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*Supplement of*

## **Estimates of exceedances of critical loads for acidifying deposition in Alberta and Saskatchewan**

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# S.1. Gas-Phase Deposition in GEM-MACH

## S.1.1 Deposition Velocity Formula

The deposition velocity of gases in GEM-MACH is given by the following land-use type and gaseous-species specific equation (Wesely and Hicks,1977):

$$V_d = (R_a + R_b + R_c)^{-1} \quad (\text{S.1})$$

where  $R_a$  is the aerodynamic resistance common to all constituents (and depends only on meteorological factors and surface roughness),  $R_b$  is the quasi-laminar sublayer resistance which depends on gas diffusivity, and  $R_c$  is the net surface resistance which depends on various environmental factors and land-use. The deposition velocity for each gas for each land-use type in each grid-square is calculated using (S.1), and then net deposition velocity for that grid-square and gas is given by sum of the land-use-fraction-weighted deposition velocities across land-use types within the grid-square.

Ozone deposition velocities calculated via (S.1) were reset for specific land use types and subject to upper limits. Wesely and Hicks (2000) noted that ozone deposition velocities over ocean are usually in the range 0.01 to 0.05  $\text{cm s}^{-1}$ , and over freshwater lakes less than or equal to 0.01  $\text{cm s}^{-1}$ , so a value of  $3 \times 10^{-2} \text{ cm s}^{-1}$  was used for these land-use classes. For ozone deposition to tundra, Wesely and Hicks (2000) noted that observational evidence suggested a typical value of 0.15  $\text{cm s}^{-1}$ , hence this value was used here. An overall upper limit of 0.1  $\text{m s}^{-1}$  was also used on the ozone deposition velocity.

## S.1.2 Net Surface Resistance, $R_c$

The net surface resistance,  $R_c$ , is given by the following formula (Jacobson (1999), Wesely (1989)):

$$\frac{1}{R_c} = \frac{1 - W_{st}}{R_{st} + R_{mx}} + \frac{1}{R_{cut}} + \frac{1}{R_{conv} + R_{exp}} + \frac{1}{R_{can} + R_{soil}} \quad (\text{S.2})$$

Where  $R_{st}$  is the stomatal resistance,  $R_{mx}$  is the mesophyll resistance,  $R_{cut}$  is the cuticle resistance,  $R_{conv}$  is the resistance of gases to buoyant convection,  $R_{exp}$  is the resistance associated with leaves, twigs, bark and other exposed surfaces in the lower canopy,  $R_{can}$  is the resistance associated with the height and density of the vegetated canopy (canopy resistance), and  $R_{soil}$  is the resistance associated with the soil, leaf litter, etc., at the surface.  $W_{st}$  is used to account for the impact of precipitation and high humidity on the stomatal and mesophyll resistance, and is set in GEM-MACH to 0.5 if the precipitation rate exceeds 1  $\text{mm hr}^{-1}$ , or the relative humidity exceeds 95%.

When the surface is snow-covered (the equivalent liquid water depth of snow is greater than 5 mm), the net surface resistance is assumed to follow the observed deposition behavior of  $\text{SO}_2$ :

$$\frac{1}{R_c} = \frac{1}{R_{cut} + exp_{Ts}} + \frac{1}{R_{conv} + R_{exp} + exp_{Ts}} + \frac{1}{R_{can} + R_{soil} + exp_{Ts}} \quad (\text{S.3})$$

Where  $exp_{Ts}$  is a temperature dependent function based on fitting to the data presented in Dasch and Cadle (1986)):

$$exp_{Ts} = 1000e^{-(T_{surf} + 4.0)} \quad (\text{S.4})$$

Where  $T_{surf}$  is the surface temperature in Celsius.

Each of the remaining terms in equations (S.2) and (S.3) are described below.

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*S.1.2.1  $R_{soil}$ : Resistance associated with soil, leaf litter, etc.*

Soil resistance for the  $i$ 'th gas and  $j$ 'th land use type and season is also calculated, largely using values from Wesely (1989):

$$R_{soil_{i,j}} = \left( \frac{\alpha_i}{R_{gd,SO2_j}} + \frac{\beta_i}{R_{gd,O3_j}} \right)^{-1} \quad (S.5)$$

10 The values of  $R_{gd,SO2}$  and  $R_{gd,O3}$  for the different land use types used in GEM-MACH are given below (Table S1), and are followed by the values of  $\alpha$  and  $\beta$  for each chemical species (Table A2). Values of zero for  $\alpha$  and  $\beta$  indicate that the given term is not used in the creation of  $R_{soil}$ ; if both are zero, no contribution from  $R_{soil}$  used for that species. Note that Wesely (1989) used values of zero for  $R_{gd,SO2}$  and  $R_{gd,O3}$  for some terms which are assigned values of 10 in Table S1: the low but non-zero values were used here to avoid division by zero error in the calculation of  $R_{soil}^{ij}$ . Wesely (1989) did not include a

15 class for ice caps and glaciers; in Table S1, the values for this land use class for  $R_{gd,O3}$  were taken from the winter values for inland water, and the most common “Winter; snow and subfreezing value” from the other land use classes,  $100 \text{ sm}^{-1}$ , was used for  $R_{gd,SO2}$

Table S1.  $R_{gd,SO_2}$  and  $R_{gd,O_3}$  values used in GEM-MACH ( $s\ m^{-1}$ )

<i>Season</i> →	Midsummer $R_{gd}$		Autumn, pre-harvest $R_{gd}$		Late Autumn, post-frost, pre-snow $R_{gd}$		Winter; snow and sub- freezing $R_{gd}$		Transitional: spring, partially green, $R_{gd}$	
<i>Land Use</i>	SO <sub>2</sub>	O <sub>3</sub>	SO <sub>2</sub>	O <sub>3</sub>	SO <sub>2</sub>	O <sub>3</sub>	SO <sub>2</sub>	O <sub>3</sub>	SO <sub>2</sub>	O <sub>3</sub>
Evergreen needle-leaf forest	500	200	500	200	500	200	100	3500	500	200
Evergreen broadleaf forest	500	200	500	200	500	200	100	3500	500	200
Deciduous needle-leaf forest	500	200	500	200	500	200	100	3500	500	200
Deciduous broadleaf forest	500	200	500	200	500	200	100	3500	500	200
Mixed Forest	100	300	100	300	200	300	100	3500	200	300
Grassland	350	200	350	200	350	200	100	3500	350	200
Crops, mixed farming	150	150	200	150	150	150	100	3500	150	150
Desert	1000	400	1000	400	1000	400	1000	400	1000	400
Tundra	400	200	400	200	400	200	50	3500	400	200
Dwarf trees, shrubs	400	200	400	200	10	200	50	3500	400	200
Wetland with plants	10	1000	10	800	10	1000	100	3500	10	1000
Ice caps and glaciers	100	2000	100	2000	100	2000	200	2000	100	2000
Inland water	10	2000	10	2000	10	2000	10	2000	10	2000
Ocean	10	2000	10	2000	10	2000	10	2000	10	2000
Urban	400	3000	400	3000	400	3000	100	600	500	300

Table S2: Values of  $\alpha$  and  $\beta$  used in GEM-MACH, by  $S_{\text{dep}}$  and  $N_{\text{dep}}$  gas species:

Species	$\alpha$	$\beta$
SO <sub>2</sub>	1	0.0
H <sub>2</sub> SO <sub>4</sub>	1	1.0
NO	0	0.01
NO <sub>2</sub>	0	0.8
HNO <sub>3</sub>	10	10
PAN	0	0.6
HONO	2	2.0
Organic Nitrate	0	0.5
NH <sub>3</sub>	1	0.0

### S.2.2 $R_{can}$ :

The canopy resistance,  $R_{can}$  (also called the aerodynamic canopy resistance) is a function of season and land use value, and is based on Zhang *et al.* (2003), given in Table S3.

Table S3.  $R_{can}$  values used in GEM-MACHv2 ( $s\ m^{-1}$ )

Season →	Midsummer	Autumn, pre-harvest	Late Autumn, post-frost, pre-snow	Winter; snow and sub- freezing	Transitional: spring, partially green
Evergreen needle-leaf forest	100	100	100	100	100
Evergreen broadleaf forest	250	250	250	250	250
Deciduous needle-leaf forest	100	85	70	60	60
Deciduous broadleaf forest	250	190	115	100	100
Mixed Forest	190	150	110	100	100
Grassland	40	40	40	10	30
Crops, mixed farming	40	40	10	10	20
Desert	0	0	0	0	0
Tundra	0	0	0	0	0
Dwarf trees, shrubs	60	60	30	20	30
Wetland with plants	20	20	20	20	20
Ice caps and glaciers	0	0	0	0	0
Inland water	0	0	0	0	0
Ocean	0	0	0	0	0
Urban	40	40	40	40	40

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### S.1.2.3 $R_{exp}$ : Lower Canopy Exposed Surface Resistance

The resistance for the lower canopy follows Wesely (1989), and is given by an equation similar to (S.5):

$$R_{exp} = \left[ 1 \times 10^{-5} \frac{H^*}{R_{exp,SO_2}} + \frac{f_0}{R_{exp,O_3}} \right]^{-1} \quad (S.6)$$

The values of  $R_{exp,SO_2}$  and  $R_{exp,O_3}$  used in GEM-MACHv2 are given in Table A4, and the values of  $H^*$  and  $f_0$  are given in Table S5.

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### S.1.2.4 $R_{mx}$ : Mesophyll Resistance

Mesophyll resistance is usually considered to be of minor importance (Zhang *et al.*, 2002, 2003 use values of 0 to 100  $s\ m^{-1}$  for  $R_{mx}$ , Baldocchi *et al.* (1987) mention its small impact on a leaf basis, quoting Hosker and Lindberg (1982) values in the

range 10 to 50  $\text{sm}^{-1}$ ), and in GEM-MACH follows the formula of Wesely (1989). Table A5 contains the values of  $H^*$  and  $f_0$  used in GEM-MACH for non-zero  $R_{\text{mx}}$ , as well as the resulting values of  $R_{\text{mx}}$ .

$$R_{\text{mx}} = (H^*/3000 + 100f_0)^{-1} \quad (\text{S.7})$$

Table S4.  $R_{\text{exp,SO}_2}$  and  $R_{\text{exp,O}_3}$  values used in GEM-MACH ( $\text{s m}^{-1}$ )

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<i>Season</i> →	Midsummer R <sub>exp</sub>		Autumn, pre-harvest R <sub>exp</sub>		Late Autumn, post-frost, pre-snow R <sub>exp</sub>		Winter; snow and sub- freezing R <sub>exp</sub>		Transitional: spring, partially green, R <sub>exp</sub>	
	SO <sub>2</sub>	O <sub>3</sub>	SO <sub>2</sub>	O <sub>3</sub>	SO <sub>2</sub>	O <sub>3</sub>	SO <sub>2</sub>	O <sub>3</sub>	SO <sub>2</sub>	O <sub>3</sub>
Evergreen needle-leaf forest	2000	1000	2000	1000	3000	1000	200	1500	2000	1500
Evergreen broadleaf forest	2000	1000	2000	1000	3000	1000	200	1500	2000	1500
Deciduous needle-leaf forest	2000	1000	9000	400	9000	400	9000	400	4000	500
Deciduous broadleaf forest	2000	1000	9000	400	9000	400	9000	400	4000	500
Mixed Forest	2000	1000	4000	600	6000	1000	400	600	3000	700
Grassland	2000	1000	9000	400	9000	400	9999	1000	4000	500
Crops, mixed farming	2000	1000	9000	400	9000	1000	9999	1000	4000	1000
Desert	9999	9999	9999	9999	9999	9999	9999	9999	9999	9999
Tundra	4000	1000	9000	400	9000	600	9000	800	8000	800
Dwarf trees, shrubs	2000	1000	9000	400	9000	400	9000	400	4000	500
Wetland with plants	2500	1000	9000	600	400	600	400	600	3000	600
Ice caps and glaciers	9999	9999	9999	9999	9999	9999	9999	9999	9999	9999
Inland water	9999	9999	9999	9999	9999	9999	9999	9999	9999	9999
Ocean	9999	9999	9999	9999	9999	9999	9999	9999	9999	9999
Urban	9999	9999	9999	9999	9999	9999	9999	9999	9999	9999

Table S5.  $H^*$  and  $f_0$  used in GEM-MACH, for  $S_{\text{dep}}$  and  $N_{\text{dep}}$  species.

Species	$H^*$	$f_0$	$R_{\text{mx}}$
SO <sub>2</sub>	$1 \times 10^5$	0.0	$3.0 \times 10^{-2}$
NO	$2 \times 10^{-3}$	0.0	$1.0 \times 10^6$
NO <sub>2</sub>	$1 \times 10^{-2}$	0.1	$1.0 \times 10^{-1}$
HNO <sub>3</sub>	$1 \times 10^{14}$	0.0	$3.0 \times 10^{-11}$
PAN	$3.6 \times 10^0$	0.1	$1.0 \times 10^{-1}$
HONO	$1 \times 10^5$	0.1	$2.3 \times 10^{-2}$
NH <sub>3</sub>	$2.0 \times 10^4$	0.0	$1.5 \times 10^{-1}$



### S.1.2.5 $R_{cut}$ : Cuticle Resistance

The dry leaf cuticle resistance is given by the formula of Wesely (1989):

$$R_{cut} = R_{cuti} [LAI(10^{-5}H^* + f_0)]^{-1} \quad (S.8)$$

- 5 Where LAI is the vertically integrated leaf area index; both LAI and the coefficient  $R_{cuti}$  are dependent on the land-use type and season, given in Table S6, below.

Table S6. LAI and  $R_{cuti}$  values used in GEM-MACHv2

	Midsummer		Autumn, pre-harvest		Late Autumn, post-frost, pre-snow		Winter; snow and sub-freezing		Transitional: spring, partially green	
	LAI	$R_{cuti}$	LAI	$R_{cuti}$	LAI	$R_{cuti}$	LAI	$R_{cuti}$	LAI	$R_{cuti}$
Evergreen needle-leaf forest	5.3	1000	5.3	1500	4.7	2000	5.5	2000	5.5	1000
Evergreen broadleaf forest	4.5	1000	4.5	1500	4.5	2000	4.5	2000	4.5	1000
Deciduous needle-leaf forest	1.1	2000	0.8	3000	0.3	8000	0.0	9999	0.0	4000
Deciduous broadleaf forest	3.4	1200	1.9	2000	0.1	9000	0.0	9999	0.0	2000
Mixed Forest	4.5	1000	3.5	1500	2.3	2000	2.3	2000	2.3	1000
Grassland	2.0	1500	1.5	2000	1.0	3000	0.5	6000	0.5	1500
Crops, mixed farming	2.0	1500	1.5	2000	1.0	3000	0.0	9999	0.0	1500
Desert	0.0	9999	0.0	9999	0.0	9999	0.0	9999	0.0	9999
Tundra	0.0	9999	0.0	9999	0.0	9999	0.0	9999	0.0	9999
Dwarf trees, shrubs	2.5	4000	2.5	1500	1.5	2000	1.2	3000	0.5	4000
Wetland with plants	0.2	6000	0.2	6000	0.1	9000	0.0	9999	0.1	6000
Ice caps and glaciers	0.0	9999	0.0	9999	0.0	9999	0.0	9999	0.0	9999
Inland water	0.0	9999	0.0	9999	0.0	9999	0.0	9999	0.0	9999
Ocean	0.0	9999	0.0	9999	0.0	9999	0.0	9999	0.0	9999
Urban	0.3	6000	0.2	6000	0.1	9000	0.0	9999	0.2	6000

*S.1.2.6 R<sub>conv</sub>: Resistance of gases to buoyant convection*

The resistance of gases to buoyant convection, and is given by (Wesely, 1989, and assuming a slope of zero on the terrain):

$$R_{conv} = 100 + \left[ 1.0 + \frac{1000}{SRAD+10} \right] \quad (S.9)$$

5 Where SRAD is the visible solar radiation ( $Wm^{-2}$ ).

*S.1.2.7 R<sub>st</sub>: Stomatal Resistance*

The stomatal resistance is generated following a similar approach to Jarvis (1976), Zhang *et al.* (2002, 2003), Baldocchi *et al.* (1987), and ValMartin *et al.* (2014), and results from several terms describing its dependence on light ( $k_s(Q_p)$ ), water vapour pressure deficit ( $k_s(\delta e)$ ), temperature ( $k_{st}$ ), CO<sub>2</sub> concentration ( $k_{sca}$ ), the leaf area index ( $LAI$ ), and the ratio of the molecular diffusivities of water to the gas being deposited ( $\frac{D_{H_2O}}{D_{gas}}$ ),

$$R_{st} = \frac{R_{s,min}}{k_s(Q_p)k_s(\delta e)k_{st}k_{sca}LAI} \frac{D_{H_2O}}{D_{gas}} \quad (S.10)$$

The leaf area index depends on the type of vegetation, and is given in Table A6. The minimum stomatal resistance varies with vegetation type; the values used in GEM-MACHv2 are given in Table A7.

15 The ratio of the molecular diffusivity of water with respect to that of the gas is given by:

$$\frac{D_{H_2O}}{D_{gas}} = \sqrt{\frac{2.608}{\left(1 + \frac{28.9644}{M_{gas}}\right)}} \quad (S.11)$$

Where  $M_{gas}$  is the molecular mass of the depositing gas.

Table S7. Values of minimum stomatal resistance ( $sm^{-1}$ ). Values of 9999 indicate no contribution of stomatal resistance due to the given land-use type at the given season.

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	Midsummer	Autumn, pre-harvest	Late Autumn, post-frost, pre-snow	Winter; snow and sub-freezing	Transitional: spring, partially green
Evergreen needle-leaf forest	130	250	250	400	250
Evergreen broadleaf forest	130	250	250	400	250
Deciduous needle-leaf forest	70	9999	9999	9999	140
Deciduous broadleaf forest	70	9999	9999	9999	140
Mixed Forest	100	800	800	800	190
Grassland	120	9999	9999	9999	240
Crops, mixed farming	60	9999	9999	9999	120
Desert	9999	9999	9999	9999	9999
Tundra	150	9999	9999	9999	300
Dwarf trees, shrubs	70	9999	9999	9999	140
Wetland with plants	80	9999	9999	9999	160
Ice caps and glaciers	9999	9999	9999	9999	9999
Inland water	9999	9999	9999	9999	9999
Ocean	9999	9999	9999	9999	9999
Urban	9999	9999	9999	9999	9999

The formulae for each of the terms in the denominator of equation (S.10) follow.

*S.1.2.7.1  $k_s(Q_p)$ , Stomatal conductance correction for photon flux density ( $Q_p$ )*

The light dependence of stomatal resistance was provided by curve-fitting to the data of Jarvis (1976), and Ellsworth and Reich, 1993), and included a conversion the input to the formula to be the solar radiation in  $\text{W m}^{-2}$  (SRAD), resulting in the following formula:

$$k_s(\text{SRAD}) = 0.205935 \ln(\text{SRAD}) - 0.6052 \quad (\text{S.12})$$

We note here that the light dependence of stomatal resistance is also described in some references by  $G_{st}(\text{SRAD})$ , the response of the stomatal resistance to visible radiation, which may be related to (S.12) via equation (S.13):

$$G_{st}(\text{SRAD}) = \frac{k_s(\text{SRAD})R_{s,min}}{\text{LAI}} \quad (\text{S.13})$$

Using (S.13), the values of the effect of light on stomatal conductance was cross-compared for different references. The values derived using (S.12) for given vegetation types are similar to those derived using the formulae of Baldocchi *et al.* (1987), but are lower than those of the formulae of Zhang *et al.* (2002), for the same land use types. For some vegetation types, the variation in the values of  $k_s(\text{SRAD})$  between Baldocchi *et al.* (1987) and Zhang *et al.* (2002) may be as high as a factor of 1.66 (e.g. for Evergreen coniferous forests, with Baldocchi *et al.* (1987) being the higher values). These differences stem from different assumptions and lighting models being used between these and other references, and probably account for much of the factor of two differences between estimates of gas-phase deposition between these references.

*S.1.2.7.2  $k_s(\delta e)$ , Stomatal conductance correction for vapour pressure deficit ( $\delta e$ )*

In GEM-MACHv2, this term is given by:

$$k_s(\delta e) = 1.0 - 0.03(1 - \text{HU}_r) 10^{\left[ \frac{0.7859 + 0.03477 T_{surf}}{1 + 0.00412 T_{surf}} \right]} \quad (\text{S.14})$$

Where  $T_{surf}$  is the surface temperature (the term in which  $T_{surf}$  appears gives the saturation vapour pressure of water in mb – a minimum value of 1mb is used here), and  $\text{HU}_r$  is the relative humidity on a 0 to 1 scale. We note that this term is also referenced as  $f_{vpd}$  in Meyers *et al.* (1998), and  $f(D)$  in Brook *et al.* (1999). Zhang *et al.* (2002) and Zhang *et al.* (2003) use vegetation-dependent values for this correction factor; here it was noted that the range of uncertainty across different references for the same vegetation types was high, so a single value was derived based on fitting to the available data.

*S.1.2.7.3  $k_{st}$ , Stomatal conductance correction for the temperature*

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The temperature dependence of the stomatal resistance in GEM-MACHv2 is given by equation (S.15):

$$k_{st} = \left[ \frac{(T_a(z) - T_{min})(T_{max} - T_a(z))}{(T_{opt} - T_{min})(T_{max} - T_{opt})} \right]^{0.6154} \quad (\text{S.15})$$

Where  $T_a(z)$  is the ambient air temperature at height ( $z$ ), and  $T_{max}$ ,  $T_{min}$ , and  $T_{opt}$  are vegetation dependent parameters; the GEM-MACHv2 values are given in Table S8 (based on Wesel (1989)). Meyers *et al.* (1998) and Zhang *et al.* (2002) use a value of  $\left( \frac{T_{max} - T_{opt}}{T_{opt} - T_{min}} \right)$  for the exponential in the formula, while Jarvis (1976) used  $\left( \frac{T_{max} - T_{opt}}{T_{max} - T_{min}} \right)$ . However, the Jarvis' exponential term use of  $T_{max}$  in the denominator is almost certainly a typo,

since its use would result in values of  $k_{st}$  greater than unity. Here, the value of 0.6154 (based on fitting of the available data, which again had a large variation between different references) was used.

Table S8. Temperature-dependent Stomatal Conductance parameters used in GEM-MACHv2. Values of 9999.0 indicate no air-surface exchange via this resistance pathway.

Land use category	$T_{max}$	$T_{min}$	$T_{opt}$
Evergreen needle-leaf forest	40.0	-5.0	15.0
Evergreen broadleaf forest	45.0	0.0	30.0
Deciduous needle-leaf forest	40.0	-5.0	15.0
Deciduous broadleaf forest	45.0	0.0	27.0
Mixed forest	42.0	-3.0	21.0
Grassland	45.0	5.0	27.0
Crops, mixed farming	45.0	5.0	25.0
Desert	9999.0	9999.0	9999.0
Tundra	9999.0	9999.0	9999.0
Dwarf trees, shrubs	43.0	0.0	21.5
Wet land with plants	45.0	5.0	25.0
Ice caps and glaciers	9999.0	9999.0	9999.0
Inland water	9999.0	9999.0	9999.0
Ocean	9999.0	9999.0	9999.0
Urban	45.0	0.0	22.0

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#### S.1.2.7.4 $k_{sca}$ , Stomatal conductance correction for the concentration of $CO_2$

The stomatal resistance correction for the presence of  $CO_2$  in GEM-MACHv2 was based on curve-fitting and conversion of units to solar radiation (SRAD) to data presented in Jarvis (1976), to derive a continuous function of the radiation and  $CO_2$  concentration data presented there:

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$$k_{sca} = \begin{cases} 1.0, [CO_2] \leq 100 \\ 1 - \{7.352 \times 10^{-4} \ln[\ln(S_{rad})] - 8.748 \times 10^{-4}\} [CO_2], 100 < [CO_2] < 1000 \\ 0.0, [CO_2] \geq 1000 \end{cases} \quad (S.16)$$

Where  $S_{rad}$  is the incoming solar radiation in  $Wm^{-2}$ . Jarvis original experiments with Sitka spruce and Douglas fir, suffered from an insufficient range of variation in the ambient  $CO_2$  concentration to be able to determine the values of the numerical constants for the coefficients for the  $CO_2$  concentration; consequently they were set to zero and the  $CO_2$  effect was thereafter neglected in that reference. However, Jarvis also presented laboratory results with varying  $CO_2$  concentrations, which suggested the impact of changes in  $CO_2$  could be large (Jarvis 1976, Figure 15). We note however, that the solar radiation dependence in (S.16), resulting from curve-fitting to Jarvis (1976), may result in some inconsistencies in the accounting for the impact of solar radiation, which also appears in (S.12). Note that  $k_{sca}$  is linked to photosynthesis, and hence depends on both  $CO_2$  and  $S_{rad}$ .

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### S.1.3 Aerodynamic Resistance, $R_a$

The aerodynamic and quasi-laminar sublayer resistances are relatively minor contributions to the overall deposition velocity compared to the surface resistance. The aerodynamic resistance is calculated using a variation on the approach of Voldner *et al.* (1986):

$$R_a = \frac{\ln\left(\frac{Z_H+z_0}{z_0}\right) - \psi_c}{ku^*} \quad (\text{S.17})$$

The values of the parameter  $\psi_c$  is given by the following formulae, where L is the Monin-Obukhov length,  $u^*$  is the friction velocity,  $z_0$  is the local (land-use dependent) roughness length, and  $Z_H$  is a reference height (10m):

$$\psi_c = \begin{cases} -5 \left( \frac{Z_H - z_0}{L} \right), & \frac{Z_H}{L} > 0.01 \\ e \left[ 0.598 + 0.39 \ln\left(-\frac{Z_H}{L}\right) - 0.18 \ln\left(-\frac{Z_H}{L}\right) \right] & \frac{Z_H}{L} < -0.01 \\ -e \left[ 0.598 + 0.39 \ln\left(-\frac{z_0}{L}\right) - 0.18 \ln\left(-\frac{z_0}{L}\right) \right] & \\ 0, & -0.01 \leq \frac{Z_H}{L} \leq 0.01 \end{cases} \quad (\text{S.18})$$

### S.1.4 Quasi-laminar sublayer resistance, $R_b$

The quasi-laminar sublayer resistance is given by (Hicks *et al.*, 1987):

$$R_b = \frac{2 \left( \frac{Sc_{gas}}{Pr} \right)^{2/3}}{ku^*} \quad (\text{S.19})$$

Where the  $Pr$  is the Prandtl number for air (0.72),  $k$  is the von Karman constant (0.4), and  $u^*$  is the friction velocity.  $Sc_{gas}$  is the Schmidt number for the gas, and is given by:

$$Sc_{gas} = 0.84 \frac{D_{H_2O}}{D_{gas}} \quad (\text{S.20})$$

The ratio of the molecular diffusivity of water to the gas is given in equation (S.11).

## S.2 Snowpack Sampling Methods

### S.2.1 Environment and Climate Change Canada oil sands snowpack sampling

#### S.2.1.1 Snowpack sampling

To assess winter-time atmospheric deposition of acidifying emissions to the oil sands region, snowpack samples were collected at varying distances from the major oil sands development area in early spring 2014 (n=130), as well as at 9-12 sites in the Peace-Athabasca River Delta (PAD) located ~200 km north of the major oil sands developments (See Figure 9(a)). Based on historical snow accumulation data for the Fort McMurray region (Environment-Canada. National Climate Data and Information Archive), the onset of permanent freezing began on November 6<sup>th</sup> of 2013, and all samples were collected within an 8 day period ending March 6<sup>th</sup>, to ensure maximum snowpack depth and minimize snowpack alterations over the course of sampling. Sampling sites were accessed by helicopter, and snow samples were collected at 50-100 m upwind of landing sites, to reduce potential contamination by helicopter exhaust. Stainless steel tools used snow collection

were acid-washed prior to use in the field and a standard two-person protocol was used to minimize potential contamination. Snow pits were dug to the bottom of the snowpack using a stainless steel shovel and 10 cm diameter custom-made stainless steel corers and stainless steel spatulas were used for snow collection, which ensured an even sampling of the complete snowpack profile. Snow sampling equipment was cleaned with snow at each site prior to collection. Snow for water chemistry and multi-element analyses was collected into 13 L pre-cleaned high density polypropylene pails. The weight and depth of ~10 cores was recorded at each site for further determination of snow water equivalents (SWE). After collection, snow was kept frozen until processing at the Canada Centre for Inland Waters (CCIW), in Burlington, Ontario, Canada. As part of QA/QC protocol, field blanks and duplicate (5% of sites) and triplicate samples (1% sites) were also collected at random sites.

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### *S.2.1.2 Water Chemistry analysis*

Snow was analyzed for water chemistry parameters, including pH, major cations, anions, and sulphate, and 45 elements including crustal elements, following standard procedures at the National Laboratory for Environmental Testing (NLET) in Burlington, Ontario, Canada. NLET is a certified member of the Canadian Association for Environmental Analytical Laboratories (CAEAL) and undergoes regular external reviews to maintain this accreditation.

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### *S.2.1.3 Snow-Water Equivalent and Loadings*

Average SWE were determined at each site and used to calculate loadings as described previously (Kelly *et al.* (2009), Kelly *et al.* (2010), Kirk *et al.* (2014), Manzano *et al.* (2016)). Briefly, equations (1), (2) and (3) were used to calculate SWE and Aerial Water Volume (AWV), which was used to obtain sulphate, nitrate, ammonium and base cations loadings, depending on the parameter used in equation (3):

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$$SWE \left( \frac{kg}{m^2} \right) = \frac{\text{snowpack weight (kg)}}{\pi[\text{corer radius (m)}]^2} \quad (1)$$

$$AWV \left( \frac{L}{m^2} \right) = \frac{SWE \left( \frac{kg}{m^2} \right)}{\rho_{\text{water}} \left( \frac{kg}{m^3} \right) \times \frac{1}{10^3} \left( \frac{m^3}{L} \right)} \quad (2)$$

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$$\sum \text{Ion loading} \left( \frac{\mu g}{m^2} \right) = AWV \left( \frac{L}{m^2} \right) \times \sum \text{Ion concentration} \left( \frac{\mu g}{L} \right) \quad (3)$$

## **S.2.2 Saskatchewan Environment Snow Sampling**

### *S.2.2.1 Sampling Design*

Snowpack surveys were conducted by Saskatchewan Ministry of Environment at 18 sites during Feb 16<sup>th</sup> - 22<sup>nd</sup> (n=13) and Apr 1<sup>st</sup> - 2<sup>nd</sup> (n=5), of 2014. Snow cores were collected at the centre of frozen lakes to minimize the influence of trees and topography on deposition and chemistry. Distances from the approximate centre of emissions in the Athabasca Oil Sands

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operations ranged from 106-291 km. Site selection in 2014 was based on criteria used to select lakes for a sediment coring study, described by Laird *et al.*, (2017).

#### *Sample collection*

5 Sampling equipment was cleaned with snow at each site prior to collection. Multiples (10-20) of intact snow cores were collected using an acrylic 7.62 cm diameter tube and a stainless steel spatula and composited into Teflon™ bags. SWE and snowpack loadings were determined as described for the ECCC snowpack samples, above. Samples were delivered frozen to the Biogeochemistry Analytical Laboratory at the University of Alberta, Edmonton.

#### *S.2.2.2 Water Chemistry analysis*

10 Samples were melted in a temperature controlled clean room and stirred prior to filtration (0.7 µm). Total and dissolved base cations were measured by ICP-MS. Other ions (ammonium, nitrate, sulphate, chloride), dissolved organic carbon, conductivity, pH, and Gran alkalinity were measured according to standard methods. Acceptance criterion of ±15% was applied to analytical charge balance.

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