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Discussion

Comment on "size distribution of sea-salt emissions as a function of relative humidity"

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Zhang et al. (2005) present a parameterization for what they term the "growth factor" of a sea-salt aerosol particle relative to its formation diameter, which they assert "is a function of relative humidity alone" and independent of an arbitrary reference relative humidity. Here, we note that this growth factor implicitly assumes an arbitrary reference relative humidity through the salinity of the seawater from which the particle is produced and thus that the diameter at formation does not uniquely represent the amount of solute mass contained in a sea-salt aerosol particle, in contrast to the equivalent dry radius (or diameter) or to the radius (or diameter) of the particle in equilibrium at a given relative humidity, typically used for this purpose. We present an alternative parameterization for the RH growth factor of sea-salt aerosol particles that is physically based, of more general applicability, more accurate, and valid at higher relative humidity.

The dependence of the size of sea-salt aerosol particles on relative humidity is important to numerous processes of interest: light scattering, gas–liquid exchange of water and trace gases, dry deposition, particle sampling, and the like, the accurate description of which requires accurate knowledge and representation of this dependence. Zhang et al. present a parameterization of the growth factor, which they define as the ratio of the diameter of a sea-salt aerosol particle at formation from seawater having salinity 35, $D_{\mathrm{form},35}$, to the diameter of the same particle in equilibrium with a given fractional relative humidity RH, D_{RH}: $C^0 \equiv D_{\mathrm{form},35}/D_{\mathrm{RH}}$; as so defined this growth factor decreases with increasing RH. The salinity S is approximately equal to the mass concentration of sea salt in grams per kilogram of seawater (Millero, 1996). Although salinity 35 is typical for much of the world ocean, there are instances for which the salinity of seawater departs substantially from 35, and for which a drop of a given formation diameter would therefore contain an amount of solute different from that of a drop at the same formation diameter formed from seawater of salinity 35. Consequently, the growth factor as defined by Zhang et al. would not be applicable to sea-salt aerosol particles formed from seawater of salinity other than 35, nor would it be equal to unity, as required, for such a sea-salt aerosol particle at formation. Because of vapor pressure lowering caused by the dissolved salts (Raoult's Law) the equilibrium relative humidity over seawater of salinity 35 is approximately 98%. By defining the growth factor C^0 relative to the diameter at formation at salinity 35, Zhang et al. have implicitly

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made the assumption that $D_{\text{form}} = D_{98}$. Thus contrary to their assertion otherwise, the growth factor as they have defined it depends on an assumed value of RH_{form}, namely 98%; that is, the growth factor of Zhang et al. is given by $C^0 \equiv D_{98}/D_{\text{RH}}$.

In general, the ratio $D_{\text{form},S}/D_{\text{RH}}$ of the diameter of a drop formed from seawater of salinity S, $D_{\text{form},S}$, to that of the drop in equilibrium at a given RH, D_{RH}, is related to $D_{\text{form},35}/D_{\text{RH}}$ (Zhang et al.'s quantity C^0) by

$$\frac{D_{\text{form},S}}{D_{\text{RH}}} = \left(\frac{D_{\text{form},35}}{D_{\text{RH}}}\right)\left(\frac{35}{S}\right)^{1/3}\left(\frac{\rho_S}{\rho_{35}}\right)^{1/3}, \tag{1}$$

where ρ_S and ρ_{35} are the densities of seawater of salinity S and salinity 35, respectively. The factor containing the density ratio $(\rho_S/\rho_{35})^{1/3}$, which is accurately approximated as $1.00000 + 0.00025(S—35)$, differs from unity by less than 1% for all situations of interest. Although for salinities 34 and 36, $D_{\text{form},S}/D_{\text{RH}}$ differs from Zhang et al.'s quantity C^0 by only about +1% and −1%, respectively, for salinity 38.5, typical of the Mediterranean, $D_{\text{form},S}/D_{\text{RH}}$ is less by ~3%; for salinity 17, typical of surface waters of the Black Sea, it is more than 20% greater than C^0; and for salinity 7, typical of the Baltic Sea, it is more than 40% greater. (Although Tang et al., 1977, reported measurements only at 25 °C, the weak temperature dependence of the density ratio and of the equilibrium relative humidity of a sea-salt aerosol particle of given concentration allows their results to be used to good accuracy over the entire temperature range of atmospheric interest.)

The parameterization of the growth factor presented by Zhang et al.:

$$\frac{D_{98}}{D_{\text{RH}}} = 28.376 - 205.44\,\text{RH} + 653.37\,\text{RH}^2 - 1031.7\,\text{RH}^3 + 803.18\,\text{RH}^4 - 247.08\,\text{RH}^5, \tag{2}$$

agrees with the results of laboratory measurements of Tang et al., on which it was based, within 2.8% for fractional relative humidity RH ranging from 0.45 (the efflorescence value of sea salt) to 0.98, but diverges sharply at higher RH, to as much as 8.6% by RH 0.99. We have recently presented (Lewis and Schwartz, 2004, p. 54) a two-parameter expression for the dependence of the radius of a sea-salt aerosol particle on relative humidity from which an expression for the growth factor defined by Zhang et al. is readily obtained:

$$\frac{D_{98}}{D_{\text{RH}}} = 3.7\left(\frac{1-\text{RH}}{2.0-\text{RH}}\right)^{1/3}. \tag{3}$$

This parameterization, which is physically based and explicitly captures the Raoult behavior at relative humidities near 100% through the factor $(1-\text{RH})^{1/3}$, agrees with results of Tang et al. to within 3% over the RH range 0.45 to greater than 0.99 (until surface tension effects require a modification of the formulation). This parameterization and that of Zhang et al. are compared to the expression presented by Tang et al. in Fig. 1. Although both parameterizations provide a good fit to the measurements over much of the RH range, the simpler, physically based parameterization yields a much more accurate representation of particle growth at high RH. This parameterization, combined with the factor presented above to take into account the formation salinity, yields the ratio of the diameter at formation from seawater of arbitrary salinity to that an any RH, again with accuracy of ~3%:

$$\frac{D_{\text{form},S}}{D_{\text{RH}}} = 3.7\left(\frac{1-\text{RH}}{2.0-\text{RH}}\right)^{1/3}\left(\frac{35}{S}\right)^{1/3}\left(\frac{\rho_S}{\rho_{35}}\right)^{1/3}, \tag{4}$$

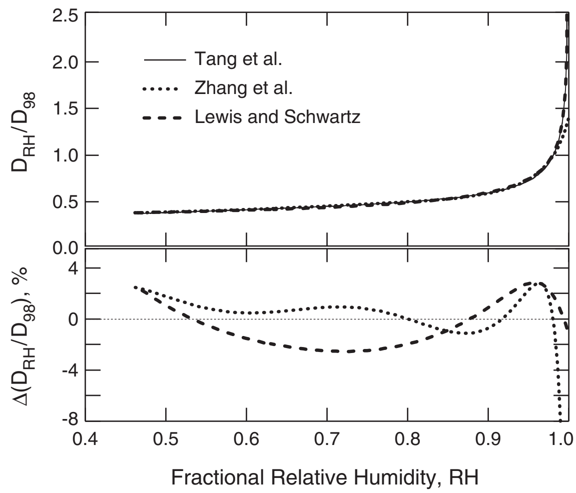

Fig. 1. Dependence of equilibrium diameter of sea-salt aerosol particle on fractional relative humidity RH. Upper panel shows ratio of particle diameter at arbitrary RH to that at RH 0.98 according to the expression of Tang et al. (1997), that given by the parameterization (Eq. (2)) of Zhang et al. (2005), and that presented here (Eq. (3)) based on Lewis and Schwartz (2004). Lower panel shows fractional departure of the two parameterizations from the Tang et al. expression, $\Delta(D_{\text{RH}}/D_{98}) = [(D_{\text{RH}}/D_{98})_{\text{param}}/(D_{\text{RH}}/D_{98})_{\text{Tang}} - 1]$, in percent.

where, as above, the factor containing the density ratio can be set to unity with little loss in accuracy.

Accurate description of the properties of sea-salt aerosol particles requires that the particles be uniquely and unambiguously identified according to some invariant physical attribute. Such an attribute is the amount of dry sea-salt mass contained in the particle, and this quantity is the identifier of choice for some considerations. However, because of the importance of particle radius (or diameter) to the physical properties of aerosol particles, several quantities involving particle radius (or diameter) are commonly employed to uniquely characterize sea-salt aerosol particles: the equivalent dry radius r_{dry}, defined by $r_{\mathrm{dry}} = [3m_{\mathrm{dry}}/(4\pi\rho_{\mathrm{ss}})]^{1/3}$, where ρ_{ss} is the density of dry sea salt (approximately $2.2\,\mathrm{g\,cm^{-3}}$); the radius of the particle in equilibrium at relative humidity 80% r_{80}; and the radius of the particle in equilibrium at relative humidity 98% r_{98}. To within about 1% the quantities are related by $D_{98} = 2r_{98} \approx 4r_{80} \approx 8r_{\mathrm{dry}}$. Thus a formulation for a quantity that depends on particle size such as sea-salt aerosol production flux given in terms of one of these quantities can readily be transformed into a formulation expressed in terms of another, for example, $\mathrm{d}F/\mathrm{d}D_{80} = (\mathrm{d}D_{98}/\mathrm{d}D_{80})(\mathrm{d}F/\mathrm{d}D_{98}) \approx 2(\mathrm{d}F/\mathrm{d}D_{98})$. In contrast, because of the dependence on seawater salinity, the radius (or diameter) of the particle at formation, r_{form} (or D_{form}), is not an unambiguous measure of the amount of sea-salt mass contained in a particle. The radius of a sea-salt aerosol particle at a given relative humidity, r_{RH}, is related to the dry mass of sea salt contained in the particle, m_{dry}, by

$$r_{\mathrm{RH}} = \left(\frac{3m_{\mathrm{dry}}}{4\pi\rho_{\mathrm{ss}}}\right)^{1/3}\left(\frac{4.0}{3.7}\right)\left(\frac{2.0-\mathrm{RH}}{1-\mathrm{RH}}\right)^{1/3}, \qquad (5)$$

where the factor 4.0 is the ratio r_{98}/r_{dry}; this parameterization is valid except where surface tension effects become important.

In conclusion, the parameterization of RH-dependent growth of sea-salt aerosol particles presented by Zhang et al. is limited to drops formed from seawater of salinity 35, cannot be used to parameterize the drop radius as a function of the dry sea-salt mass and relative humidity, and exhibits substantial error at high RH. The expression presented by Lewis and Schwartz (2004) and extended here is physically based, is applicable to all salinities, provides an unambiguous relation between drop radius and dry sea-salt mass, and is accurate over virtually the entire range of RH pertinent to aqueous sea-salt aerosol in the atmosphere.

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References

Lewis, E.R., Schwartz, S.E., 2004. Sea Salt Aerosol Production: Mechanisms, Methods, Measurements, and Models: A Critical Review. American Geophysical Union, Washington, DC.

Millero, F.J., 1996. Chemical Oceanography, second ed. CRC Press, Boca Raton, FL.

Tang, I.N., Tridico, A.C., Fung, K.H., 1997. Thermodynamic and optical properties of sea salt aerosols. Journal of Geophysical Research—Atmospheres 102, 23,269–23,275.

Zhang, K.M., Knipping, E.M., Wexler, A.S., Bhave, P.V., Tonnesen, G.S., 2005. Size distribution of sea-salt emissions as a function of relative humidity. Atmospheric Environment 39, 3373–3379.