector ($n \times 1$) containing the residuals which, for validity, should be approximately normally distributed with zero mean, however, is permitted to covary with adjacent values according to V – a positive definite, symmetric covariance matrix, to accommodate possible autocorrelation between adjacent months. Correlated errors between adjacent months are represented by a first order autoregressive model of e , which can be expressed as:

$$e_t = \phi e_{t-1} + w_t \quad t = 1, \dots, n, \quad w \sim N(0, \sigma^2 I) \quad (3)$$

where, the residual e_t for month t is a fraction \emptyset of the previous month's residual e_{t-1} with a white noise component w_t which, for validity, should be approximately normally distributed with zero mean, constant variance and independent. We deseasonalized the monthly time series by subtracting the climatological monthly median prior to regression. Note, the trend is more heavily weighted toward summer when observations are more frequent.

3 Results & Discussion

Figure 1 shows the spatial distribution of mean OMI-derived ground-level SO₂ over North America for the periods of 2005-2007, 2008-2010, 2011-2015 and 2005-2015. The major SO₂ hot-spots (that is, locations of high SO₂ associated with a large nearby source) are primarily located in the Eastern US from coal-fired power plants and industrial activities (Krotkov et al., 2016). There are far fewer sources in the western US and Canada, with a few notable exceptions such as Flin Flon (54.77° N, 101.88° W; copper smelter), ~~Snow Lake~~, Sudbury (46.52° N, 80.95° W; copper and nickel smelter), Thompson (55.74° N, 97.85° W; metal ore mining), Montreal (45.50° N, 73.56° W), the oil sands region in northern Alberta and power plants nearby Edmonton. The spatial distribution of annual mean OMI-derived ground-level SO₂ for each year is shown in supporting information Figure S1. A noticeable decrease in OMI-derived ground-level SO₂ is apparent from Figure 1 during 2008-2010 and 2011-2015 compared to 2005-2007. These US reductions correspond with the installation of flue-gas desulfurization (FGD) units at many power plants to meet stricter emissions limits introduced by the Clean Air Interstate Rule. The closure of Flin Flon (54.77° N, 101.88° W) copper smelter in June 2010 is also apparent in OMI-derived ground-level SO₂ during 2011-2015 (Figure 1). The OMI-derived ground-level SO₂ concentrations over large geographical area could be useful to assess its impact on human health and environment. It can also provide valuable information to policy makers where air quality network measurements are not available.

To verify these satellite findings, we compared the OMI-derived ground-level SO₂ concentrations with in-situ measurements over North America for the period of 2005-2015. The original OMI-derived ground-level SO₂ concentration (black circles) moderately correlates with collocated in-situ measurements ($r = 0.61$), but have a significant difference in slope (slope = 0.39) (Fig 2). The departure from unity of the slope is a common feature of virtually all satellite-surface comparisons of this kind (Kharol et al., 2015), and can be a result of both the in-situ monitor placements (i.e. mainly located in the cities and close to pollution sources) and differences in the spatial sampling of the two types of observations. To quantify this inhomogeneity effect we utilized output from the GEM-MACH model at high-resolution (2.5 km x 2.5 km; supporting information Fig S2) over a region in central Canada. These high-resolution GEM-MACH SO₂ columns at the locations of the in-situ monitors were taken as representative of point (in-situ) measurements. The model SO₂ columns were then progressively averaged up (smoothed) to 30 km x 30 km, approximately representing the spatial size of an OMI pixel. The smoothed columns are regressed against the unsmoothed columns. The slope and correlation coefficient continue to decrease

from unity as the smoothing is increased. We used this estimate of the spatial inhomogeneous sampling obtained from the original (2.5 km) vs smoothed (30 km) GEM-MACH SO₂ column (supporting information Fig S3) to derive a scaling factor (in-situ scaled = $0.52 \times (\text{in-situ}) + 0.04$, $R = 0.83$) that is used to adjust the in-situ measurements to be representative of the OMI pixel size over all of North America. We noticed ~92% increase in slope to 0.75 when comparing the spatial inhomogeneity adjusted in-situ measurements with the OMI ground-level SO₂ (red circles in Fig. 2). In comparison to previous studies, Lee et al., (2011), comparing ground-level SO₂ mixing ratios derived from SCIAMACHY and OMI with in-situ measurements from US-EPA AQS and NAPS monitoring networks over the United States and Canada for the year of 2006, reported slightly higher correlation ($r = 0.86$, slope = 0.91 for SCIAMACHY and $r = 0.80$, slope = 0.79 for OMI). In their study they used 15 km coincidence criterion and included only AQS sites measuring less than 6 ppbv at satellite overpass times. Nowlan et al., (2011) estimated ground-level SO₂ from GOME-2 and compared with in-situ measurements over North America from Clear Air Status and Trends Network (CASTNET; $r = 0.85$) and US-EPA AQS and NAPS ($r = 0.40$) for 2008.

We determined the trend in ground-level SO₂ from OMI using the monthly time series from January, 2005 to December, 2015. Figure 3 illustrates the spatial distribution of OMI-derived ground-level SO₂ trend over North America for the period of 2005-2015. We noticed a strong decreasing trend in ground-level SO₂ over eastern US and Flin Flon in Canada. The observed decrease in ground-level SO₂ concentration in the eastern US corresponds to more strict pollution control laws implemented to reduce SO₂ emissions and the installation of FGD devices in power plants (Fioletov et al., 2011; Krotkov et al., 2016). Furthermore, we estimated the trend in ground-level SO₂ at in-situ locations collocated with OMI. The upper panel of Fig 4 shows the trend in ground-level SO₂ from OMI and collocated in-situ measurements over North America for the period of 2005-2015. Both in-situ and OMI-derived ground-level SO₂ mixing ratios show a strong decreasing trend over eastern US mainly located at locations close to power plants. The lower panel of Fig 4 shows the scatter plot of trends in ground-level SO₂ from collocated in-situ measurements and OMI. The OMI-derived trends are significantly correlated ($r = 0.74$) with collocated in-situ trends. As expected the slope of 0.43 is similar to the absolute concentrations slope (Fig. 2) and reveals the difference in absolute trend.

Figure 5 shows the percentage change compared to 2005 in annual mean ground-level SO₂ concentration from coincidentally-sampled OMI and in-situ measurements and total SO₂ emissions from power plants over eastern US. The geographical locations of stations considered over the eastern US are shown inside the blue color box within the inset map. Both OMI and in-situ measurements shows $-81 \pm 19\%$ and $-86 \pm 13\%$ decrease in ground-level SO₂ over the eastern US, respectively. Earlier OMI SO₂ columns studies reported a 40% (Fioletov et al., 2011) and 80% (Krotkov et al., 2016) decrease near power plants in Eastern US and Ohio River Valley for the period of 2005-2010 and 2005-2015, respectively. Furthermore, we derived a ~~-64±18%~~ decrease of 64±18% from spatially averaged OMI-derived ground-level SO₂ (Fig. 3) over the eastern US from entire domain (blue box in Fig. 5). The observed decrease in ground-level SO₂ from OMI and in-situ measurements is in

agreement with the US EPA reported decrease of about 70% in total US SO₂ emissions (<https://www3.epa.gov/airtrends/aqtrends.html>). Figure 6 shows that bottom-up SO₂ emissions and OMI-derived ground-level SO₂ concentrations are temporally correlated even for larger individual point sources, namely the Bowen power plant (34.13° N, 84.92° W), USA, and Flin Flon copper smelter (54.77° N, 101.88° W), Canada. The bottom-up emission data for these sites are obtained from the US EPA (2016), and National Pollutant Release Inventory (NPRI, 2017), respectively.

Recently Philip et al. (2014) analyzed the PM_{2.5} chemical composition over North America from the satellite data and reported that sulfate aerosols contribute ~30% in ground-level PM_{2.5} mass concentration over the eastern US. Here, the ground-level sulfate PM_{2.5} mass concentration is estimated by applying the sulfate fraction from Philip et al., (2014) to the total PM_{2.5} mass concentration inferred using the method of van Donkelaar et al. (2010), which uses information from satellites, models and monitors. Figure 76 shows the spatial distribution of OMI ground-level SO₂ mixing-ratio/vertical column density (left panel) and sulfate PM_{2.5} mass concentration over eastern US for the period of 2005-2008. The locations of large (>18.98 kt[SO₂]/yr in 2006) power plants (largest contributor to SO₂ emissions) and 2005-2008 average boundary-layer winds from an ECMWF (European Center for Medium range Weather Forecasting) reanalysis (Dee et al., 2011) are overlaid on the plots as circle and arrows respectively. This demonstrates that ground-level SO₂ VCD influence air quality locally due to its shorter atmospheric lifetime. However, sulfate PM_{2.5} with a longer atmospheric lifetime, influences air quality locally as well as downwind through long-range transport. It is evident from Figure 76 that column SO₂ and sulfate PM_{2.5} hotspots are collocated around and downwind of power plant locations. There is only a moderate spatial correlation ($r = 0.60$) between OMI SO₂ and sulfate PM_{2.5} but given that sulfate is largely a secondary pollutant, this is not surprising. It was also found that there is a saturation effect at high SO₂ mixing-ratios/VCDs (Supporting Information Fig S4).

4 Conclusions

We examined the spatial and temporal characteristic of the ground-level SO₂ concentration from OMI over North America during the period from 2005-2015. OMI-derived ground-level SO₂ concentrations and trend correlates well with in-situ measurements ($r = 0.61$ and 0.74 , respectively) with a significant bias in slope. Once the in-situ observations are adjusted, based on nested GEM-MACH model results, to account for the spatial sampling differences between the in-situ and OMI spatial resolution there is a notable increase (~92%) in slope to a value of 0.75 . The observed reduction in ground-level SO₂ concentration from OMI ($-81 \pm 19\%$) is consistent with in-situ measurements ($-86 \pm 13\%$) over Eastern US for the period of 2005-2015. The observed decreasing trend in ground-level SO₂ could lead to considerable reduction in sulfate aerosols, and thus play a major role in improving air quality thereby minimizing its deleterious health impact. The long-term spatial distribution maps of ground-level SO₂ from OMI provide policy-makers with SO₂ pollution monitoring at locations where ground measurements are not available. Future satellite missions like TEMPO (Tropospheric Emissions: Monitoring Pollution) will provide better coverage of SO₂, and other pollutants, as it will have higher spatial resolution, and hourly

frequency over the North American continent during daytime (especially USA and parts of Canada). ~~Whereas~~ Also TROPospheric Monitoring Instrument (TROPOMI) is scheduled to launch in 20176 and will provide daily global coverage of tropospheric SO₂ and other pollutants with a high spatial resolution of 7x7 km².

Acknowledgement

- 5 We acknowledge the National Aeronautics and Space Administration (NASA) for the availability of OMI SO₂ tropospheric column data. We would like to thank Natural Sciences and Engineering Research Council of Canada (NSERC) for funding support.

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OMI SO₂ Surface Mixing Ratio

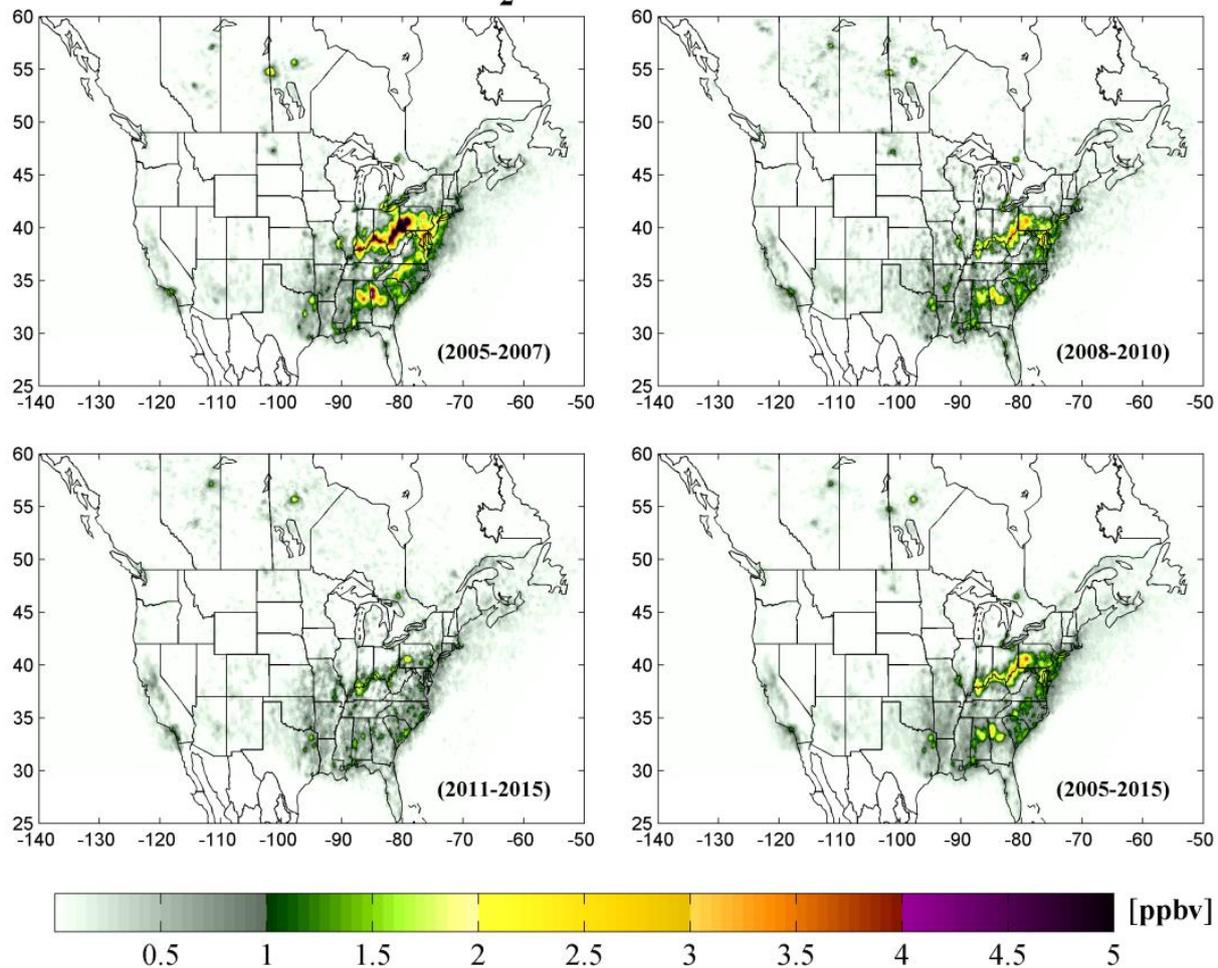


Figure 1: Spatial distribution of mean OMI-derived ground-level SO₂ mixing ratio over North America for the period of 2005-2007, 2008-2010, 2011-2015 and 2005-2015.

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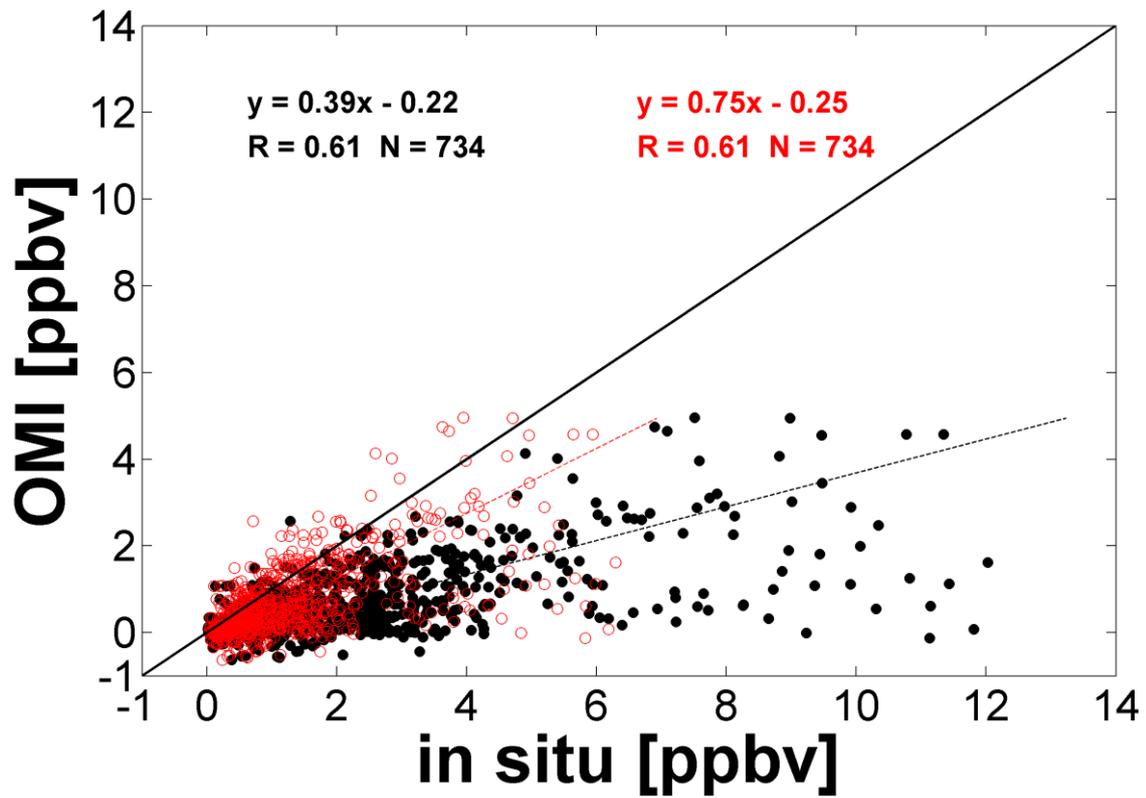


Figure 2: Scatter plot of the annual mean OMI-derived ground-level SO₂ versus collocated in-situ measurements for the years of 2005-2015. Filled black circles represent the original in-situ values, and red circles represent the comparison with spatially inhomogeneity adjusted in-situ values.

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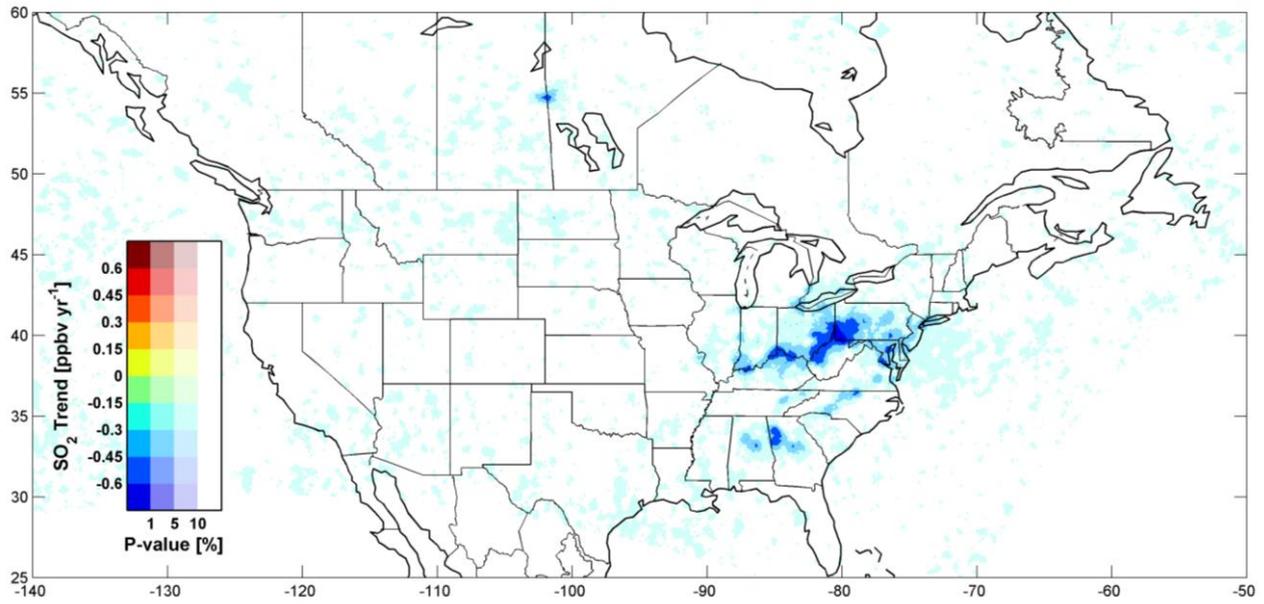


Figure 3: Spatial distribution of OMI-derived surface SO₂ trend at 0.1° × 0.1° over North America for the year of 2005-2015. Statistical significance is shown in the form of a two sided P-value, tested against null being zero trend.

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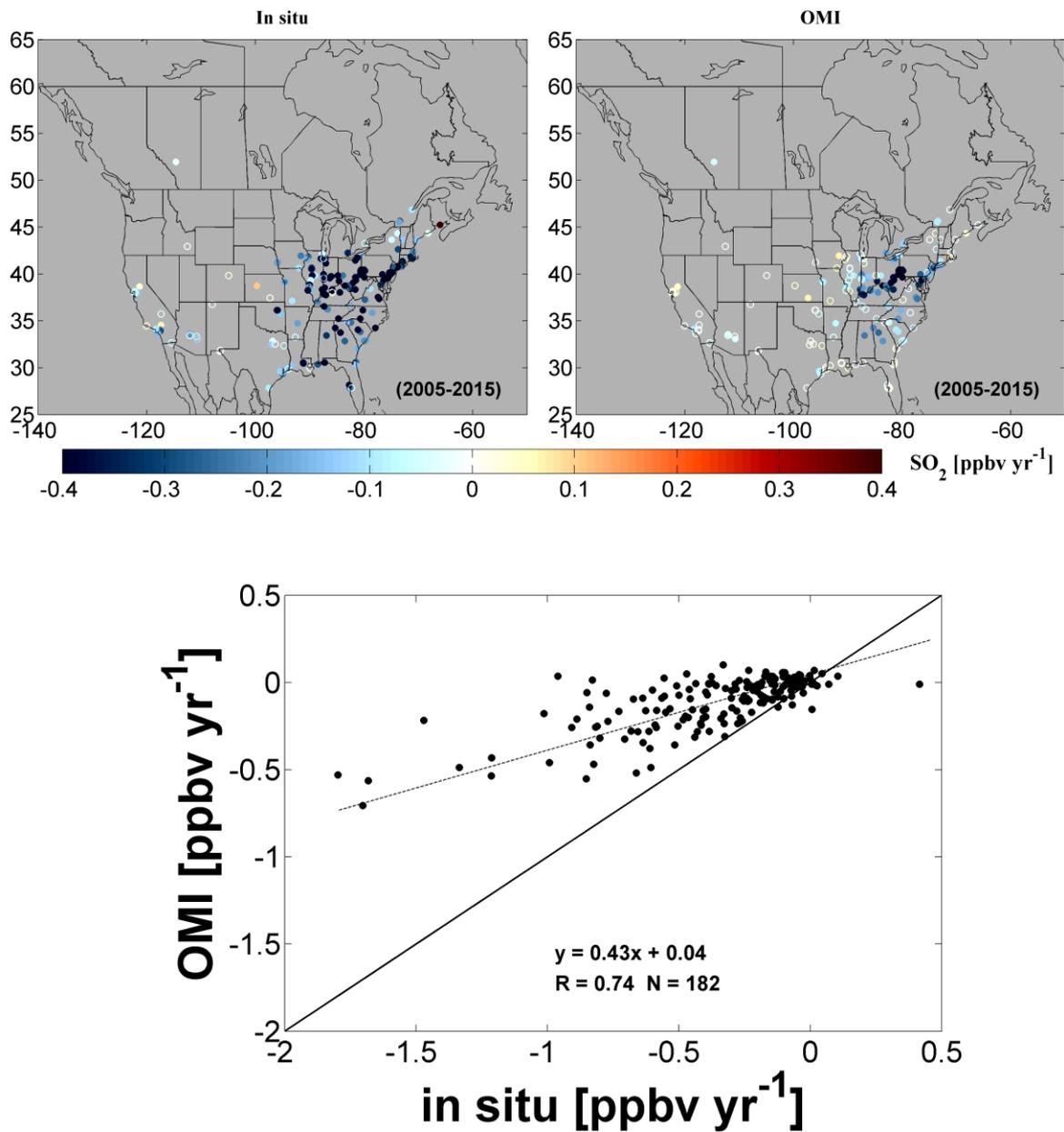


Figure 4: Trends in ground-level SO₂ for the period of 2005-to-2015. The top row shows trends inferred from in-situ measurements at OMI overpass and from OMI for the period of 2005-2015. The filled circle represents where trend p-value < 0.05 and trend p-values > 0.05 are shown as empty circle. The bottom panel contains scatter plots of trends for the period of 2005-2015.

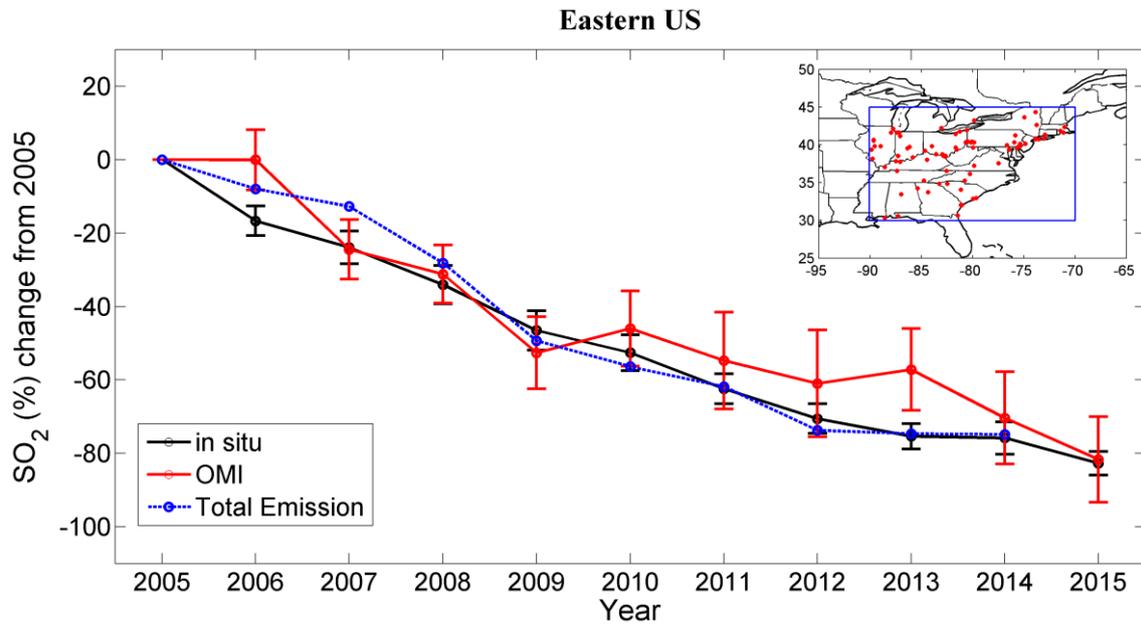


Figure 5: Percent change in ground-level SO₂ mixing ratio from 2005 over Eastern US and southern Ontario, Canada. The in-situ and OMI ground-level SO₂ percent change are shown in black and red color, respectively. Blue circles show changes in total SO₂ emissions. The locations of in-situ measurement stations over Eastern US and southern Ontario, Canada (blue box) are shown in the inset map. The error bars represent the 1-standard error of the mean.

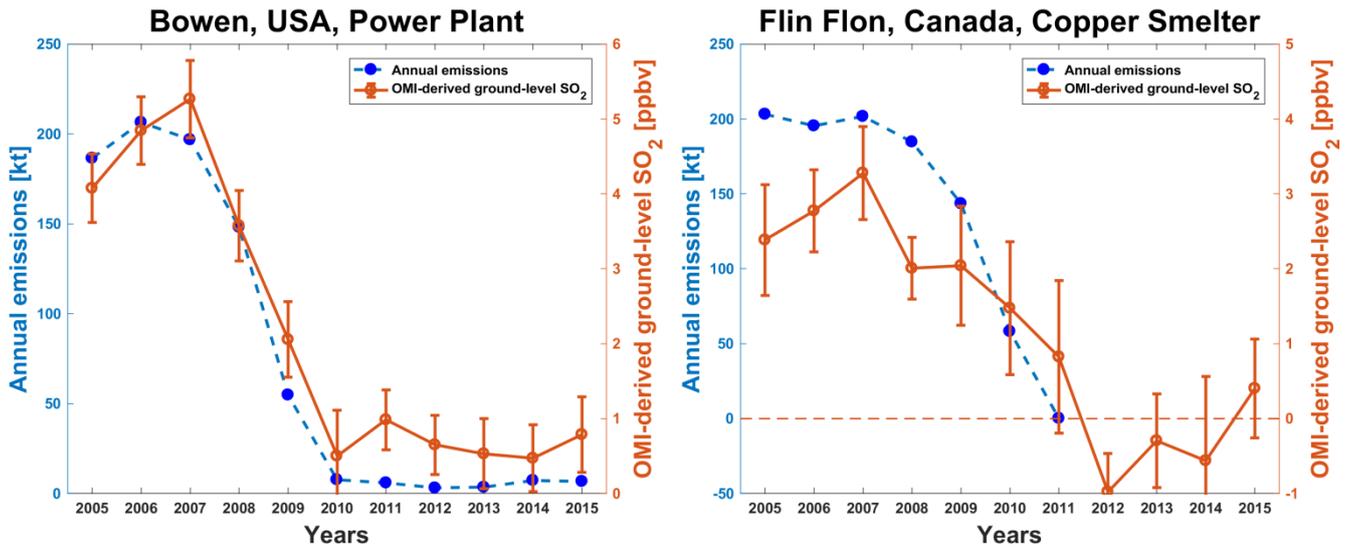
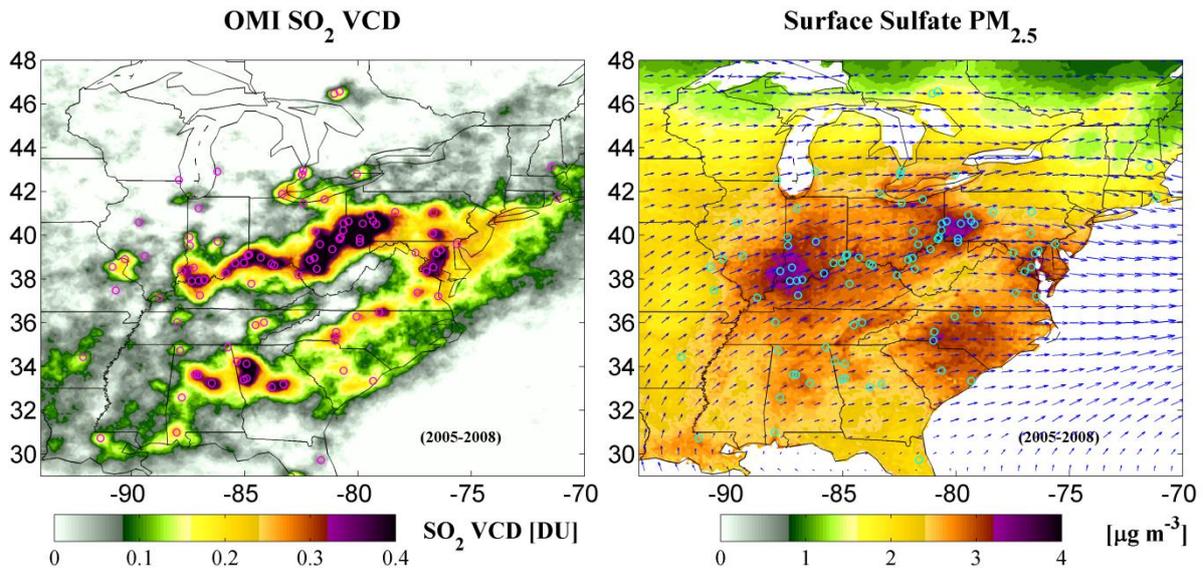


Figure 6: Time series of bottom-up annual SO₂ emissions and OMI-derived ground-level SO₂ concentration for Bowen power plant (34.13° N, 84.92° W), USA, and Flin Flon copper smelter (54.77° N, 101.88° W), Canada. The dashed orange line represents the zero line in Flin Flon, Canada plot. Bottom-up SO₂ emissions data are not available after 2011 due to closer of Flin Flon copper smelter. The error bars represent the 1-standard error of the mean.



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Figure 76: Spatial distribution of satellite derived SO₂ vertical column density (VCD) and sulfate PM_{2.5} mass concentration over eastern US and southern Ontario, Canada. The power plant locations overlaid on both panels are shown as circle. ECMWF model derived ground-level winds are overlaid on sulfate PM_{2.5} mass concentration map are shown with arrows.