

6. Discussion

6.1 Comparison of LTADS Deposition Estimates with Previous Estimates

Estimates of deposition to Lake Tahoe based upon a variety of methods have been published. These methods include measuring quantities of N and P containing compounds collected on surrogate surfaces, observed ambient concentrations combined with literature values of deposition velocity, and finally modeling of ambient concentrations and deposition utilizing estimates of emissions, boundary conditions, and meteorological conditions. This chapter presents available historical analyses and compares their results with the preliminary LTADS estimates of dry deposition.

6.1.1 Historical Surrogate Surface Measurements

Deposition in the Tahoe Basin has historically been observed at land sites using snow tubes and wet/dry bucket samplers with automated covers. The deposition samplers used in Tahoe are modifications of the sampler employed in the National Acid Deposition Program (NADP). Mid-lake measurements (on buoys) are made during the precipitation months with a tube having a smaller diameter than the wet/dry deposition buckets and having pointed vertical protrusions around the mouth (to prevent birds from perching). During the dry season, the snow tube for collecting bulk deposition is replaced by a buoy dry deposition bucket (the same as the traditional bucket but shorter). The sampling protocol followed at Tahoe for water year 1989 and later changed from the NADP method in that distilled water is now added to the dry deposition buckets to increase retention of particles and to better simulate deposition to a water surface. With this change in procedure, the measured annual rate of dry deposition increased by a factor of 3 to 4, depending on the chemical species and year; the enhancement was greater for NH_4^+ than for NO_3^- and soluble reactive phosphorus (SRP). Because ammonia (NH_3) is soluble in water, its concentrations are likely deposited on water and surfaces with substantial water content such as leaves and needles. Ammonia is also relatively abundant in the atmosphere. Dry dep buckets are less likely than the water column or surfaces with water content to adequately capture available significant ambient concentrations of ammonia. The standard dry dep bucket method thus likely underestimates deposition of ammonia to the Lake.

Additional modifications to the traditional deposition sampling protocol were made to accommodate the unique sampling conditions in the Tahoe Basin. For example, the buoy bucket also includes baffling to prevent loss of water during periods of wave action. In addition, the on-shore "dry" buckets now also include a heater during the winter months to prevent freezing of the distilled water collection surface.

Because these surrogate surface methods, adapted for conditions at Tahoe, provide a rich record for analysis of trends, it is anticipated that these surrogate surfaces will likely continue to be employed in the Tahoe Basin. However, the limitations and problems of measuring deposition using multiple surrogate surfaces and methods raise some

concerns about quantitative use of these historical data. A primary concern with the use of deposition buckets in general is the effect of turbulence induced by air flowing over the bucket and sampling structure. Another concern is having water in the dry dep bucket (good from a deposition to lake perspective) and its effect on the retention of particles and on attracting insects and birds.

6.1.2 Interpretation of Surrogate Surface Observations

Using the surrogate surfaces described above, Jassby et al. (1994) reported measurements of wet and dry deposition during the period of 1983-1992. Their important and widely referenced conclusions were that atmospheric deposition likely provides over half of the dissolved inorganic nitrogen and total nitrogen inputs to Lake Tahoe and that atmospheric deposition probably contributes significant loading of soluble reactive phosphorus and total phosphorus to the Lake. They note that the observed shift in the lake's phytoplankton production from co-limitation by N and P to persistent P limitation would be consistent with these conclusions. They suggested that this shift may be the result of a slow, decadal change in the relative sizes of the Lake's N and P reservoirs and hypothesize that the change may have been caused by the relatively greater atmospheric deposition of N than of P.

The validity of the estimates depends upon whether the surrogate surfaces are adequate to quantify deposition to natural surfaces. Additional investigation is motivated by the obvious importance and far-reaching implications of the conclusions by Jassby et al. (1994) with respect to lake clarity and by ambiguity regarding the relationship between observed rates of deposition on various surrogate surfaces and deposition to the surface of the Lake.

As part of LTADS, CARB staff collocated various surrogate surface samplers in an attempt to determine relationships among four dry deposition sampling methods: standard NADP dry bucket, TRG-modified dry bucket with water, TRG-bulk tube sampler, and a water surface sampler with an aerodynamic shape. Sampling difficulties limited the number of sample sets to less than 20 and shipping and handling problems further reduced the number of valid samples. Final results from the methods comparison experiment, which are not likely to be definitive because of the low number of samples, will be reported in the LTADS final report.

6.1.3 Deposition Rates Inferred from Concentrations

Tarnay *et al.* (2001) inferred deposition rates from preliminary measurements of gaseous and aerosol N concentrations made during the dry summer season. They concluded that dry deposition of HNO_3 is the dominant source of N deposition to the Lake surface but dry deposition of NH_3 may also be important.

Tarnay *et al.* (2001) estimated dry deposition of N to the lake surface during the dry seasons (July-September) of 1997 and 1998. They estimated dry deposition of N in the amount of 30-61 MT-N in the form of HNO_3 (27-34 MT-N), NH_3 (2.9-22 MT-N), and

NH_4NO_3 (0.1–4.9 MT-N). They note that this is a rate of 1.2 to 8.6 kg N/ha for the July-September season and that this is comparable to the annual wet deposition (1.7 to 2.9 kg N/ha) that was reported by Jassby *et al.* (1994).

6.1.4 Modeling Estimates of Deposition to Lake Tahoe

Air quality modeling by Koracin *et al.* (2003) also suggests that local sources of NO_y are important contributors to ambient HNO_3 concentrations and deposition. However, citing limitations in the meteorological data available for model inputs, they recommended additional investigation to confirm this conclusion. Other model inputs may also be a concern, such as boundary conditions and emissions estimates.

A cursory review of the N deposition in the above table indicates a wide variety of estimates regarding N deposition to Lake Tahoe. As noted in Chapter 3, ambient concentration data for nitrogen species are consistent with previous record of nitrogen species measurements at Tahoe. The LTADS deposition estimates for nitrogen species are comparable to previous estimates based on shoreline measurements at the Wallis Residence and, as anticipated, higher than the buoy-based estimates. As noted earlier in this chapter, standard dry deposition measurement methods may underestimate ammonium due to the solubility of ammonia. As noted in Chapter 3, gaseous nitrogen denuder measurements often have high blank values and positive artifacts. Thus, the LTADS nitrogen species deposition estimates agreement with the surrogate surface deposition measurements may be fortuitous.

Table 6-1 indicates that previous P deposition estimates are generally higher than estimated from LTADS. As noted previously, difficulties face every measurement system attempting to measure atmospheric P concentrations above method uncertainty. These difficulties are accentuated because nearly all ambient P concentrations at Tahoe are likely in the O-LOD range of 10 to 15 ng/m^3 . Thus, the range of P deposition estimates from LTADS (assuming average P concentrations throughout the Basin are between 10 and 40 ng/m^3 ; 10 ng/m^3 being the effective detection limit and 40 ng/m^3 being the maximum observed anywhere during LTADS) is very comprehensive. The LTADS range of P deposition estimates is comparable to the range of deposition estimates provided by historical and recent deposition measurements and estimates. However, as noted in Chapter 3, the assumed peak concentration of 40 ng/m^3 is slightly higher than the highest ever observed at Tahoe and definitely represents an extreme upper limit for all sites in the basin during all times of the year. Therefore, the highest deposition estimates provided are purely for bounding purposes and CARB's best estimate of P deposition is much closer to the lower bound than the upper bound.

**Table 6-1. Estimates of Annual Direct Atmospheric Deposition to Lake Tahoe
(metric tons/year)**

Data Source *	Nitrogen			Phosphorus			Particulate Matter		
	Dry	Wet	TOT	Dry	Wet	TOT	Dry	Wet	TOT
ARB (LTADS 2004)	160 (110-230)			1 (0.7-6)			1300 (850-1800)		
ARB (EI 2003)**			148			3.4			2636
TRG 4-site (1982)			55			4.8			
TRG 3-site (1982)	26	36	62	2.7	2.3	5.0			
mean corrected	90	36	127	8.6	2.3	10.9			
slope corrected	75	36	112	10.5	2.3	12.9			
TRG 3-site (1983-1984)	17	44	61	3.8	2.4	6.2			
TRG (1989-91)			234	8.7	3.7	12.4 (12-13)			
TRG (1989-91) dry 2-buoys	59								
TRG (1989-91;WLL-upper bound)				11.7 (11-12)	5.1 (4-6)	16.8 (15-18)			
Liu Wallis (2000)				35.1					
DRI (2000) – over-water turbulence = on-shore turbulence			238 (183-293)						
DRI (2000) – wind speed			49 (37-62)						
Liu 7-site (2000)				40.0					
Tarnay (2001)			(117-240)						
TRG (4-buoy 2002-2003)	102								
TRG Wallis (2003)		54	215	23.0	0.7 ⁺	23.7			
TRG 2-buoy (2003)						6.0			
TRG 4-buoy (summer 2003)	200		316	8.0 (5-11)	0.2 ⁺⁺ (0-1)	8.2 (5-12)			
Cahill (2004)						(7.4-13.7)			

* all data except, ARB data, are from informal summary by Reuter *et al.*, 2004. Units were converted to metric tons per year.

** emission inventory estimate is only for California portion of the Tahoe Air Basin.

+ assumes 55 days with precipitation during year.

++ assumes 6 days with precipitation during summer.

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Table 6.1 indicates that previous P deposition estimates are generally higher than estimated from LTADS. As noted previously, difficulties face every measurement system attempting to measure atmospheric P concentrations above method uncertainty. These difficulties are accentuated because nearly all ambient P concentrations at Tahoe are likely in the O-LOD range of 10 to 15 ng/m³. Thus, the range of P deposition estimates from LTADS (assuming average P concentrations throughout the Basin are between 10 and 40 ng/m³; 10 ng/m³ being the effective detection limit and 40 ng/m³ being the maximum observed anywhere during LTADS) is very comprehensive. The LTADS range of P deposition estimates is comparable to the range of deposition estimates provided by historical and recent deposition measurements and estimates. However, as noted in Chapter 3, the assumed peak concentration of 40 ng/m³ is slightly higher than the highest ever observed at Tahoe and definitely represents an extreme average for all sites in the basin during all times of the year. Therefore, the highest deposition estimates provided are purely for bounding purposes and CARB's best estimate of P deposition is much closer to the lower bound than the upper bound.

6.2 Implications of Higher Phosphorus at Buoys

What are implications of "seeing" more P at buoys than at piers/shoreline? These samples were collected over 30 hours at a 5 liters per minute (lpm) flow rate. Furthermore, the P detects at the buoys occurred primarily during the winter and spring on about 25% of the samples. Samples forwarded to ALS may shed more light confirming or altering these and other P detection above uncertainty data. We provide four alternative explanations for this phenomenon, but we note insufficient information to prefer one alternative to the next.

Volatilization of P associated with organic materials – As noted earlier, the TWS, and to a lesser extent MVS, samplers lose organic materials due to volatilization. The lengthy measurement period provides a wide window of opportunity for volatilization to occur. It is possible that P associated with combustion processes may leave the TWS and MVS filter pack. Buoy measurements, which are based on shorter sampling times, may have far less loss of material via volatilization. The extent of volatilization, likely to dominate during Summer months, during Winter and Spring is a subject of further study.

Greater accumulation during extended hours of offshore flow - During the absence of storms in the winter, cold air drainage off the mountain slopes to the Lake would occur for about 16 hours per day. This drainage flow would carry road dust and wood smoke with it over the Lake. During stagnant periods, the net flow of air would be onto the Lake. Each evening, fresh input of smoke and dust would add to the pollutant burden in the air over the Lake. If the buoy samples happen to be taken on a day following several stagnant days (featuring offshore flows during many hours of darkness and weak onshore flows during relatively few hours of daylight), they would detect a sample enriched in fine soils, potassium, and P.

Down-mixing of transported air aloft - Any particles that might be transported to the Tahoe Basin in the surface layer of air would necessarily be in the fine size fraction (would have deposited before reaching the Lake otherwise). Particles transported in the free troposphere above surface effects could include larger particles. With the water temperature relatively warmer than the air temperature and the convergence of drainage air over the Lake, vertical mixing would be induced over the Lake. If the air aloft were enriched in P relative to Tahoe air (e.g., Asian dust) and if the vertical mixing were sufficiently deep to tap into any enriched transported air, then the buoys might detect higher P concentrations than the shoreline sites.

Less soil (silicon) in buoy samples - Soil is rich in Si and Si tends to be in larger particle sizes. Because large particles would tend to deposit before arriving at the buoy sampling sites, the buoy samples would tend to have proportionately more fine smoke particles and fewer large soil particles. Because Si is an abundant element in soil and because the XRF analytical method for measuring elements receives a strong signal from Si that overlaps with the P signal, the P signal from the on- and near-shore samples is frequently overwhelmed by the Si signal. Because there is less soil (Si) in the air at the buoys, the buoys are able to detect the P more readily.

As we noted earlier, there is currently insufficient information to prefer any alternative over another in explaining the six high P buoy detects during LTADS.

6.3 Recommendations for Additional Refinement

Additional efforts beyond the scope of LTADS may be warranted to improve estimates of atmospheric deposition in the Tahoe Basin depending upon the relative importance of atmospheric deposition compared to other avenues of nutrient input to the Lake. Potential additional efforts, which are discussed in this section, include refinements to the deposition estimation methodology used by CARB staff and improvements in phosphorus measurement techniques. When adequate funding is available, the greater scientific community (including instrumentation, monitoring, and laboratory groups) should work with local groups (e.g., Lake Tahoe Scientific Advisory Group, Lake Tahoe Federal Advisory Committee, TRPA's Air Quality Working Group) to address the research recommendations.

6.3.1 Refinements to Deposition Estimates

By not fully accounting for the depletion of material with distance from the shoreline, LTADS estimates of atmospheric deposition might be positively biased. In other words, the assumption of constant concentrations over the surface of the Lake is unreasonable if deposition is occurring. This simplification implies that the transport or emission of pollutants replenishes the atmosphere as fast as material deposits out of the atmosphere. This “steady-state” assumption might be reasonable when ambient concentrations are near background levels but is not likely to be true for large particles above the Lake. Because the large particles tend to have high deposition rates and to contribute most to the total mass being deposited, this simplifying assumption will overestimate the amount of deposition occurring.

This is particularly true in the central portion of the Lake where emission sources are limited and replenishment of the larger particles that have deposited is unlikely. The impact on the current estimate however is moderated by use of an over-water roughness approach for most of the lake surface and by relatively good mixing over the Lake due to the relatively warmer water temperature compared to air temperature during many hours of the year.

Recommendation: Incorporate a parameter in the deposition model that accounts for the deposition of particles, especially PM_{large}, without replenishment. In the next upgrade to deposition estimates, incorporation of a concentration depletion parameter is recommended.

6.3.2 Improve understanding and characterization of atmospheric processes.

An upper air network for characterizing synoptic and meso-scale meteorological processes was established during LTADS. This effort consisted of Radar Wind Profilers with Radio Acoustic Sounding Systems (RWP/RASS) for determining the vertical profiles of winds and temperatures outside and within the Tahoe Basin. These data need to be further analyzed to document the depth and frequency of mixing over Lake Tahoe and the potential for mixing potentially polluted air aloft into the air mass over the Lake.

During LTADS, CARB also established a network of mini-sodars for characterizing the frequency, duration, direction, and, most importantly, the depth of the diurnally varying slope flows toward and from the Lake. These data need to be analyzed in context with the RWP/RASS data to document the scale of mixing and air circulation cells over Lake Tahoe. For example, the well-documented up-slope/down-slope flows associated with heating during the day and cooling during the night need to be summarized for the development of conceptual air flow patterns and for evaluating the performance of meteorological models. The thickness (depth) of the surface air flows will have a significant impact on the scale of air circulation patterns in the Basin and the resultant air quality and deposition values.

Recommendation: Thoroughly review the meteorological data for conditions aloft and the associated surface conditions. Future deposition estimates should incorporate the results of the atmospheric processes aloft.

Recommendation: Investigate whether the current state-of-the-art meteorological models are capable of replicating the complex meteorological conditions within the Tahoe Basin. Future deposition estimates should incorporate an analysis and recommendation on meteorological models appropriate for the Lake Tahoe Air Basin.

6.3.3 Perform additional validation of LTADS data

The administrative timeline for providing annual atmospheric deposition estimates precluded detailed validation of the air quality and meteorological data collected during LTADS. Data were essentially screened to minimize the occurrence of physically unreasonable data. Level_II data validation efforts are needed to ensure that the data are consistent with other measurements taken at the same monitoring site. Level_II validation procedures are particularly appropriate for BAM and TWS data collected in multiple size fractions. For example, internal consistency problems are known to exist with the Lake Forest BAM data, particularly in the spring. Given the spatial and temporal complexity of the emissions and meteorological processes in the Tahoe Basin, a Level_III validation effort, where data are reviewed for consistency with regional processes, is recommended only for selected periods of particular interest.

Recommendation: Thoroughly review the air quality and meteorological data (with priority on BAM and TWS measurements) for internal and regional consistency. Future deposition estimates should incorporate high quality input data.

6.3.4 Improve the estimation of deposition velocities.

The initial analysis of atmospheric deposition reported here assumed that the deposition velocity for gases was determined solely by the aerodynamic resistance (i.e., the diffusivity resistance across the thin layer of air above the water's surface is 0). For our primary gases of interest (HNO_3 and NH_3), this is a reasonable assumption. Although the deposition velocity becomes very large when the aerodynamic resistance is small ($V_d = 1/R_a$), the net impact is relatively small as indicated by our upper bound estimates compared to our best estimate where the maximum hourly deposition velocity is capped at 6 cm/sec. However, a more precise estimate could be made with the incorporation of the boundary layer resistance and a term incorporating the effects of humidity and spray from waves.

Recommendation: Incorporate "minor terms" (e.g., R_b , humidity, spray from interaction of wind and waves) in the calculation of deposition velocities to derive more precise estimates of the atmospheric deposition.

6.3.5 Improve the estimation of the concentrations for the conceptual model.

A conceptual model of seasonal concentrations was developed based on ambient concentrations. A conceptual model of concentrations was used rather than actual ambient concentrations because data from some sites were incomplete or had data quality issues. By using seasonal averages, the impact of questionable or missing data was minimized.

Recommendation: After Level_II validation of the BAM and TWS data has occurred, recreate the conceptual model of seasonal concentrations and compare with the current conceptual model based on the initial screening of the data. If appropriate, future estimates should recreate the conceptual model. The next would be to incorporate the refined conceptual model of seasonal concentrations into the deposition model, revise the deposition estimates, and compare with the earlier results.

Recommendation: Apply the CalMet and CalPuff models for the air over Lake Tahoe to independently assess the results. If the meteorological processes can be properly represented, concentrations measured on the shorelines could be used as boundary condition inputs to the model and the deposition to the Lake estimated by the model. Future deposition estimates, if given sufficient resources, should incorporate an independent assessment of meteorological processes.

6.4 Recommendations for Additional Research

Additional scientific research will likely be needed to address some outstanding issues. Given the relatively clean air quality in the Tahoe Basin with respect to health-based ambient air quality standards, these research needs are not a high priority during the current period of limited resources.

6.4.1 Improve the detection of phosphorus (P)

The accurate detection of P in the Tahoe basin is complicated by at least 3 factors:

- a) the low P concentrations associated with the relatively clean air in the Basin,
- b) the low source strengths of wood smoke and road dust for P (i.e., P is a low percentage of the total emissions), and
- c) the difficulty of detecting a small P signal from much larger overlapping Si and S signals.

Recommendation: Collect larger PM samples - Although the frequency of P detects during LTADS was comparable to the historical frequency observed with the long-term IMPROVE sampling program at Lake Tahoe, a sampling program dedicated to P measurements is appropriate. Such a program should feature high volume samplers that can collect a large amount of material. The samplers should operate on a 24-hour basis to provide information on the short-term variability of concentrations and to minimize the frequency of filters becoming overloaded with material.

In addition to the typical difficulty in siting monitoring equipment to collect representative samples, the high-volume (hi-vol) type of sampler tends to generate significantly more noise and would impose an additional constraint on siting. The Xontec 950 sampler

used in ARB's toxic monitoring program is also a potential option because of its high sampling volume and the possibility of using existing equipment and sample analysis protocols in the toxics sampling program. However, larger sample volumes do not necessarily guarantee more frequent detection of P. Even the concentrated samples of smoke and road dust sources collected during LTADS failed to consistently detect significant amounts of P.

Recommendation: Improve chemical analysis procedures - Improved sample analysis methods are needed to increase the confidence of the P measurements. Multiple efforts were undertaken during LTADS (e.g., higher intensity XRF beams, synchrotron XRF with advanced signal processing) but more radical approaches should be considered (e.g., processing of samples to selectively remove S and, if possible, Si).

6.4.2 Additional chemical analyses of road dust, prescribed fires, and, as safe and feasible, wild fires.

A limited number of source samples were collected during LTADS but the results were not always self-consistent or unambiguous. Additional samples and analyses are needed to provide more confidence in the emission profiles of these sources. LTADS wood smoke chemical speciation results for P were similar to previous analyses in other areas. Thus, residential wood-burning does not appear to be the dominant source of P in ambient measurements. Furthermore, the limited road dust experiments indicate a small contribution to ambient P concentrations. Limited measurements in recent years however, indicate that P emissions are higher with the burning of live or recently cut vegetation.

Recommendation: Collect more samples of prescribed and wild fires and analyze to confirm the higher percentage of P emissions from these sources. Using mini-volume, or other easy to deploy, samplers equipped with denuders and backup filters would help generate a more detailed and consistent database.

6.4.3 Identification of additional sources of phosphorus.

LTADS design assumed that the primary form of P would be as PO_4^- . However, recent literature indicates that reduced forms of P (e.g., phosphine, PH_3) are present in anaerobic environments such as wastewater treatment facilities and water-saturated soils. However, the phosphine emissions likely react relatively rapidly in most environments to become PO_4^- .

Recommendation: Conduct sampling and analysis in areas that are oxygen-deprived at times to estimate the potential magnitude of atmospheric concentrations of phosphine.

Another potential source of P is wildlife. The year-round Canadian Geese population of the Tahoe Basin is rumored to have increased in recent years. Because they live on and near the Lake, P in their excrement could have direct impact on nutrients in the

Lake. A back-of-the-envelope assessment indicates that this source of P is very small (~100 pounds/year) but the assessment was based on many assumptions.

Recommendation: Research/collect information on the number of geese and other waterfowl that reside on/near the Lake, the number of waterfowl that migrate to the Lake & the duration of their visit, as well as the frequency, density, and P content of their droppings.

Another potential source of P is pollen from plants and trees. In particular, pine pollen is known to cover the lake in late spring and early summer.

Recommendation: Determine the P content of pollen and its solubility to address the potential magnitude and impact of this biological source.

6.4.4 Improve characterization of biases between the different deposition sampling methods historically used in the Tahoe Basin.

Although LTADS included a small component to investigate potential deposition measurement differences due to differences in sampler design and operation, the effort was less than successful due to sampling and handling difficulties. More research is needed to identify the processes at work and to quantify the methodological differences.

Recommendation: Conduct a side-by-side comparison of the different deposition sampling methods used in the Tahoe Basin.

Recommendation: Include, as part of the methods comparison, a water surface sampler (similar to the Holsen design) that uses water to better represent deposition to a water surface but also has a streamlined aerodynamic design to minimize the effect of eddies around the deposition surface.

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