

Appendix H

Staff Responses to the Major Comments Received from the University of California Peer Reviewers Regarding the CARB Interim Report (AKA Technical 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 more substantive comments of the peer reviewers are repeated with responses and comments of the staff interspersed here in Appendix H.

Summary of the Major Comments Received from Professor Keith Stolzenbach with CARB Staff Responses

General Comments

Comment: 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.

Response: *Thank you. Although extensive measurements were made in the field program, our initial assessments of dry deposition are based on a subset of the total observations. In addition, wet deposition estimates during LTADS are still being prepared.*

Comment: 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.

Response: *Staff acknowledges that the focus of its efforts was direct deposition to the lake surface. Although the surface area of the Lake Tahoe is large compared to most watersheds, atmospheric deposition to land surfaces would still be significant compared to the direct atmospheric deposition of materials to the lake. The indirect atmospheric contribution is a component of a watershed analysis contracted by the Lahontan Water Quality Control Board. Other inputs being quantified in the watershed analysis include storm water runoff, stream flows, ground water inputs, and shore erosion. Those inputs would include the migration to the Lake of any nutrients deposited to from the atmosphere to land surfaces. With extensive biotic assimilation of atmospheric nutrients and the small amount of atmospheric particulate matter compared to sediment transport in water runoff and erosion, staff suspects the indirect atmospheric contribution to the loading of Lake Tahoe is small. Because the CARB measurements were primarily made near the shoreline and on the Lake, estimates of the atmospheric deposition to land surfaces would require additional assumptions about the air quality and meteorology on the mountain slopes ringing the Lake. Crude atmospheric deposition estimations could be made in the future to assess the reasonableness of the indirect atmospheric deposition estimates from the watershed modeling.*

Staff will clarify in the final report that the LTADS goal was to provide an estimate of atmospheric deposition directly to the Lake surface. The final report will also reiterate that the estimates of direct deposition to the Lake surface provided by LTADS will be

used in the TMDL process along with the estimated lake inputs by other mechanisms (being provided by Lahontan RWQCB and their contractors).

Comment: In my judgment, the precision of these deposition estimates can not be considered to be better than about $\pm 30\text{-}50\%$. 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.

Response: *Staff concurs that the precision of its deposition estimates is at best $\pm 30\text{-}50\%$ but believes it likely is less than $\pm 100\%$. In addition to uncertainty regarding the spatial and temporal variations in concentrations of nitrogen, phosphorus, and PM, the estimates of deposition velocity for individual hours may have an uncertainty of a factor of two. However, we expect spatially and temporally averaged deposition velocities to be much less uncertain. Because staff intentionally made some conservative assumptions in generating the deposition estimates, staff expects that more refined analyses would likely decrease these estimates of annual deposition.*

Specific Comments

Comment: 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 $20\ \mu\text{m}$. The literature is full of measurements that indicate substantial mass of aerosols larger than $20\ \mu\text{m}$. In making our own deposition estimates here in LA we used an upper bound of $60\ \mu\text{m}$ 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.

Response: *The sentence on page 44 will be revised for clarity. From several types of observations made in LTADS, the mass of particles larger than $10\ \mu\text{m}$ seemed to be dominated by particles smaller than $25\ \mu\text{m}$. Staff is reviewing results from several studies in other areas that may be relevant to particle size at Lake Tahoe. The LTADS observations included particle counts converted to mass concentrations for size bins of $0.5 - 1$, $1 - 2.5$, $2.5 - 5$, $5 - 10$, $10 - 25$, and $> 25\ \mu\text{m}$. In addition, based upon observations made with the TWS and the BAMs, the difference between mass concentrations of TSP and PM10 were generally less than the difference between masses of PM10 and PM2.5. Those observations suggest that particles larger than $25\ \mu\text{m}$ would not dominate the mass concentration or rate of deposition. Although larger particle sizes have been observed in urban areas of southern California, re-suspension of large particles is more likely in that area due to more predominant hard man-made surfaces and the mechanical re-suspension by vehicles. Based on additional analysis*

of the LTADS data, staff may revise the assumed effective sizes of PM_{large} (15, 20, and 25 μm respectively for the Lower Bound, Best Estimate, and Upper Bound calculations). Staff will present details of the information leading to the final assumptions of representative sizes for PM_{large} .

Comment: 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.

Response: *Staff will clarify that the aerosol concentrations used in the analysis came from land-based stations. The TWS inlets were 2 m above ground level except at Sandy Way where the inlet was 2 m above the roof of the shelter. The wind measurements were on piers at 6 to 7 m above water level and on a buoy at 2 m above water level. Staff also does not expect the mid-lake aerosol concentrations to be maintained at the concentrations observed near the shoreline. However, that assumption was made to provide a conservative upper estimate of deposition to the Lake surface. Staff does not have sufficient information about vertical extent of concentrations to make reliable estimates of the amount by which mid-lake concentrations might be depleted by deposition. Staff does have some limited evidence that suggests vertical mixing of roadway emissions might be about 5 –7 m directly downwind of the roads but does not have a means to estimate concentrations at altitudes not directly influenced by the roadway emissions. Staff considered making bounding calculations using assumptions about the extent of vertical mixing but were concerned that those could be speculative and potentially problematic (misleading or inflammatory) without reliable supporting data. Staff will seek additional information regarding vertical mixing and will incorporate estimates based on measurements of vertical mixing if possible or assumptions if necessary in the final report.*

Comment: 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.

Response: *In making a conservative estimate of deposition to the lake surface (i.e., one that is unlikely to be revised upwards with future refinements), staff assumed a quasi-laminar layer resistance (R_b) of zero for gases as many authors have done (e.g., Valigura, 1995). The standard formulation for particles includes the smooth surface treatment of quasi-laminar layer resistance and that may introduce some error. Because wind speeds are low for most hours we expect only a small impact from the effects of broken surfaces and spray. The recent work of Sarah Pryor suggests that the Williamson model would overestimate increases in deposition associated with particle growth, broken surfaces, and spray. The final report will include revised estimates, which take into account the effects of broken surfaces and spray. Staff will also review available information on the effects of surfaces and include a comparison of calculations for both smooth and rough surfaces.*

Comment: 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).

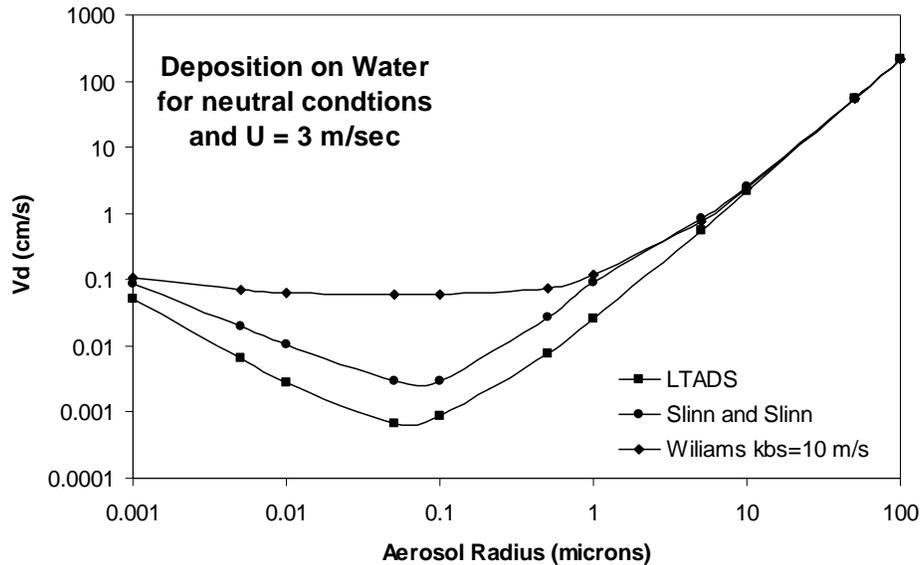
Response: *Formulations for atmospheric stability based on a single air temperature and a single water temperature (in this case at 2 cm depth) have been widely applied for over-water situations but are merely an approximation. For comparison purposes, staff will provide more detailed treatment of atmospheric stability in the final report. Staff has requested additional data from NASA on skin temperature of the Lake surface for comparison with the water temperature measured at a depth of 2 cm. Staff also plans to estimate differences in temperature between the surface water temperature and the air temperature directly above the water based on an energy balance approach. Because the skin temperature data requires labor-intensive processing, it is unlikely that those data will be available before the final report is due. Staff has access to some limited eddy covariance data that may be helpful for the purpose of comparing estimates of fluxes provided by the current approach and the more detailed energy balance modeling. If completed in time, this work would be incorporated into the final report.*

Regarding the appropriate extent of the log wind profile assumption, the value of Z_0 is sufficiently small over open water (on the order of 0.0001 m) that the assumption is reasonable at heights below the height of the wind and air quality measurements. Likewise with onshore flow, the value of Z_0 is small near the shore where wind measurements are made on the piers. However, this is not the case during periods of offshore flow. For those conditions, staff adopted a larger value of Z_0 to represent advection of turbulence from land to water. With that assumption and the assumption that deposition velocity is $1/Ra$ (i.e., that $R_b = 0$ and $R_c = 0$), the resulting deposition velocity estimates are excessive and are arbitrarily capped at 6 cm/s based on literature values for another reactive soluble gas (SO_2). Thus, during offshore flow the actual values of Z_0 near shore are not used directly in calculation of the deposition velocity, but they do cause the capping value of 6 cm/s to be invoked.

Comment: 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.

Response: *Thank you for the reference. Staff will obtain and review the paper by Giorgi and compare calculations for smooth and rough surfaces to quantify the effect that the implicit assumption of smooth surfaces has on the estimate of deposition rates. As you suggest may be the case, staff expects that the effect will be minor on the estimates of deposition rates.*

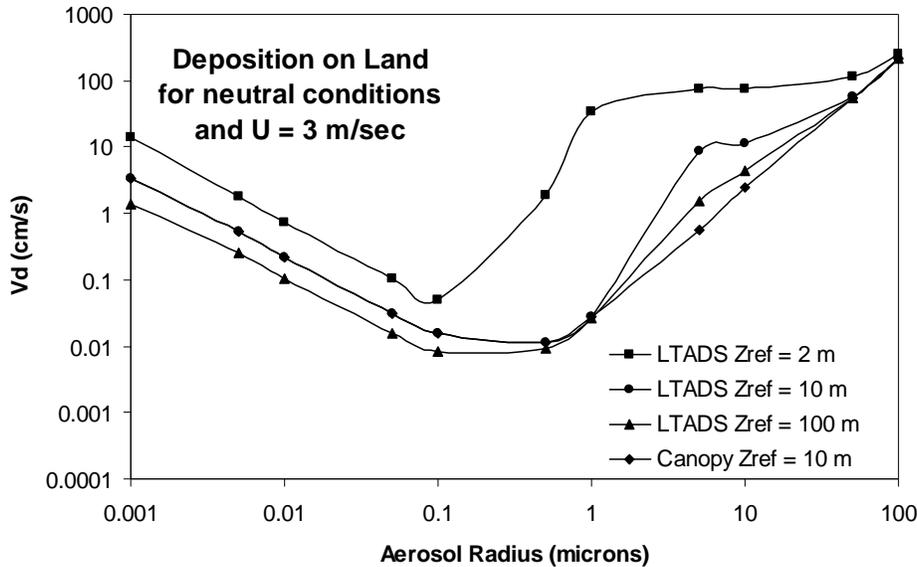
Comment: Deposition of aerosols on water surfaces is particularly problematic, primarily because many of the assumptions underlying theories for transport to a solid fixed surface do not hold at a water surface, which can move in response to stress and which can fragment into droplets of spray. It is 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.



Response: *With inclusion of the depositional effects of spray and broken surfaces, the estimate of deposition to the Lake surface could increase. Staff expects this effect to be small based on generally low wind speeds and the work of Sarah Pryor; however, staff intends to quantify the potential effects in the final report. Staff will investigate differences in deposition estimates using smooth surface and rough surface formulations and provide a comparison of results in the final report.*

Comment: 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.



Response: *The first point is important especially for patchy vegetation where bluff surfaces are presented to the wind flow and the standard formulations would likely significantly underestimate the rate of deposition to surfaces under those conditions. However, we do not expect this to be a major issue over open waters of Lake Tahoe. The second point has two aspects, calculation of Z_o and inertial impaction near shore and use of U and U^* at 10 m. The application of the bulk coefficient method was intended only for comparison with results using the log wind profile with stability corrections but the methods were inadvertently mixed due to an error in coding. Calculation of wind speed at 10 m was intended for consistency with the formulation for calculation of the bulk coefficient for momentum flux. The code is being corrected to calculate Z_o , U_{star} , and Ra using the log wind profile and stability functions based on the observed air-water temperature differences. Those results will be incorporated in the final deposition calculations. The deposition velocity will be calculated for heights consistent with the measurement height for concentration. It may also be that it will be appropriate to estimate values of aerodynamic resistance for a range of heights for which the observed concentration may be considered representative. This would be a means to consider the sensitivity of aerodynamic resistance to the assumed representativeness of concentration observations. These questions will be addressed in the final report.*

Comment: I have a number of questions about the actual code used in computing deposition and have already communicated these..., 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 $u_{10} = u_Z * [\log(10/Z_o) + \Phi_M] / [\log(z/Z_{oInitial}) + \Phi_M]$. My question is why the use of $Z_{oInitial}$ rather than the values calculated earlier for land and water?

Response: *Thank you for catching this error in the computer program used to calculate deposition. The mistake will be corrected in future calculations. This programming error also led to your comment below. The revised code will calculate deposition rates based on the U_{star} from the log wind law and those results will be compared with estimates calculated using the bulk coefficient method.*

- 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.

Response: *The original intent was to also calculate U_{star} with the bulk coefficient formula and enable comparison of that U_{star} estimate with the log law estimate for quality assurance purposes. Calculations using the bulk coefficient method will be replaced with calculations based solely upon the log wind profile and stability correction functions in time for the final report. Revisions should have small effects on the estimated deposition.*

Summary of the Major Comments Received from Professor Akula Venkatram with CARB Staff Responses

Comment: 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.

Response: *Thank you for your reminder of the most appropriate formulation for calculation of deposition velocities of aerosols (i.e., one that includes the fundamental constraint of conservation of mass). As you showed, the formulation that staff used, and that previously has been widely accepted and is commonly applied in air quality models (e.g., CALPUFF), violates mass conservation. Staff agrees that it is important to use the best formulation of deposition velocity, not only for accuracy but also for the credibility of the LTADS findings and the TMDL process. Staff will run the deposition model with the updated formulation in Equation (1) and will compare those results with results from the traditional formulation used in the first draft. It is anticipated that any differences observed between the results of the two formulations will be for a limited range of particle size and will likely have only minor impact on the overall deposition results and conclusions. In addition, staff will add equation numbers in the final report to facilitate cross-referencing.*

Comment: 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.

Response: *Staff agrees that the values of wind speed and friction velocity utilized for calculation of the aerodynamic resistance (based on similarity to turbulent transport of*

momentum) should be representative of the height of the concentration measurements. For most LTADS sites, the TWS sampled concentrations at 2 m agl. At Sandy Way, the TWS sampled at 2 m above the shelter roof. Staff will minimize, to the extent possible, mismatches between the concentration measurement heights and heights at which aerodynamic resistance, r_a , is estimated. Staff calculated aerodynamic resistance by using observed wind speed and assuming a log wind profile with stability corrections to then calculate friction velocity and wind speed at a reference height. Staff will compare those primary estimates of aerodynamic resistance with values estimated by bulk coefficient method. The former (log-profile) method can be used to make estimates at heights for which the observed concentrations are deemed representative. Staff's understanding is that the alternative calculation method (based upon a bulk coefficient formulation) was designed for use with winds observed at 10 m. Thus, in applying that method, staff made an implicit assumption that the concentrations measured over land at 2 m are reasonably representative (or at least do not seriously underestimate) concentrations over the Lake at 10 m.

Comment: The authors claim that $r_a > r_b$ 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.

Response: *Staff's assumption that $r_a \gg r_b$ for deposition of gases over water, is supported by added references to Valigura (1995) and Pryor (2000). Calculation of V_d as $1/r_a$, instead of as $1/(r_a + r_b)$, is thus only slightly conservative as an estimate for the deposition velocity of the gases (i.e., NH_3 and HNO_3). Staff's statement regarding the relative importance of wind speed versus air-water temperature difference for determining r_a is meaningful within the context of the observed ranges of wind speeds and air-water temperature differences during LTADS. Because the statement was not essential to the LTADS results or conclusions, as time allows, this point may be either expanded and supported by further discussion of the observations or merely deleted from the final report.*

Comment: 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.

Response: *A clarification to the text has been provided to indicate that the formulation used for calculation of L is recommended for use with air and water temperature observations. The formulation has previously been applied (in CALMET) with observed air and water temperatures for calculation of momentum flux over water. The observational data used in LTADS were air temperature measured above the piers and water temperature measured at a depth of 2 cm.*

Staff agrees that the subsurface (2-cm) water temperature will differ from the water skin temperature. However, differences between skin and 2-cm depth temperatures are observed to be very small except during periods of calm or very low speed winds coinciding with strongly positive or negative net radiation. During daylight periods having a positive net radiation balance at the surface (and typically characterized by upslope or onshore flow) the surface temperature and thermally induced mixing may be slightly higher than estimated from observed water temperature at 2 cm depth. Conversely, during periods of negative net radiation (typically characterized by drainage and offshore flow) the skin temperature and thermally induced atmospheric mixing will be slightly lower than estimated with the temperature at 2 cm depth. Staff also agrees that the water skin temperature may differ from the air temperature at the air-water interface. However, these differences are small and the effect on calculation of annual average deposition is expected to be very small.

If skin temperature or air temperature at the air-water interface were continuously measured or modeled there could be a potential for improved treatment of atmospheric stability. However, observations are not available for direct use or for model testing. In the absence of such observations, staff thinks that the temperatures measured at 2 cm depth and the formulation provided are reasonable for estimation of L.

Staff appreciates the reference to the model of Valigura (1995) and notes that it provides the theoretical framework for calculation of heat flux but notes further that Valigura reported results were inconclusive due to discrepancies between observations and model output. After consideration of the difficulties reported, limitations in observational data for model confirmation within LTADS, and limitations in available time and resources, staff elected not to pursue a surface energy balance modeling approach for estimation of stability.

Although the assumption of similarity between turbulent transport of heat and chemical species is a good approach for estimation of r_a , staff is not aware of empirical evidence that it is necessarily more accurate for estimation of turbulent transport of chemical species than the assumption of similarity with the turbulent transport of momentum. Furthermore, heat flux may be more difficult than momentum flux to estimate from the measurements available to LTADS. Data to support estimation of heat flux are limited, for example, there is limited information on the type and height of cloud cover. Observational data to validate estimation of heat flux at Lake Tahoe are very limited spatially and temporally and do not overlap the LTADS monitoring period. Similarly, although desirable for validation of such modeling, measurements of air temperature at the air-water interface are not available to LTADS. Some satellite-based radiometric measurements of water skin temperature were sought from NASA scientists but turned out to generally not be available due to the labor-intensive requirements for processing of the raw observations. Modeling estimates of either momentum flux or heat flux could potentially be validated against direct measurements by the eddy covariance (E-C) method. Some E-C data exist for one Lake site and could potentially be used subject to quality assurance and analysis.

Although selection of the most appropriate analog for estimating turbulent transport of chemical species is of research interest, staff expects that the uncertainties associated with that choice is overshadowed by uncertainty in ambient concentrations and their spatial variability.

Although the location of the near-surface air temperature measurement or its estimation may be a source of bias, staff's understanding is that the formula for L that was applied here is intended for use with water temperature.

Staff will clarify in the final report that the data used for calculation of thermal stability of the atmosphere were water temperature measured at 2 cm depth and air temperature measured approximately 6 meters above the water surface with instruments on piers (or 3 m on buoys). The explicit assumption was made that the measured water temperature adequately approximates the air temperature near the water surface. Staff agrees that this is a source of uncertainty or bias and that near surface air temperature might be better approximated by modeling based on an energy balance. Staff will include a discussion of the potential biases introduced by using the 2-cm water temperature as a surrogate for air temperature near the water surface.

Comment: 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.

Response: *Typos and coding will be corrected to accurately represent the intended calculations. Our intention was to calculate aerodynamic resistance using two methods (both based upon estimation of momentum flux) and compare the results. These methods were the bulk coefficient method utilized in CALMET for calculation of momentum flux over water and a standard formulation for momentum flux based upon a log wind profile with stability corrections. However, there was a coding error in the calculations for the draft report and the calculations were inadvertently made as a composite of the two methods. The code will be corrected and rerun and revised results will be included in the final report. Use of the bulk coefficient method was intended merely for a point of comparison with estimates of R_a based upon calculation of friction velocity assuming a logarithmic wind profile. The bulk coefficient method*

used in CALMET is specified as applicable for use with 10 m winds. The corrections will affect the calculation of friction velocity (U_{star}) and differences in heights used for wind speed inputs to the bulk coefficient and the log profile methods. Based on preliminary calculations, staff expects the revision to have only a minor impact on the estimated deposition rates. The treatment of the stability parameter L will be clarified and any corrections made as necessary.

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

Response: Additional discussion will be provided on the conditions under which J. Sun observed evidence of air turbulence, generated by the surface roughness over land, being advected over coastal waters.

Comment: 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.

Response: Additional references in the peer-reviewed literature will be provided to supplement the Scire et al. (2000) reference and to reduce the need to report programming codes.

Comment: 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.

Response: Staff concurs that direct deposition measurements would have helped to provide a solid foundation for the deposition estimates by indicating the appropriateness of the assumptions used in the analyses. Unfortunately, the funding and staffing resources for doing so were not available for LTADS. Staff conducted a few experiments (e.g., dust experiments) to enable some assessments of the micro-scale variations. More details about atmospheric processes and parameters that affect the deposition estimates will be provided in the final report.

Summary of the Major Comments Received from Professor Anthony Wexler with CARB Staff Responses

Comment: 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.

Response: *Total ammonium was calculated by adding the ammonium measured by the Two-Week-Sampler (TWS) to the estimated ammonium associated with the volatilized nitrate measured on the nylon backup filter by the TWS. The assumption is that the volatilized nitrate originated from volatilized ammonium-nitrate (NH_4NO_3) particles. The molar equivalency equates to a mass ratio of 18:63 and 17:63, when assuming that all of the NH_4 originated from NH_3 . This calculation will be explained in more detail in the final report.*

Comment: 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.

Response: *Staff agrees that the ammonia data appear more reliable than the nitric acid data and that equilibrium theory could help refine the nitric acid data. Although staff has not had time to perform a detailed comprehensive analysis, it appears that substantial concentrations of ammonium sulfate would impact the equilibrium theory and would require additional refinements that staff cannot conduct within the present schedule for delivery of deposition estimates and reports.*

Comment: Section 3.3.1, page 23, paragraph 2: if no phosphorus was detected in PM2.5 doesn't this lend support to the later contention that wood smoke is not a significant source?

Response: *The absence of P detections in fine particulate matter lends some circumstantial support to the hypothesis that wood smoke is not a significant source of P. However, the limited mass and the ubiquitous presence of silicon and sulfur in the ambient samples, would likely cause any P present in the sample to be reported as Si or S by the XRF method. It is interesting to note that the majority of the phosphorus detects during LTADS were in the buoy samples. Although it is possible that the Lake itself is the source of the P or that transported P is mixed down to the lake surface (not likely because most of the detects did not occur during summer when transport is more likely), the most likely explanation is that the abundant Si and S particles observed in*

on-shore measurements, often deposit before reaching the buoys and thus do not interfere with the P measurement on the buoy samples. In this case, the P data from the buoys probably represent a minimum concentration present in the Tahoe Basin because it primarily represents fine particulate matter.

Comment: 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.

Response: *Staff concurs and will follow the advice.*

Comment: 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.

Response: *Staff concurs and will incorporate the more appropriate formulation in the deposition calculations for the final report.*

Comment: 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.

Response: *As noted elsewhere, the staff believes that the direct atmospheric deposition to Lake Tahoe greatly exceeds the indirect atmospheric deposition. The final report will include more discussion of the assumptions and justifications associated with the analyses of atmospheric deposition to Lake Tahoe.*

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

Response: *Staff will provide improved documentation in the final report.*

Comment: 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.

Response: *Staff concurs and will extensively revise, expand, and reorganize this chapter.*

Comment: 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.

Response: *Staff will include a more comprehensive discussion of the volatility of particulate matter and the equilibrium of some particles with gaseous constituents.*

Comment: 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.

Response: *Staff concurs and will provide seasonal as well as annual deposition estimates.*

Comment: 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.

Response: *Staff concurs and will revise discussion and elaborate further in the final report.*

References

Pryor S.C. and Sorensen L.L. (2000), "Nitric acid-sea salt reactions: Implications for nitrogen deposition to water surfaces," *Journal of Applied Meteorology*, **39** No. 5, 725-731.

Valigura, R.A. (1995), "Iterative bulk exchange model for estimating air-water transfer of HNO₃" *Journal of Geophysical Research Atmosphere*, **100**, 26045-26050.