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Alkaline dust deposition to foliage surfaces likely enhances the dry deposition velocity of SO_2: An investigation in the Alberta Oil-Sands Region using the GEM-MACH air-quality model

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S1.0 Appendix A: Theoretical Development and Description of the Carbonate Adjustment Module CALCCO3

Table S1: Chemical species in gas, aqueous and solid phases and their thermodynamic properties assumed in CALCCO3 (Fountoukis & Nenes 2007; Meng et al., 1995).

Species	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	C_p° (J mol^{-1} K^{-1})
$NH_3(aq)$	-26.500	-80.290	79.900
$NH_4^+(aq)$	-79.310	-132.510	79.900
$H^+(aq)$	0.000	0.000	0.000
$OH^-(aq)$	-157.244	-229.994	-148.500
$HSO_4^-(aq)$	-755.910	-887.340	-84.000
$SO_4^{2-}(aq)$	-744.530	-909.270	-293.000
$CO_2(g)$	-394.359	-393.509	37.11
$CO_2(aq)$	-385.980	-413.80	277.64
$Na_2CO_3(s)$	-1044.44	-1130.68	112.30
$K_2CO_3(s)$	-1063.5	-1151.02	114.43
$CaCO_3(s)$	-1128.79	-1206.92	81.88
$MgCO_3(s)$	-1012.1	-1095.8	75.52
$HCO_3^-(aq)$	-586.77	-691.99	88.43
$CO_3^{2-}(aq)$	-527.81	-677.14	-234.52
$Mg^{2+}(aq)$	-454.800	-466.850	-
$Ca^{2+}(aq)$	-553.580	-542.830	-
$K^+(aq)$	-283.270	-252.830	21.800
$Na^+(aq)$	-261.905	-240.120	46.400

The equilibrium constants for reversible reactions vary with temperature according to the van't Hoff equation:

$$K(T) = \exp\left(-\frac{\Delta G^\circ}{RT_0}\right)\exp\left[-\frac{\Delta H^\circ(T_0)}{RT_0}\left(\frac{T_0}{T}-1\right)-\frac{\Delta C_p^\circ}{R}\left(1+\ln\left(\frac{T_0}{T}\right)-\frac{T_0}{T}\right)\right].$$

where $K_0 = \exp\left(-\frac{\Delta G^\circ}{RT_0}\right)$, $H_0 = \frac{\Delta H^\circ(T_0)}{RT_0}$ and $C_{p_0} = \frac{\Delta C_p^\circ}{R}$, $T_0 = 298.15\ \text{K}$, $R = 8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}$

ΔG°, ΔH° and ΔC_p° represent the Gibbs free energy, enthalpy and specific heat a constant pressure respectively, due to reactions from the lefthand side to righthand side of the reversible reaction formulae (Table S2). They are derived from thermodynamic properties of the species involved in the reactions (Table S1). For example, for the equilibrium reaction $NH_4^+ \leftrightarrow H^+ + NH_3(aq)$:

$$\Delta G^\circ = \Delta_f G^\circ_{NH_3} + \Delta_f G^\circ_{H^+} - \Delta_f G^\circ_{NH_4^+} = -26.500 + 0.000 - (-79.310) = 52.810\ \text{kJ mol}^{-1},$$

$$\Delta H^\circ = \Delta_f H^\circ_{NH_3} + \Delta_f H^\circ_{H^+} - \Delta_f H^\circ_{NH_4^+} = -80.290 + 0.000 - (-132.510) = 52.220\ \text{kJ mol}^{-1} \text{ and}$$

$$\Delta C_p^\circ = \Delta C^\circ_{p_{NH_3}} + \Delta C^\circ_{p_{H^+}} - \Delta C^\circ_{p_{NH_4^+}} = -79.900 + 0.000 - (-79.900) = 0.0\ \text{J mol}^{-1}\ \text{K}^{-1}.$$

Table S2: Reversible chemical reactions and their equilibrium constants (K_0) at a standard temperature of 298.15 K, and parameters H_0 and C_{p_0} describing the temperature dependence considered in CALCCO3.

Equilibrium Reaction	Equilibrium Expression	K_0	H_0	C_{p_0}	Units
$H_2O \leftrightarrow H^+ + OH^-$	$K_w = [H^+][OH^-]$	1.01×10^{-14}	-22.52	26.92	$mol^2\ kg^{-2}$
$HSO_4^- \leftrightarrow H^+ + SO_4^{2-}$	$K_{HSO_4} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]}$	1.015×10^{-2}	8.85	25.14	$mol\ kg^{-1}$
$NH_4^+ \leftrightarrow H^+ + NH_3(aq)$	$K_{NH_4} = \frac{[NH_3]_{(aq)}[H^+]}{[NH_4^+]}$	5.599×10^{-10}	21.07	0.00	$mol\ kg^{-1}$
$CO_2(g) \leftrightarrow CO_2(aq)$	$K_{CO_2} = \frac{[CO_2(aq)]}{p_{CO_2}}$	3.404×10^{-2}	-8.1858	28.9307	$mol\ kg^{-1}\ atm^{-1}$
$CO_2(aq) + H_2O \leftrightarrow H^+ + HCO_3^-$	$K_{HCO_3} = \frac{[HCO_3^-][H^+]}{[CO_2(aq)]}$	4.299×10^{-7}	3.0821	-31.8139	$mol\ kg^{-1}$
$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$	$K_{CO_3} = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]}$	4.678×10^{-11}	5.9908	-38.8440	$mol\ kg^{-1}$
$CaCO_3(s) \leftrightarrow Ca^{2+} + CO_3^{2-}$	$K_{CaCO_3} = [Ca^{2+}][CO_3^{2-}]$	4.959×10^{-9}	-	-	$mol^2\ kg^{-2}$
$MgCO_3(s) \leftrightarrow Mg^{2+} + CO_3^{2-}$	$K_{MgCO_3} = [Mg^{2+}][CO_3^{2-}]$	6.812×10^{-6}	-	-	$mol^2\ kg^{-2}$
$K_2CO_3 \leftrightarrow 2K^+ + CO_3^{2-}$	$K_{K_2CO_3} = [K^+]^2[CO_3^{2-}]$	2.541×10^5	-12.4575	-36.7272	$mol^3\ kg^{-3}$
$Na_2CO_3 \leftrightarrow 2Na^+ + CO_3^{2-}$	$K_{Na_2CO_3} = [Na^+]^2[CO_3^{2-}]$	18.11	-10.7713	-30.5533	$mol^3\ kg^{-3}$

Model inputs to CALCCO3 are concentrations C (except water) in units of mol m^{-3} air and the liquid water content denoted L_w in units of kg m^{-3}, whereas equilibrium expressions in Table S2 require concentrations (X) to have units of mol kg^{-1} (i.e., molalities, where the solvent here is water). Thus, the inputs are converted as follows:

$$X\left(\frac{\mathrm{mol}}{\mathrm{kg}}\right) = \frac{C\left(\frac{\mathrm{mol}}{\mathrm{m}^3}\right)}{L_W\left(\frac{\mathrm{kg}}{\mathrm{m}^3}\right)}.$$

CALCCO3 solves the electroneutrality equation iteratively using the bisection method, where the bisected variable is $[H^+]_B$. All concentrations are in mol kg^{-1} water and partial pressures are in atm. Equilibrium constants follow the same units as the species in their expressions (see Table S2). The electroneutrality equation is

$$[H^+]_B + [NH_4^+] + 2[Ca^{2+}] + 2[Mg^{2+}] + [K^+] + [Na^+] = [OH^-] + [HSO_4^-] + 2[SO_4^{2-}] + [Cl^-] + [NO_3^-] + [HCO_3^-] + 2[CO_3^{2-}]. \quad \text{(S1)}$$

The initial aqueous speciation used as inputs for CALCCO3 are obtained from HETP, where

$$\mathrm{TS} = [SO_4^{2-}] + [HSO_4^-] \quad \text{(S2a)}$$

$$\mathrm{TA} = [NH_4^+] + [NH_3]_{(aq)} \quad \text{(S2b)}$$

$$\mathrm{TCl} = [Cl^-] \quad \text{(S2c)}$$

$$\mathrm{TN} = [NO_3^-], \quad \text{(S2d)}$$

and initially $[NH_3]_{(aq)} = 0$. HETP assigns part of base cations to protons being associated with strong acid and base anions, other than HCO_3^- and CO_3^{2-}, denoted here by a subscript i. Any remaining free (excess) base cations that are not assigned with an anion (i.e., T_{MgCO_3}, T_{CaCO_3}, $T_{K_2CO_3}$, $T_{Ca_2CO_3}$) are assumed to be matched by carbonate (CO_3^{2-}). These enter CALCCO3 initially as solid carbonates magnesium carbonate, calcium carbonate, potassium carbonate and sodium carbonate, represented below by T_{MgCO_3}, T_{CaCO_3}, $T_{K_2CO_3}$, $T_{Na_2CO_3}$ respectively. The total magnesium, total calcium, total potassium and total sodium are, respectively,

$$\mathrm{TMg} = [Mg^{2+}]_i + T_{MgCO_3} \quad \text{(S2e)}$$

$$\mathrm{TCa} = [Ca^{2+}]_i + T_{CaCO_3} \quad \text{(S2f)}$$

$$T_{\mathrm{K}} = [\mathrm{K}^+]_i + T_{\mathrm{K_2CO_3}} \tag{S2g}$$

$$T_{\mathrm{Na}} = [\mathrm{Na}^+]_i + T_{\mathrm{Na_2CO_3}} \tag{S2h}$$

The following expressions are used reduce the number of unknown variables in Eq. (S1). For hydroxide (OH^-), we use

$$[\mathrm{OH}^-] = \frac{\mathrm{K_w}}{[\mathrm{H}^+]} \tag{S3}$$

From Eq. (S2a), $\mathrm{TS} - [\mathrm{HSO_4^-}] = [\mathrm{SO_4^{2-}}]$, hence

$$K_{\mathrm{HSO_4}} = \frac{[\mathrm{H}^+][\mathrm{SO_4^{2-}}]}{[\mathrm{HSO_4^-}]} = \frac{[\mathrm{H}^+](\mathrm{TS} - [\mathrm{HSO_4^-}])}{[\mathrm{HSO_4^-}]}$$

which can be rearranged to

$$[\mathrm{HSO_4^-}] = \frac{\mathrm{TS}}{1+\frac{\mathrm{K_{HSO_4}}}{[\mathrm{H}^+]}} \tag{S4}$$

$$[\mathrm{SO_4^{2-}}] = \mathrm{TS} - [\mathrm{HSO_4^-}]. \tag{S5}$$

Similarly form equation (S2b), $\mathrm{TA} - [\mathrm{NH_4^+}] = [\mathrm{NH_3}]_{(\mathrm{aq})}$, hence

$K_{\mathrm{NH_4}} = \frac{[\mathrm{NH_3}]_{(\mathrm{aq})}[\mathrm{H}^+]}{[\mathrm{NH_4^+}]} = \frac{[\mathrm{H}^+](\mathrm{TA}-[\mathrm{NH_4^+}])}{[\mathrm{NH_4^+}]}$, which can be rearranged to

$$[\mathrm{NH_4^+}] = \frac{\mathrm{TA}}{1+\frac{\mathrm{K_{NH_4}}}{[\mathrm{H}^+]}}. \tag{S6}$$

$$[\mathrm{NH_3}]_{(\mathrm{aq})} = \mathrm{TA} - [\mathrm{NH_4^+}] \tag{S7}$$

Next, we define the total dissolved inorganic carbon (TC) as

$$\mathrm{TC} = [\mathrm{CO_2(aq)}] + [\mathrm{HCO_3^-}] + [\mathrm{CO_3^{2-}}]$$

where we assume initially that ${\mathrm{CO_2}}_{\mathrm{aq}}$ is in equilibrium with the gas-phase CO2 via dissolution or volatilization, so

$$K_{\mathrm{CO_2}} = \frac{[\mathrm{CO_2(aq)}]}{p_{CO_2}}$$

hence

$$[\mathrm{CO_2(aq)}] = K_{\mathrm{CO_2}} p_{CO_2}. \tag{S8}$$

And $[\mathrm{HCO_3^-}]$ and $[\mathrm{CO_3^{2-}}]$ follow

$$K_{\mathrm{HCO_3}} = \frac{[\mathrm{HCO_3^-}][\mathrm{H}^+]}{[\mathrm{CO_2(aq)}]}$$

hence

$$[\mathrm{HCO_3^-}] = \frac{K_{\mathrm{HCO_3}}[\mathrm{CO_2(aq)}]}{[\mathrm{H}^+]}, \tag{S9}$$

and

$$K_{\mathrm{CO_3}} = \frac{[\mathrm{CO_3^{2-}}][\mathrm{H}^+]}{[\mathrm{HCO_3^-}]}$$

hence

$$[\mathrm{CO_3^{2-}}] = \frac{K_{\mathrm{CO_3}}[\mathrm{HCO_3^-}]}{[\mathrm{H^+}]} = \frac{K_{\mathrm{CO_3}}K_{\mathrm{HCO_3}}[\mathrm{CO_2(aq)}]}{[\mathrm{H^+}]^2} \tag{S10}$$

By using Eq. (S9) and Eq. (S10), TC can be rewritten as a function of $[\mathrm{CO_2(aq)}]$ and $[\mathrm{H^+}]$:

$$\mathrm{TC} = [\mathrm{CO_2(aq)}]\left(1 + \frac{K_{\mathrm{HCO_3}}}{[\mathrm{H^+}]} + \frac{K_{\mathrm{CO_3}}K_{\mathrm{HCO_3}}}{[\mathrm{H^+}]^2}\right) \tag{S11}$$

By using a relation between TC and $[\mathrm{CO_2(aq)}]$ from Eq. (S11), Eq. (S9) can be rewritten to represent a relation between TC and $[\mathrm{HCO_3^-}]$

$$[\mathrm{HCO_3^-}] = \frac{\mathrm{TC}K_{\mathrm{HCO_3}}[\mathrm{H^+}]}{[\mathrm{H^+}]^2 + [\mathrm{H^+}]K_{\mathrm{HCO_3}} + K_{\mathrm{CO_3}}K_{\mathrm{HCO_3}}}. \tag{S12}$$

Similarly, by combining Eq. (S10) and Eq. (S11), we obtain

$$[\mathrm{CO_3^{2-}}] = \frac{\mathrm{TC}K_{\mathrm{CO_3}}K_{\mathrm{HCO_3}}}{[\mathrm{H^+}]^2 + [\mathrm{H^+}]K_{\mathrm{HCO_3}} + K_{\mathrm{CO_3}}K_{\mathrm{HCO_3}}}. \tag{S13}$$

Solubility-limited, stepwise solid carbonate dissolution is then assumed, and applied according to

$$[\mathrm{Ca^{2+}}]_d = \min\left(T_{\mathrm{CaCO_3}}, \frac{K_{\mathrm{CaCO_3}}}{[\mathrm{CO_3^{2-}}]}\right) \tag{S14}$$

where $[\mathrm{CO_3^{2-}}]$ is calculated from Eq. (S13), and $\mathrm{TC} = \mathrm{TC} + [\mathrm{Ca^{2+}}]_d$ since additional $[\mathrm{CO_3^{2-}}]$ has been added through dissolution. Following this, $[\mathrm{CO_3^{2-}}]$ is then recalculated from Eq. (S13) and $MgCO_3$ dissolution is performed according to

$$[\mathrm{Mg^{2+}}]_d = \min\left(T_{\mathrm{MgCO_3}}, \frac{K_{\mathrm{MgCO_3}}}{[\mathrm{CO_3^{2-}}]}\right). \tag{S15}$$

Once again, TC is updated as $\mathrm{TC} = \mathrm{TC} + [\mathrm{Mg^{2+}}]_d$. Thereafter, K_2CO_3 and Na_2CO_3 dissolution is performed as

$$[\mathrm{K^+}]_d = \min\left(T_{\mathrm{K_2CO_3}}, 2\left[\frac{K_{\mathrm{K_2CO_3}}}{4}\right]^{1/3}\right) \tag{S16}$$

and

$$[\mathrm{Na^+}]_d = \min\left(T_{\mathrm{Na_2CO_3}}, 2\left[\frac{K_{\mathrm{Na_2CO_3}}}{4}\right]^{1/3}\right) \tag{S17}$$

and TC is updated to $\mathrm{TC} = \mathrm{TC} + [\mathrm{K^+}]_d + [\mathrm{Na^+}]_d$. Using the final updated TC, a final $[\mathrm{CO_3^{2-}}]$ is recalculated from Eq. (S13). Subsequently, a final $[\mathrm{HCO_3^-}]$ is calculated from Eq. (S12). Finally, base cations are calculated from

$$[\mathrm{Ca^{2+}}] = [\mathrm{Ca^{2+}}]_i + [\mathrm{Ca^{2+}}]_d \tag{S18}$$

$$[\mathrm{Mg^{2+}}] = [\mathrm{Mg^{2+}}]_i + [\mathrm{Mg^{2+}}]_d \tag{S19}$$

$$[\mathrm{K^+}] = [\mathrm{K^+}]_i + 2[\mathrm{K^+}]_d \tag{S20}$$

$$[\mathrm{Na^+}] = [\mathrm{Na^+}]_i + 2[\mathrm{Na^+}]_d. \tag{S21}$$

Thus, (S2c), (S2d), (S3), (S4), (S5), (S6), (S12), (S13), (S18), (S19), (S20) and (S21) fully define all ion speciation required to solve (S1) as an electroneutrality error δ_E

$$\delta_E = [\mathrm{H^+}]_\mathrm{B} + [\mathrm{NH_4^+}] + 2[\mathrm{Ca^+}] + 2[\mathrm{Mg^{2+}}] + [\mathrm{K^+}] + [\mathrm{Na^+}] - ([\mathrm{OH^-}] + [\mathrm{HSO_4^-}] + 2[\mathrm{SO_4^{2-}}] + [\mathrm{Cl^-}] + [\mathrm{NO_3^-}] + [\mathrm{HCO_3^-}] + 2[\mathrm{CO_3^{2-}}]). \tag{S23}$$

Once $\delta_E < 1 \times 10^{-12}$ convergence is achieved, and pH is derived from a final $[\mathrm{H^+}]_\mathrm{B}$ calculated from Eq. (S23).

Appendix B: Additional figures and tables

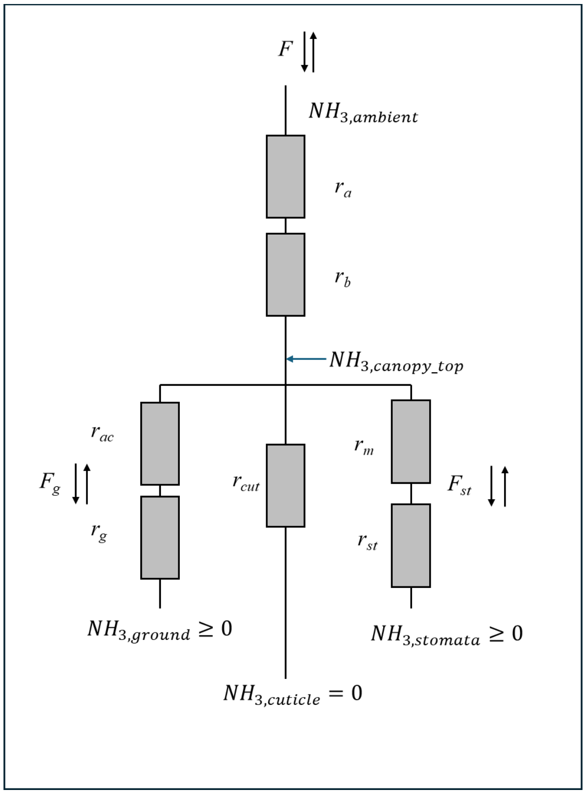


Figure S1: NH_3 bidirectional flux resistances (after Zhang et al., 2010).

145 Note that the deposition flux via the cuticle pathway depends on the concentration of NH_3 at the top of the canopy; this is referred to as $\boldsymbol{C}_{\mathbf{NH_3}}^{\boldsymbol{canopy\_top}}$ in the text.

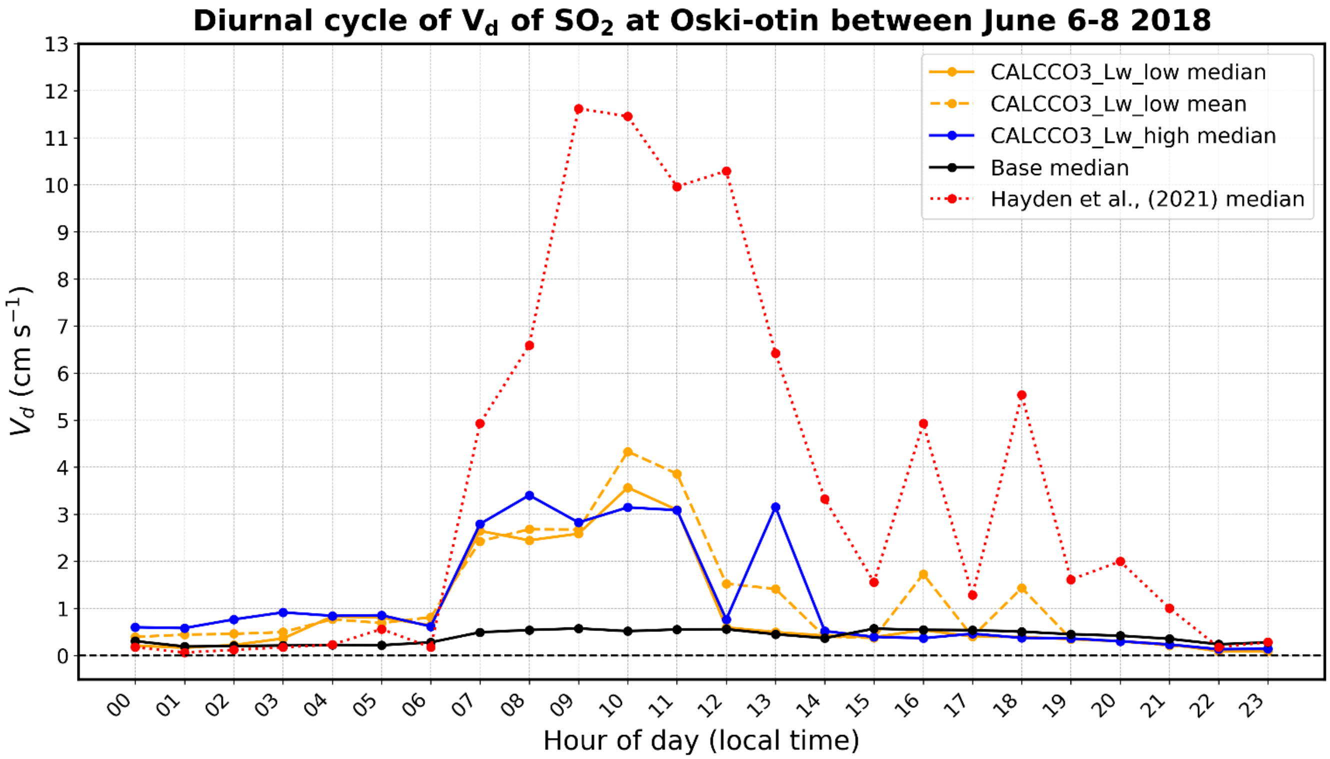


Figure S2: The diurnal cycle (in local time) of the deposition velocity of SO_2 (cm s^{-1}) calculated over June 6 to June 8 at Oski-otin.

150 The dashed red line shows the median $V_{d_{SO_2}}$ inferred from stationary tower measurements as reported in the supplemental material of Hayden et al., (2021). The remaining lines are various GEM-MACH model predictions – the orange line is CALCCO3_Lw_low (the solid line is the median and the dashed line is the mean); the solid blue line is the median of CALCCO3_Lw_high, and the solid black line is the median of the Base Case.

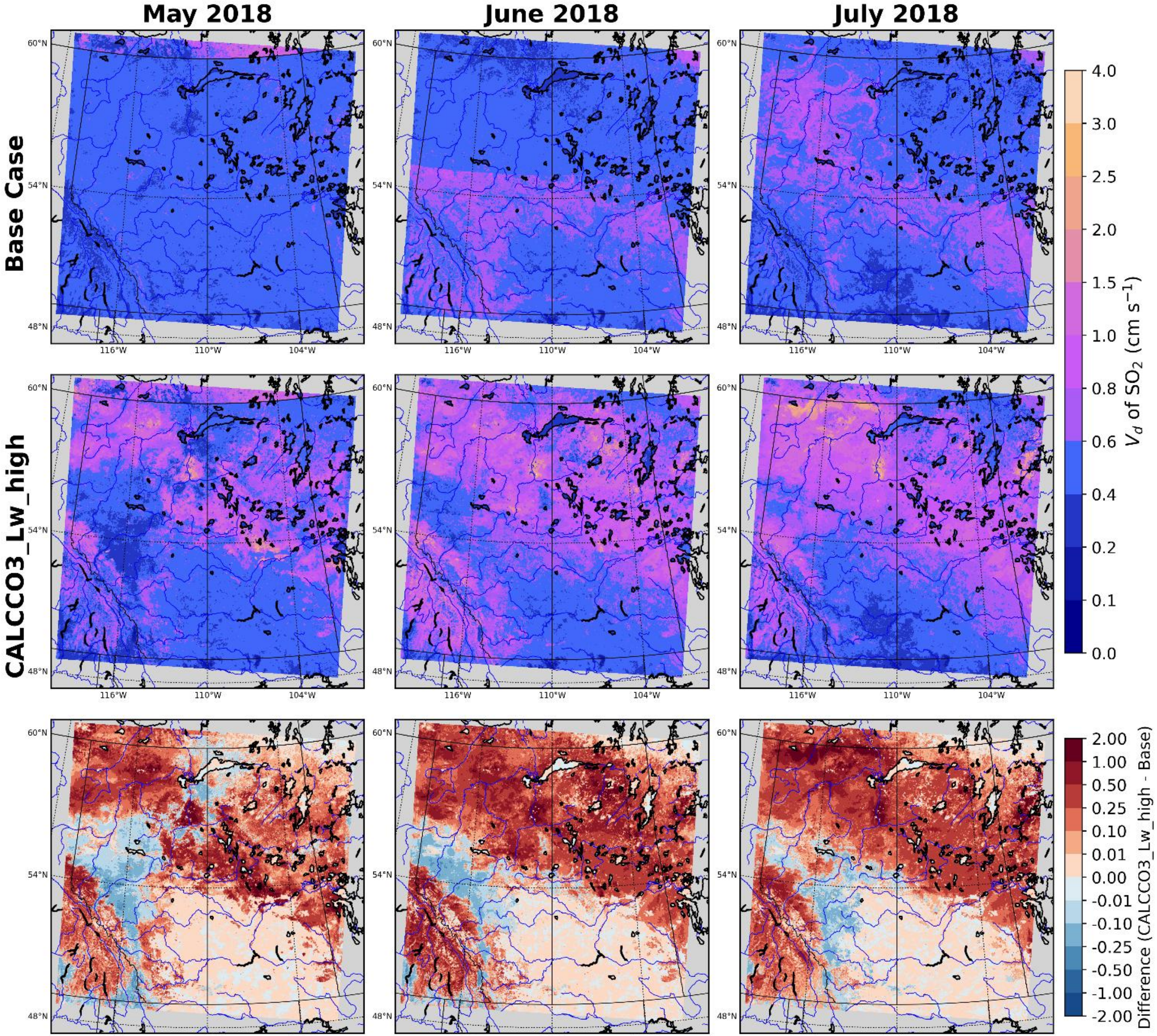
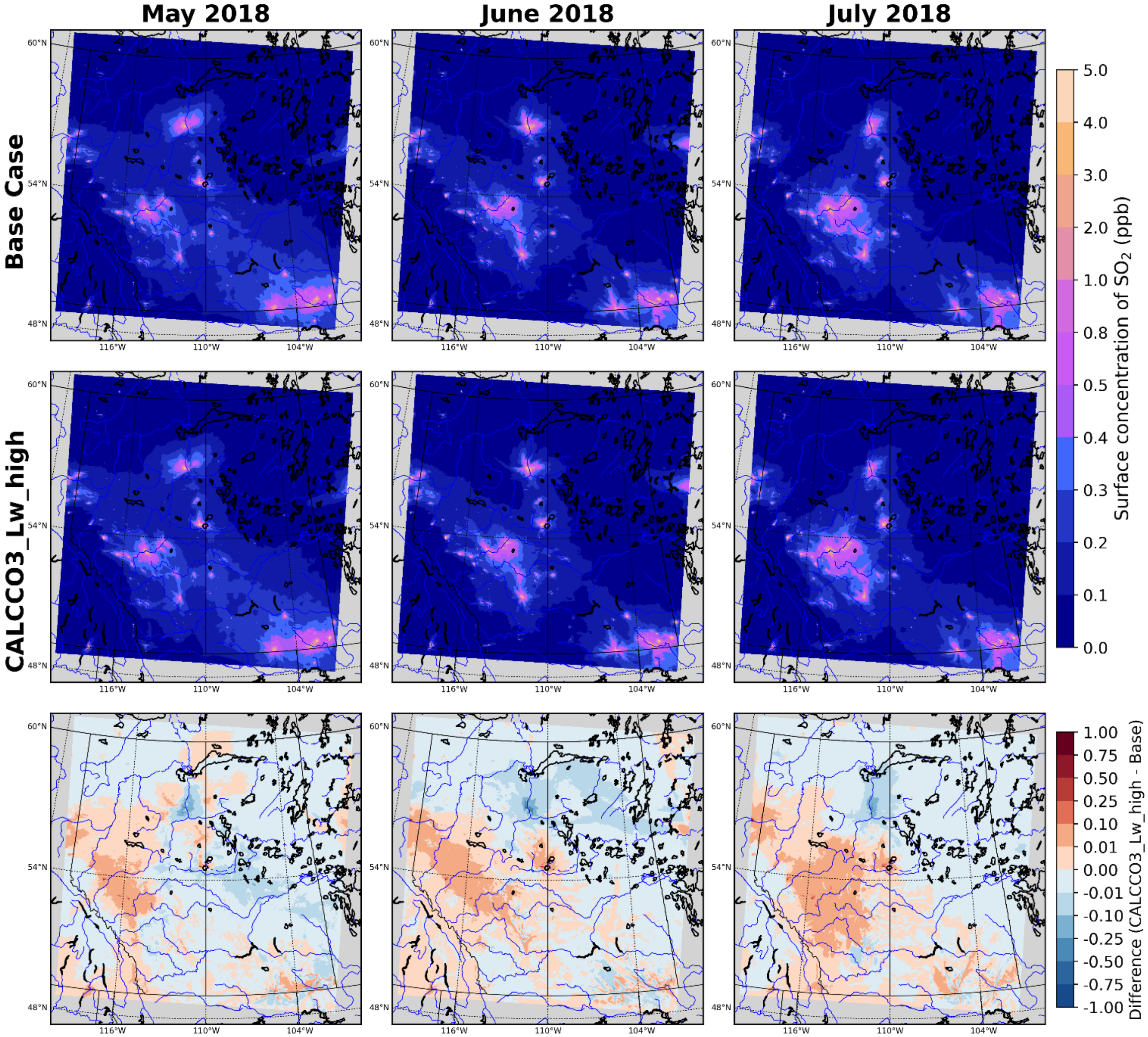


Figure S1: Identical to Fig. 8, except now the final row shows the difference (cm s^{-1}) between CALCCO3_Lw_high and the Base Case.

The difference plots have units of cm s^{-1}.



160 **Figure S2: Identical to Fig. 13, except now the final row shows the difference (ppb) between CALCCO3_Lw_high and the Base Case.**

The difference plots have units of ppb.

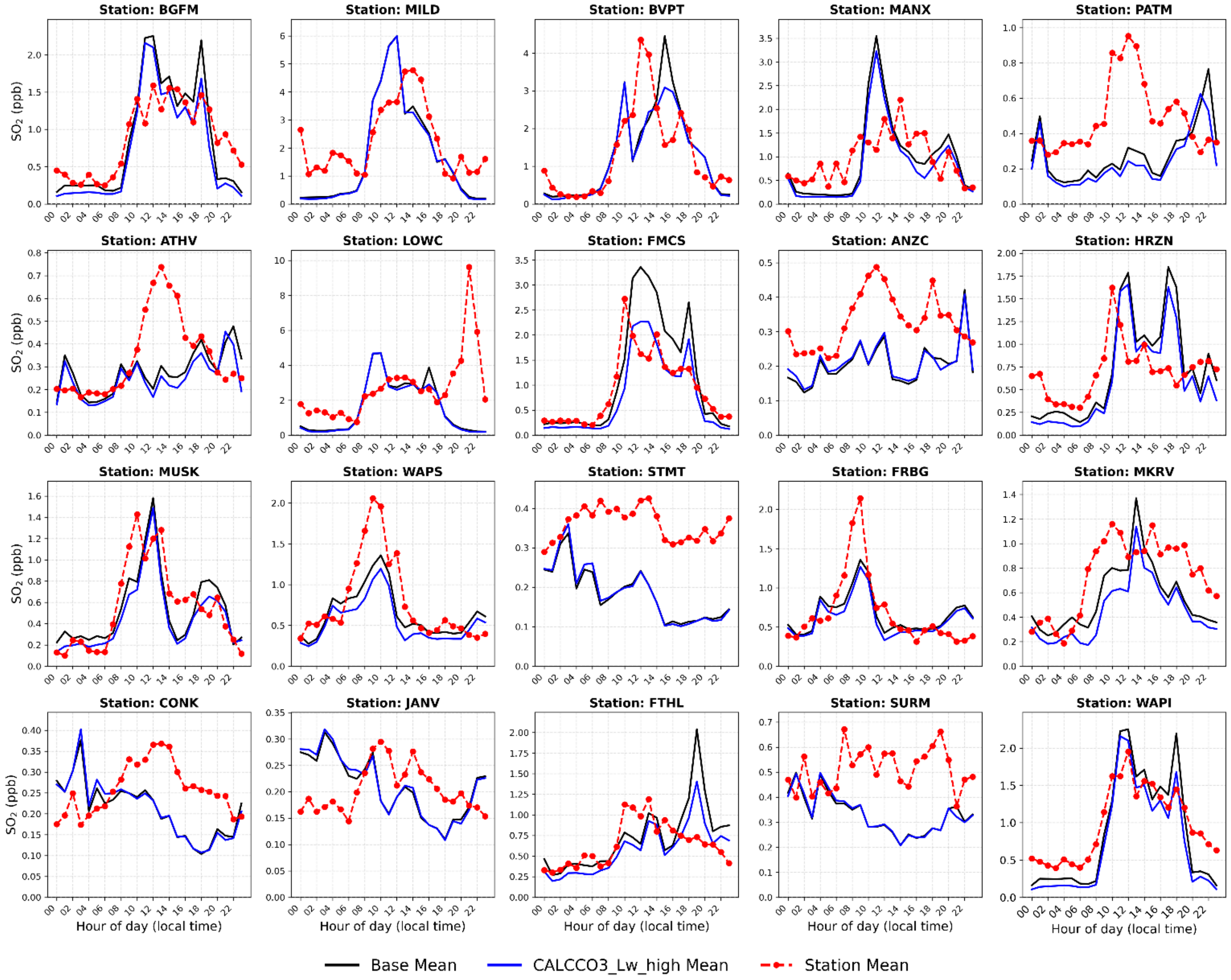


Figure S3: Identical to Fig. 11 except now for May 2018. Also shown in each plot is the surface SO$_2$ concentration predicted by CALCCO3_Lw_low (orange line).

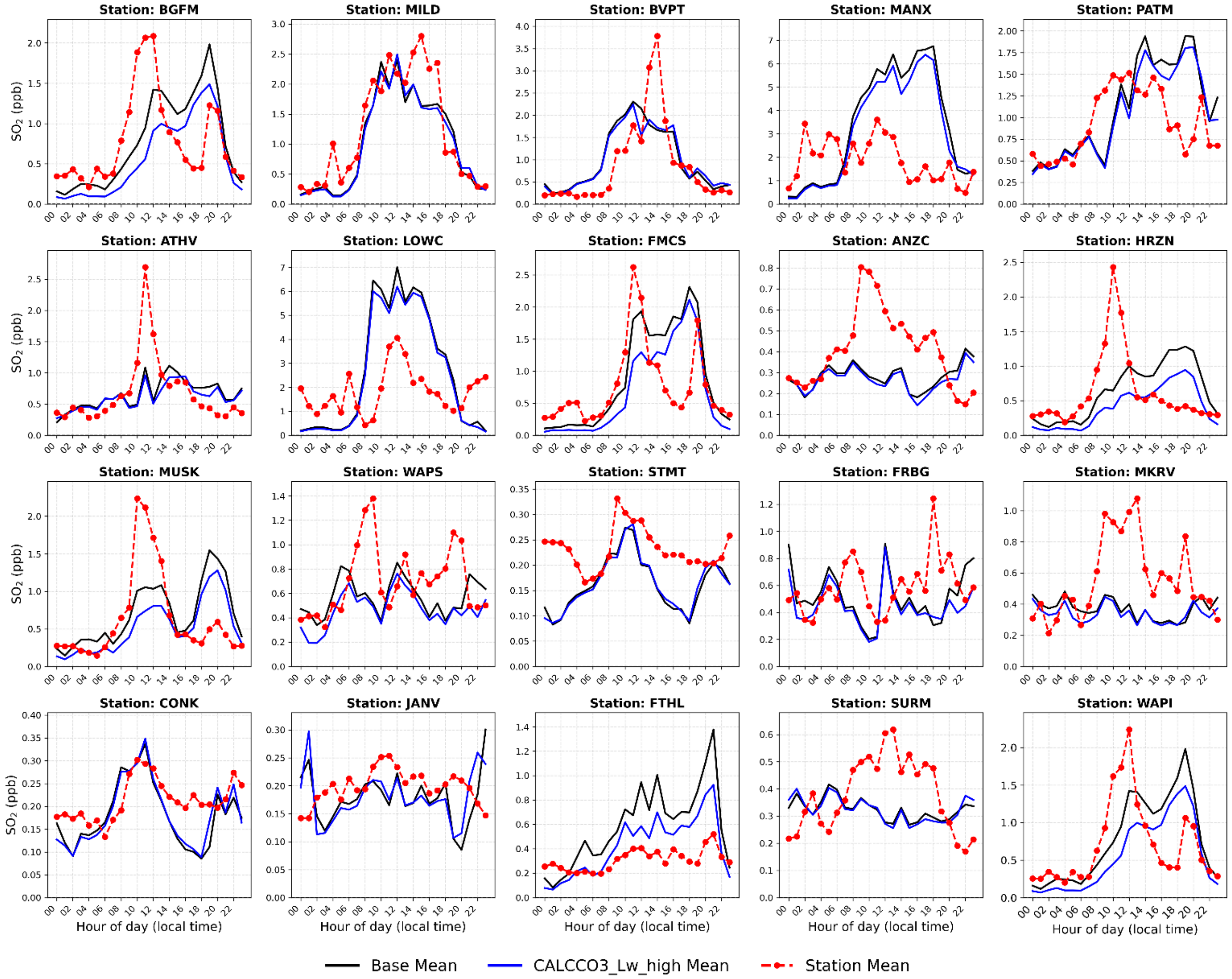


Figure S4: Identical to Fig. 11 except now for July 2018. Also shown in each plot is the surface SO_2 concentration predicted by CALCCO3_Lw_low (orange line).

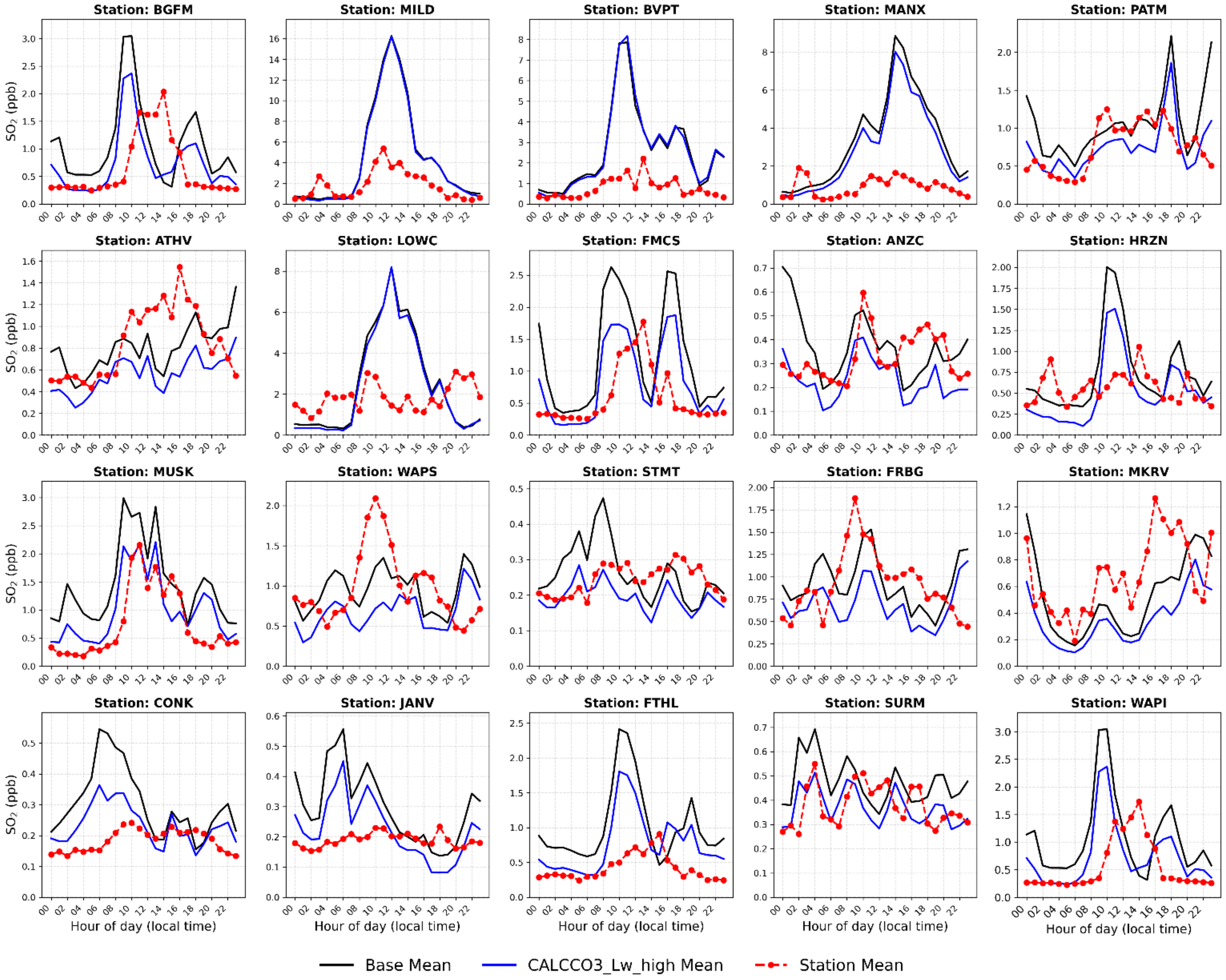


Figure S5: Identical to Fig. 11 except now for August 2018.

Table S3: Formulae used to perform statistical evaluaton of the modelled SO_2 surface concentrations compared to observations.

Variable (Abbreviation)	Formulae	Definition	Ideal score
n	-	Number of hourly model-observation pairs used in the evaluation	-
o_i	-	Observed value at time i	-
m_i	-	Modelled value at time i	-
$\bar{o}$	$\bar{o} = \frac{1}{n}\sum_{i=1}^{n} o_i$	Average (mean) of the observed values.	-
$\bar{m}$	$\bar{m} = \frac{1}{n}\sum_{i=1}^{n} m_i$	Average (mean) of of the modelled values.	$\bar{m} = \bar{o}$
σ_O	$\sigma_o = \left(\frac{\sum_{i=1}^{n}(o_i - \bar{o})}{n-1}\right)^{\frac{1}{2}}$	Sample standard deviation of the observed values.	-
σ_m	$\sigma_m = \left(\frac{\sum_{i=1}^{n}(m_i - \bar{m})}{n-1}\right)^{\frac{1}{2}}$	Sample standard deviation of the modelled values.	$\sigma_m = \sigma_o$
NSD	$\mathrm{NSD} = \frac{\sigma_m}{\sigma_O}$	Normalized standard deviation (NSD). The standard deviation of the model normalized by the standard deviation of the observations.	NSD = 1.0
r	$r = \frac{1}{n-1}\sum_{i=1}^{n}\left[\left(\frac{m_i - \bar{m}}{\sigma_m}\right)\left(\frac{o_i - \bar{o}}{\sigma_O}\right)\right]$	The Pearson correlation coefficient which describes the degree of linear dependence between the modelled and observed values.	$r = 1.0$
NMB	$\mathrm{NMB} = \frac{\sum_{i=1}^{n}(m_i - o_i)}{\sum_{i=1}^{n} o_i} \times 100\ \%$	Normalized mean bias (NMB), representing the average of the difference (model minus observation) for all data pairs normalized by the average of the observations. Negative (positive) values indicate the model value is lower (greater) than the observations. Expressed as a percentage.	NMB = 0.0 %
RMSE	$\mathrm{RMSE} = \left[\frac{\sum_{i=1}^{n}(m_i - o_i)}{n}\right]^{\frac{1}{2}}$	Root-mean square error (RMSE), representing the standard deviation of differences between the model and observations.	RMSE = 0.0
NRMSE	$\mathrm{NRMSE} = \frac{\mathrm{RMSE}}{\bar{o}} \times 100\ \%$	Normalized root-mean square error (NRMSE). The RMSE normalized by the average of the observations. Expressed as a percentage.	NRMSE = 0.0 %
MAE	$\mathrm{MAE} = \frac{1}{n}\sum_{i=1}^{n}\lvert m_i - o_i\rvert$	Mean absolute error (MAE).	MAE = 0.0 %
NMAE	$\mathrm{NMAE} = \frac{1}{n}\sum_{i=1}^{n}\frac{\lvert m_i - o_i\rvert}{o_i}$	Normalized mean absolute error (NMAE).	NMAE = 0.0 %
IOA	$\mathrm{IOA} = 1.0 - \frac{\sum_{i=1}^{n}\lvert m_i - o_i\rvert}{2\sum_{i=1}^{n}\lvert o_i - \bar{o}\rvert}$	Index of agreement (IOA).	IOA = 1.0