

Appendix I (a) –Comments Received from the University of California Peer Reviewers Regarding the CARB Deposition Memo

CARB received comments on its draft report titled “Annual Atmospheric Deposition of Nitrogen, Phosphorous, and Particulate Matter to Lake Tahoe” from Peer Reviewers selected by the University of California Office of the President. Comments were received from Professors Stolzenbach (UC Los Angeles), Venkatram (UC Riverside), and Wexler (UC Davis). The comments are presented in their entirety in here. Staff’s responses to the comments in presented in Appendix I (b).

Comments Received from Professor Keith Stolzenbach, UC Los Angeles

This letter is to transmit my review of the document “Annual Atmospheric Deposition of Nitrogen, Phosphorous, and Particulate Matter to Lake Tahoe,” which I performed as a part of the Lake Tahoe Atmospheric Deposition Study per the Interagency Agreement No. 98004-TO between the University of California and the Air Resource Board. Note that my comments reflect my professional areas of expertise, particularly the deposition of aerosols on land and water. I have not addressed issues of the sampling methodologies for nitrogen or phosphorous.

General Comments

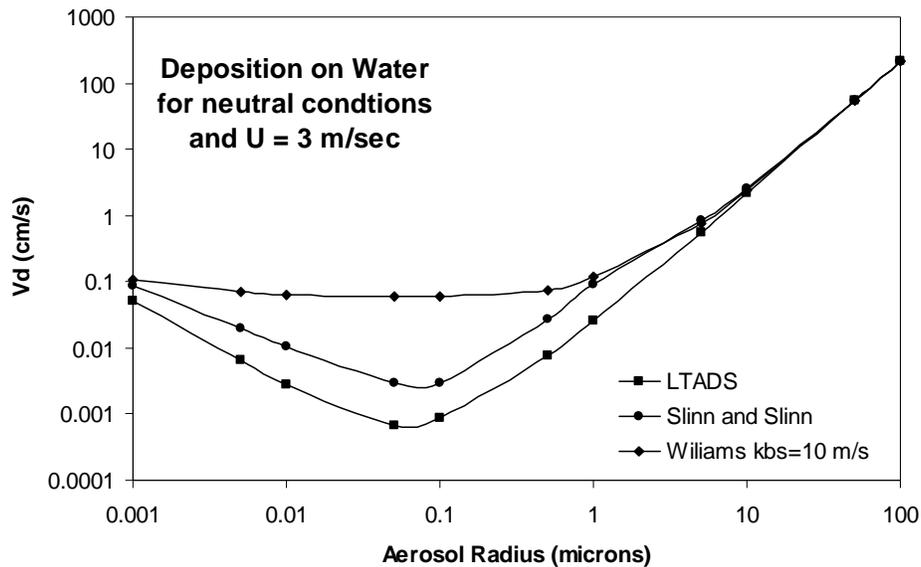
- The general approach of estimating atmospheric deposition rates by using observed atmospheric concentrations in conjunction with theoretical deposition velocities is a well-established methodology (e.g. Brook et al. 1999; Smith et al. 2000, Lu et al. 2003). The quantity and quality of the concentration and meteorological data (used as a basis for the deposition velocity calculation) in this study greatly exceeds that of previous studies in other regions.
- This report focuses entirely on direct deposition to the water surface. In a study of atmospheric deposition in the LA area (Lu et al. 2003), we found that the atmospheric loading to streams and water bodies was more influenced by deposition on the watershed that is then washed off than by direct deposition on the water surface. Of course, Lake Tahoe has a large surface area relative to its watershed, so this may be less so there. Also, storm water inputs to the lake may be accounted for in other components of the overall study.
- I have a number of detailed comments below that raise questions about the methodology used for the deposition estimates. However, there are several pieces of evidence that indicate the estimates are within the range to be expected. First, the range of deposition velocities mentioned at the end of page 37 of the report are consistent with the findings of other studies, including Lu et al. (2003), with which I am most familiar. Second, I have used the PM concentration data in Figure 3-2 and the computed annual PM loading to the lake given in section 5.6 (page 46) to compute an effective average deposition velocity for particulate matter. If 1700 metric tons of particulate matter (the best estimate) is deposited on a lake surface area of 495 km² (<http://tahoe.usgs.gov/facts.html>), and if the typical total PM concentration is 30 µg/m³, then the effective deposition velocity is about 0.4 cm/sec, which is entirely consistent with results from other studies with which I am familiar.
- In my judgment, the precision of these deposition estimates can not be considered to be better than about ±30-50%. Some of this is because of the uncertainty in the temporal and spatial distribution of the atmospheric concentration of the substances of interest, but a large part of the uncertainty comes from the inadequacies of the theoretical formulations for predicting deposition. I discuss this in more detail below.

Specific Comments

- The report describes in detail how time-resolved meteorological and atmospheric concentration data was used to produce estimates of average deposition rates. These procedures for averaging temporally and spatially, which I have reviewed somewhat quickly compared to other aspects of the report, seem reasonable.
- As mentioned in the report, deposition estimates based on atmospheric concentrations specified by aerosol size are particularly sensitive to the concentration of the larger size classes. In this regard, I am not quite sure why the report states on page 44 that “the same cannot generally be said for PM large.” Additionally, it is not clear why the PM large size fraction was assumed to cap at 20 μm . The literature is full of measurements that indicate substantial mass of aerosols larger than 20 μm . In making our own deposition estimates here in LA we used an upper bound of 60 μm based on direct measurements of aerosol sizes. The computed deposition estimates will be sensitive to the assumed upper bound on aerosol size, and the value used in this report may lead to an underestimate of deposition rates.
- As far as I can tell, the aerosol concentrations used in the deposition calculations were all measured at land-based stations, although the meteorological data came from anchored buoys. One of our hypotheses here in LA is that large aerosols generated from land surfaces by traffic and by wind tend to deposit within a kilometer or so from the source, but then are commonly resuspended again, resulting in the significant measured large aerosol fraction in the atmosphere. For a lake the size of Tahoe, it seems possible that the large aerosol fraction may not be maintained in the center of the lake because there will be no resuspension from the water surface. For this study, this would result in an overestimate of total deposition on the lake surface. I am not sure how significant this source of error is; perhaps there is information regarding the vertical extent of the measured atmospheric concentration profile. The higher the aerosols are in the air column, the farther out into the lake they will deposit. For example, for a large particle depositing with a velocity of 1 cm/sec in an offshore wind with a velocity of 2 m/sec would have to start at a height of 50 meters to reach a point 10 km from shore before depositing.
- It is important to note the uncertainties in the theoretical formulations for deposition velocity. All agree that the major processes involved in deposition are atmospheric turbulence, gravitational settling, inertial impaction, and Brownian motion, but representing deposition by these processes on surfaces as complicated as a wavy water surface (with spray) or a typical natural or urban land surface is challenging, particularly given the lack of good data for validation of theoretical concepts.
 - The formulation for atmospheric turbulent transport of both gases and aerosols used in this study is the standard one based on the logarithmic velocity profile assumption modified by atmospheric stability. However, even with this process there are uncertainties. First, the calculation of the atmospheric stability parameter L from one air measurement and a water surface temperature measurement is approximate. I am not sure how

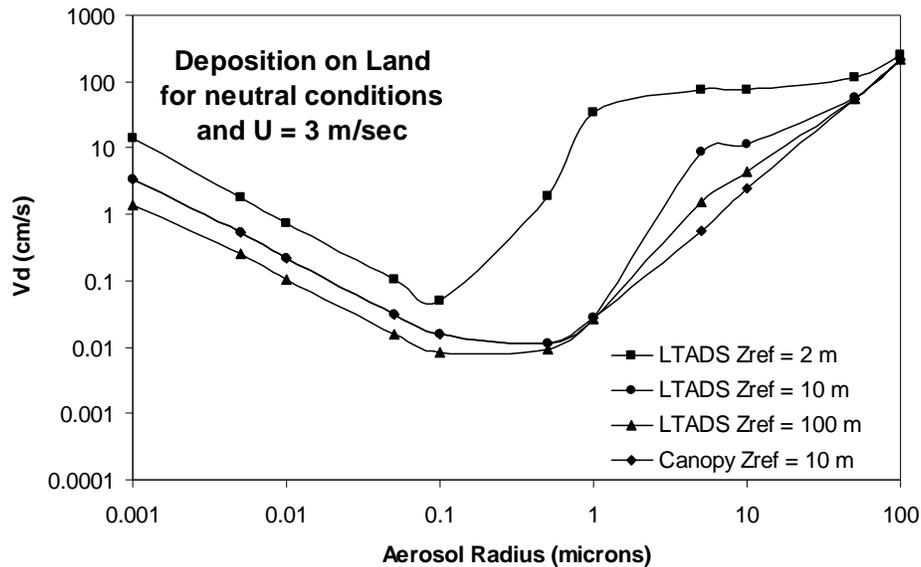
much error this can introduce, but the stability functions are not very “steep” near neutral stability, so perhaps this is not a major effect. More problematic is the assumption that the logarithmic velocity profile extends to the wind measurement height. This assumption is used implicitly in the part of the calculation where the wind speed at the measurement height is extrapolated to a standard 10 meters height using the log law. It is well-known that the logarithmic wind profile a surface with a roughness height z_0 is not valid below about $50z_0$ (Brutsaert, 1982). For a land surface calculation for with $z_0 = 1$ meter, the value used in this report, use of the logarithmic profile below 50 meter height is theoretically not valid. This constraint is widely ignored in the literature, largely because for most uses of the logarithmic profile little error is introduced. But this turns out not to be the case for the calculation of inertial deposition (see below).

- Brownian motion of aerosols is represented by the $Sc^{2/3}$ term in the expression for the boundary resistance. Sc is a dimensionless quantity representing (inversely) the relative importance of molecular diffusion processes. In general, as the aerosol size decreases, Brownian diffusion increases, Sc decreases, and the boundary resistance decreases, resulting in larger deposition velocities for the smallest aerosols. The formulation used here is quite standard, but is actually theoretically applicable to smooth surfaces only. This limitation is also ignored throughout the literature. There are formulations applicable to rough surfaces, and some papers correctly use them (Giorgi, 1986). Here again I am not too concerned about the error introduced into the deposition calculation because I suspect that aerosols in the size range affected by these assumptions do not contribute much to the total deposition. Again, this can be checked by calculations using rough surface expressions.
- Deposition of aerosols on water surfaces is particularly problematic, primarily because many of the assumptions underlying theories for transport to a solid fixed surface do not hold at a water surface, which can move in response to stress and which can fragment into droplets of spray. It is difficult to measure accumulated deposition on a large water surface, and there are few data to verify theories. The figure below shows the predictions of Slinn and Slinn (1980), Williams (1982), and this study for aerosol deposition on a water surface with an assumed wind speed of 3 m/sec. The larger deposition rate for the Williams model results from his inclusion in the model of a “broken surface” effect. For illustration, a relatively large but not unrealistic value of this effect is used here.



- For aerosols deposition may also occur by inertial impaction, which results when the aerosols initially moving with a flow toward a solid surface are unable to follow the flow away from or around the surface. Theoretical formulations have been developed for inertial deposition occurring because of turbulent motions in a boundary layer and steady flow around obstacles, the latter sometimes being referred to as canopy deposition. The study in this report uses a boundary layer formulation developed by Slinn and Slinn (1980). There are two problems with this methodology. First, boundary layer analyses, and supporting data, are restricted to relatively uniform roughness patterns, and it is not clear whether these formulations accurately predict deposition on complex natural and constructed surfaces. I find it significant that formulations for canopy deposition predict little effect of inertia for typical wind speeds (see figure below with a canopy formulation from Nho-Kim, et al. (2004)). Second, the equations used in this report are extremely sensitive to the measurement height specified for the wind speed, largely because the Stokes number used in the inertial deposition term is proportional to the square of the friction velocity, which is in turn very sensitive to the relative values of surface roughness and wind measurement height (see figure below). Extremely high rates of inertial deposition result when the measurement height of the wind speed is close to the specified roughness height, which is apparently the case for the calculation of deposition velocity on land, which is then extended some distance into the lake. I believe that this is an artifact of a high land surface roughness (1 meter) combined with a low wind measurement height (2 meters). Applying the same wind speed at a 10 meter height results in significantly less inertial

deposition. However, this error may not be reflected in the actual reported deposition rates because of a mistake in the computer code as discussed below.



- I have number of questions about the actual code used in computing deposition and have already communicated these to Jim Pederson of your office. He has responded to some of my questions, but the following remain unanswered:
 - In the main calculation for Ra, the sequence seems to be to specify $Z_{oInitial} = 0.0001$ and then to use this in a log law to calculate u_{Star} using u_z and then to use that u_{Star} to calculate u_{10} . But the calculation for u_{10} uses Z_o not $Z_{oInitial}$. The effective result is $u_{10} = u_z * [\log(10/Z_o) + \Phi_i M] / [\log(z/Z_{oInitial}) + \Phi_i M]$. My question is why the use of $Z_{oInitial}$ rather than the values calculated earlier for land and water?
 - Following the calculation of u_{10} , the bulk coefficient formula is used to calculate u_{Star} using u_{10} and the comments say that this is the final u_{Star} to be used from that point on. My question is why use the bulk coefficient when you already have a log law estimate for u_{Star} (although based on $Z_{oInitial}$)? Why not use Z_o right from the start to get u_{Star} ?

Apparently the answer to the second question is that the u_{Star} calculated from the log law (although using $Z_{oInitial}$) is not used at all and instead a Calmet bulk transfer coefficient ($0.75 + 0.067 * u$) is used. This might explain why the deposition estimates are not affected by the issue relating to the logarithmic law addressed above.

I hope that this review is useful in your future planning and execution of the project. Please contact me with any questions you may have.

Very truly yours,



Keith D. Stolzenbach
Professor of Civil and
Environmental Engineering

References Cited:

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Comments Received from Professor Akula Venkatram, UC Riverside

I will confine most of my comments to section 4 on the calculation of dry deposition velocities. As the attached paper shows, the electrical analogy does not apply to the calculation of dry deposition velocity of particles. The correct expression for v_d is

$$v_d = \frac{v_s}{(1 - e^{-v_s r})}, \quad (1)$$

where v_s is the settling velocity of the particle, and the r is

$$r = r_a + r_b + r_c. \quad (2)$$

In practice, estimates from Equation (1) might not differ from that used by ARB, but this needs to be checked out. It would be useful to number all the equations in the report to facilitate cross-referencing.

The atmospheric resistance is defined as

$$r_a = \frac{U}{u_*^2}. \quad (3)$$

This expression is valid only if the turbulent transport of chemical species is similar to that of momentum. Empirical evidence (see Valigura, 1995) indicates that transport of chemicals is similar to that of heat. The authors should check whether the correct formulation was used in the code to estimate dry deposition velocities. If Equation (3) is used, the wind speed U in the expression should correspond to the height at which the concentration is measured rather than 10 m as suggested in the report.

The authors claim that $r_a \gg r_b$ for most substances of interest. This should be supported with some calculated values of these two resistances. The statement that r_a is more sensitive to wind speed than to air-water temperature difference should be similarly supported with calculations.

The method used to calculate r_a and r_b over water requires an iterative solution and a surface energy balance as shown in Valigura (1995). This is because the subsurface water temperature is not the same as the near surface air temperature. It is not clear from the equation for L on page 35 that this distinction was made. Page 33 states that these temperatures are assumed to be the same. Please justify using results from other studies. Here are some minor points of concern raised by the equations on Page 35:

1. There appears to be typo in the equation for the 10 meter wind speed, whose significance is not clear to me.
2. When $L > 0$, u_* does not account for stability effects. Why?

3. How was u^* calculated when $L < 0$?
4. How was the dry deposition velocity calculated over land? The calculation of atmospheric resistance requires temperature measurements at two heights and/or a surface energy balance. I did not think that the temperature was measured at two heights over land.

I would have liked to see more details on accounting for turbulence being advected from the land on to the lake surface.

The equations used to calculate the dry deposition velocities are based on those in CALMET (Scire et al, 2000). It might be more useful to point the reader to peer reviewed journal literature for the dry deposition formulations. The code attached to the report does not convey much information to this reader.

It is clear that substantial resources have been spent on collecting the concentration data relevant to N, P, and PM deposition. However, these concentrations cannot be translated into deposition without reliable estimates of deposition velocities. It is difficult to comment on the magnitudes of the deposition estimates without an understanding of the uncertainties in the relevant micrometeorological variables. This is especially important because the report does not present any direct measurements of dry deposition. The report can be improved by including more details on the micrometeorology that was used to estimate deposition.

Comments Received from Professor Anthony Wexler of UC, Davis

Overall, the report is well written and well organized. CARB staff should be commended for accomplishing a lot with limited resources. Below, I present my suggested improvements to each chapter, divided into Substantive (science) and Editorial (organization, presentation, typos) sections.

Substantive

Section 3.2.1, page 16, paragraph 3: It was not clear from this discussion or later discussions how ammonium T was estimated from ammonium M and what uncertainties are introduced. This should be expanded.

Section 3.2.2, page 17 and 18: If the ammonium and nitrate are in the particles as ammonium nitrate (as opposed to being bound with other compounds – see my Section 5.3 comment below), they imposed a partial pressure product (assuming equilibrium) that may help constrain some of the uncertainties in the gas phase measurements. These calculations can be done using AIM (<http://mae.ucdavis.edu/wexler/aim>) or you can consult the paper by Stelson and Seinfeld. For instance, the TWS ammonia data appear to be more reliable than the nitric acid data, so the ammonia may be able to estimate the nitric acid if the equilibrium assumption and ammonium nitrate assumptions apply.

Section 3.3.1, page 23, paragraph 2: if no phosphorus was detected in PM_{2.5} doesn't this lend support to the later contention that wood smoke is not a significant source?

Chapter 4. This chapter is poorly organized, poorly written, and needs a major overhaul. The Appendix should not be included in the report – it is a lot of pages that are not providing useful information. Probably better to post on the web for those who want to examine the workings of the code or try it out. The material in section 4.1 does not agree with that in 4.3, and misleads the reader. I suggest removing 4.1 altogether. The first couple of paragraphs of 4.4 repeat what has already been stated. These editorial comments are no reflection on the science, which appears well founded and thorough, but good science does not stand with out comparable presentation.

Page 30 and page 35: According to Seinfeld and Pandis, the settling velocity does not simply add to the deposition velocity (note that Figure 4-1 is right out of their text on page 960) as shown in their equation 19.7 because the settling velocity may be thought to operate in parallel to the other processes.

Chapter 4: there is an implicit assumption that deposition to the lake surface dominates transport. In other words, deposition of material to trees, streets, soil and other non-

lake surfaces with subsequent transport to the lake by rain or melting snow is not a significant source. I think this assumption is valid but it should be stated explicitly.

Chapter 4: there are very few references to the literature. Support the algorithms and formulas with references.

Section 4.2 should be merged with 4.3.

Section 4.3 should be explained and written out. V_e is introduced and then set to zero – remove it. State units for all the parameters and variables.

Section 4.3, section 3d, page 36: hygroscopic growth has a number of effects on R_b – it increases Brownian resistance but decreases that due to impaction, which should dominate for this size range. Also, settling increases which will also tend to increase deposition.

Page 38, renumber figure 4.2 to 4.3.

Section 5.3, page 42, end of first paragraph: I don't know much about the thermodynamics of phosphate, what cation it comes with, if any, and the mineral salt composition of the coarse and large fractions, but these may have an influence on the size partitioning of the ammonium nitrate and volatility of the phosphate. For instance, the volatility of the phosphate may change if it is bound to ammonium instead of a non-volatile cation. Similarly, if ammonia or nitrate bind to the mineral content in the coarse or large fractions, their vapor pressures will be decreased. This may change the size distribution of these nitrogen containing compounds to the large fraction, that may increase their deposition.

Section 5.6, page 46: Since the seasonal depositions were calculated seasonally, they should be reported seasonally. The annual average is the bottom line but the seasonal values may be important to subsequent investigations.

Section 6.2, page 51: if volatilization of phosphorous occurs at all, it seems that it would most likely occur in the warmer months, not during winter and spring when the buoys had detects.

Editorial

Section 2.4: Change “the” to “then” on line 3 and “Chapter 3” to “Chapter 4” on line 4.

Section 3, page 11, last paragraph, line 2, change “a” to “as”.

Section 3.2.1, page 15, last paragraph, line 2: change “computer” to “computed”

Section 3.2.3, page 20, line 3: change “Figure 1” to “Figure 3.2”

Section 3.3.1, page 24, line 2: remove “to”

Page 41, paragraph 3, line 4 – insert “to” to read “used to represent”

Section 5.4, page 43: change “Sunn” to “Sun”

Section 6.1.1, page 47: insert “measured” to read “the measured annual rate”

Section 6.1.4, page 49: number the figure on page 50 and refer to it that way. Also the last two paragraphs in this section are repeats of the second and third.