

1 New Methodology Shows Short Atmospheric Lifetimes of 2 Oxidized Sulfur and Nitrogen due to Dry Deposition

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14 **Abstract**

15
16 The atmospheric lifetimes of pollutants determine their impacts on human health, ecosystems
17 and climate and yet, pollutant lifetimes due to dry deposition over large regions have not been
18 determined from measurements. Here, a new methodology based on aircraft observations is used
19 to determine the lifetimes of oxidized sulfur and nitrogen due to dry deposition over $(3-6) \times 10^3$
20 km^2 of boreal forest in Canada. Dry deposition fluxes decreased exponentially with distance
21 from the Athabasca oil sands sources, located in northern Alberta, resulting in lifetimes of 2.2-26
22 hours. Fluxes were 2-14 and 1-18 times higher than model estimates for oxidized sulfur and
23 nitrogen, respectively, indicating dry deposition velocities which were 1.2-5.4 times higher than
24 those computed for models. A Monte-Carlo analysis with five commonly used inferential dry
25 deposition algorithms indicates that such model underestimates of dry deposition velocity are
26 typical. These findings indicate that deposition to vegetation surfaces are likely under-estimated
27 in regional and global chemical transport models regardless of the model algorithm used. The
28 model-observation gaps may be reduced if surface pH, and quasi-laminar and aerodynamic
29 resistances in algorithms are optimized as shown in the Monte-Carlo analysis. Assessing the air
30 quality and climate impacts of atmospheric pollutants on regional and global scales requires
31 improved measurement-based understanding of atmospheric lifetimes of these pollutants.

32

33 **1 Introduction**

34 Deposition represents the terminating process for most air pollutants and the starting
35 point for ecosystem impacts. Understanding deposition is critical in determining the atmospheric
36 lifetimes and spatial scale of atmospheric transport of pollutants, which in turn, dictates their
37 ecosystem (WHO, 2016; Solomon et al., 2007) and climate (Samset et al., 2014) impacts. In
38 particular, atmospheric lifetimes (τ) of oxidized sulfur and nitrogen compounds influence their
39 concentrations and column burdens in air, which affect air quality and hence human exposure
40 (WHO, 2016). Furthermore, the lifetime of these species affects their contributions to
41 atmospheric aerosols, with a consequent influence on climate via changes to radiative transfer
42 through scattering and cloud formation (Solomon et al., 2007). In addition, their deposition can
43 exceed critical load thresholds causing aquatic and terrestrial acidification, and eutrophication in
44 the case of nitrogen deposition (Howarth, 2008; Bobbink et al., 2010; Doney, 2010; Vet et al.,
45 2014; Wright et al., 2018). Quantifying τ and deposition thus provides a crucial assessment of
46 these regional and global impacts.

47 Deposition occurs through wet and dry processes. While wet deposition fluxes can be
48 measured directly (Vet et al., 2014), there are few validated methods for dry deposition fluxes
49 (Wesley and Hicks, 2000), and none which estimates deposition over large regions. Dry
50 deposition fluxes (F) may be obtained using micrometeorological measurements for pollutants
51 for which fast response instruments are available. However, these results are only valid for the
52 footprints of the observation sites, typically hundreds of meters (Aubinet et al., 2012), and their
53 extrapolation to larger regions may suffer from representativeness issues. As a result,
54 atmospheric lifetimes τ with respect to dry deposition have not been determined through direct
55 observations. On a regional scale, dry deposition fluxes are typically derived using an inferential

56 approach by multiplying network-measured or model-predicted air concentrations with dry
57 deposition velocities (V_d) (Sickles and Shadwick, 2015; Fowler et al., 2009; Meyers et al., 1991),
58 which are derived using resistance-based inferential dry deposition algorithms (Wu et al., 2018),
59 and compared with limited micrometeorological flux measurements (Wesley and Hicks, 2000;
60 Wu et al., 2018; Finkelstein et al., 2000; Matsuda et al., 2006; Makar et al., 2018) for validation.
61 When applied to a regional scale, an inferential-algorithm derived V_d may have significant
62 uncertainties (Wesley and Hicks, 2000; Aubinet et al., 2012; Wu et al., 2018; Finkelstein et al.,
63 2000; Matsuda et al., 2006; Makar et al., 2018; Brook et al., 1997). For example, inferred V_d for
64 SO_2 , despite being the most studied and best estimated, may be underestimated by 35% for forest
65 canopies (Finkelstein et al., 2000). Underestimated V_d for SO_2 and nitrogen oxides can
66 contribute to model over-prediction of regional and global SO_2 concentrations (Solomon et al.,
67 2007; Christian et al., 2015; Chin et al., 2000), or under-prediction of global oxidized nitrogen
68 dry deposition fluxes (Paulot et al., 2018; Dentener et al., 2006).

69 Here, a new approach is presented to determine τ with respect to dry deposition and F for
70 total oxidized sulfur (**TOS**, the sulfur mass in SO_2 and particle- SO_4 (pSO_4)) and total reactive
71 oxidized nitrogen (**TON**, the nitrogen mass in NO , NO_2 , and others designated as NO_z) on a
72 spatial scale of $(3-6) \times 10^3 \text{ km}^2$, using aircraft measurements. This approach provides a unique
73 methodology to determine τ and F over a large region. Coupled with analyses for chemical
74 reaction rates (for **TOS** compounds), the average V_d for **TOS** and **TON** over the same spatial
75 scale were also determined. The airborne measurements were obtained during an intensive
76 campaign from August to September 2013 in the Athabasca Oil Sands Region (AOSR) (Gordon
77 et al., 2015; Liggio et al., 2016; Li et al., 2017; Baray et al., 2018; Liggio et al., 2019) in northern

78 Alberta, Canada. Direct comparisons with modelled dry deposition estimates are made to assess
79 their uncertainties and the spatial-temporal scales of air pollutant impacts.

80 **2 Methods**

81 **2.1 Lagrangian Flight Design**

82 Details of the airborne measurement program have been described elsewhere (Gordon et
83 al., 2015; Liggio et al., 2016; Li et al., 2017; Liggio et al., 2019; Baray et al., 2018). Briefly, an
84 instrumented National Research Council of Canada's Convair-580 research aircraft was flown
85 over the AOSR in Alberta, Canada from August 13 to September 7, 2013. The flights were
86 designed to determine emissions from mining activities in the AOSR, assess their atmospheric
87 transformation processes and gather data for satellite and numerical model validation. Three
88 flights were flown to study transformation and deposition processes by flying a Lagrangian
89 pattern so that the same pollutant air mass was sampled at different time intervals downwind of
90 emission sources for a total of 4-5 hours and up to 107-135 km downwind of the AOSR sources.
91 Flights 7 (F7, Aug 19), 19 (F19, Sep 4) and 20 (F20, Sep 5) took place during the afternoon
92 when the boundary layer was well established. The flights were conducted in clear sky
93 conditions so wet deposition processes were insignificant. As shown in Fig. 1, the aircraft flew
94 tracks perpendicular to the oil sands plume at multiple altitudes between 150 to 1400 m agl and
95 multiple intercepts of the same plume downwind. Vertical profiles conducted as spirals were
96 flown at the centre of the plume which provided information on the boundary layer height and
97 extent of plume mixing. The flight tracks closest to the AOSR intercepted the main emissions
98 from the oil sands operations; there were no other anthropogenic sources as the aircraft flew
99 further downwind of the AOSR.

100 2.2 Aircraft Measurements

101 A comprehensive suite of detailed gas- and particle-phase measurements were made from
102 the aircraft. Measurements pertaining to the analysis in this paper are discussed below.

103 **SO₂ and NO_y.** Ambient air was drawn in through a 6.35 mm (1/4") diameter PFA sampling line
104 taken from a rear-facing inlet located on the roof towards the rear of the aircraft. The inlet was
105 pressure-controlled to 770 mm Hg using a combination of a MKS pressure controller and a
106 Teflon pump. Ambient air from the pressure-controlled inlet was fed to instrumentation for
107 measuring SO₂ and NO_y. The total sample flow rate was measured at 4988 cm³ min⁻¹ of which
108 SO₂ and NO_y were 429 and 1085 cm³ min⁻¹, respectively. SO₂ was detected via pulsed
109 fluorescence with a Thermo 43iTLE (Thermo Fisher Scientific, Franklin, MA, USA). NO_y (also
110 denoted as Total Oxidized Nitrogen (TON)) was measured by passing ambient air across a
111 heated (325 °C) molybdenum converter that reduces reactive nitrogen oxide species to NO. NO
112 was then detected through chemiluminescence with a modified Thermo 42iTL (Thermo Fisher
113 Scientific, Franklin, MA, USA) run in NO_y mode. An inlet filter was used for SO₂ to exclude
114 particles, but NO_y was not filtered prior to the molybdenum converter. NO_y includes NO, NO₂,
115 HNO₃ and other oxides of nitrogen such as peroxy acetyl nitrate and organic nitrates (Dunlea et
116 al., 2007; Williams et al., 1998). Although there was no filter on the NO_y inlet to exclude
117 particles, the inlet was not designed to sample particles (i.e. rear-facing PFA tubing). As a result,
118 pNO₃ was not included as part of NO_y (TON) The conversion efficiency of the heated
119 molybdenum converter and inlet transmission was evaluated with NO₂ and HNO₃ and found to
120 be near 100 % and >90 %, respectively. Previous studies conducted by Williams et al. (1998)
121 showed similar molybdenum converter efficiencies including that of n-propyl nitrate near 100%.
122 Interferences from alkenes or NH₃ were assumed to be negligible (Williams et al., 1998; Dunlea

123 et al. 2007). Species like NO₃ radical and N₂O₅ are expected to be low in concentration as they
124 photolyze quickly during daytime. Zeros were performed 3-5 times per flight for both the SO₂
125 and NO_y instruments by passing ambient air through an in-line Koby King Jr cartridge for ~5
126 minutes. For the NO_y measurements pre-reactor zeroes (dynamic instrument zero) were also
127 obtained periodically throughout each flight using either ambient air or a Koby King Jr. air
128 purifier. Multiple calibrations were conducted before, during and after the study using National
129 Institute Standards and Technology reference standards. Data were recorded at a time resolution
130 of 1 second and corrected for a sampling time delay of 1-3 seconds depending on the instrument.
131 Detection limits were determined as 2 times the standard deviation of the values acquired during
132 zeroes; NO_y was 0.09 ppbv and SO₂ was 0.70 ppbv (Table S1).

133 **Aerosols.** Multiple aerosol instruments sub-sampled from a forward facing, shrouded, isokinetic
134 particle inlet (Droplet Measurement Technologies, Boulder, CO, USA). A Time-of-Flight High
135 Resolution Aerosol Mass Spectrometer (AMS) (Aerodyne Research Inc.) was used to measure
136 non-refractory submicron aerosol components including pSO₄, pNO₃, pNH₄, and p-organics.
137 Details of the AMS and its operations have been published elsewhere (DeCarlo et al., 2006).
138 The instrument was operated in mass spectrometry V-mode with a sampling time resolution of
139 10 seconds. Filtered measurements were taken 4-5 times per flight to determine background
140 signals. Detection limits of 0.048, 0.036, 0.235 and 0.236 $\mu\text{g m}^{-3}$ for pSO₄, pNO₃, pNH₄ and p-
141 organics were determined using 3 times the standard deviation of the average of filtered time
142 periods for all flights (Table S1). Ionization efficiency calibrations using monodisperse
143 ammonium nitrate were performed during the study with an uncertainty of $\pm 9\%$. Data were
144 corrected for a sampling time delay of 10 seconds by comparing with faster response instruments
145 e.g. a wing-mounted Forward Scattering Spectrometer Probe Model 300 (FSSP-300) and an in-

146 board Ultra High Sensitivity Absorption Spectrometer (UHSAS) (both from Droplet
147 Measurement Technologies). The FSSP and UHSAS instruments measure particle diameters
148 that range from 300 nm-20 μm and 50 nm-1 μm , respectively. The AMS data were processed
149 using AMS data analysis software (Squirrel, version 1.51H and PIKA, version 1.10H). The
150 particle collection efficiency (CE) of the AMS was determined through comparisons of the total
151 AMS-derived mass with the mass estimated from the size distribution measurements of the
152 UHSAS assuming a density based on the chemical composition. The CE for F7 and F20 was 0.5
153 for both flights, and for F19 it was 1.0. The CE was applied to all AMS species for the duration
154 of each flight (Fig. S1). Since the AMS measures only particle mass $< 1 \mu\text{m}$ (PM_1) in diameter,
155 the mass of SO_4 formed through OH oxidation was scaled upward to account for all particle sizes
156 that H_2SO_4 vapor could potentially condense on. The scaling factor was determined using the
157 surface area ratio of $\text{PM}_1/\text{PM}_{20}$ from the aircraft particle measurements, assuming that the
158 condensation process is approximately proportional to the surface area. PM_1 measurements were
159 from the UHSAS and PM_{20} were from the FSSP300. As the ratio did not vary significantly in
160 the plumes, one single value was used between each set of screens; in F19 the ratio between
161 screens ranged from 0.6 to 0.8, in F20 the ratio ranged from 0.8 to 0.9, and in F7 the ratio ranged
162 from 0.7 to 0.9 (Liggio et al., 2016).

163 Measurements are discussed in terms of total oxidized sulfur (TOS, the sulfur mass in SO_2 from
164 the Thermo SO_2 instrument and particle- SO_4 (pSO_4) from the AMS instrument) and total
165 reactive oxidized nitrogen (TON, the nitrogen mass in reactive oxidized nitrogen species, from
166 the Thermo NO_y instrument, often denoted NO_y).

167 **Volatile Organic Compounds (VOCs).** Selected VOCs were used to estimate the OH
168 concentrations used for determining oxidation rates for SO_2 . VOCs were measured with a proton

169 transfer reaction time-of-flight mass spectrometer (PTR-ToF-MS, Ionicon Analytik GmbH,
170 Austria) as well as through discrete canister grab samples. The PTR-ToF-MS and its operation,
171 along with the details of the canister sampling and lab analyses during the study were described
172 in detail previously (Li et al., 2017). Briefly, the PTR-ToF-MS used chemical ionization with
173 H_3O^+ as the primary reagent ion. Gases with a proton affinity greater than that of water were
174 protonated in the drift tube. The pressure and temperature of the drift tube region were
175 maintained at a constant 2.15 mbar and 60 °C, respectively for an E/N of 141 Td (Townsend, 1
176 $\text{Td}=10^{-17} \text{ V cm}^2$). E/N refers to the reduced electric field parameter in the drift tube; E is the
177 electric field and N is the number density of the gas in the drift tube. The E/N ratio can affect the
178 reagent ion distribution in the drift tube and VOC fragmentation (de Gouw and Warneke; 2007).
179 The protonated gases were detected using a high-resolution time of flight mass spectrometer at a
180 time resolution of 2 seconds. Instrumental backgrounds were performed in flight using a
181 custom-built zero-air generating unit. The unit contained a catalytic converter heated to 350 °C
182 with a continuous flow of ambient air at a flow rate of one litre per minute. The data were
183 processed using Tofware software (Tofwerk AG). Calibrations were performed on the ground
184 using gas standard mixtures from Ionicon, Apel-Reimer and Scott-Marrin for 22 compounds.
185 The canister samples were collected in pre-cleaned and passivated 3L stainless steel canisters
186 that were subsequently sent to an analytical laboratory for GC-FID/MS analyses for a suite of
187 150 hydrocarbon compounds.

188 **Meteorology and aircraft state parameters.** Meteorological measurements have been
189 described elsewhere (Gordon et al., 2015). In brief, 3-D wind speed and temperature were
190 measured with a Rosemount 858 probe. Dew point was measured with an Edgetech hygrometer
191 and pressure was measured with a DigiQuartz sensor. Aircraft state parameters including

192 positions and altitudes were measured with GPS and a Honeywell HG1700 unit. All
193 meteorological measurements and aircraft state parameters were measured at a 1 s time
194 resolution.

195

196 **2.3 Mass transfer rates in the atmosphere**

197 Mass transfer rates (T) across flight screens (Fig. 1) were determined using an extension
198 of the Top-down Emission Rate Retrieval Algorithm (TERRA) developed for emission rate
199 determination using aircraft measurements (Gordon et al., 2015). Briefly, at each plume
200 interception location, the level flight tracks were stacked to create a virtual screen. Background
201 subtracted pollutant concentrations and horizontal wind speeds normal to the screen were
202 interpolated using kriging. The background for SO₂ was ~0 ppb and pSO₄ was 0.2-0.3 μg m⁻³
203 which was subtracted from the pSO₄ measurements before mass transfer rates were calculated
204 (Liggio et al., 2016). Integration of the horizontal fluxes across the plume extent on the screen
205 yields the transfer rate T in units of t hr⁻¹. Using SO₂ as an example,

$$206 \quad T_{SO_2} = \int_{s_1}^{s_2} \int_{z_1}^{z_2} C(s, z) u_n(s, z) ds dz \quad (1)$$

207 where $C(s, z)$ is the background subtracted concentration at screen coordinate s and z , which
208 represent the horizontal and vertical axes of the screen. The $u_n(s, z)$ is the horizontal wind speed
209 normal to the screen at the same coordinates.

210 Since the lowest flight altitude was 150 magl, it was necessary to extrapolate the data to
211 the surface as per the procedures described previously (Gordon et al., 2015). Extrapolation to the
212 surface methods were compared and differences were included in the uncertainty estimates. The
213 main sources of SO₂ were from elevated facility stacks associated with the desulfurization of the

214 raw bitumen (Zhang et al., 2018). The stacks with the biggest SO₂ emissions range in height
 215 from 76.2 to 183.0 m. Since the main source of SO₂ is from the elevated facility stacks, the
 216 uncertainty for a single screen is estimated at 4% (Gordon et al., 2015). NO_y was also
 217 extrapolated linearly to the surface and the mass transfer rates were similarly compared to other
 218 extrapolation methods. NO_y sources include the elevated facility stacks and surface sources such
 219 as the heavy hauler trucks operating in the surface mines. The uncertainty in the resulting
 220 transfer rate T for a single screen is estimated to be larger at 8 %, as a larger fraction of the NO_y
 221 mass may be below the lowest measurement altitude (Gordon et al., 2015). Sulfur and nitrogen
 222 data were also extrapolated linearly to background values from the highest altitude flight tracks
 223 upwards to the mixed layer height, which was determined from vertical profiles of pollutant
 224 mixing ratios, temperature and dew point (Table 1).

225 Changes in the mass transfer rate T (denoted ΔT) in units of t hr⁻¹ were then calculated as
 226 the differences in T between pairs of virtual screens. The uncertainty in ΔT was estimated as 8
 227 % for **TOS** and 26 % for **TON** as supported by emission rate uncertainties determined for box
 228 flights (Gordon et al., 2015). The uncertainty analysis for box flights is applicable to ΔT here, as
 229 both account for uncertainties with an upwind and a downwind screen. The ΔT uncertainties
 230 were propagated through subsequent calculations.

231 Knowing the change in mass transfer rate ΔT , and accounting for the net rates of
 232 chemical loss and formation between screens for SO₂ and pSO₄, the deposition rates (and
 233 subsequently the deposition flux in tonnes S (or N) km⁻² hr⁻¹, Sect. 2.4 were determined for the
 234 sulfur compounds as follows:

$$235 \quad \Delta T_{SO_2} = T_{SO_2}(t_2) - T_{SO_2}(t_1) = X_{SO_2} - D_{SO_2} \quad (2)$$

$$236 \quad \Delta T_{pSO_4} = T_{pSO_4}(t_2) - T_{pSO_4}(t_1) = X_{pSO_4} - D_{pSO_4} \quad (3)$$

237
$$\Delta T_{TOS} = T_{TOS}(t_2) - T_{TOS}(t_1) = -D_{TOS} \quad (4)$$

238 where X_{SO_2} is the rate of chemical reaction loss of sulfur mass in SO_2 , X_{pSO_4} is the rate of
 239 chemical formation of sulfur mass as pSO_4 , D_{SO_2} and D_{pSO_4} are deposition rates of sulfur mass in
 240 SO_2 and pSO_4 respectively, and t_1 and t_2 are plume interception times at Screen 1 and Screen 2,
 241 respectively. Note that the chemical loss rate of SO_2 is set to be equivalent to the formation rate
 242 of pSO_4 i.e. $X_{SO_2} = X_{pSO_4}$. Eq. (4) for TOS can also similarly be written as shown in Eq. (5).

243
$$\Delta T_{TOS} = \Delta T_{SO_2} + \Delta T_{pSO_4} = -D_{SO_2} - D_{pSO_4} \quad (5)$$

244 Units in Eq. (2 to 5) are all in $t \text{ hr}^{-1}$. Reaction with the OH radical was considered to be the most
 245 significant chemical loss of SO_2 and the most significant path for the formation of pSO_4 . X_{SO_2}
 246 and X_{pSO_4} were determined using estimated OH radical concentrations, which were estimated
 247 using the methodology described in SI Sect. S4. Although TON encompasses a range of
 248 different N species with expected differences in their deposition rates, it was not possible to
 249 quantitatively separate their chemical formation/losses from their deposition rates with this
 250 method. For total oxidized sulfur **TOS** (i.e., sulfur in $SO_2 + pSO_4$) and total oxidized nitrogen
 251 **TON** (i.e., nitrogen in NO_y) the chemistry term is not relevant, and thus, the dry deposition rate
 252 D_{TOS} was directly determined from ΔT_{TOS} using Eq. (4), and respectively for **TON**.

253

254 **2.4 Dry deposition fluxes and dry deposition velocities**

255 Average dry deposition fluxes (F) for **TOS** and **TON** were obtained by dividing the
 256 deposition rates D in $t \text{ hr}^{-1}$ with the footprint surface area of the plume between two adjacent
 257 screens (Fig. 1 grey shaded regions), as shown in Eq. (6) for the dry deposition flux F_{TOS} of **TOS**
 258 (in $t \text{ S km}^{-2} \text{ hr}^{-1}$):

259
$$F_{TOS} = \frac{D_{TOS}}{Area} \quad (6)$$

260 where the surface area, *Area*, was identified as the geographic area under the plume extending to
261 the edges of the plume where concentrations fell to background levels (i.e. SO₂ to ~0 ppb; SO₄
262 ~0.2 ug m⁻³). This approach was similarly used to derive deposition fluxes from an air quality
263 model, Global Environmental Multiscale – Modelling Air-quality and Chemistry (GEM-MaCH)
264 (Moran et al., 2010; also see SI Sect. S5 for details). The geographic surface area uncertainty is
265 estimated at 5 %. Dry deposition fluxes between the sources and the first screen were also
266 estimated using change in mass transfer rate ΔT based on the extrapolated transfer rates back to
267 the source region (‘extended’ region). The surface area boundaries for these ‘extended’ regions
268 were determined using latitude and longitude coordinates that were weighted by emissions. This
269 was done by first using the average wind direction from Screen 1 and creating a set of parallel
270 back trajectories (~20) starting at different parts of Screen 1 back across the source region. For
271 **TON**, the NO_x emission sources along each back trajectory were weighted by their NO_x
272 emissions to obtain an emissions-weighted center location with latitude and longitude
273 coordinates for each back trajectory. The line connecting these emissions-weighted center
274 locations formed the boundary of the extended surface area. The extended surface area was
275 similarly determined for **TOS** based upon the known locations of the major SO₂ point sources.
276 The uncertainty of the ‘extended’ regions is estimated at 10 % based on repeated optimizations
277 of the geographical area. Surface areas are visualized as grey shaded regions between screens in
278 Fig. 1 and tabulated in SI Table S1.

279 Spatially-averaged dry deposition velocities, V_d , based on the aircraft measurements were
280 determined over the surface area between screens using average plume concentrations across
281 pairs of screens at about 40 meters above the ground for **SO₂** and **TON** (e.g. Eq. (7) for SO₂ in

282 units of cm s^{-1}). Although TOS includes the S in both SO_2 and pSO_4 , only SO_2 is used in the
283 calculation of V_d since the deposition behaviour of gases and particles differ substantially, and
284 particles additionally have size-dependent deposition rates (Emerson et al., 2020). As the
285 dominant form of TOS is SO_2 (>92 %) the deposition behaviour of TOS is expected to be largely
286 driven by that of SO_2 . The measured TON does not include pNO_3 .

$$287 \quad V_d = \frac{F_{\text{SO}_2}}{[\text{SO}_2]} \quad (7)$$

288 The largest source of uncertainty in V_d calculated this way was the determination of
289 concentration at 40 meters above the surface as the measurements were extrapolated from the
290 lowest aircraft altitude to the surface and interpolated concentrations were used. The
291 measurement-derived V_d are compared with those from the air quality model GEM-MACH
292 which uses inferential methods.

293

294 **2.5 Monte-Carlo simulations of dry deposition velocities using multiple resistance-based** 295 **parameterizations**

296 Parameterization of dry deposition in inferential algorithms is commonly based on a
297 resistance approach with dry deposition velocity depending on three main resistance terms as
298 below:

$$299 \quad V_d = \frac{1}{R_a + R_b + R_c} \quad (8)$$

300

301 where R_a , R_b and R_c represent the aerodynamic, quasi-laminar sublayer and bulk surface
302 resistances respectively. Although these resistance terms are common among many regional air
303 quality models (Wu et al., 2018), the formulae used (and inputs in to these formulae) to calculate
304 the individual resistance terms differ significantly among the inferential deposition algorithms.
305 To assess the potential for a general underestimation of V_d across different inferential deposition
306 algorithms, and to compare with the aircraft-derived V_d , five different inferential deposition
307 algorithms, including that used in the GEM-MACH model for calculating V_d (Wu et al., 2018)
308 were incorporated into a Monte-Carlo simulation for V_d for SO_2 . NO_y was not considered here,
309 as its measurement includes multiple reactive nitrogen oxide species with different individual
310 deposition velocities. We note that many of the inferential algorithms are based on observations
311 of SO_2 and O_3 deposition made at single sites, and the extent to which a chemical is similar to
312 SO_2 or O_3 features into its V_d calculation – the comparison thus has relevance for species aside
313 from SO_2 . The five deposition algorithms considered are denoted ZHANG, NOAH-GEM,
314 C5DRY, WESLEY and GEM-MACH and are compared in Wu et al. (2018) (except the
315 algorithm in GEM-MACH). The five algorithms all use a big-leaf approach for calculating V_d
316 i.e. V_d is based on the resistance-analogy approach for calculating dry deposition velocity where
317 V_d is the reciprocal sum of three resistance terms R_a , R_b and R_c . Although the approach is
318 similar, the formulations of R_a , R_b and R_c between the algorithms are substantially different
319 (Table 1 in Wu et al., 2018). Results from Wu et al (2018) suggest that the differences in R_a+R_b
320 between different models would cause a difference in their V_d values on the order of 10-30% for
321 most chemical species (including SO_2 and NO_2), although the differences can be much larger for
322 species with near-zero R_c such as HNO_3 .

323 To perform the simulations, formulae for the first four algorithms were taken from Wu et
324 al. (2018) and for GEM-MACH taken from Makar et al. (2018). The stomatal resistance in the
325 ZHANG algorithm was from Zhang et al. (2002). The GEM-MACH formula (Eq. (8.7) in the SI
326 of Makar et al. (2018)) for mesophyll resistance R_{mx} contained a typo (missing the Leaf Area
327 Index (LAI)) and was corrected for as follows:

$$328 R_{mx} = [LAI(H^*/3000 + 100 f_0)]^{-1} \quad (9)$$

329 Prescribed input values were constrained by the range of possible values consistent with the
330 conditions during the aircraft flights and are shown in SI Table S3 with associated references.
331 Calculations for the R_a term were based on unstable and dry conditions as observed during the
332 aircraft flights. The Monte-Carlo simulation generated a distribution of possible V_d values,
333 based on randomly generated values of the input variables to each algorithm and selected from
334 Gaussian distributions with a range of 3 sigma for all input parameters. All simulations were
335 performed with the same input values that were common between the algorithms.

336 **3 Results and Discussion**

337 **3.1 Meteorological and Emissions Conditions during the Transformation Flights**

338 Three aircraft flights, Flights 7 (F7), 19 (F19) and 20 (F20) were conducted in
339 Lagrangian patterns where the same plume emitted from oil sands activities was repeatedly
340 sampled for a 4-5 hour period and up to 107-135 km downwind of the AOSR. The first screen of
341 each flight captured the main emissions from the oil sands operations with no additional
342 anthropogenic sources between subsequent screens downwind. The main sources of nitrogen
343 oxides were from exhaust emissions from off-road vehicles used in open pit mining activities and
344 sulfur and nitrogen oxides from the elevated facility stack emissions associated with the

345 desulfurization of raw bitumen (Zhang et al., 2018). As depicted in Fig. 1, F7 and F19 captured
346 a plume that contained both sulfur and nitrogen oxides. The westerly wind direction and
347 orientation of the aircraft tracks on F20 resulted in the measurement of two distinct plumes; one
348 plume exhibited increased levels of sulfur and nitrogen oxides mainly from the facility stacks,
349 and the other plume contained elevated levels of nitrogen oxides, mainly from the open pit
350 mining activities, and no SO₂.

351 During the experiments, the dry deposition rates (D) (t hr⁻¹) were quantified under
352 different meteorological conditions and emissions levels of **TOS** and **TON** (E_{TOS} and E_{TON}) for
353 the three flights (see Table 1). These differences played important roles in the observed pollutant
354 concentrations and resulting dry deposition fluxes for F7, F19 and F20. Mixed layer heights
355 (MLH) were derived from aircraft vertical profiles that were conducted in the centre of the
356 plume at each downwind set of transects. The profiles of temperature, dew point temperature,
357 relative humidity and pollutant mixing ratios were inspected for vertical gradients indicating a
358 contiguous layer connected to the surface. The highest MLH was determined for F7 at 2500
359 magl whereas F19 had the lowest MLH at 1200 magl (Table 1). In F20, the MLH was 2100
360 magl. The combination of a high MLH in F7 with the highest wind speeds resulted in the lowest
361 pollutant concentrations of the three flights. In F19, lower wind speeds and the lowest mixed
362 layer heights led to the highest pollutant levels. F20 had emissions and meteorological
363 conditions that were in between F7 and F19 resulting in pollutant concentrations between those
364 of F7 and F19.

365 Emission rates of SO₂ and NO_x (designated as E_{TOS} and E_{TON}) from the main sources in
366 the AOSR were estimated from the aircraft measurements and varied significantly between the
367 three flight days. The measurement-based emission rates of E_{TOS} and E_{TON} were taken from the

368 mass transfer rates of T_{SO_2} and T_{NO_y} (described in Methods) by extrapolating backwards to the
369 source locations in the AOSR using exponential functions (Fig. 2, Sect. 3.2). For **TOS**, the
370 source location was set at 57.017N, -111.466W, where the main stacks for SO₂ emissions are
371 located. For **TON**, the source locations were determined from geographically weighted
372 locations. Emission rates E_{TOS} and E_{TON} for each flight are shown in Table 1.

373 Model-based E_{TOS} and E_{TON} were also obtained from the 2.5 km x 2.5 km gridded
374 emissions fields that were specifically developed for model simulations of the large AOSR
375 surface mining facilities (Zhang et al., 2018) i.e. Suncor Millenium, Syncrude Mildred Lake,
376 Syncrude Aurora North, Shell Canada Muskeg River Mine & Muskeg River Mine Expansion,
377 CNRL Horizon Project and Imperial Kearn Mine. The emissions fields have been used in GEM-
378 MACH (described in SI Sect. S5) to carry out a number of model simulations (Zhang et al.,
379 2018; Makar et al., 2018) including for the present study. In this work, emissions were summed
380 from various sources including offroad, point (Continuous Emissions Monitoring (CEMS)), and
381 point (non-CEMS) for the surface mines to obtain total AOSR hourly emission rates for the
382 flight time periods of interest (Table 2). The standard deviations reflect the emissions variations
383 during the simulated flight.

384 **3.2 Mass Transfer Rates**

385 The mass transfer rates T (in t hr⁻¹) across the virtual flight screens for all three flights are
386 shown for **TOS** and **TON** in Fig. 1 and plotted in Fig. 2. In F20, two distinct **TON** plumes were
387 observed, allowing separate T calculations for **TON**. Monotonic decreases in T were observed
388 for both **TOS** and **TON** during transport downwind in all flights, clearly showing dry
389 depositional losses. The deposition rate D (Methods, Sect. 2.3) was used to estimate the
390 cumulative deposition of **TOS** and **TON** as a fraction of E_{TOS} or E_{TON} and is shown in Fig. 3 for

391 F7, F19 and F20 for transport distances of up to 107-135 km downwind of the sources. Curves
392 were fitted to the **TOS** and **TON** dry deposition cumulative percentages from which $d_{1/e}$ and τ
393 were determined (SI Table S1). The transport e-folding distance ($d_{1/e}$) was determined where
394 63.2% of E_{TOS} (or E_{TON}) was dry deposited, i.e., $\sum_{d=0}^{d_{1/e}} D(d) = 0.368E_{TOS}$. The atmospheric
395 lifetimes (τ) were derived as $\tau = d_{1/e}/u$, where u was the average wind speed across the distance
396 $d_{1/e}$. These estimates were compared with predictions from the regional air quality model GEM-
397 MACH (Makar et al., 2018; Moran et al., 2010; SI Sect. S5) using facility emission rates (Table
398 2). For **TOS** during F19, (Fig. 3b, e), the observed cumulative deposition at the maximum
399 distance accounted for 74 ± 5 % vs. the modelled 21 % of E_{TOS} . The measurements indicate that
400 the cumulative deposition of TOS was due mostly to SO_2 dry deposition where SO_2 was ~ 100 %
401 of TOS closest to the oil sands sources decreasing to 94 % farthest downwind. Although the
402 modelled cumulative deposition of TOS was significantly lower than the observations, the
403 fractional deposition of SO_2 was similar, decreasing from ~ 100 % to 95 % of TOS. Fitting a
404 curve to D and interpolating the cumulative deposition fraction to the 63.2 % E_{TOS} loss leads to a
405 $d_{1/e}$ of 71 ± 1 km, versus 500 km for the model prediction. Under the prevailing wind conditions,
406 the observed distance indicates a τ for **TOS** of approximately 2.2 hours, whereas the model
407 prediction indicated 16 hours. Large observation-based values and model prediction differences
408 in lifetime were also evident for the other flights (SI Table S1). Clearly, the model predictions
409 significantly underestimated deposition and vastly overestimated $d_{1/e}$ and τ . The observation-
410 based values for τ are also lower than average lifetimes of 1–2 days for SO_2 and 2–9 days for
411 pSO_4 derived from global models (Chin et al., 2000; Benkovitz et al., 2004; Berglen et al., 2004),
412 which include the effects of wet deposition and chemical conversion for SO_2 , thus making their
413 implicit residence times with respect to dry deposition even longer.

414 For **TON** in F19 (Fig. 3h, l), the observed cumulative deposition accounted for 49 ± 11 %
415 of E_{TON} at the maximum flight distance, versus 19 % predicted by the model. Similar model
416 underestimates for cumulative deposition fractions were found for F7 and F20. Extrapolating to
417 the 63.2% cumulative deposition fraction, $d_{1/e}$ was estimated to be 190 ± 7 km for F19 versus a
418 predicted 650 km from the model, implying a τ of approximately 5.6 hours for the measurement-
419 based results and 23 hours for the model prediction. Again, analogous differences for F7 and
420 F20 were found (SI Table S1). Similar to TOS, the measurement-based $d_{1/e}$ and τ values for
421 TON were significantly smaller than commonly accepted lifetimes of a few days for nitrogen
422 oxides in the boundary layer (Munger et al., 1998).

423 **3.3 Dry Deposition Fluxes F**

424 Using the deposition rate D (in tonnes S or N hr^{-1}), the average dry deposition fluxes, F
425 (in tonnes S or N $\text{km}^{-2} \text{hr}^{-1}$), were calculated by dividing D by the plume footprint surface areas
426 estimated by extending to the plume edges where the concentrations fell to background levels
427 (Methods, Sect. 2.4). These footprints are shown as the gray shaded geographic areas in Fig. 1,
428 totaling 3500, 5700 and 4200km^2 for F7, F19, and F20 plumes, respectively; see SI Table S1 for
429 **TON** plume areas). Fig. 4a shows F_{TOS} values for all three flights, exhibiting exponential
430 decreases with increasing distance away from the sources and showing e-folding distances for
431 F_{TOS} of 18, 27, and 55 km for F7, F19, and F20, respectively. More than 90% of the decreases in
432 F_{TOS} were accounted for by F_{SO_2} . Similarly, F_{TON} decreased exponentially with increasing
433 transport distances in all flights (Fig. 4c), exhibiting e-folding distances of 18 and 33 km for F7
434 and F19, and 55 and 189 km for the south and north **TON** plumes during F20, respectively.
435 These e-folding distances were similar to those for F_{TOS} , indicating similar rates of decreases in
436 F_{TON} with transport distances.

437 The potential for other processes to contribute to the derived TOS and TON fluxes were
438 considered including losses from the boundary layer to the free troposphere and re-emission of
439 TOS or TON species from the surface back to the gas-phase. Two different approaches, a finite
440 jump model and a gradient flux approach (Stull, 1988; Degrazia et al., 2015), were used to
441 estimate the potential upward loss across the interface between the boundary layer and the free
442 troposphere for sulfur and nitrogen. In both approaches, the upward S flux was a minor loss at <
443 $45 \text{ g km}^{-2} \text{ hr}^{-1}$, about 3 orders of magnitude lower than the several to many $\text{kg km}^{-2} \text{ hr}^{-1}$
444 horizontal advective transport that were determined using TERRA. For N, the upward flux
445 was estimated to be $\sim 570 \text{ g km}^{-2} \text{ hr}^{-1}$, so although a larger flux than S, it is about factor of 18
446 lower than the TON fluxes derived from observations.

447 As expected from the τ and transport e-folding distance $d_{1/e}$ comparisons, the GEM-
448 MACH model F_{TOS} were significantly lower than the measurement-based F_{TOS} results (Fig. 4a),
449 with the model F_{TOS} e-folding distances usually large: 133, 797, and 57 km for F7, F19, and F20,
450 respectively, or 7.4, 29.5, and 1.1 times longer than the corresponding measurement results. Part
451 of the differences between model and measurement F_{TOS} could be explained by differences in
452 actual versus model emissions, E_{TOS} (Tables 1 vs 2). To remove the influence of emissions, an
453 emission-normalized flux ($=F_{TOS}/E_{TOS}$ and F_{TON}/E_{TON}) was calculated for both measurement and
454 model (SI Fig. S2). Fig. 4b shows the ratios of measurement to model normalized emissions for
455 TOS. The model emission-normalized fluxes F_{TOS}/E_{TOS} were lower than the measurement-
456 based values by factors of 2.5-14, 1.8-3.4, and 2.0-3.0 for F7, F19, and F20, respectively,
457 decreasing with increased transport distances. However, they coalesce to a factor of 2 at the
458 furthest distances sampled by the aircraft, indicating that the model F_{TOS} estimates were biased
459 low by similar factors. The decreasing trends suggest that at distances further downwind, model

460 fluxes may exceed measurement-based fluxes, albeit at magnitudes lower than those shown in
461 Fig. 4a, which is consistent with earlier study results (Makar et al., 2018). For F_{TON} , the model-
462 predicted values were also lower than the measurement results, especially near the sources (Fig.
463 4c), and showed little variation with transport distances from the oil sands sources for all flights,
464 in strong contrast to the exponential decays observed from the aircraft. However, the emission-
465 normalized fluxes ($=F_{TON}/E_{TON}$) for the model approached those from measurements within
466 maximum flying distances for F19 and F20, although still significantly lower for F7 ($>10x$) (Fig.
467 4d).

468 **3.4 Dry Deposition Velocities V_d**

469 The shorter $d_{1/e}$ and τ , and larger deposition fluxes F near the sources determined from
470 the aircraft measurements compared to predictions by the GEM-MACH model indicate that the
471 model dry deposition velocities V_d was underestimated. Gas-phase V_d in the model is predicted
472 with a standard inferential “resistance” algorithm (Wesley, 1989; Jarvis, 1976), with resistance to
473 deposition calculated for multiple parameters including aerodynamic, quasi-laminar sublayer and
474 bulk surface resistances (Baldocchi, 1987). To demonstrate the model underestimation in V_d ,
475 comparisons between the measurement-based and model V_d were made where an evaluation of
476 V_d for TOS and TON was possible. All F_{SO_2} were converted into V_{d-SO_2} by dividing F_{SO_2} by
477 interpolated SO_2 concentrations at 40 meters above ground, averaging 1.2 ± 0.5 , 2.4 ± 0.4 , and
478 3.4 ± 0.6 $cm\ s^{-1}$ for F7, F19 and F20, respectively, across the plume footprints (Methods, Sect. 2.4
479 and SI Table S2). The corresponding model V_{d-SO_2} derived in the same way as the observations
480 was 0.72 , 0.63 , and 0.58 $cm\ s^{-1}$, 1.7-5.4 times lower than observations (SI Sect. S5; SI Table S2).
481 Interestingly, the median V_d for SO_2 of 4.1 $cm\ s^{-1}$ determined using eddy covariance/vertical
482 gradient measurements from a tower in the AOSR is higher than the mass balanced method

483 showing an even larger discrepancy compared to the model (SI Sect. S3; Fig. S5). Similarly,
484 derived V_{d-TON} averaged 2.8 ± 0.8 , 1.6 ± 0.5 , 4.7 ± 1.4 and 2.2 ± 0.7 cm s^{-1} F7, F19, F20 south plume,
485 and F20 north plume, respectively (SI Table S2), 1.2-5.2 times higher than the corresponding
486 modelled V_{d-TON} of 1.4, 1.3, 0.92, and 0.90 cm s^{-1} .

487 Using the observations, it was not possible to derive individual TON deposition rates
488 separate from their chemical formation/losses. In previous modelling work, Makar et al. (2018),
489 use the GEM-MACH model and describe the relative contributions of different TOS and TON
490 species towards total S and N deposition in the AOSR. TON was dominated by dry NO_2 (g)
491 deposition fluxes close to the sources (>70 % of total N close to the sources), and dry HNO_3 (g)
492 deposition increases with increasing distance from the sources (remaining < 30 % of total N),
493 and other sources of TON having minor contributions to deposition (< 10 %). Although TON
494 encompasses a range of different N species with expected differences in their deposition rates,
495 comparisons of V_{d-TON} with the model show, nevertheless, that overall large differences do exist.

496 **3.5 Monte-Carlo simulations of V_d for SO_2**

497 To further demonstrate observation-model differences, V_d distributions of SO_2 from five
498 common inferential dry deposition algorithms (Wu et al., 2018; Makar et al., 2018) were
499 determined for the conditions encountered during the flights using a Monte-Carlo approach as
500 described in Methods, Sect. 2.5). Results for the V_d simulations algorithms are shown in Fig. 5a.
501 Histograms for all five algorithms have peak V_d values at ~ 1 cm s^{-1} or lower. Probability
502 distributions for the individual resistance terms, R_a , R_b , and R_c showed that the dominant
503 resistance driving V_d was the R_c term (SI Fig. S3). Also shown in Fig. 5a are the measurement-
504 derived V_d for Flights 7, 19 and 20, and that from the Oski-ötin ground site. The observed V_d
505 values are larger than the V_d values for most of the simulations, with the exception of Flight 7,

506 where the Zhang et al. (2002), NOAA-GEM (Wu et al., 2018) and C5DRY (Wu et al., 2018)
507 algorithms' distributions agree with the observations. All algorithms are biased low relative to
508 the observations for the remaining flights, and the Oski-ôtin ground site. It is noted that the
509 ground-site observations that were derived using a standard flux tower methodology (SI Sect.
510 S3) at a single site, appeared to be higher than all other V_d ; nevertheless, these observations are
511 closer to the aircraft values than the algorithm estimates. These results indicate that an
512 underestimation of V_d relative to both aircraft and ground based measurements in the AOSR is
513 not unique to the GEM-MACH model or its dry deposition algorithm; similar results would
514 occur with the other algorithms included in the Monte-Carlo simulations, all of which are used
515 within other regional models.

516 To investigate the possible reasons behind the low model V_d relative to the observations,
517 a series of sensitivity tests using SO_2 were conducted. Differences in model V_d have been shown
518 to be mainly due to differences in the calculated R_c (Wu et al., 2018), and sensitivity tests here
519 indicated that R_c is particularly sensitive to the cuticular resistance R_{cut} . Hence, factors causing
520 R_{cut} to change can have significant impact on model V_d . In some of the algorithms, R_{cut} and
521 other resistance terms are dependent on the effective Henry's Law constant K_H^* for SO_2 . The
522 Monte-Carlo simulations for Fig. 5 assumed a surface pH= 6.68 resulting in a K_H^* of 1×10^5 for
523 SO_2 . Additional Monte-Carlo simulations were performed for the GEM-MACH dry deposition
524 algorithm by adjusting K_H^* assuming different pH with small variations from a pH=6.68
525 significantly changing R_c , R_{cut} , and V_d (SI Fig. S4). In Fig. 5b – red dashed line, with a surface
526 pH change from 6.68 to 8, consistent with possible alkaline surfaces in the AOSR (Makar et al.,
527 2018), in the GEM-MACH simulation, the V_d distribution is moved to larger values) with its
528 peak value shifting from 0.6 to 1.4 cm s^{-1} . These results show that model V_d may be highly

529 sensitive to assumed surface pH, at least when using some inferential dry deposition algorithms
530 which are pH-dependent. However, Fig. 5b shows that this pH-associated increase in V_d is still
531 insufficient to encompass the range of measurement-derived V_d . Increasing pH to 8 for the
532 GEM-MACH simulation reduces R_{cut} , hence R_c , to values much smaller than R_a and R_b ,
533 suggesting that model V_d cannot further increase without reductions in both R_a and R_b . In other
534 words, R_a and R_b were probably overestimated in the current deposition velocity algorithms. By
535 using the Zhang et al. (2002) R_a and the NOAH-GEM (Wu et al., 2018) R_b parameterizations in
536 the GEM-MACH algorithm, a further shift of the GEM-MACH V_d distribution to larger values
537 was found, with the range encompassing most of the observations (Fig. 5b, pink dashed line).
538 Using the Zhang and NOAH-GEM parameterizations, rather than the GEM-MACH
539 parameterization, would decrease the R_a and R_b for the momentum, heat and moisture fluxes as
540 well, but still remain within the range of what is expected based on published parameterizations
541 (Wu et al., 2018 and references therein).

542 The potential for re-emission of TOS and TON species was also considered. Fulgham et
543 al. (2020) report that the bidirectional fluxes of volatile organic acids are driven by an
544 equilibrium partitioning between surface wetness and the atmosphere. The observations
545 presented here represent the net flux of all processes including the effects of deposition and any
546 potential re-emissions of TOS and TON compounds should this process occur. As the results
547 show a net downward flux (i.e. net deposition), if any re-emission was occurring, it would be
548 smaller than the deposition fluxes observed here, which are themselves higher than shown by
549 currently available deposition algorithms. This implies that the deposition part of the flux must
550 be even larger than the net observed flux and the measured net fluxes presented here should then
551 be considered as minimum values. The current deposition algorithms do not include

552 bidirectional fluxes for inorganics, and adjustments related to pH in some situations may not be
553 sufficient to parameterize deposition fluxes. A bidirectional approach may be needed that would
554 include not only $[H^+]$, but surface heterogeneous reactions, to determine near-surface equilibrium
555 concentrations of co-depositing gases such as ammonia and nitric acid.

556 It is clear from the Monte-Carlo simulations for SO_2 V_d comparisons, inferential dry
557 deposition algorithms as used in regional and global chemical transport models need to be further
558 validated and improved, especially over large geographic regions. Here, the role of pH was
559 identified for improvement in some algorithms along with possible improvement in aerodynamic
560 and quasi-laminar sublayer resistance parameters. Yet, for other algorithms and for **TON**
561 compounds, the model low-biases in V_d remain to be investigated.

562 The underestimates suggest that the applications of these algorithms in regional or global
563 models may significantly underestimate predictions of **TOS** dry depositional loss from the
564 atmosphere. Underestimates in V_d are the result of a combination of uncertainties in the
565 parameterizations of each algorithm. In the case of the algorithm used in GEM-MACH, by
566 adjusting the assumed surface pH from 6.68 to 8 (justifiable given the considerable dust
567 emissions in the region (Zhang et al., 2018)), the model V_d moved closer to the aircraft-derived
568 values (Fig. 5b), reducing the model-observation gap by approximately 2/3. In addition,
569 substituting the aerodynamic resistance and quasi-laminar sublayer resistance parameterizations
570 in the GEM-MACH algorithm with that from Zhang et al. (2002) and NOAA-GEM (Wu et al.,
571 2018), respectively, resulted in a further increase in the model V_d distribution that encompasses
572 most of the observations (Fig. 5b). Clearly, different algorithms respond differently to changes
573 in the parameterizations, and validation and adjustment to each algorithm needs measurement-
574 based results over large regions such as derived here.

575 **4 Conclusions**

576 The atmospheric transport distances and lifetimes $d_{1/e}$ and τ determined from the aircraft
577 measurements are substantially shorter than the GEM-MACH model predictions, and the dry
578 deposition fluxes F and velocities and V_d near sources are larger compared to the predictions by
579 GEM-MACH and five inferential dry deposition velocity algorithms, respectively. There are
580 important implications for these measurement-model discrepancies. Such discrepancies indicate
581 that regional or global chemical transport models using these algorithms are biased low for local
582 deposition and high for long-range transport and deposition, and **TOS** and **TON** loss from the
583 atmosphere are significantly under-predicted, resulting in overestimated lifetimes. While the
584 measurements took place over a relatively short time period, these results indicate that **TOS** and
585 **TON** may be removed from the atmosphere at about twice the rate as predicted by current
586 atmospheric deposition algorithms. This, in turn, implies a potentially significant impact on
587 deposition over longer time scales (potentially weeks to months) and relevance towards
588 cumulative environmental exposure metrics such as critical loads and their exceedance. A faster
589 near-source deposition velocity for emitted reactive gases may imply less S and N mass being
590 available for long range transport, reducing concentrations and deposition further downwind.
591 The near-source higher deposition velocity, thus has the important implication of a reduction in
592 more distant and longer timescale deposition for locations further from the sources. Moreover,
593 emissions assessed through network measurements or budget analysis of atmospheric **TOS** and
594 **TON** (Sickles and Shadwick, 2015; Paulot et al., 2018; Berglen et al., 2004) may be
595 underestimated due to lower V_d used in these estimates, and may require reassessing the
596 effectiveness of control policies. Shorter τ for **TOS** and **TON** reduces their atmospheric spatial
597 scale and intensity of smog episodes, potentially reducing human exposures (Moran et al., 2010).

598 Importantly, shorter τ for **TOS** and **TON** reduces their contribution to atmospheric aerosols;
599 consequently, the negative direct and indirect radiative forcing from these sulfur and nitrogen
600 aerosols are reduced, reducing their cooling effects on climate (Solomon et al., 2007). These
601 impacts suggest that more measurements to determine τ and F for these pollutants across large
602 geographic scales and different surface types are necessary to better quantify their climate and
603 environmental impacts in support of policy. While in the past such determination was difficult
604 and/or impossible, the present study provides a viable methodology to achieve such a goal.

605

606

607 **Table 1.** Average observed meteorological conditions and facility emission rates of **TOS** (E_{TOS})
 608 and **TON** (E_{TON}), (determined from extrapolated (to distance=0) transfer rates; Figure 1) for
 609 **TOS** and **TON** during the F7, F19 and F20 flights. SP=south plume; NP=north plume.

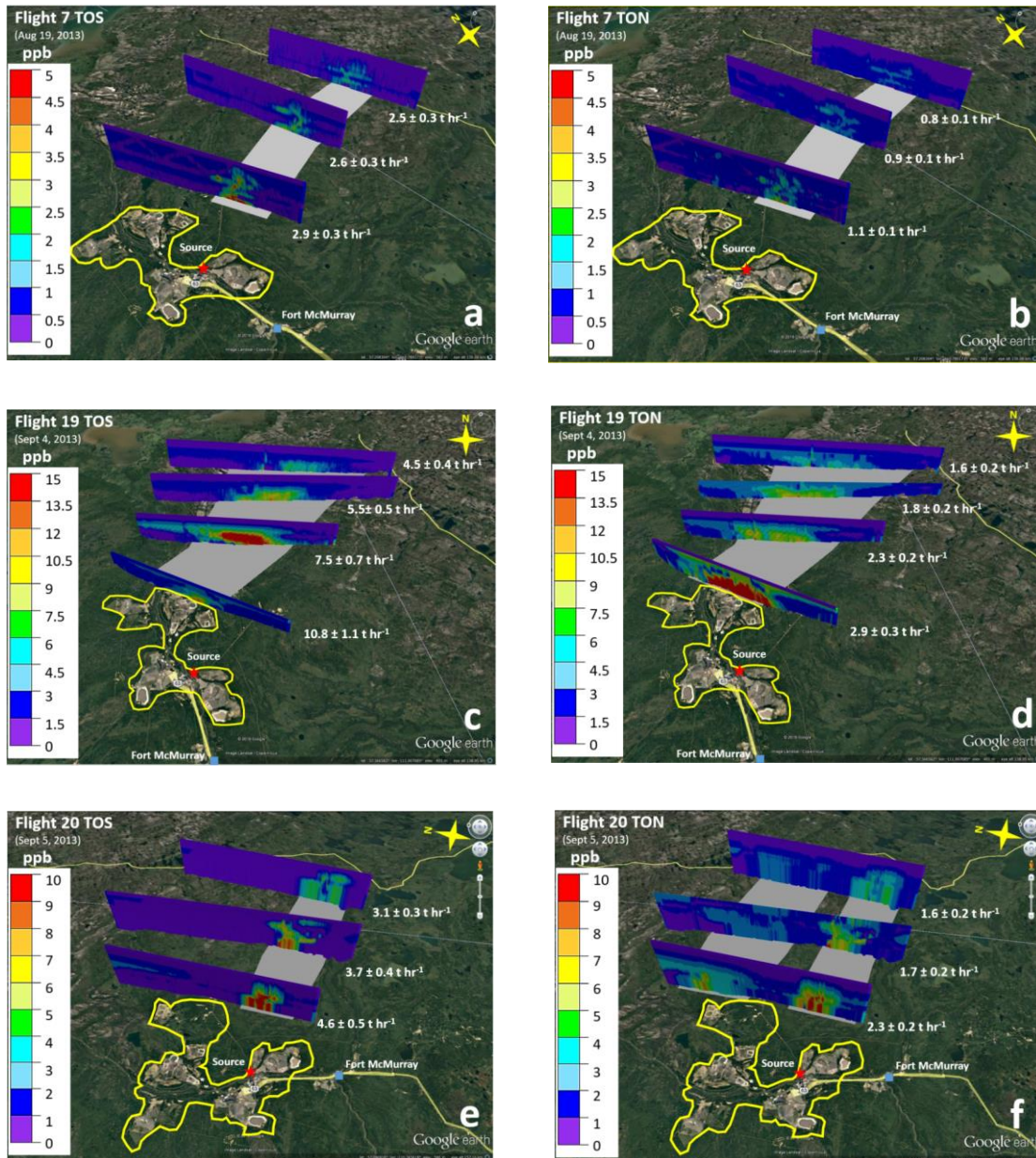
Flight	Date	Time (UTC)	Mean wind speed (m/s)	Mean wind direction (°)	Mixed layer height (m agl)	E_{TOS} (t/hr)	E_{TON} (t/hr)
7	Aug 19/13	2007–0108	13.0±1.0	256±11.7	2500±100	3.4	1.2
19	Sep 4/13	1854–2353	9.5±1.9	218±16	1200±100	18.5	3.9
20	Sep 5/13	1933–2436	8.9±1.2	281±11	2100±100	5.8	2.2 (SP) 1.2 (NP)

610

611 **Table 2.** Model average meteorological conditions and facility emission rates of **TOS** (E_{TOS}) and
 612 **TON** (E_{TON}) during the F7, F19 and F20 flights as described above. SP=south plume; NP=north
 613 plume.

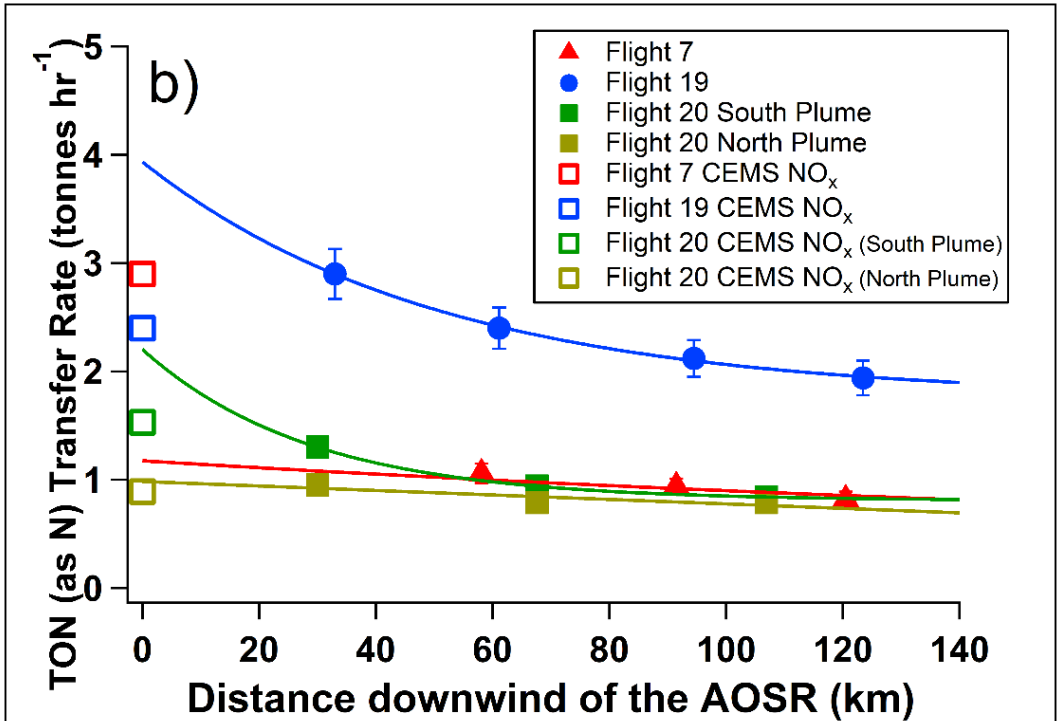
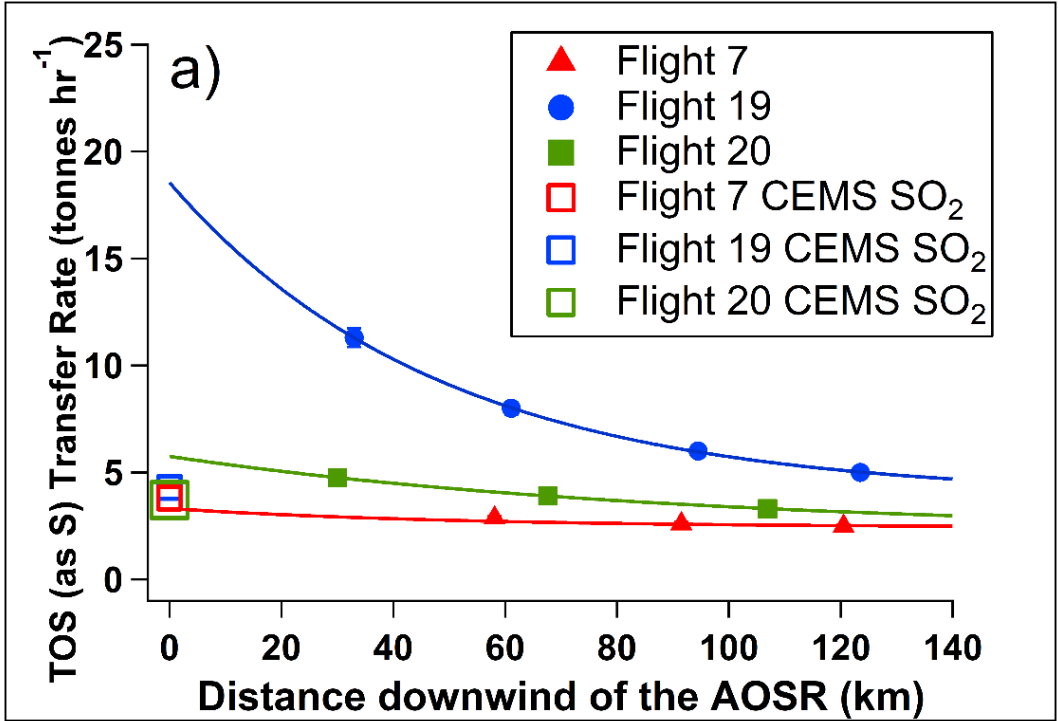
Flight	Date	Time (UTC)	mean wind speed (m/s)	mean wind direction (°)	mixed layer height (m agl)	E_{TOS} (t/hr)	E_{TON} (t/hr)
7	Aug 19/13	2007–0108	12.6±0.3	253±5.0	1670±80	3.8	2.9
19	Sep 4/13	1854–2353	8.1±1.0	225±4.6	1450±43	4.3	2.4
20	Sep 5/13	1933–2436	9.1±0.7	275±1.6	1590±42	3.7	1.5 (SP) 0.9 (NP)

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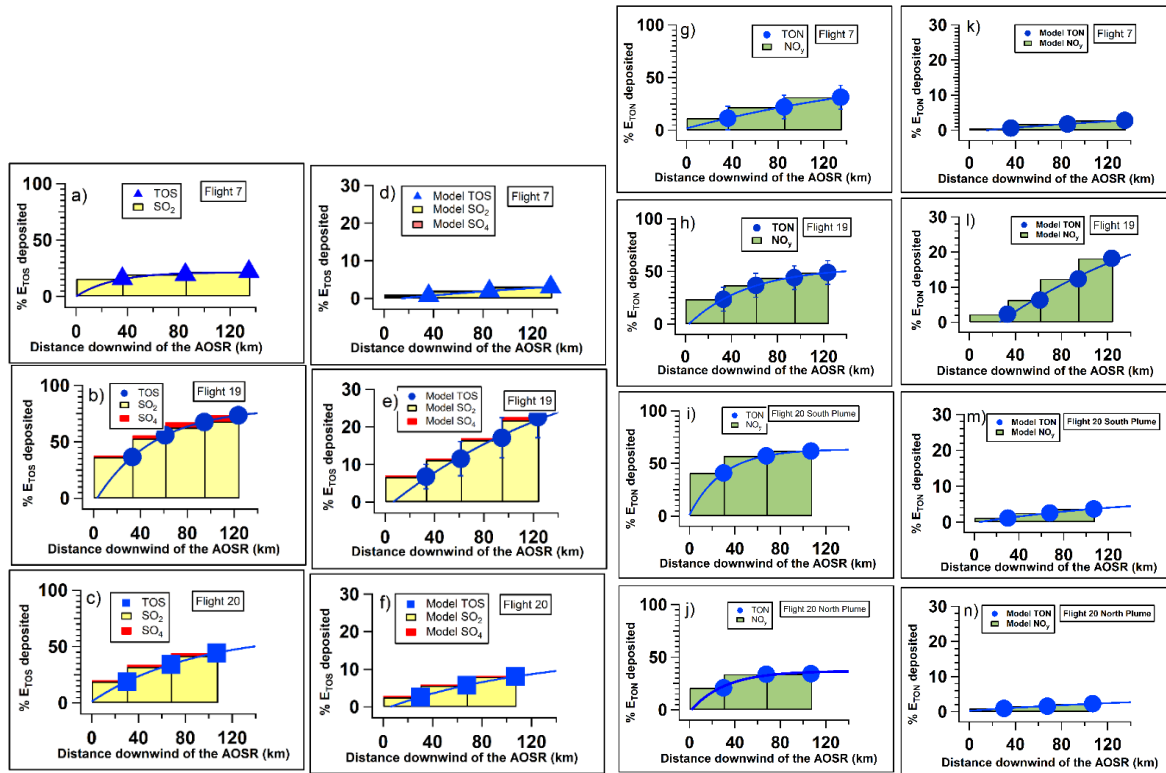
Figure 1. TOS (total oxidized sulfur) and TON (total oxidized nitrogen) plumes downwind of the AOSR during three Lagrangian flights, F7, F19 and F20. The AOSR facilities are enclosed by the yellow outline. The transfer rates T in t S or N hr^{-1} across each screen are shown. The grey shaded surface areas are identified as the geographic footprint under the plumes. Data: Google Image © 2018 Image Landsat / Copernicus.



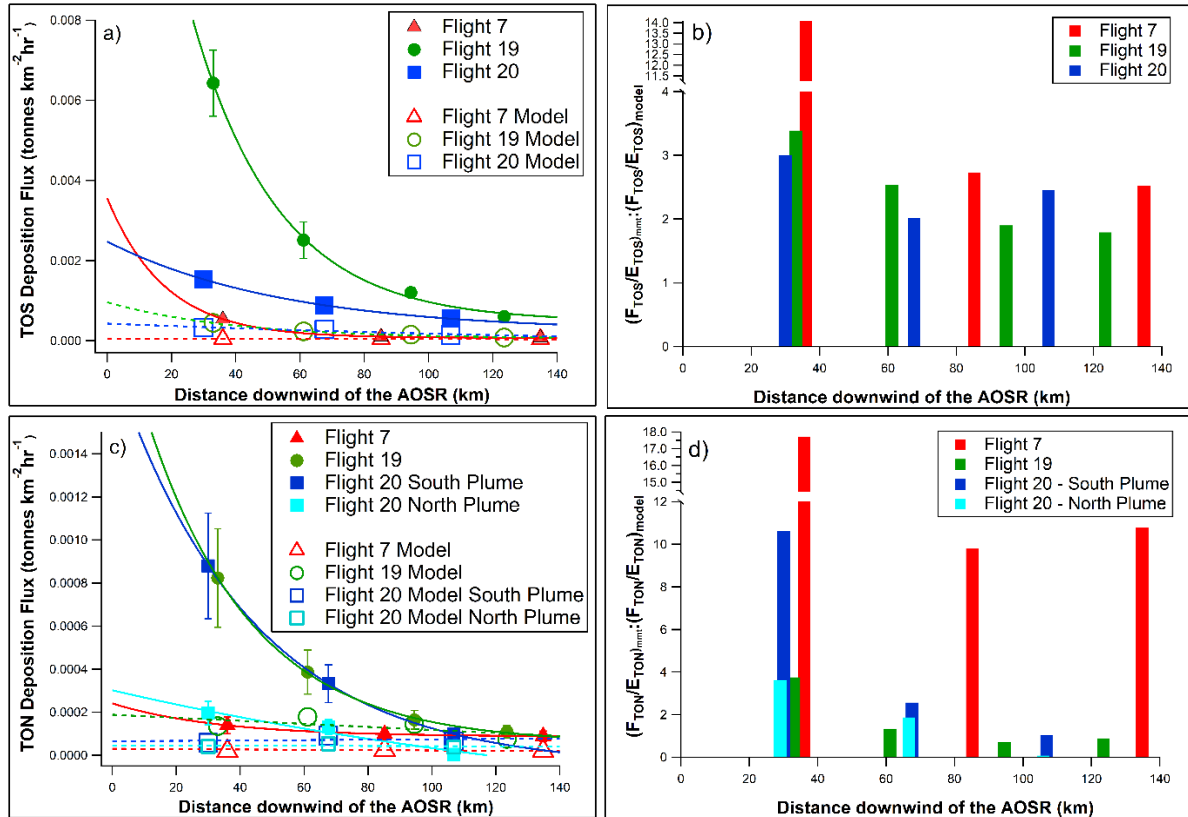
622

623 **Figure 2.** TERRA-derived transfer rates of (a) TOS and (b) TON for F7, F19 and F20. The
 624 vertical bars indicate the propagated uncertainties. The model emission rates E_{TOS} and E_{TON} are
 625 shown by the open symbols.

626



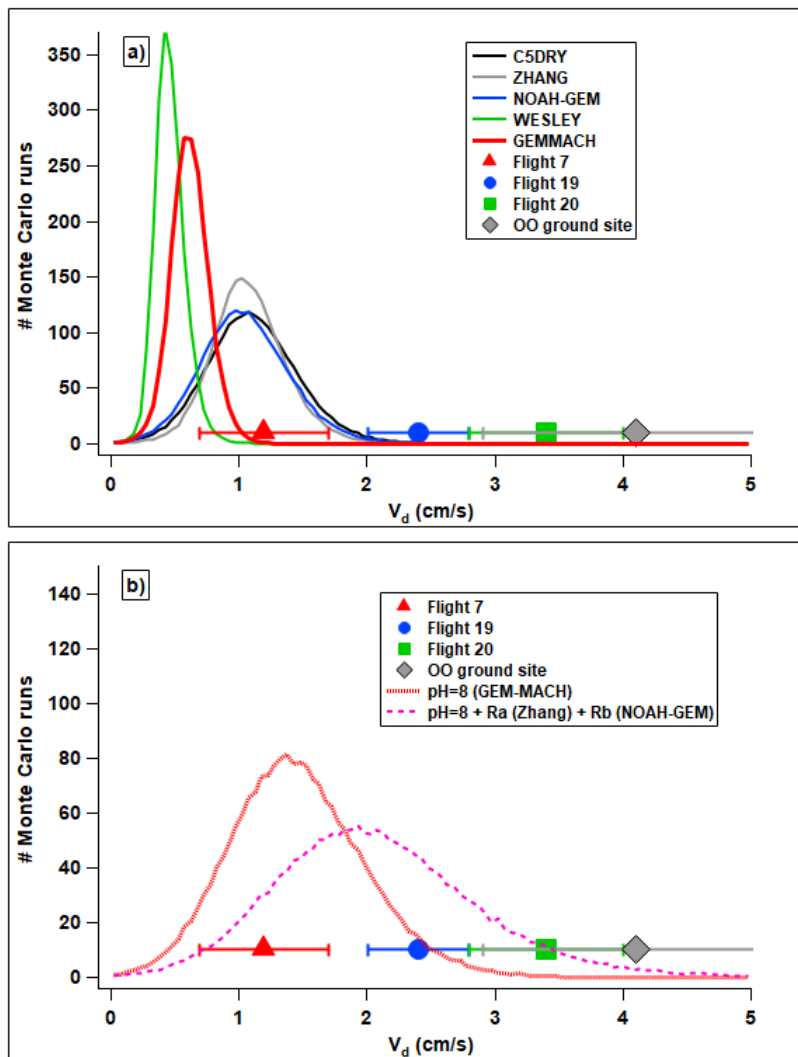
627 **Figure 3.** Cumulative dry deposition as a percentage of emissions E_{TOS} (a to f) or E_{TON} (g to n)
 628 for F7, F19 and F20 measurements with corresponding GEM-MACH model predictions. The
 629 bars show the dry deposition due to SO_2 and pSO_4 . The curves were fitted to the TOS and TON
 630 dry deposition percentages from which $d_{1/e}$ and τ were determined.



631

632 **Figure 4.** Dry deposition fluxes F_{TOS} and F_{TON} (in $t\ km^{-2}\ hr^{-1}$) determined from measurements
 633 (solid symbols) and GEM-MACH model predictions (open symbols). (a) F_{TOS} , (b) ratios of
 634 measurement to model normalized emissions F_{TOS}/E_{TOS} , (c) F_{TON} , and (d) ratios of measurement
 635 to model normalized emissions F_{TON}/E_{TON} .

636



637

638 **Figure 5.** (a) Distributions of V_d for SO_2 from Monte-Carlo simulations using 5 different
 639 deposition parameterizations (Wu et al., 2018; Makar et al., 2018) and (b) Monte-Carlo
 640 simulations for the GEM-MACH algorithm using a pH=8 and using a pH=8 plus replacing the
 641 GEM-MACH algorithm R_a and R_b formulae with that from Zhang et al. (2002) and NOAH-GEM
 642 (Wu et al., 2018), respectively. Aircraft-derived V_d for F7, F19 and F20 as well as the median
 643 value for the Oski-ôtin ground site (SI Figure S5) are shown in both (a) and (b) for comparison.
 644

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830 **Code availability**

831 All the computer code associated with the TERRA algorithm, including for the kriging of
832 pollutant data, a demonstration dataset and associated documentation is freely available upon
833 request. The authors request that future publications which make use of the TERRA algorithm
834 cite this paper, Gordon et al., Liggio et al., or Li et al. as appropriate.

835 **Data availability**

836 All data used in this publication are freely available on the Canada-Alberta Oil Sands
837 Environmental Monitoring Information Portal: [https://www.canada.ca/en/environment-climate-](https://www.canada.ca/en/environment-climate-change/services/oil-sands-monitoring/monitoring-air-quality-alberta-oil-sands.html)
838 [change/services/oil-sands-monitoring/monitoring-air-quality-alberta-oil-sands.html](https://www.canada.ca/en/environment-climate-change/services/oil-sands-monitoring/monitoring-air-quality-alberta-oil-sands.html)
839

840 **Author contribution**

841 KH, SML, JL, SM, RM, RS, JO, MW all contributed to the collection of aircraft observations in the field.
842 KH, RM and JO made the SO₂, NO_y and pSO₄ measurements and carried out subsequent QA/QC of data.
843 RM analyzed canister VOCs and provided OH concentration estimates. SM provided OH estimates from
844 MCM modelling as a comparison. AD contributed to the development of TERRA. JL wrote the Monte

845 Carlo code. PM and AA ran the model and provided model analyses. JZ provided emissions data. LZ and
846 RS provided deposition algorithm parameters. RS made and provided the ground site deposition velocity
847 measurements. KH and SML wrote the paper input from all co-authors.
848

849 **Competing Interests**

850 The authors declare no competing interests.

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857
858