

### 3. Atmospheric Concentrations

This section is intended to provide support and clarification to the preliminary deposition estimates for nitrogen, phosphorus, and particles presented elsewhere in this memorandum. As such the level of detail and analysis presented in each section is determined by the use of that data in constructing that estimate and the degree to which previous reports have addressed them.

Six general types of air quality data were used to develop the LTADS deposition estimates. They are:

- 1) Historical and current regulatory air quality gas and aerosol data: intermittent 24-hour integrated TSP, PM10, PM2.5 aerosol mass and chemistry, and hourly gaseous pollutant data collected by the States of California and Nevada.
- 2) Historical and current visibility monitoring data: 24-hour integrated PM10 and PM2.5 filter samples collected by the federal IMPROVE Network and TRPA (following IMPROVE protocols).
- 3) 24<sup>+</sup>-hour integrated aerosol filter samples collected by the LTADS team using portable “Mini-volume” samplers (MVS) around the basin and on buoys anchored on the lake.
- 4) Two-week time integrated aerosol and gas chemical speciation samples collected by the LTADS team using ARB’s Two-Week Samplers (TWS) located at selected LTADS monitoring sites.
- 5) Hourly TSP, PM10, and PM2.5 mass concentrations measured by Beta Attenuation Monitors (BAMs) collected by the LTADS team.
- 6) Minute to hourly size-resolved ambient particle counts (six size ranges) collected in specialized short term “dust” experiments by the LTADS team.

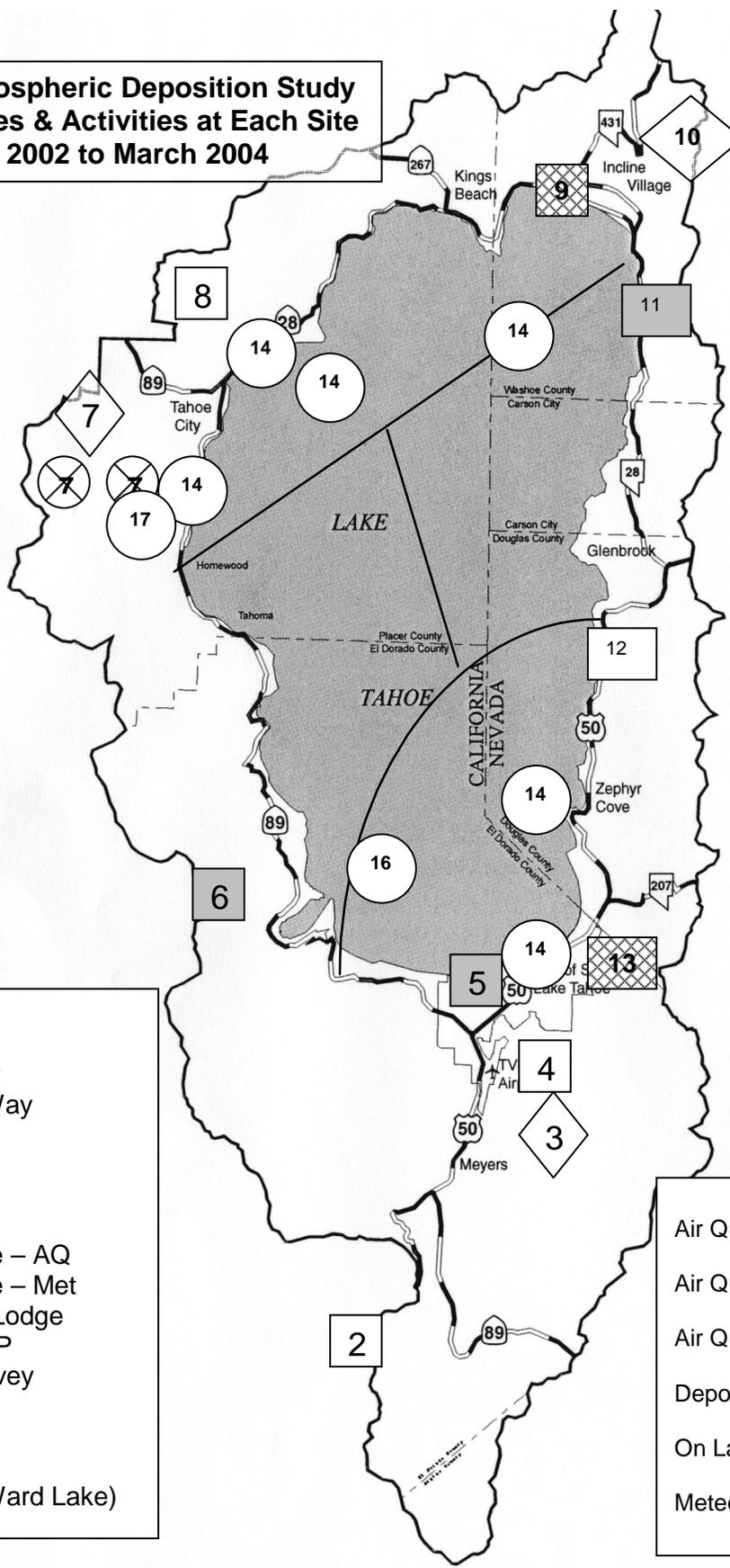
**Table 3-1 Lake Tahoe Atmospheric Deposition Study (LTADS) Two Week Sampler (TWS) Mini Volume Sampler (MVS) Network Locations**

Site Name	Geography	Lakeshore Distance	Network	Size Cuts	Duration
Lake Forest (LF)	Tahoe City North Lake Shore	Hwy 28 Adjacent	TWS	TSP, PM10, PM2.5	2 Weeks
Coast Guard Pier	Tahoe City North Lake Shore	Pier 200 Meters from LF	MVS	TSP	1 Week
Thunderbird	East Lake Shore - Distant from Hwy 28	Elephant House 10 Meters	TWS	TSP, PM10, PM2.5	2 Weeks
Zephyr Cove	Zephyr Cove Marina, East Lake Shore	Pier 200 Meters from Hwy 50	MVS	TSP	1 Week
SOLA	South Lake Tahoe, South Lake Shore	1 Meter from Hwy 50	TWS	TSP, PM10, PM2.5	2 Weeks
Timber Cove	South Lake Tahoe, South Lake Shore	Pier 800 Meters from SOLA	MVS	TSP	48 Hours
Sandy Way	South Lake Tahoe, South Lake Inland	10 Meter from Hwy 50	TWS	TSP, PM10, PM2.5	2 Weeks
Bliss State Park	West Lake Shore Inland Mountain	10 Meter from Hwy 89	MVS	TSP	1 Week
Wallis Residence Tower	West Lake Shore	10 Meter from Hwy 89	MVS	TSP	1 Week
Wallis Residence Pier	West Lake Shore	Pier 50 Meters from Tower	MVS	TSP	1 Week
Buoy TB1 East	Mid Lake North East	-	MVS	TSP	24 Hours
Buoy TB1 West	Mid Lake North West	-	MVS	TSP	24 Hours
Big Hill	Outside the Basin Near Loon Lake	25 miles SW of DL Bliss	TWS	TSP, PM10, PM2.5	2 Weeks

A detailed description of TWS and MVS measurements is provided in Table 3-1. The map on the next page shows the location of all the monitoring and meteorological sites used as part of LTADS.

15

**Lake Tahoe Atmospheric Deposition Study  
Map of Study Sites & Activities at Each Site  
November 2002 to March 2004**



1. Big Hill
2. Echo Summit
3. Tahoe Airport
4. SLT-Sandy Way
5. SLT - SOLA
6. DL Bliss SP
7. Tahoe City
8. Lake Forest
9. Incline Village – AQ
10. Incline Village – Met
11. Thunderbird Lodge
12. Cave Rock SP
13. Stateline Harvey
14. Buoys/Piers
15. Grass Valley
16. TDR2
17. Wallis Pier (Ward Lake)

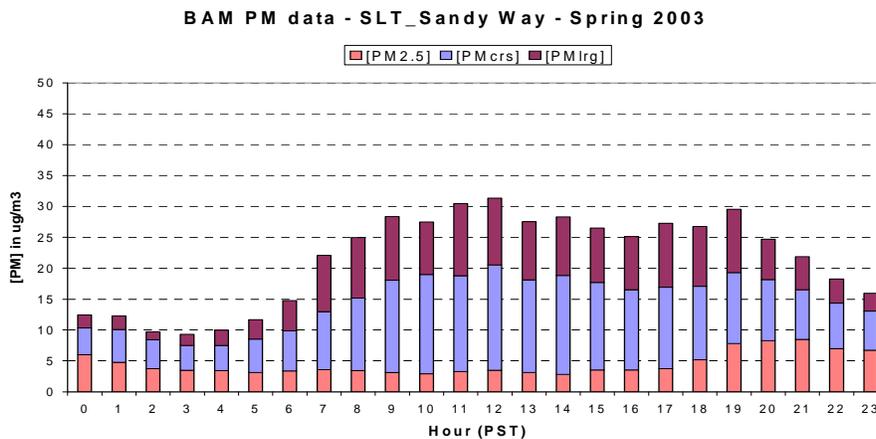
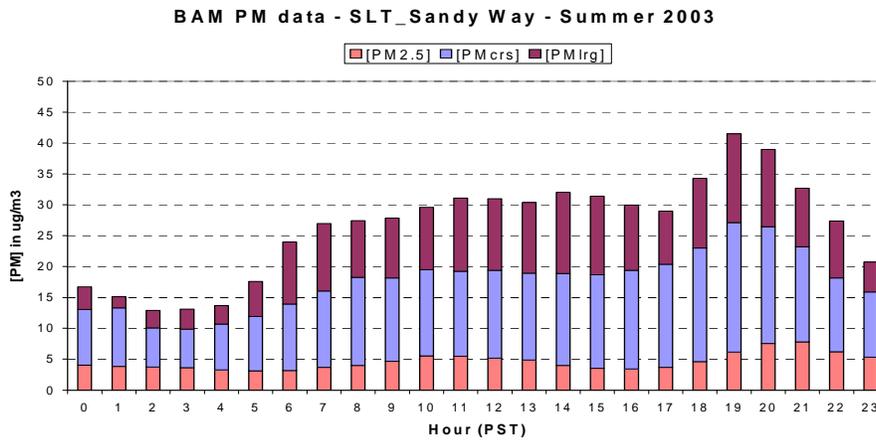
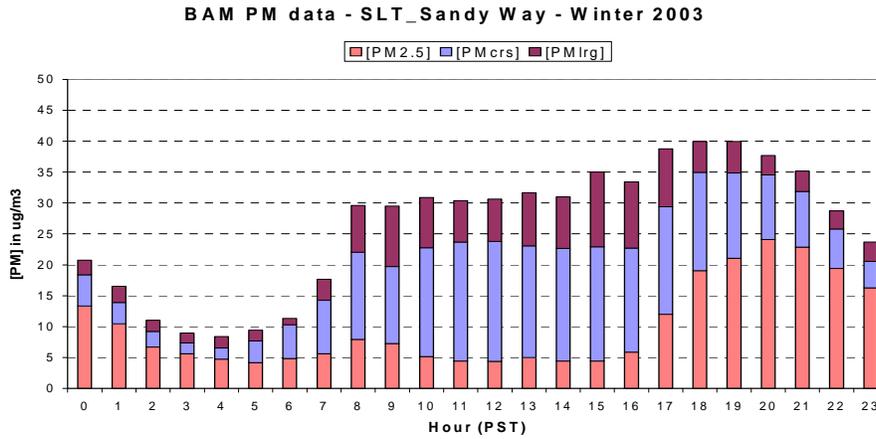
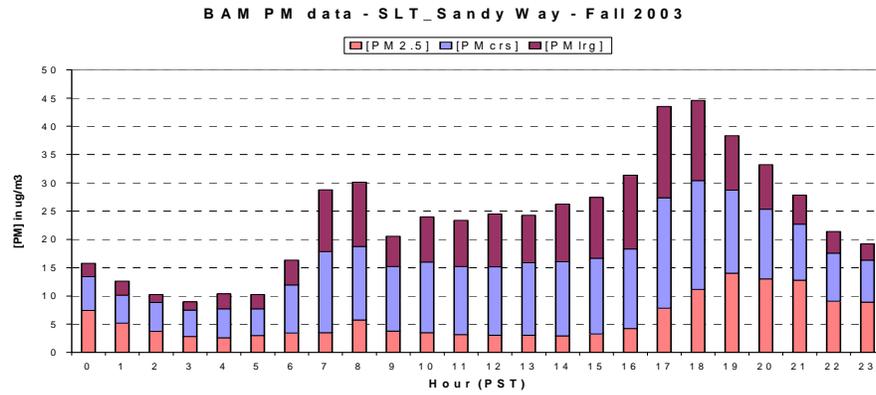
Air Quality Gas & PM	
Air Quality PM	
Air Quality Single Gas	
Deposition	
On Lake	
Meteorology Aloft	

### 3.1 TWS, MVS, and BAM Data

To develop deposition estimates that dynamically account for Tahoe Basin meteorology, hourly deposition velocities as a function of hourly wind speeds, wind direction, air and water temperatures, and mixing depths are required. Deposition estimates require concentration and deposition velocity data for the same locations and for the same time units. Diurnal concentration profiles are required to match the temporal resolution of the meteorological data.

The TWS and MVS networks provide for sampling periods as short as 24 hours and as long as two weeks for chemical composition data. The BAM network collected hourly concentration data in TSP, PM10, and PM2.5 size fractions at several, though not all, stations. The BAM network's diurnal profiles were used to parse seasonal TWS and MVS data and to arrive at seasonal hourly concentration data for TSP, PM10, and PM2.5. Figure 3-2 below provides a synopsis of BAM diurnal profiles for each of the four seasons at Sandy Way. Because the BAM instruments collect all particles below a specified cut-point or size, the concentrations include overlapping measurements. For sites with all three size measurements the data can be segregated into three non-overlapping size fraction by subtracting the PM10 measurement from the TSP measurement to give the concentration of particles larger than PM10 (referred to as "PM\_Large"). In a similar manner, the PM2.5 concentration can be subtracted from the PM10 to give the concentration of particles of size greater than 2.5  $\mu\text{m}$  and smaller than 10  $\mu\text{m}$  (referred to as "PM\_Coarse").

**Figure 3-2 Seasonal Diurnal Profiles at Fine, Coarse and Large Particulate Matter South Lake Tahoe (Sandy Way)**



BAM data from various sites indicate a relatively small diurnal variation in PM<sub>2.5</sub> mass when averaged for a season. In contrast, the BAM data indicate that PM-coarse and PM-large both varied markedly with hour of day, being higher around sunrise and sunset when the air is more stable and traffic activities tend to be greater. The PM chemical constituents were assumed to have diurnal variations similar to the variations in total mass.

Hourly concentrations were estimated as:

$$\text{seasonal TWS (or MVS) concentration} \quad \times \quad \frac{\text{seasonal hourly BAM mass}}{\text{seasonal BAM mass}}$$

The selection of the denominator in the expression above was as follows:

The diurnal variation of PM<sub>2.5</sub> was normalized to the seasonal average BAM PM<sub>2.5</sub> while the diurnal variation of PM-coarse was normalized to the sum of BAM PM-coarse and BAM PM-large. This was done to ensure that the conceptual hourly PM concentrations met the physical constraint of PM<sub>2.5</sub> < PM<sub>10</sub> < TSP, or stated differently, that PM-coarse (PM<sub>10</sub> – PM<sub>2.5</sub>) and PM-large (TSP – PM<sub>10</sub>) would not have negative concentrations.

## 3.2 Nitrogen Species

Nitrogen species are a key input to the Lake and deposit from the atmosphere in both aerosol and gaseous forms. This section will first discuss aerosol nitrogen species and then gaseous nitrogen components.

### 3.2.1 Aerosol Nitrogen

The most common nitrogen-containing aerosol species are ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) and ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>). Both are water soluble and readily deposit to water. Ammonium (NH<sub>4</sub><sup>+</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), and sulfate (SO<sub>4</sub><sup>=</sup>) ionic concentrations in LTADS samples were measured by extracting a portion of an aerosol filter in water, then analyzing the liquid by ion chromatography (IC).

Aerosol nitrate (NH<sub>4</sub>NO<sub>3</sub>) is not chemically stable; rather, it exists in equilibrium with the gas-phase concentrations of its precursors, ammonia (NH<sub>3</sub>) and nitric acid (HNO<sub>3</sub>) and water vapor. Collecting nitrate particles on a filter can produce a negative bias if the air flow shifts away from the equilibrium point and some of the nitrate on the filter returns to the gas phase and is lost. If gas-phase precursors in the air stream condense on the filter to form “new” nitrate, nitrate particle collection can create a positive bias. In the TWS, air entering the sampler first passed through a carbonate-coated “denuder” that removed nitric acid vapor, preventing any positive artifact formation on the filters. Any ammonium nitrate that volatilized as nitric acid vapor was captured by the nylon backup filter. Volatilized ammonia was estimated as the equal mole concentration of the volatilized nitrate captured on the backup. This assumption provides an upper estimate of ammonium because some of the particulate nitrates are undoubtedly associated with calcium, magnesium, sodium, etc.

Total nitrate was computed for the TWS network as the sum of primary and backup filter. Total ammonium was computed as the sum of primary filter ammonium and the estimated volatilized ammonium from the backup filter. IMPROVE  $\text{NH}_4^+$  and  $\text{NO}_3^-$  data are based on the same type of collection and lab analyses. Neither denuders nor backup filters can be used with the standard design of MVSs as they would decrease the airflow and change the particle size cutpoints when used for PM<sub>2.5</sub> or PM<sub>10</sub> sampling. Although the MVSs used during LTADS were for TSP sampling, which is less sensitive to airflow variations, the short study timeline precluded the design, construction, and testing of a more sophisticated MVS sampling system.

The nitrate/ammonium sampling and analytical procedures lead to six nitrogen measurement numbers which are as follows:

- 1) Nitrate M: nitrate measured with the TWS.
- 2) Nitrate V: volatilized nitrate measured with the TWS.
- 3) Ammonium M: ammonium measured with the TWS.
- 4) Ammonium V: volatilized ammonium estimated from Nitrate V.
- 5) Nitrate T: total nitrates equal to Nitrate M + Nitrate V.
- 6) Ammonium T: total ammonium equal to Ammonium M + Ammonium V.

It is unlikely that all volatilized nitrates are ammonium nitrate and therefore Ammonium V estimates that assume mole for mole of ammonium ion for volatilized nitrate ion overestimate Ammonium V and Ammonium T ambient concentrations. We need to additionally assume that ammonium nitrate, does not dissociate to ammonia and nitric acid, and remains at equilibrium. Because these are two-week average measurements, ammonium nitrate equilibrium is not likely maintained. As noted later, relative humidities above 62% tends to create circumstances for aqueous instead of gas phase chemistry for ammonium nitrate. Further and within the proper relative humidity regimes, gaseous particulate phase partition coefficient (dissociation constant) is temperature dependent. Clearly, substantial temperature swings within a two-week period occur that argue against a steady-state ammonium-nitrate equilibrium throughout the sample collection period.

As the MVS collected only Ammonium M, we have estimated Ammonium T for the MVS network from Ammonium M and the difference was designated as Ammonium V for the MVS network. Estimated Nitrate V for the MVS network is assumed to be molar equal to Ammonium V, leading to the Nitrate T estimates for the MVS network. This approach allows common use of TWS and MVS particulate nitrogen data for seasonal and annual deposition calculations. However, the MVS flow rate was 5 liters per minute (lpm) compared to TWS flow rate of 1.3 lpm. MVS samplers ran about 30 hours at mid-lake and 168 hours at piers while TWS samples ran for about 300 hours. We thus recommend caution in comparing individually imputed Ammonium V and Nitrate V values between MVS and TWS. MVS Ammonium T, Nitrate T, and Nitrogen Total Filter (TF) were calculated based on this treatment (Table 3-2).

Both nitrate and ammonium concentrations at Big Hill are higher than at any site within the Tahoe Basin. Comparing to the IMPROVE network, the Big Hill PM<sub>2.5</sub> nitrate

loadings are halfway between the averages for two transport-influenced sites in the southern Sierra Nevada - Yosemite ( $0.36 \mu\text{g}/\text{m}^3$ ) and Sequoia ( $1.3 \mu\text{g}/\text{m}^3$ ), suggesting that transport is an important component at Big Hill. The annual mean at Big Hill is somewhat uncertain. Most of the samples collected there are from the warm seasons when upslope transport from the Sacramento Valley is strongest (sampling began February 26, 2003), so much of the low nitrate winter period was likely missed. The Big Hill average is thus better viewed as an upper bound on the true annual average.

PM<sub>2.5</sub> nitrate data from the TWS compare well with data from the IMPROVE network. At Bliss, IMPROVE nitrate averaged  $0.22 \mu\text{g}/\text{m}^3$ , essentially the same as LTADS' TWS nitrate for Bliss,  $0.24 \mu\text{g}/\text{m}^3$ . The Coast Guard, Wallis Tower, Wallis Pier, Thunderbird, and Lake Forest sites all show average nitrates concentrations of 0.2 to  $0.7 \mu\text{g}/\text{m}^3$ , much lower than the  $1.29 \mu\text{g}/\text{m}^3$  observed at Big Hill. Even the SOLA and Sandy Way sites in South Lake Tahoe, despite strong local motor vehicle and urban emissions, only averaged about  $1 \mu\text{g}/\text{m}^3$  of nitrate. Although divorced from a more substantive meteorological assessment, aerosol nitrogen concentrations within the basin appear to be largely influenced by in-basin emissions, which is consistent with conclusions of Tarnay *et al.* (2002).

**Table 3-2.** Seasonal and Study Avg. NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, and total particulate nitrogen concentrations from LTADS filter sampling.

Lake Tahoe Atmospheric Deposition Study Nitrogen Total Particulate, Nitrates, Ammonium (ug/m3)							
Site	Nitrogen Particulate (N)					Nitrates (mass)	Ammonium (mass)
	Winter	Spring	Summer	Fall	Study Average		
Big Hill PM2.5	0.26	<u>0.45</u>	0.60	<u>0.34</u>	0.51	0.73	0.44
Big Hill PM10	<u>0.50</u>	0.45	0.71	0.34	0.55	0.93	0.44
Big Hill TSP	0.34	0.54	0.96	0.69	0.70	1.29	0.52
Bliss State Park TSP	<u>0.11</u>	-	-	0.22	0.20	0.24	0.19
Coast Guard TSP	0.22	0.27	0.33	0.27	0.27	0.27	0.26
Lake Forest PM2.5	0.26	<u>0.20</u>	<u>0.35</u>	0.31	0.29	0.37	0.26
Lake Forest PM10	0.25	0.33	0.38	<u>0.31</u>	0.31	0.47	0.26
Lake Forest TSP	0.26	0.34	0.46	0.37	0.37	0.57	0.31
NASA Raft, TB1 (east) TSP	0.41	0.51	0.45	<u>0.58</u>	0.46	0.62	0.41
NASA Raft, TB1 (west) TSP	0.39	0.49	0.41	<u>0.52</u>	0.43	0.59	0.38
Sandy Way PM2.5	0.51	0.35	0.44	0.50	0.47	0.76	0.38
Sandy Way PM10	0.57	0.43	0.49	0.51	0.51	0.89	0.40
Sandy Way TSP	0.55	0.54	0.69	0.63	0.60	1.06	0.46
SOLA PM2.5	0.50	0.36	0.44	0.46	0.45	0.67	0.38
SOLA PM10	0.46	0.38	0.49	0.48	0.46	0.80	0.36
SOLA TWS TSP	0.52	0.51	<u>0.53</u>	0.53	0.52	0.92	0.40
SOLA MVS TSP*	0.29	-	<u>0.36</u>	0.32	0.31	0.54	0.25
TDunderbird PM2.5	<u>0.24</u>	<u>0.24</u>	<u>0.35</u>	<u>0.24</u>	0.26	0.34	0.23
TDunderbird PM10	0.24	0.21	0.34	0.26	0.27	0.39	0.24
TDunderbird TSP	0.25	0.34	0.57	0.33	0.39	0.62	0.32
Timber Cove TSP	0.42	0.47	<u>0.29</u>	-	0.42	0.47	0.41
Wallis Pier TSP	0.11	0.27	0.32	0.26	0.26	0.24	0.27
Wallis Tower TSP	<u>0.09</u>	0.25	0.36	0.25	0.26	0.22	0.27
Zephyr Cove TSP	0.40	0.40	0.46	0.29	0.36	0.37	0.36
<b>Maximum Basinwide (excludes Big Hill)</b>					2.57	2.57	1.04
<b>2nd Maximum Lakewide (excludes Big Hill)</b>					1.21	2.24	0.91
<b>Average Lakewide (excludes Big Hill)</b>					0.60	0.60	0.34
<b>Median Basinwide (excludes Big Hill)</b>					0.50	0.50	0.32
<b>Minimum Basinwide (excludes Big Hill)</b>					0.04	0.04	0.04

Underlined data presented are estimates or rely on too few data points; \*SOLA MVS higher flow & lower NH<sub>4</sub><sup>+</sup> DRI ARB QA Review

### 3.2.2 Gaseous Nitrogen

Gaseous nitric acid and ammonia were measured with the TWS by denuders. Nitric acid was found by extracting captured nitrate from the carbonate denuders, and ammonia by extracting citric acid denuders. Due to the long integration time of the TWS, stoichiometric balance among the gases and aerosols were not expected, and statistics among the species show only weak relationships. This lack of systematic relationships eliminates any basis for estimating nitric acid or ammonia for the MVS network. Gas-phase nitrogen calculations are therefore entirely based on the TWS network data.

Review and analysis of the TWS data identified several occasions when nitric acid data were atypically low and deemed suspect. DRI reviewed the laboratory calculations, identified errors, and corrected the suspect values.

Comparative measurements for gaseous nitrogen species were collected using laser-induced fluorescence (LIF) at the Big Hill site by a research group from UC Berkeley. Those measurements also include alkyl nitrates, peroxy-acetyl nitrates, and nitrogen dioxide.

Difficulties in measuring nitric acid were significantly enhanced due to positive artifacts for denuder samplers, and large uncertainties in the denuder method for the low ambient nitric acid concentrations at all the LTADS sites. Denuder measurements can be biased upwards by conversion of nitrous acid into nitric acid within the denuder, and they also have significant uncertainties in nitric acid collection efficiency at low concentrations, in laboratory extraction efficiency, and the whole analytical process suffers from occasional high blank values. These uncertainties are usually small compared to ambient nitric acid levels in the urban areas where this technology was developed, but at very low concentrations, such as those in the Lake Tahoe Basin, they presented substantial challenges to achieving high data quality.

Thermal stability is key to LIF operations. For a substantial amount of time at Big Hill, the power failed and the LIF unit was off line leading to difficulties in maintaining thermal stability. Quality assurance issues for both databases remain. DRI and UC Berkeley continue to work on improving the quality of both databases.

TWS ammonia data quality control review indicated fewer problems than seen with nitric acid, and TWS-based seasonal and annual ammonia estimates are thought to be more reliable. Gaseous nitrogen measurements are summarized in Table 3-3.

Ammonium nitrate equilibrium would suggest that from ammonia concentrations and knowledge of ambient temperature and relative humidity, one could estimate the dissociation constant  $K$  and consequently one could estimate nitric acid concentrations from the following equations (Stelson and Seinfeld, 1982):

$$K = P_{\text{HNO}_3} \times P_{\text{NH}_3}$$

$$\ln K = 84.6 - (24,220/T) - 6.1 \ln (T/298)$$

where  $T$  = Temperature in degrees Kelvin and  $RH$  is lower than 62%. The dissociation constant,  $K$ , is in units of  $(\text{ppbV})^2$ .

A two-week sampling schedule suggests that the ammonium nitrate equilibrium assumption might be unreasonable. Average two-week temperature and relative humidity data do not adequately describe second-to-second temperature and relative humidity profiles that likely govern nitric acid and ammonia concentrations, even if the ammonium nitrate equilibrium held. The 1997 Southern California Ozone Study data have suggested that theoretical  $K$  values ought to consider dilution and the aerosol matrix of surfaces where ammonium nitrate reactions might take place (Hughes et al., 2002). LTADS data do not include sufficient time resolution and sufficient aerosol matrix and plume dilution information necessary for proper assessment of  $K$ . Whether or not equilibrium is maintained and the concentrations are balanced is a question for future study.

**Table 3-3.** Gaseous nitrogen from the LTADS TWS network.

Lake Tahoe Atmospheric Deposition Study Nitrogen Total Gas, Nitric Acid, Ammonia (ug/m3)							
Site	Nitrogen Gas (N)					Nitric Acid (Mass)	Ammonia (Mass)
	Winter	Spring	Summer	Fall	Study Average		
Big Hill	0.21	0.23	1.04	0.82	0.69	0.72	0.64
Lake Forest	0.58	0.37	0.80	0.86	0.68	0.45	0.71
Sandy Way	0.90	0.76	1.04	1.32	1.02	1.01	0.96
SOLA	1.96	0.93	1.51	2.21	1.79	0.99	1.90
Thunderbird	0.10	0.11	0.36	0.26	0.22	0.33	0.18
<b>Maximum Basinwide (excludes Big Hill)</b>					3.58	2.93	4.08
<b>2nd Maximum Basinwide (excludes Big Hill)</b>					3.26	1.91	3.59
<b>Average Basinwide (excludes Big Hill)</b>					0.92	0.71	0.92
<b>Median Basinwide (excludes Big Hill)</b>					0.85	0.65	0.81
<b>Minimum Basinwide (excludes Big Hill)</b>					0.04	0.08	0.00

### 3.2.3 Total Nitrogen

Because a total nitrogen calculation is only possible for locations with both gas and particle phase concentrations, the data summaries are confined to TWS sites (Table 3-4).

**Table 3-4.** Total nitrogen from TWS aerosol and gas measurements.

Lake Tahoe Atmospheric Deposition Study Nitrogen Total, Nitrates, Ammonium Ion, Nitric Acid, Ammonia (ug/m3)									
Site	Nitrogen Particulate & Gas (N)					Nitrates (Mass)	Ammonium (Mass)	Nitric Acid (Mass)	Ammonia (Mass)
	Winter	Spring	Summer	Fall	Study Average				
Big Hill	0.55	0.78	2.00	1.52	1.39	1.29	0.52	0.72	0.57
Lake Forest	0.85	0.71	1.26	1.23	1.05	0.56	0.30	0.45	0.71
Sandy Way	1.45	1.30	1.74	1.95	1.61	1.06	0.46	1.01	0.95
SOLA	2.48	1.45	2.05	2.74	2.31	0.89	0.39	0.99	1.76
Thunderbird	0.35	0.45	0.93	0.59	0.61	0.60	0.31	0.33	0.18
<b>Maximum Basinwide (excludes Big Hill)</b>					6.15	2.57	1.04	2.93	4.08
<b>2nd Maximum Basinwide (excludes Big Hill)</b>					4.47	2.24	0.91	1.91	3.59
<b>Average Basinwide (excludes Big Hill)</b>					1.52	0.59	0.34	1.01	0.83
<b>Median Basinwide (excludes Big Hill)</b>					1.35	0.52	0.32	0.89	0.74
<b>Minimum Basinwide (excludes Big Hill)</b>					0.08	0.04	0.04	0.00	0.00

There is a wide variation across these sites. In winter, the populated sites in the basin are clearly highest, with the south shore (Sandy Way, SOLA) much higher than the other sites. In summer, the south shore still is highest, but the difference from winter is modest, while the north shore (Lake Forest) and western slope (Big Hill) rise significantly. The unpopulated east shore (Thunderbird) shows the least seasonal signal and is the lowest year-round.

The split among the gas and aerosol species is also highly variable across the network. Total nitrogen distributions (percent of N) are shown in Table 3-5.

Table 3-5. Contributions of nitrogen species from TWS measurements.							
	Nitrates	Ammonium	Nitric Acid	Ammonia	NH <sub>4</sub> +NH <sub>3</sub>	HNO <sub>3</sub> +NO <sub>3</sub> -	Total N (ng/m <sup>3</sup> )
Site	% of Total	% of Total	% of Total	% of Total	% of Total	% of Total	Study Average
Big Hill	22	31	12	35	66	34	1390
Lake Forest	12	22	10	56	78	22	1054
Sandy Way	15	22	14	49	71	29	1615
SOLA	9	14	10	67	81	19	2306
Thunderbird	23	40	12	25	65	35	609

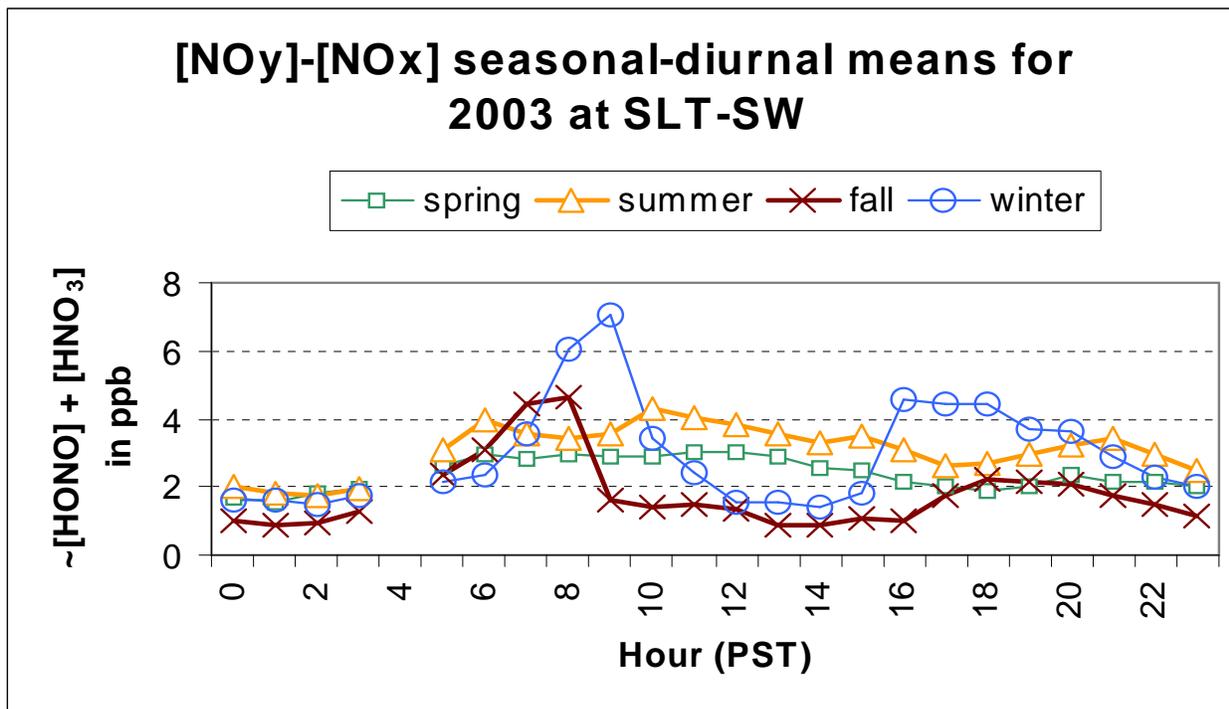
The aerosol fraction (nitrate + ammonium) is greatest at the less-populated sites (Thunderbird and Big Hill), while the ammonia gas fraction peaks in the populated areas (SOLA/Sandy Way and Lake Forest). Nitric acid, by contrast, is a relatively constant fraction at all sites. On average, 70% or more of total N is from ammonia plus ammonium, with over 50% of total N from ammonia alone. Thus, total atmospheric N is primarily determined by the supply of ammonia, regardless of its site-specific aerosol-gas partitioning.

As noted earlier, hourly concentration profiles are required. For nitric acid, using NO<sub>y</sub>-NO<sub>x</sub> differences from South Lake Tahoe station at Sandy Way, such a diurnal profile has been assembled and is shown in Figure 3-2 below.

Total reactive nitrogen includes total oxides of nitrogen plus such species as peroxy acetyl and other organic nitrates, as well as, nitric and nitrous acids. Formulation of diurnal profiles presumes that nitric acid (plus nitrous acid, the positive artifact of nitric acid measurements) well exceeds other constituents of NO<sub>y</sub>. Based on the day/night TWS samples, no diurnal variation was assumed for ammonia concentrations.

As noted on the map, Lake Tahoe was divided into four quadrants for deposition estimation. Using average concentration profiles from TWS sites to characterize four quadrants of the Lake based on population/activity densities, “dry” atmospheric N deposited to Lake Tahoe is estimated in Chapter 5. As indicated by the above table, approximately 70% of the dry N deposition is likely to come from the deposition of gaseous NH<sub>3</sub> and HNO<sub>3</sub>, both being highly water soluble.

Figure 3-2. LTADS HNO<sub>3</sub> (+HNO<sub>2</sub>) Diurnal Profile Developed from Sandy Way Station. HNO<sub>3</sub> + HNO = Total Reactive Nitrogen Species (NO<sub>y</sub>) – Total Oxides of Nitrogen NO<sub>x</sub>



### 3.2.4 LTADS vs. Other Tahoe Basin N-species Reports

Tarnay *et al.* (2001 and 2003) collected denuder gaseous nitric acid and ammonia data at remote forested locations in Bliss State Park and a high alpine forest near Incline Village (Table 3-6). Ammonium nitrate data reported in the 2001 paper is from the IMPROVE network's Bliss site, thus most relevant to rural, elevated, undeveloped regions of Tahoe Basin. Tarnay *et al.* (2003) expanded the network to several other stations but still only covered the summer months (July-September).

Table 3-6. N-Species as reported by Tarnay *et al.*, 2001 and 2003.

Tarnay et al. (2001) Bliss State Park & Incline Village Alpine Forests					LTADS (2004)	
Nitrogen Species	Mean Daytime	Mean Night	Mean Daytime	Mean Night	Study Median	Study Max
	nmol N/m3	nmol N/m3	ng N/m3	ng N/m3	ng N/m3	ng N/m3
HNO3	26	11	364	154	198	906
NH3	20	49	280	686	609	3,357
NH4NO3* Bliss Tarnay	7	7	101	101	365	1,388
NH4NO3* Bliss LTADS (MVS Average)			165			
Tarnay et al. (2003)					LTADS (2004)	
HNO3	17	13	238	182	198	906
NH3	21	10	294	140	609	3,357

\* Tarnay et al. incorporated from IMPROVE network summer and fall 1990-1996

Please note that different years indicate opposite day/night relationships for ammonia. This is most likely the product of the difficulties we have noted in gaseous N species measurements using denuders. Nitric acid concentrations observed during LTADS are in the range of those reported by Tarnay *et al.* (2001 and 2003). However, LTADS observed substantially higher ammonia concentrations than were reported by Tarnay *et al.* (2003). In general, LTADS results are similar to those reported by Tarnay *et al.* (2001). LTADS reported substantially higher ammonium nitrate concentrations than those reported from IMPROVE network for Bliss State Park and at SOLA, for summer and fall seasons of 1990-96. LTADS data from the remote site Bliss agree with ammonium nitrate concentrations reported by Tarnay *et al.* (2001).

Zhang *et al.* (2002) reported limited aircraft sampling in and near the Tahoe Basin. These show a wide range, but are within the range of LTADS reported concentrations. Note that ammonium plus ammonia concentrations reported in aircraft measurements are between LTADS reported median and maximum values (Table 3-7).

**Table 3-7.** Aircraft measurement of N-species from Zhang *et al.* (2002) & Carroll *et al.* (2003).

Zhang <i>et al.</i> (2002)			LTADS (2004)			
Nitrogen Species	3 Representative Samples		Study Median	Study Max		
	n mol N/m <sup>3</sup>	ng N/m <sup>3</sup>	ng N/m <sup>3</sup>	ng N/m <sup>3</sup>		
HNO <sub>3</sub> (gas) + NO <sub>3</sub> <sup>-</sup> (particle)	30	420	315	1,487		
NH <sub>3</sub> (g) + NH <sub>4</sub> (p)	95	1,330	857	4,164		
ON (g) + ON (p)	15	210	-	-		
Total N (g) + (p)	140	1,960	1,349	6,152		
Carroll <i>et al.</i> (2003)						
	Range		Range		Study Median	Study Max
	n mol N/m <sup>3</sup>	n mol N/m <sup>4</sup>	ng N/m <sup>3</sup>	ng N/m <sup>3</sup>	ng N/m <sup>3</sup>	ng N/m <sup>3</sup>
Ammonium Nitrate	6	51	84	714	365	1,388
Gas Phase Nitrogen	26	310	364	4,310	807	4,263
Ammonia as fraction of Total N	55%				52%	

Carroll *et al.* (2003) performed detailed air and boat sampling over and on Lake Tahoe in coordination with LTADS. They noted high blank values and other analytical difficulties that the TWS have also encountered. Nevertheless, using averages of the ensemble of denuder filter pack samples, it appears that ammonia increased slightly with height above the lake while nitric acid gas decreased slightly with height. The ammonium nitrate and gaseous nitrogen concentration range from Carroll *et al.* (2003) are between TWS reported median and maximum values. Please also note that ammonia fraction of nitrogen species from Carroll *et al.* (2003) and TWS agree quite well.

### 3.3 Phosphorus

Phosphorus (P) in either gaseous or aerosol form is not commonly a focus of air quality monitoring. We are not aware of any gaseous P measurements in California. California has a limited set of aerosol P data collected as part of the Toxic Air Contaminant (TAC) monitoring program. As part of this program, TSP samples are collected at sites

throughout the state. Filters are then available for elemental analyses by ARB. P data is also available from ARB's Dichot network for PM<sub>2.5</sub> and PM<sub>coarse</sub>. The IMPROVE network reports P concentrations for PM<sub>2.5</sub>, but does not use it in computing aerosol composition statistics or quality assurance calculations. LTADS attempted to measure aerosol P, but had only limited success (see below). This section summarizes the P data available from the IMPROVE and LTADS sampling in the Tahoe Basin and, drawing on other P data and published scientific literature, constructs a rough conceptual model for P concentrations in the basin.

### 3.3.1 Constraints on Aerosol P measurement

LTADS, IMPROVE, and ARB's TAC program rely on X-ray fluorescence (XRF) analysis of Teflon filters to measure aerosol P. For ambient aerosols, P detection is hampered by chronically small P concentrations and by strong interference from two common elements, sulfur (S) and silicon (Si).

The S interference is driven by three factors. 1) The strongest spectral fluorescence lines for P and S are separated by only a little more than the minimum energy resolution of typical fluorescence detectors (about 1.5 times the minimum resolution); allowing for some electronic "noise," the two peaks nearly overlie one another; 2) S fluoresces more strongly than P does; and finally, 3) S is usually present at several times the concentration of P. Together these factors often cause the S signal to overwhelm the P signal.

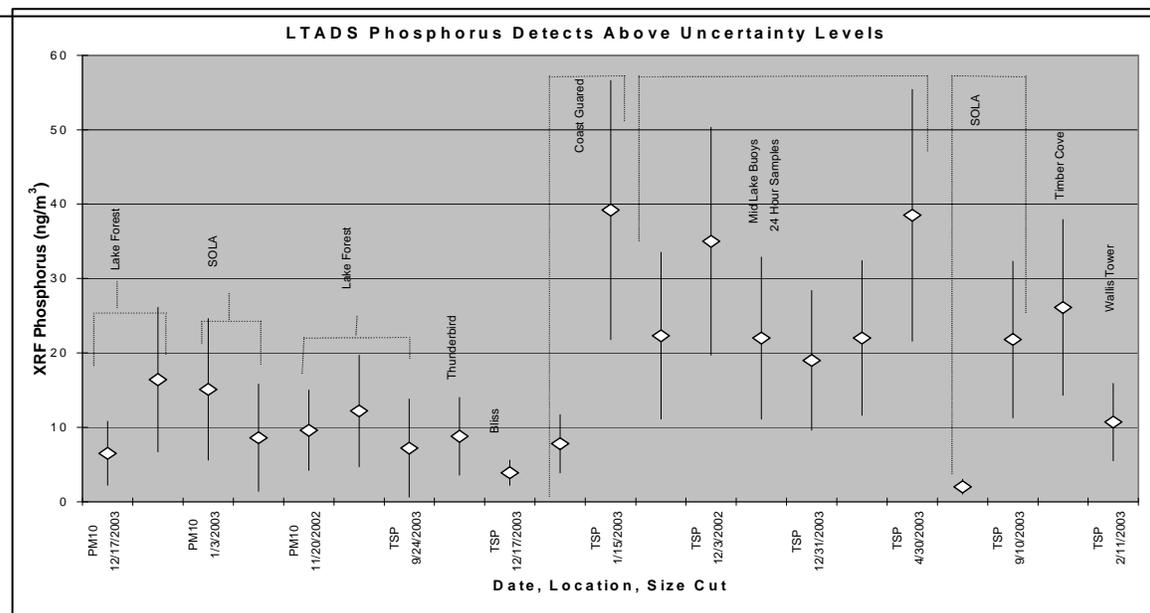
The Si interference is not as intrinsically strong, because the peak energies are separated more (nearly 3 times typical detector energy resolution), but Si is generally present in much higher concentrations than P, and the large concentration peaks have wider electronic "noise" footprints, so the net effect is similar to that for S.

The relatively clean air and likely low P concentrations in the Tahoe Basin accentuates the P detection problem. Although P can accurately be measured in pure standards, low P concentrations and interferences in ambient samples makes detecting P concentrations above measurement uncertainties in most XRF systems difficult to achieve in the best of circumstances. During the LTADS sampling program, 596 filters were analyzed by XRF. Of those, only 88 had P values greater than zero (i.e., there was a distinguishable P signal), and only 23 of those were above measurement uncertainty limits. Two of the samples with P above uncertainty ( $P > U$ ) were compromised by other sampling problems, leaving 21 "valid" P measurements. These are presented in Figure 3-3. The mean P concentrations for the 21 measurements was  $17.6 \text{ ng/m}^3$  and the maximum observed was less than  $40 \text{ ng/m}^3$ .

None of the 21 P detects were in the PM<sub>2.5</sub> size fraction. Comparison of the 21  $P > U$  and P detects below uncertainties indicates the XRF operational limit of detection (O-LOD) for P was about  $2\text{-}11 \text{ ng/m}^3$  for LTADS. The experience of LTADS, TAC program, and other XRF P measurements in the TSP fraction suggest that  $10\text{-}15 \text{ ng/m}^3$  is a reasonable O-LOD. O-LOD denotes a statistical likelihood of detection. This is a distinct concept from an absolute detection limit. An O-LOD of 15 would not preclude a

P > U detection of 1 ng/m<sup>3</sup>; however, this would be a low probability event. Detecting P concentrations above 15 ng/m<sup>3</sup> would be nearly certain. Note that although LOD reported by other studies can be in the range of 1 to 5 ng/m<sup>3</sup>, analytical difficulties noted here and generally low P concentrations result in O-LOD of 10-15 ng/m<sup>3</sup>. As noted before, P non-detects likely occur due to S and Si interference. The aerosol sample matrix may be the governing factor on whether or not XRF measurements successfully detect P. LTADS finding of no P detects in the PM2.5 size fraction conveys a likelihood that such concentrations were below the O-LOD. LTADS finds no quantitative information on likely ambient concentrations of P in the fine aerosols at Tahoe. Therefore, conclusions on P concentrations in wood smoke and other combustion sources thought to dominate the fine fraction emissions would be premature. A phosphorus-specific measurement campaign at Tahoe might be insightful.

Figure 3-3. All 21 LTADS measurements for P greater than the uncertainty.



**Table 3-8.** Tahoe Basin IMPROVE P statistics with comparative S/P, Si/P ratios, and total PM2.5 and PM10 concentrations.

IMPROVE 1989-2000 Lake Tahoe Air Basin						
	P	S/P	Si/P	PM2.5 ALL	PM2.5	P-DETECT
	SOLA ng/m <sup>3</sup>					
Min	5.39	2.48	2.63	1495		1752
Max	21.52	33.35	42.81	37382		21281
Mean	11.84	12.38	16.25	8841		9113
Median	10.99	9.91	16.25	7272		8287
Std. Dev.	4.06	7.85	10.76	5370		4900
Std. Err. of Mean	0.73	1.43	1.96	197		880
95 Conf Int. of Population	1.49	2.93	4.02	387		1797
Valid Obs.	31	30	30	743		31
Total Obs.	751	751	751	751		751
	BLIS					
Min	1.03	2.92	0.31	350		367
Max	9.61	57.62	72.09	13654		6338
Mean	4.56	18.43	11.97	3447		2324
Median	4.75	16.88	9.63	3138		2098
Std. Dev.	2.11	11.90	13.64	2060		1614
Std. Err. of Mean	0.38	2.17	2.49	88		305
95 Conf Int. of Population	0.79	4.44	5.09	174		626
Valid Obs.	30	30	30	542		28
Total Obs.	571	571	571	571		571

The LTADS P detection efficiency was comparable with that experienced by other aerosol sampling systems. From 1989 to 2000, the IMPROVE sampling network collected 750 PM2.5 filters at Bliss State Park, reporting 31 P detects above uncertainty. Among 571 PM2.5 filters that were collected at SOLA over the same period, IMPROVE reported 30 P detects above uncertainty. The minimum detected P for IMPROVE appears to be around 1 ng/m<sup>3</sup>. The IMPROVE O-LOD is likely much higher than 1 ng/m<sup>3</sup> because similar interferences from S and Si are expected and the percent of P observations is similar to that observed in LTADS. These data are summarized in Table 3-8.

In urban South Lake Tahoe, the IMPROVE data report a maximum concentration of 21.5 ng/m<sup>3</sup> P at SOLA (PM2.5), which agrees well with the maximum of 21.8 ng/m<sup>3</sup> reported by LTADS for SOLA (TSP). It may well have been that SOLA PM2.5 in fact includes much of the P mass that would be identified in the LTADS MVS and TWS networks as elements of PM10 (PM3 to PM5). In a more rural area in the basin, the IMPROVE data recorded a maximum concentration of 9.6 ng/m<sup>3</sup> P at Bliss State Park (PM2.5), a site well above lake level and on western side of the Lake. LTADS (TSP) reported 3.9 ng/m<sup>3</sup> at Bliss and 8.8 ng/m<sup>3</sup> at Thunderbird Lodge, which is located in a similarly unpopulated area on the east shore.

**3.3.2 LTADS vs. Other Phosphorus Measurements**

Although not taken in the Tahoe Basin additional P measurements are available from the ARB Toxic Air Pollutants (TAC) monitoring network (Table 3-9).

In the most urban regions of California, median P concentrations do not exceed 60 ng/m<sup>3</sup>. In well over a decade of sampling at more than 20 stations not impacted by obvious agricultural or dairy impacts (e.g., avoiding phosphine PH<sub>3</sub> emissions), only once (Azusa, 2002) has the reported P concentration exceeded 200 ng/m<sup>3</sup> (ARB, 2002).

<b>Table 3-9.</b> Representative California aerosol P statistics from TAC and other studies.		
<b>ARB Studies Proximate to Tahoe Air Basin Potential Transport</b>		
<b>Dichot PM Program</b>		
Site	Season	Average (ng/m <sup>3</sup> )
Roseville Sacramento Valley Urban Region TSP Limit of Detection 15 ng/m <sup>3</sup>	Winter	26.9
	Spring	47.4
	Summer	41.8
	Fall	45.1
	Study Average	41.6
Truckee Dichot PM10 (Fine Non Det) Limit of Detection 15 ng/m <sup>3</sup>	Winter	44.5
	Spring	38.3
	Summer	33.7
	Fall	31.0
	Study Average	35.7
<b>ARB Air Toxics P Detections 1989-2002 (ADAM Database)</b>		
Site	Median (ng/m <sup>3</sup> )	
Azusa, Los Angeles Urban Region	60.4	64
Santa Barbara Coastal Urban Region	11.2	45.4
Roseville Sacramento Valley Urban Region	26.1	38
<b>Transport of Acidic Air Pollutants &amp; Oxidants Sierra Nevada Study</b>		
<b>Summer 1990 (3-hour samples) PM10 (Gertler et al. 1993)</b>		
Site	Average (ng/m <sup>3</sup> )	Max (ng/m <sup>3</sup> )
Yosemite	1.6	14.3
Sequoia	1.8	11.9
<b>San Joaquin Valley Air Quality Study Phase II Volume I</b>		
<b>Report Published October 1990 PM10 &amp; PM2.5 (Chow et al. 1990)</b>		
Site	Size	Average (ng/m <sup>3</sup> )
Crows Landing	PM10	42
	PM2.5	3.3
Fresno Urban Center	PM10	87
	PM2.5	13
Kern Wildlife Refuge	PM10	41
	PM2.5	6.2

Annual statewide medians have ranged from 29.6 to 70.5 ng/m<sup>3</sup> from 1991 to 2002.

**3.3.3 Uncertainty of Atmospheric P Concentrations at Lake Tahoe**

Overall, the P data capture rates are low in all sampling systems we examined. This situation suggests using caution when interpreting what concentrations might be on days when analytical limitations prevent reportable measurements.

In an effort to improve on XRF analyses for the LTADS program, a set of 100 LTADS filters have been submitted for X-ray analysis using the much more powerful synchrotron X-ray beam at the Advance Light Source (ALS) at Lawrence Berkeley Laboratory. Results of those analyses are expected in early 2005 (Cliff, 2004).

Pending the outcome of ALS experiments, we prefer not to assert that the 21 LTADS P values are a representative sample of all days, and thus we do not offer an estimate of average P concentration. We believe that the data from Tahoe and elsewhere indicate that annual average P concentrations in the Tahoe Basin are no more than 40 ng/m<sup>3</sup> and quite likely are far less (the maximum P concentrations observed during LTADS was 39.5 ng/m<sup>3</sup>). The O-LOD for most P detection systems is from 10 to 15 ng/m<sup>3</sup>. We suggest that bounding numbers (10 and 40 ng/m<sup>3</sup>) be used for estimating deposition to the Lake until more refined P estimates are available. The average study P concentration, based on the 21 valid P measurements, is 18 ng/m<sup>3</sup>.

**3.3.4 Phosphorus in the Fine Fraction**

LTADS data included no P detects above uncertainties in the fine fraction (PM2.5). IMPROVE has reported P detects in the fine fraction. We are uncertain if this difference between LTADS and IMPROVE has to do with statistics of obtaining a P XRF peak free of S and Si interference or whether the IMPROVE fine P data reflect truly representative ambient P concentrations at Tahoe. Similar to LTADS and between 1992 and 2000, ARB dichot sampling network in mountain counties found no P in the fine fraction. Values of 7.5 ng/m<sup>3</sup> in the fine fraction in Table 3-10 are merely ½ of LOD (15 ng/m<sup>3</sup>) and in essence denote no P detects.

Year	PM coarse + PM fine	PM coarse	PM fine <sup>*</sup>	Site
1992	32.1	24.6	7.5	Truckee
1993	38.7	31.2	7.5	Truckee
1992	29.8	22.3	7.5	Quincy
1993	28.9	21.4	7.5	Quincy
1997	15.0	7.5*	7.5	Portola
1998	34.1	26.6	7.5	Portola
1999	32.8	25.3	7.5	Portola
2000	35.0	27.5	7.5	Portola
Mean:	30.8	23.3	7.5	

+ the dichot sampler measures PM in 2 size cuts – PM\_fine, particles with aerodynamic diameters < 2.5 microns and PM\_coarse, particles with aerodynamic diameters between 2.5

and 10 microns. The sum of the two sizes is equivalent to the concentration in the PM10 size cut (aerodynamic diameters < 10 microns)

\* all PM<sub>fine</sub> samples were P non-detects; [P]<sub>fine</sub> assumed to be ½ LOD or 7.5 ng/m<sup>3</sup>

Source: CARB dichot sampling network in Mountain Counties Air Basin

The dichot data presented in Table 3-10 show that P concentrations in the fine fraction almost never exceed 20% of the P mass in the PM10 or TSP fraction.

### 3.4 “Inert” Particles

Particles depositing from the atmosphere can dissolve in the lake water (the rate can vary) providing SO<sub>4</sub><sup>-</sup>, PO<sub>4</sub><sup>-</sup>, and NO<sub>3</sub><sup>-</sup> that act as nutrients, stimulating biological growth, which can adversely impact water clarity and aesthetics. Insoluble particles depositing to the water will scatter and absorb light, thus also reducing visibility into the water. Little is quantitatively known at this time about the relative fates of atmospheric particles once they enter the water. As a crude estimate, the analysis of atmospheric particles by ion chromatography (water soluble analysis of particulate matter) would provide an indication of the soluble fraction of particulate matter. An upper estimate of the inert particles would then be the difference between the total atmospheric PM and the soluble portion identified by ion chromatography. Even further, we have combined SO<sub>4</sub><sup>-</sup>, PO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, Cl<sup>-</sup>, Ca<sub>2</sub><sup>+</sup>, K<sup>+</sup>, Na<sup>+</sup>, and a few other potentially soluble species concentrations to arrive at a total soluble fraction. On a study average basis (TSP, PM10, and PM2.5), the LTADS soluble fraction is about 35% of the sum of species.

Very small particles produce Rayleigh scattering while larger particles undergo geometric scattering (Finlayson-Pitts and Pitts 1986) and particles in the middle of the size spectrum may undergo Mie scattering. Rayleigh scattering occurs equally in the forward and backward directions, geometric scattering is about light refraction through large particles and is handled by classic optics, Mie scattering is non-uniform forward scattering and has a refraction index of 1.333 in water. In essence, to properly judge inert particle light scattering in the water column, very specific particle size (as many size cuts as possible), particle counts in each size, and particle concentration information in each size would be required. Particle composition and particle shape would also be extremely useful. Usual angle of radiation, rates of accumulation, conglomeration, and settling within the water column would be additionally required information. Collecting these types of information was beyond the scope of LTADS. To begin assessment of inert particle light scattering and absorption for various water columns at Lake Tahoe, LTADS soluble fraction information is a very approximate starting point.

### 3.5 Summary

Staff has confidence in the LTADS atmospheric dry particulate matter concentration results in the TSP, PM10, and PM2.5 size fractions. Staff believe the LTADS nitrogen species concentrations (gas and particulate) in all size fractions are representative of Tahoe Basin atmospheric chemistry and processes. The LTADS phosphorus observations are representative of the difficulties all present analyses of ambient P have, but we have confidence that the P concentrations are between our bounding limits. Because the chosen upper limit of 40 ng/m<sup>3</sup> is greater than any observed

concentration from LTADS, it is probably an overestimation. The LTADS scope did not include collection of information to study inert particles in detail but enables a maximum bounding estimate.