2014

A corrected formulation of the Multilayer Model (MLM) for inferring gaseous dry deposition to vegetated surfaces

Rick Saylor
NOAA Air Resources Laboratory, Atmospheric Turbulence and Diffusion Division

Glenn Wolf
University of Maryland Baltimore County, NASA Goddard Space Flight Center, Atmospheric Chemistry and Dynamics Laboratory

Tilden Meyers
NOAA Air Resources Laboratory, Atmospheric Turbulence and Diffusion Division

Bruce Hicks
Metcorps

Atmospheric Environment 92 (2014) 141–145

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Technical note

A corrected formulation of the Multilayer Model (MLM) for inferring gaseous dry deposition to vegetated surfaces

Rick D. Saylor [a,*], Glenn M. Wolfe [b,c], Tilden P. Meyers [a], Bruce B. Hicks [d]

[a] NOAA Air Resources Laboratory, Atmospheric Turbulence and Diffusion Division, 456 S. Illinois Ave., Oak Ridge, TN 37830, USA
[b] NASA Goddard Space Flight Center, Atmospheric Chemistry and Dynamics Laboratory, Greenbelt, MD 20771, USA
[c] Joint Center for Earth Systems Technology, University of Maryland Baltimore County, Baltimore, MD 21250, USA
[d] Metcorps, Norris, TN 37828, USA

HIGHLIGHTS

- MLM contains a non-physical formulation of the leaf-level boundary layer resistance.
- A revised, physically consistent formulation of MLM is proposed.
- Deposition estimates of SO_2 and O_3 are only slightly reduced with the revised MLM.
- HNO_3 deposition is reduced by as much as 38% during midday.
- A reevaluation of estimated deposition of total nitrogen in the U.S. is recommended.

ARTICLE INFO

Article history:
Received 4 November 2013
Received in revised form
24 March 2014
Accepted 26 March 2014
Available online 1 April 2014

Keywords:
Dry deposition
Nitric acid
Sulfur dioxide
Ozone
Multi-layer model
Canopy
CASTNet

ABSTRACT

The Multilayer Model (MLM) has been used for many years to infer dry deposition fluxes from measured trace species concentrations and standard meteorological measurements for national networks in the U.S., including the U.S. Environmental Protection Agency's Clean Air Status and Trends Network (CASTNet). MLM utilizes a resistance analogy to calculate deposition velocities appropriate for whole vegetative canopies, while employing a multilayer integration to account for vertically varying meteorology, canopy morphology and radiative transfer within the canopy. However, the MLM formulation, as it was originally presented and as it has been subsequently employed, contains a non-physical representation related to the leaf-level quasi-laminar boundary layer resistance that affects the calculation of the total canopy resistance. In this note, the non-physical representation of the canopy resistance as originally formulated in MLM is discussed and a revised, physically consistent, formulation is suggested as a replacement. The revised canopy resistance formulation reduces estimates of HNO_3 deposition velocities by as much as 38% during mid-day as compared to values generated by the original formulation. Inferred deposition velocities for SO_2 and O_3 are not significantly altered by the change in formulation (<3%). Inferred deposition loadings of oxidized and total nitrogen from CASTNet data may be reduced by 10–20% and 5–10%, respectively, for the Eastern U. S. when employing the revised formulation of MLM as compared to the original formulation.

1. Introduction

The Multilayer Model (MLM; Meyers et al., 1998; Cooter and Schwede, 2000) has been used for many years to infer dry deposition fluxes from measured trace species concentrations and selected meteorological measurements for U.S. national networks (Clarke et al., 1997; Finkelstein et al., 2000; Schwede et al., 2011; USEPA, 2013). MLM has been evaluated (Meyers et al., 1998; Finkelstein et al., 2000; Sickles and Shadwick, 2002) as well as modified (Wu et al., 2003a,b) but the version as described by Cooter and Schwede (2000) is currently employed to infer dry deposition fluxes from measurements made in the CASTNET network (Schwede et al., 2001; Baumgardner et al., 2002; Sickles and Shadwick, 2007; Bowker et al., 2011; USEPA, 2013). Conceptual components of the original model have also been used to simulate the bi-directional exchange of ammonia between vegetation and the atmosphere (Wu et al., 2009).

* Corresponding author.
E-mail address: Rick.Saylor@noaa.gov (R.D. Saylor).

http://dx.doi.org/10.1016/j.atmosenv.2014.03.056
1352-2310/

Nomenclature

h_c	height of the canopy (m)
$LAI(z)$	leaf area index (single-sided) of the canopy at height z (m^2 m^{-2})
R_a	aerodynamic resistance (s m^{-1})
$r_{a,soil}$	subcanopy aerodynamic resistance for deposition to soil (s m^{-1})
$r_b(z)$	leaf boundary layer resistance at height z (s m^{-1})
$r_c(z)$	total resistance of canopy elements at height z (s m^{-1})
r_{cut}	leaf cuticular resistance (s m^{-1})
$r_l(z)$	total leaf surface resistance at height z (s m^{-1})
r_{meso}	leaf mesophyll resistance (s m^{-1})
$r_s(z)$	leaf stomatal resistance at height z (s m^{-1})
r_{soil}	soil uptake resistance (s m^{-1})
$S(z)$	general local sink term for trace species deposition to the canopy (s^{-1})
$S^{orig}(z)$	local sink term of the original MLM formulation for trace species deposition to the canopy (s^{-1})
$S^{rev}(z)$	local sink term of the revised MLM formulation for trace species deposition to the canopy (s^{-1})
V_d	whole canopy deposition velocity (m s^{-1})
z	vertical coordinate from ground surface upward (m)

MLM utilizes the ubiquitous Ohm's Law (i.e., resistance) analogy to calculate deposition velocities appropriate for whole vegetative canopies, while employing a multilayer integration within the canopy to account for vertically varying meteorology, canopy morphology and radiative transfer. However, close inspection of the MLM formulation, as it is presented by Meyers et al. (1998) and as it is typically employed (Finkelstein et al., 2000; Finkelstein, 2001; Baumgardner et al., 2002; Sickles and Shadwick, 2007; Schwede et al., 2011), reveals a representation of the leaf-level quasi-laminar boundary layer resistance, r_b, that is non-physical. In this technical note, we explore the impact of this non-physical formulation and suggest a revised formulation that is more consistent with the accepted conceptual model of multilayer resistance-based dry deposition.

2. Multilayer model description and revised formulation

Within the MLM, hourly estimates of deposition velocities (V_d) for each deposited trace species are calculated from

$$V_d = \left[R_a + \left(\int_0^{h_c} S(z)\mathrm{d}z + \frac{1}{r_{soil} + r_{a,soil}} \right)^{-1} \right]^{-1} \tag{1}$$

and

$$S(z) = S^{orig}(z) = \frac{LAI(z)}{r_c(z)} \tag{2}$$

with

$$\frac{1}{r_c(z)} = \frac{1}{r_b(z) + r_s(z) + r_{meso}} + \frac{2}{r_b(z) + r_{cut}}. \tag{3}$$

Parameterizations for the various resistances in Eqs. (1)–(3) are as specified in Meyers et al. (1998) or Cooter and Schwede (2000).

In this formulation, the aerodynamic resistance, R_a, is in series with the whole canopy and ground surface resistances, which are represented by the parenthetical term in Eq. (1). At each level, the total canopy resistance, $r_c(z)$, is calculated as the sum of parallel resistances due to diffusion into the leaf stomata and absorption into the plant mesophyll and to adsorption onto the leaf cuticle (the factor of 2 appearing because adsorption may occur on either side of the leaf, while stomata are typically found only on the underside of leaves for hypostomatous plants). As represented in Eq. (3), the leaf boundary layer resistance r_b, exists in series with each of these possible pathways for trace species deposition to a leaf. However, this representation of r_b as occurring in series *individually* with each leaf deposition pathway is inherently non-physical.

As a trace species molecule approaches a leaf it must first diffuse through any existing laminar boundary layer next to the leaf surface. At that juncture, the molecule can then *either* be deposited onto the leaf's cuticle (on the top or bottom of the leaf) *or* it can diffuse into a stoma and be absorbed into the mesophyll. Given this conceptual picture, it is clear that the boundary layer resistance is in series *independent* of the two subsequent parallel pathways for trace species deposition (i.e., onto the leaf cuticle or through the stoma into the leaf mesophyll), so that the canopy resistance should be formulated as

$$r_c(z) = r_b(z) + r_l(z) \tag{4}$$

where,

$$\frac{1}{r_l(z)} = \frac{1}{r_s(z) + r_{meso}} + \frac{2}{r_{cut}}, \tag{5}$$

or after rearrangement,

$$r_l(z) = \frac{r_{cut}(r_s(z) + r_{meso})}{r_{cut} + 2(r_s(z) + r_{meso})}. \tag{6}$$

Then,

$$r_c(z) = r_b(z) + \frac{r_{cut}(r_s(z) + r_{meso})}{r_{cut} + 2(r_s(z) + r_{meso})}, \tag{7}$$

and the revised local canopy sink becomes

$$S^{rev}(z) = LAI(z)\left(r_b(z) + \frac{r_{cut}(r_s(z) + r_{meso})}{r_{cut} + 2(r_s(z) + r_{meso})} \right)^{-1}. \tag{8}$$

3. Analysis of the original and revised formulations

Consideration of limiting cases of the two formulations for $r_c(z)$ (Eqs. (3) and (7)) is instructive. First, in the case where the cuticular and mesophyllic resistances approach zero and the boundary layer resistance is much larger than the stomatal resistance -

$$\begin{aligned} &r_{cut} \to 0 \\ &r_{meso} \to 0 \\ &r_b(z) >> r_s(z) \end{aligned} \tag{9}$$

then the leaf-level resistance at height z, from Eq. (3) is given by

$$\frac{1}{r_c(z)} = \frac{1}{r_b(z) + r_s(z) + r_{meso}} + \frac{2}{r_b(z) + r_{cut}} \to \frac{1}{r_b(z)} + \frac{2}{r_b(z)} = \frac{3}{r_b(z)}. \tag{10}$$

On the other hand, the leaf-level resistance from Eq. (7) reduces to

$$\frac{1}{r_c(z)} = \frac{1}{r_b(z) + \frac{r_{\text{cut}}(r_s(z)+r_{meso})}{r_{\text{cut}}+2(r_s(z)+r_{meso})}} \rightarrow \frac{1}{r_b(z)}. \quad (11)$$

Clearly, the original MLM limiting case result given by Eq. (10) is inconsistent with the conceptual idea that as the surface resistances become vanishingly small the overall local canopy resistance should approach the boundary layer resistance. However, the correct limiting case result (Eq. (11)) is produced from the revised formulation of Eq. (7).

Alternatively, in the limiting case where the boundary layer resistance approaches zero -

$$r_b \rightarrow 0 \quad (12)$$

then $r_c(z)$ from Eq. (3) becomes

$$\frac{1}{r_c(z)} = \frac{1}{r_b(z) + r_s(z) + r_{\text{meso}}} + \frac{2}{r_b(z) + r_{cut}} \rightarrow \frac{1}{r_s(z) + r_{\text{meso}}} + \frac{2}{r_{\text{cut}}} \quad (13)$$

and from Eq. (7) we obtain the identical limiting result

$$\frac{1}{r_c(z)} = \left(r_b(z) + \frac{r_{\text{cut}}(r_s(z) + r_{\text{meso}})}{r_{\text{cut}} + 2(r_s(z) + r_{\text{meso}})} \right)^{-1} \rightarrow \left(\frac{r_{\text{cut}} + 2(r_s(z) + r_{\text{meso}})}{r_{\text{cut}}(r_s(z) + r_{\text{meso}})} \right) = \frac{1}{r_s(z) + r_{\text{meso}}} + \frac{2}{r_{\text{cut}}}. \quad (14)$$

4. Impact of the revised formulation on MLM whole canopy deposition velocities

The revised formulation of $r_c(z)$ as presented in Eq. (7) was implemented into the version of MLM as described by Cooter and Schwede (2000). All other elements of MLM, including all resistance parameterizations, were left the same as specified in Cooter and Schwede (2000). A test meteorological data set was used to generate V_d values for six monitoring sites (Table 1) representing a sampling of different vegetation species and morphology. Identical meteorological data were used for all sites to allow a direct assessment of how differing site characteristics affect V_d values calculated by the new formulation. Fig. 1 presents a comparison of deposition velocities generated with the original and revised formulations for SO_2, O_3 and HNO_3 for Oak Ridge, TN. For these three gaseous species, only the V_d values for HNO_3 are significantly affected by implementation of the revised r_c formulation. For SO_2 and O_3, the boundary layer resistance is smaller than the leaf surface resistances (r_s, r_{cut} and r_{meso}) and thus the calculated V_d values for these species are altered only slightly during the day (−3%). On the other hand, for HNO_3 with an effective Henry's law coefficient of $>10^{12}$ M atm^{-1}, the cuticular and mesophyllic resistances are essentially zero so that the deposition velocities for HNO_3 are reduced by as much as 38% during mid-day and 32% on average between 6:00 am and 6:00 pm LST. Similar results are obtained for the other five sites as shown in Table 1 over a variety of vegetation types and leaf area index (LAI) values. HNO_3 V_d reductions across the sites range from 10% at the low LAI site Pawnee Grasslands to 32% at Oak Ridge and 27–28% at the other locations. O_3 and SO_2 values are reduced by 3% or less at all sites.

Table 1
Percent difference in 6:00 am–6:00 pm mean total deposition velocity (V_d) between the revised and original formulations of MLM.

Site	Lat/Lon (deg)	Vegetation	LAI (m^2 m^{-2})	HNO_3 (%)	O_3 (%)	SO_2 (%)
Oak Ridge	35.96N/84.28W	White oak Loblolly pine	5.0	−32.1	−3.3	−2.9
Bondville	40.05N/88.37W	Maize	4.0	−26.9	−2.8	−1.6
Sequoia National Park	36.58N/118.75W	Grass Ponderosa pine	4.6	−26.7	−2.4	−1.5
Pawnee Grasslands	40.82N/104.77W	Bluegrass	0.6	−10.1	−1.3	−0.2
Howland National Forest	45.17N/68.77W	Spruce White birch	5.8	−28.2	−3.0	−2.5
Everglades	25.00N/80.50W	Cattails Sawgrass	4.0	−28.6	−2.9	−2.0

Interestingly, evaluations of MLM against measurements have not noted biases of the magnitude as are suggested here (Meyers et al., 1989; Cooter and Schwede, 2000; Baumgardner et al., 2002; Schwede et al., 2011), although Meyers et al. (1998) did report that mean biases for daytime estimates of V_d for HNO_3 were positive and ranged from 0.09 cm s^{-1} for corn canopies to 0.47 cm s^{-1} for pastures. However, the reported precisions of these biases for HNO_3 were much larger, ranging from ±0.88 cm s^{-1} for corn to ±1.5 cm s^{-1} for pasture. The difficulties of obtaining accurate measurements of HNO_3 are well known (Huey et al., 1998; Kita et al., 2006), so that measurement uncertainties likely obscured the biases reported here.

5. Summary, implications and recommendations

In this work, the non-physical representation of the canopy resistance as originally formulated in MLM has been noted and a revised, physically consistent, formulation has been suggested as a replacement. The revised canopy resistance formulation reduces estimates of HNO_3 deposition velocities by as much as 38% during mid-day as compared to values generated by the original formulation. Deposition velocities for SO_2 and O_3 are only slightly altered by the change in formulation (<3%). The MLM is used by the U.S. Environmental Protection Agency's (U. S. EPA's) Clean Air Status and Trends Network (CASTNet) to derive deposition velocities for CASTNet-based deposition estimates (Cooter and Schwede, 2000; U.S. EPA, 2013). Implementation of the revised, physically consistent, formulation into MLM will result in reduced estimates of dry deposition of gaseous HNO_3. Dry deposition of HNO_3 represents 35–40% of total oxidized nitrogen deposition and roughly one-quarter of total nitrogen (i.e., oxidized + reduced forms) deposition in the Eastern U.S. (Sickles and Shadwick, 2007). If the results of Table 1 and Fig. 1 are typical (10–30% reduction in HNO_3 deposition), estimated oxidized and total nitrogen deposition loadings would be reduced by as much as 10–20% and 5–10%, respectively, for the Eastern U. S. A re-evaluation of estimated deposition for total nitrogen over the U. S. should be undertaken (U.S. EPA,2013; Baumgardner et al., 2002; Sickles and Shadwick, 2007) to correct the historical record or at minimum to provide an indication of the sensitivity of large-scale loadings to the way in which field measurements are interpreted. Furthermore, observations of surface–atmosphere exchange of reactive nitrogen species, particularly nitric acid, are needed to better constrain the parameterizations used to estimate total nitrogen deposition. Ideally, such efforts would leverage recent advances in *in situ* techniques (Neuman et al., 2000; Farmer et al., 2006; Veres et al., 2008) to directly measure nitric acid fluxes via eddy covariance over a range of vegetated environments.

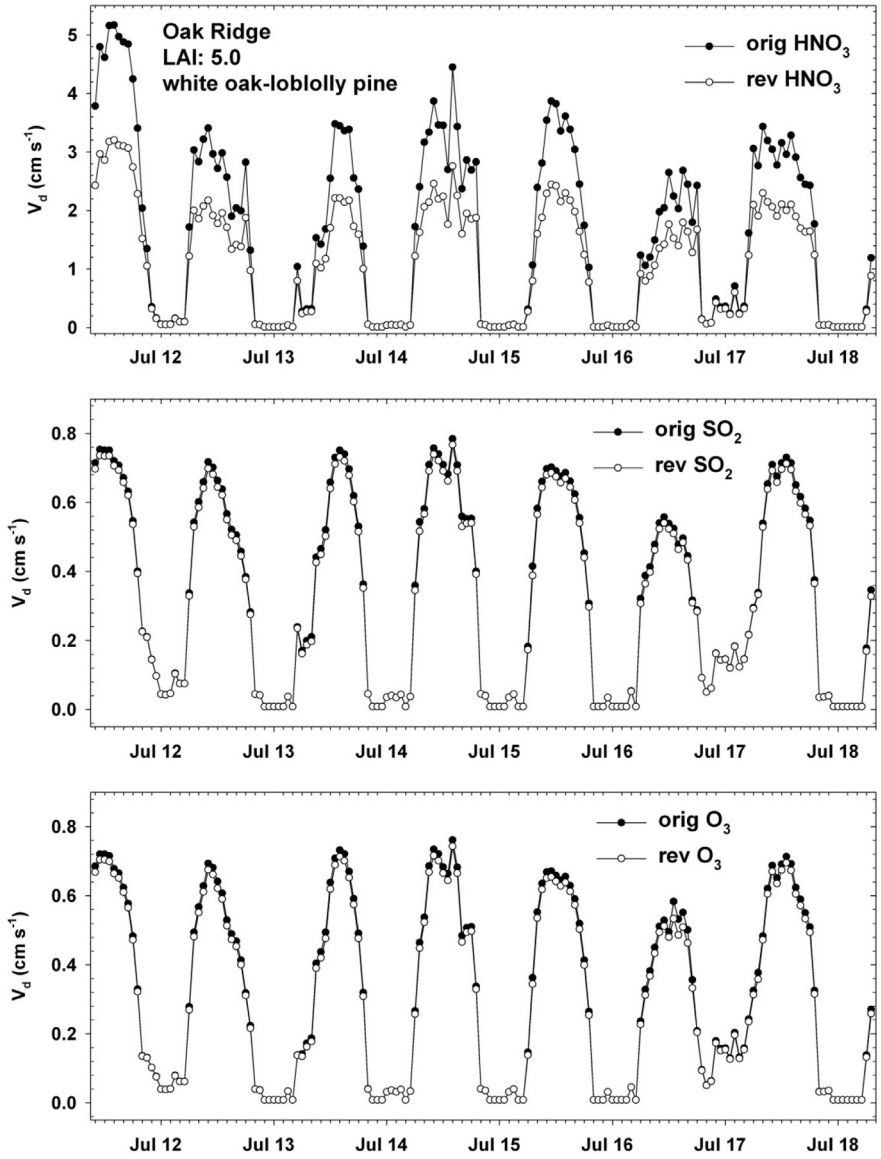

Fig. 1. Hourly deposition velocities for HNO_3, SO_2 and O_3 predicted by the original and revised formulations of MLM for a test meteorological data set applied to the Oak Ridge, TN, forest canopy.

Acknowledgments

One author (RS) performed this work with support from the U.S. Weather Research Program within the NOAA/OAR Office of Weather and Air Quality.

References

Baumgardner Jr., R.E., Lavery, T.F., Rogers, C.M., Isil, S.S., 2002. Estimates of atmospheric deposition of sulfur and nitrogen species: clean air status and trends network, 1990–2000. Environmental Science and Technology 36, 2614–2629.

Bowker, G.E., Schwede, D.B., Lear, G.G., Warren-Hicks, W.J., Finkelstein, P.L., 2011. Quality assurance decisions with air models: a case study of imputation of missing input data using EPA's multi-layer model. Water, Air, and Soil Pollution 222, 391–402.

Cooter, E.J., Schwede, D.B., 2000. Sensitivity of the National Oceanic and Atmospheric Administration multilayer model to instrument error and parameterization uncertainty. Journal of Geophysical Research 105 (D5), 6695–6707.

Clarke, J.F., Edgerton, E.S., Martin, B.E., 1997. Dry deposition calculations for the clean air status and trends network. Atmospheric Environment 31, 3667–3678.

Farmer, D.K., Wooldridge, P.J., Cohen, R.C., 2006. Application of thermal-dissociation laser induced fluorescence (TD-LIF) to measurement of HNO_3, ∑alkyl nitrates, ∑peroxy nitrates, and NO_2 fluxes using eddy covariance. Atmospheric Chemistry and Physics 6, 3471–3486.

Finkelstein, P.L., Ellestad, T.G., Clarke, J.F., Meyers, T.P., Schwede, D.B., Hebert, E.O., Neal, J.A., 2000. Ozone and sulfur dioxide dry deposition to forests: observations and model evaluation. Journal of Geophysical Research 105 (D12), 15365–15377.

Finkelstein, P.L., 2001. Deposition velocities of SO_2 and O_3 over agricultural and forest ecosystems. Water, Air, and Soil Pollution: Focus 1, 49–57.

Huey, L.G., Dunlea, E.J., Lovejoy, E.R., Hanson, D.R., Norton, R.B., Fehsenfeld, F.C., Howard, C.J., 1998. Fast time response measurements of HNO_3 in air with a chemical ionization mass spectrometer. Journal of Geophysical Research 103 (D3), 3355–3360.

Kita, K., Morino, Y., Kondo, Y., Komazaki, Y., Takegawa, N., Miyazaki, Y., Hirokawa, J., Tanaka, S., Thompson, T.L., Gao, R.-S., Fahey, D.W., 2006. A chemical ionization mass spectrometer for ground-based measurements of nitric acid. Journal of Atmospheric and Oceanic Technology 23, 1104–1113.

Meyers, T.P., Huebert, B.J., Hicks, B.B., 1989. HNO_3 deposition to a deciduous forest. Boundary-Layer Meteorology 49, 395–410.

Meyers, T.P., Finkelstein, P., Clarke, J., Ellestad, T.G., Sims, P.F., 1998. A multilayer model for inferring dry deposition using standard meteorological measurements. Journal of Geophysical Research 103 (D17), 22645–22661.

Neuman, J.A., Gao, R.S., Schein, M.E., Ciciora, S.J., Holecek, J.C., Thompson, T.L., Winkler, R.H., McLaughlin, R.J., Northway, M.J., Richard, E.C., Fahey, D.W., 2000. A fast-response chemical ionization mass spectrometer for in situ measurements of HNO_3 in the upper troposphere and lower stratosphere. Review of Scientific Instruments 71, 3886–3894. http://dx.doi.org/10.1063/1.1289679.

Schwede, D.B., Leduc, S.K., Otte, T.L., 2001. Using meteorological model output as a surrogate for on-site observations to predict deposition velocity. Water, Air, and Soil Pollution: Focus 1, 59–66.

Schwede, D., Zhang, L., Vet, R., Lear, G., 2011. An intercomparison of the deposition models used in the CASTNET and CAPMoN networks. Atmospheric Environment 45, 1337–1346.

Sickles II, J.E., Shadwick, D.S., 2002. Precision of atmospheric dry deposition data from the clean air status and trends network. Atmospheric Environment 36, 5671–5686.

Sickles II, J.E., Shadwick, D.S., 2007. Seasonal and regional air quality and atmospheric deposition in the eastern United States. Journal of Geophysical Research 112, D17302. http://dx.doi.org/10.1029/2006JD008356.

U. S. Environmental Protection Agency, 2013. Clean air status and Trends Network (CASTNET): 2011 Annual Report. USEPA Office of Air and Radiation, Clean Air and Markets Division, Washington, DC. http://epa.gov/castnet/javaweb/index.html.

Veres, P., Roberts, J.M., Warneke, C., Welsh-Bon, D., Zahniser, M., Herndon, S., Fall, R., de Gouw, J., 2008. Development of negative-ion proton-transfer chemical-ionization mass spectrometry (NI-PT-CIMS) for the measurement of gas-phase organic acids in the atmosphere. International Journal of Mass Spectrometry 274, 48–55. http://dx.doi.org/10.1016/j.ijms.2008.04.032.

Wu, Y., Brashers, B., Finkelstein, P.L., Pleim, J.E., 2003a. A multilayer biochemical dry deposition model 1. Model formulation. Journal of Geophysical Research 108 (D1), 4013. http://dx.doi.org/10.1029/2002JD002293.

Wu, Y., Brashers, B., Finkelstein, P.L., Pleim, J.E., 2003b. A multilayer biochemical dry deposition model 2. Model evaluation. Journal of Geophysical Research 108 (D1), 4014. http://dx.doi.org/10.1029/2002JD002306.

Wu, Y., Walker, J., Schwede, D., Peters-Lidard, C., Dennis, R., Robarge, W., 2009. A new model of bi-directional ammonia exchange between the atmosphere and biosphere: ammonia stomatal compensation point. Agricultural and Forest Meteorology 149, 263–280.