

## Appendix A

### Comparison of Surrogate Surface Methods of Measuring Dry Deposition

Measurement of the deposition of gases and aerosols from the atmosphere to surfaces is difficult and fraught with complexities associated with disturbances during sampling, reaction/transformation/contamination during sampling and before chemical analysis, analytical detection of small quantities, etc. Measurement of deposition to a water surface is further complicated by access and logistical challenges. Staff of the Tahoe Research Group (TRG) has maintained a limited program of surrogate surface sampling for many years now, near and on Lake Tahoe. To better represent deposition to a water surface, TRG modified, in 1989, the standard wet/dry bucket sampler method developed for the National Deposition Assessment Program by adding water to the dry bucket sampler. Ratios of the dry deposition means before and after the changeover indicate that this modification significantly increased the dry deposition measurements (**Table A-1**). Furthermore, in a cold environment like Tahoe during the winter when water in the sampler could freeze, it was necessary to install a small heater to keep the water ice-free. Warming of the water in turn may affect the dynamics of deposition at the air-water interface. This modification and potential side-effect, however, is not unreasonable given the large thermal mass of Lake Tahoe, which also causes the water temperature to be greater than the air temperature during most of the winter and during most summer nights.

Questions have historically been raised about the representativeness of deposition measurements associated with surrogate surface deposition samplers like the bucket sampler, particularly for dry deposition. It is believed that the wet bucket measurements are reasonably realistic, assuming proper siting of the equipment away from buildings and trees. Although initially planned, the LTADS field study did not include additional wet/dry bucket sampling to supplement the historical and on-going sampling by the TRG. The LTADS bucket sampling in the Tahoe Basin was not initiated due to siting and servicing complications and constraints. The LTADS surrogate surface deposition sampling effort was then restricted to a limited assessment of methodological differences between dry deposition sampling methods. The dry deposition methods comparison study was conducted on the rooftop of ARB's 13<sup>th</sup> & T Street ambient air quality monitoring station in Sacramento.

CARB staff pursued a dry deposition methods comparison study to better characterize the potential differences between surrogate surface sampling methods that are or could be used for dry deposition measurements. After conducting this collocated study of different surrogate surfaces for measuring dry deposition, staff has a much greater appreciation for the efforts and dedication of the field personnel doing field sampling under a variety of difficult environmental situations. Staff also thanks Scott Hackley of TRG, Thomas Holsen of Clarkson University, and Ying Hsu for their generosity in

loaning sampling equipment and providing guidance for the study. Staff also thanks Jacque Landy of the Lahontan Water Quality Control Board for providing laboratory and staffing resources for processing (e.g., storing, filtering, shipping) samples and Patty Bucknell and her staff of the TRG laboratory for chemically analyzing the samples.

The four types of surrogate surface deposition samplers used in this comparison were:

- 1) the standard wet/dry deposition bucket sampler (Stnd),
- 2) the standard wet/dry bucket sampler but with the TRG modification of water in the dry deposition bucket (TRG),
- 3) the TRG bulk deposition tube sampler (Tube), and
- 4) the Clarkson water surface sampler (WSS).

**Figure A-1** is a photograph of the deposition samplers used in the study. The standard wet/dry deposition bucket sampler used in the National Deposition Assessment Program is shown in the right side of the photograph. Precipitation causes the hood (bucket cover) to move to the right and protect the dry deposition sample. Wet deposition samples in the wet bucket on the left side of the sampler were not collected or analyzed during this study of dry deposition differences. To the left, is the WSS designed at Clarkson University to better represent dry deposition to a water surface. The WSS is a research-grade instrument that has been used in other deposition studies, such as the Lake Michigan Ozone Study. Next to the left, is the bulk deposition snow tube (Tube) that is used by TRG to collect samples on a buoy, which cannot be serviced to differentiate between wet and dry deposition samples, and also to accommodate large snow volumes at terrestrial sites during some winter storms. Furthest left, is the TRG-modified sampler. Structurally and operationally, it is the same as the Stnd sampler but the dry deposition bucket has been modified (shortened) and is initially filled with 4 liters of de-ionized water. This water-based dry deposition bucket has also been used on buoys with interlocking plastic panels that serve as baffling to minimize spillage during wave action and servicing.

**Figure A-2** shows the water surface sampler and the TRG-modified dry bucket sampler in more detail. The WSS has a peristaltic pump that circulates water from a 4-liter reservoir up to an opening on the top where the water flows out from the center of an ~14-inch diameter disc toward the edge. The water flows over the edge, into the collection bowl, and drains via tubing to the bottle reservoir. An approximately 12-inch flange is mounted around the collection bowl to minimize sampler-induced turbulence near the sampling surface, which by its design is already less than that induced with the Standard or TRG-modified wet/dry deposition bucket sampler. The TRG bucket has the same diameter as the Standard deposition bucket but has been modified to be shorter. The TRG design reduces the depth from the top of the sampling bucket to the deposition surface compared to the Standard arrangement and better represents the real-world setting. It is not known how the baffles, which float in the water and extend above the water's surface, affect the deposition across the boundary layer between the air and the water. On a few occasions when large aerosols were present, more ash appeared to be present in the TRG bucket than the Stnd bucket. That appearance may have been due to better contrast, material not escaping the water bucket once it was

deposited, or to enhanced deposition (air flow impedance allowing settling of large particles or, conversely, enhanced turbulence).

One of the criticisms of the bucket deposition sampler is that its design generates turbulence, which perturbs the actual deposition processes. Turbulence is generated by the bulk and size of the sampler and the amount and type of turbulence varies by the direction of the wind relative to the sampler orientation. This type of turbulence is less with the design of the Tube and WSS deposition samplers. Another type of turbulence is created as the air flows over the mouths of the bucket and Tube samplers. Additional disturbance of the deposition processes may also be created by the plastic baffling in the TRG bucket. The WSS's aerodynamic design reduces all three potential types of turbulence/disturbance associated with the TRG-modified bucket sampler. Staff believes that the WSS's aerodynamic design and use of water enable that method to theoretically provide the best characterization of actual deposition to a water surface (e.g., lake).

Nearly 20 sets of deposition samples were collected during periods of anticipated dry weather (**Table A-2**). Several sample sets were aborted or discarded due to rain or mechanical failures. On a few occasions near the end of the study, samples were lost in shipment or the frozen samples thawed during shipping to the labs. Because the sample bottles were sealed with limited air space, it is believed that the quality of those samples was not compromised due to chemical reaction or contamination. Although the WSS was conceptually the best design for characterizing dry deposition to a water surface like Lake Tahoe, the equipment reliability suffered (e.g., cracked plastic tubing) under the intense sunshine during the hot summer in Sacramento. Thus, the number of samples with WSS data as part of the measurement suite was limited to only five.

The study results are summarized in the following figures showing the analytes from the non-traditional sampling methods (Y-axis) plotted against the analytes from the Standard sampling method (X-axis).

The results of lab duplicate analyses (i.e., sample was reanalyzed) are shown in **Figure A-3**. As can be seen, the original and reanalyzed results are generally very comparable and indicate good, consistent laboratory protocols. Any deviations in the measurements of the duplicate field samples therefore are probably real or associated with sample contamination during processing and shipping.

Duplicate field samples (i.e., side-by-side measurements with the same method) were made with the Standard and TRG samplers. Technically, the second TRG sampler was not a duplicate because it consisted of a deposition bucket of standard depth filled with 10 liters of de-ionized water to raise the water level to the same depth from the rim as the other TRG bucket. Furthermore, the second TRG bucket also did not include the baffling. The results of field duplicate samples for the Standard method indicate reasonable precision except for a couple of samples. The only valid duplicate sample collected for the TRG method indicated differences, particularly for phosphorus.

A simple comparison of the non-standard methods with the Standard dry deposition method is presented in **Table A-3**. The cell with the predominant relationship/pattern is shaded. Of interest is the tendency for the TRG water-based method to measure higher amounts of N and P than with the Standard method. The WSS method tended to have variable results but, except for TKN, tended to yield comparable results on average with the standard method. Although the Tube method also had variable results, its P results were similar, but its N results were higher, when compared with the Standard method. Staff anticipated that the water-based sampling methods would yield more ammonium because ammonia gas ( $\text{NH}_3$ ) is relatively abundant in the atmosphere and is also water-soluble and thereby depositing to water surfaces but not the standard dry bucket. If this were the case, a water-based deposition sampling method would be more representative of nitrogen deposition to a lake than the Standard dry bucket method. Interestingly however, although the TRG method usually detected more ammonium ( $\text{NH}_4$ , the presumed product of  $\text{NH}_3$  deposition) than the Standard method, the other water-based method (WSS) detected similar  $\text{NH}_4$ . It is not known if the difference is due to the limited number of samples (5) or if the air turbulence induced by the bucket sampler caused more deposition of  $\text{NH}_3$  to its water surface. Another interesting pattern is that the phosphorus measurements with the WSS and Tube methods were comparable to the Standard method but the phosphorus from the TRG method tended to be comparable to or higher than with the Standard method.

Matched method samples are shown by analyte in **Figures A8-A10** to provide more detail about the relationships between pollutants and the dry deposition methods. In general, the relationships between the methods are not well defined and tend to have significant scatter. However, the alternative methods all tend to “see” more nitrogen species and comparable phosphorus species than the standard dry deposition method.

Given the apparent shift in N and P results when TRG changed dry deposition methods in 1989 and the limited results from the Dry Deposition to Surrogate Surfaces Comparison Study, additional work to quantify the differences between sampling methods and to understand the reasons for the differences is warranted.

**Table A-1.** Precipitation (cm) and atmospheric deposition rates ( $\mu\text{moles}/\text{m}^2/\text{day}$ ) at Ward Lake Level (aka Wallis Tower).

WY*	Precip	NO <sub>3</sub>		NH <sub>4</sub>		SRP	
		Wet	Dry	Wet	Dry	Wet	Dry
1983	167.6	13.1	2.3	9.6	2.0	0.42	0.27
1984	129.2	11.9	2.5	6.7	1.6	0.27	0.33
1985	73.8	13.5	2.5	11.5	2.5	0.48	0.45
1986	160.2	24.7	3.3	19.2	2.2	0.68	0.32
1987	49.7	11.0	2.2	9.2	1.8	0.23	0.37
1988	56.1	12.3	1.8	11.2	1.2	0.29	0.30
1989**	120.3	20.0	10.2	17.4	9.6	0.57	0.97
1990	78.5	21.7	6.1	20.0	6.7	0.35	0.91
1991	75.0	14.1	6.1	11.4	7.2	0.23	0.92
1992	65.3	12.9	7.0	9.8	8.8	0.19	1.46
1983-88 mean	106.1	14.4	2.4	11.2	1.9	0.4	0.3
1989-92 mean	84.8	17.2	7.4	14.7	8.1	0.3	1.1
'83-88 mean / '89-92 mean	1.251	1.191	3.021	1.304	4.288	0.848	3.132

**Source:** Jassby et al., *Water Resources Research*, Vol. 30, No. 7, pp. 2207-2216, July 1994.

\* Water Year from Oct. 1 through Sept. 30

\*\* sampling changed to water-based dry deposition method

**Table A-2.** Summary of samples collected during the Dry Deposition Method Comparison Study.

Sample Set #	Period (2003/2004)	AeroChem Standard	AeroChem Standard #2	AeroChem TRG	AeroChem TRG #2	TRG – tube	H <sub>2</sub> O Surface Sampler
1	3/6 – 3/11/03	S-X	NS	S-X	NS	NS	S-IV (malfunction)
2	3/28 – 4/7	S-X	NS	S-X	NS	S-IV (rain)	S-IV (rain)
3	4/7 – 4/11	S-X	NS	S-X	NS	S-X	S-IV (malfunction)
4	5/14 – 6/3	S-X	NS	S-X*	NS	S-X	NS (broken)
5	6/3 – 6/10	S-X	NS	S-X	NS	S-X	NS (broken)
6	6/10 – 6/17	S-X	NS	S-X	NS	S-X	NS (broken)
7	6/17 – 6/24	S-X	NS	S-X	NS	S-X	NS (broken)
8	10/10 – 10/14	S-X	NS	S-X	NS	S-IV (toppled)	S-X
9	10/14 – 10/17	S-X	S-X	S-X	NS	S-X	S-X
10	10/17 – 10/20	S-\RL	S-X	S-X	S-/FL	S-IV (lost)	S-X
11	10/20 – 10/24	S-X	S-X	S-X	S-X	S-X	S-X
12	10/24 – 10/28	S-\RL	S-X	S-/FL	NS	S-X	S-/FL
13	10/28 – 10/31	S-/FL	S-X	S-X	NS	S-/FL	S-X
14	10/31 – 11/10	S-X	NS	S-X	NS	S-IV (rain)	S-IV (rain)
15	11/10 – 11/14	S-X	NS	S-X	NS	S-X	S-X
16	12/15 – 12/19/03	S-IV (damgd)	NS	S-IV (damgd)	NS	S-IV (damgd)	S-IV (damgd)
17	2/9 – 2/13/04	S-IV (damgd)	NS	S-IV (damgd)	NS	S-IV (damgd)	S-IV (lost)
18	5/11 – 5/17	S-IV (lost)	NS	S-IV (lost)	NS	S-IV (lost)	S-IV (leak)
19	5/17 – 5/21/04	S-IV (lost)	NS	S-IV (lost)	NS	S-IV (lost)	S-IV (lost)
<b># collected</b>		<b>19</b>	<b>5</b>	<b>19</b>	<b>2</b>	<b>18</b>	<b>15</b>
<b># analyzed</b>		<b>15</b>	<b>5</b>	<b>15</b>	<b>2</b>	<b>10</b>	<b>7</b>

\* sample dry due to long collection period during warm weather; 1 liter de-ionized water added before sample collection.

**Abbreviations:**

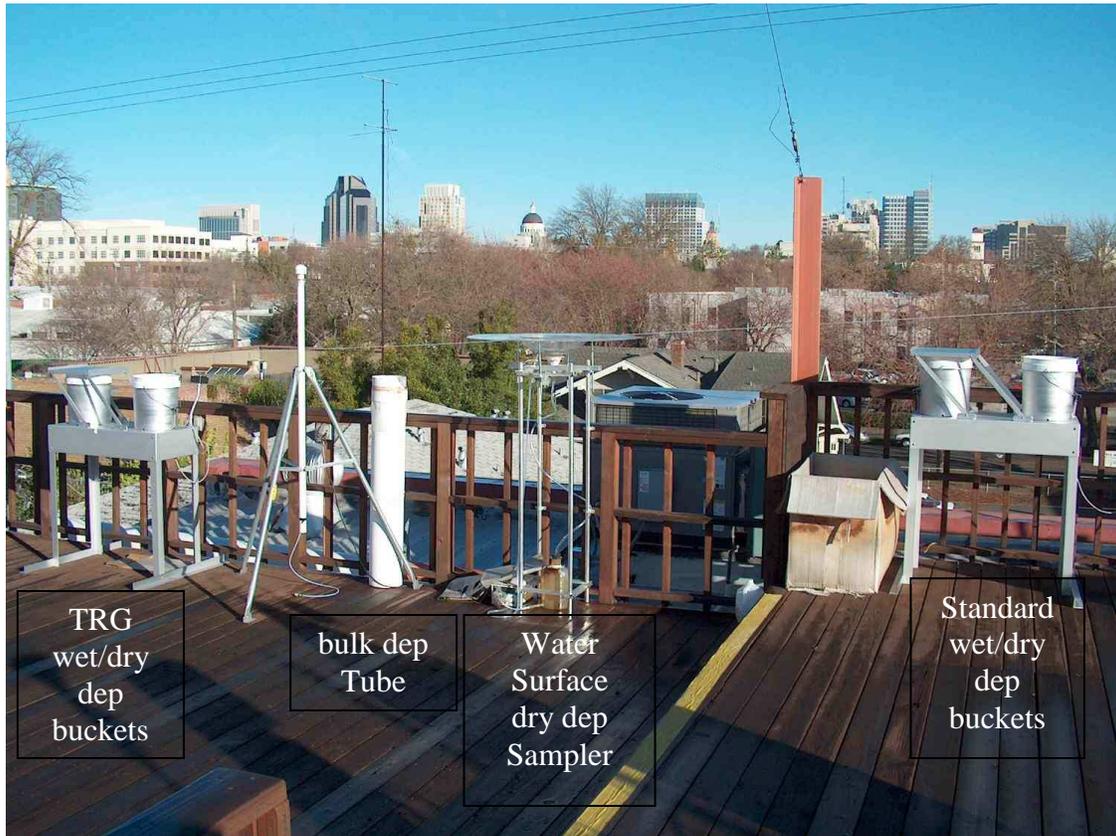
NS – no sample collected; S – sample collected; IV – invalid sample; / - raw sample analyzed; \ - filtered sample analyzed  
 dmgd – damaged (sample labels not legible due to water damage)  
 lost – lost in shipment; FL – filtered sample lost; RL – raw sample lost

**Table A-3.** Comparison summary of dry deposition measurement results from various surrogate surface methods and the Standard Dry Deposition Bucket method.

<b>Specie \ Measurement Method</b>	<b>MM &gt; Stnd</b>	<b>MM ≈ Stnd</b>	<b>MM &lt; Stnd</b>	<b>Data Pairs</b>
<b>Total Kjeldahl Nitrogen</b>				
WSS	5	0	0	5
TRG	13	0	0	13
Tube	6	3	0	9
<b>Total Ammonium</b>				
WSS	1	3	1	5
TRG	10	2	0	12
Tube	9	0	0	9
<b>Total Nitrite/Nitrate (as NO<sub>3</sub>)</b>				
WSS	3	0	2	5
TRG	10	1	1	12
Tube	7	2	0	9
<b>Total Phosphorus</b>				
WSS	1	1	3	5
TRG	6	3	3	12
Tube	3	5	1	9
<b>Dissolved Phosphorus</b>				
WSS	1	3	1	5
TRG	7	0	3	10
Tube	2	3	3	8
<b>Soluble Reactive Phosphorus</b>				
WSS	0	4	1	5
TRG	3	4	4	11
Tube	1	3	4	8

Note: shading indicates the relative tendency of the measurements with various dry deposition methods compared to the standard dry deposition bucket sampling method.

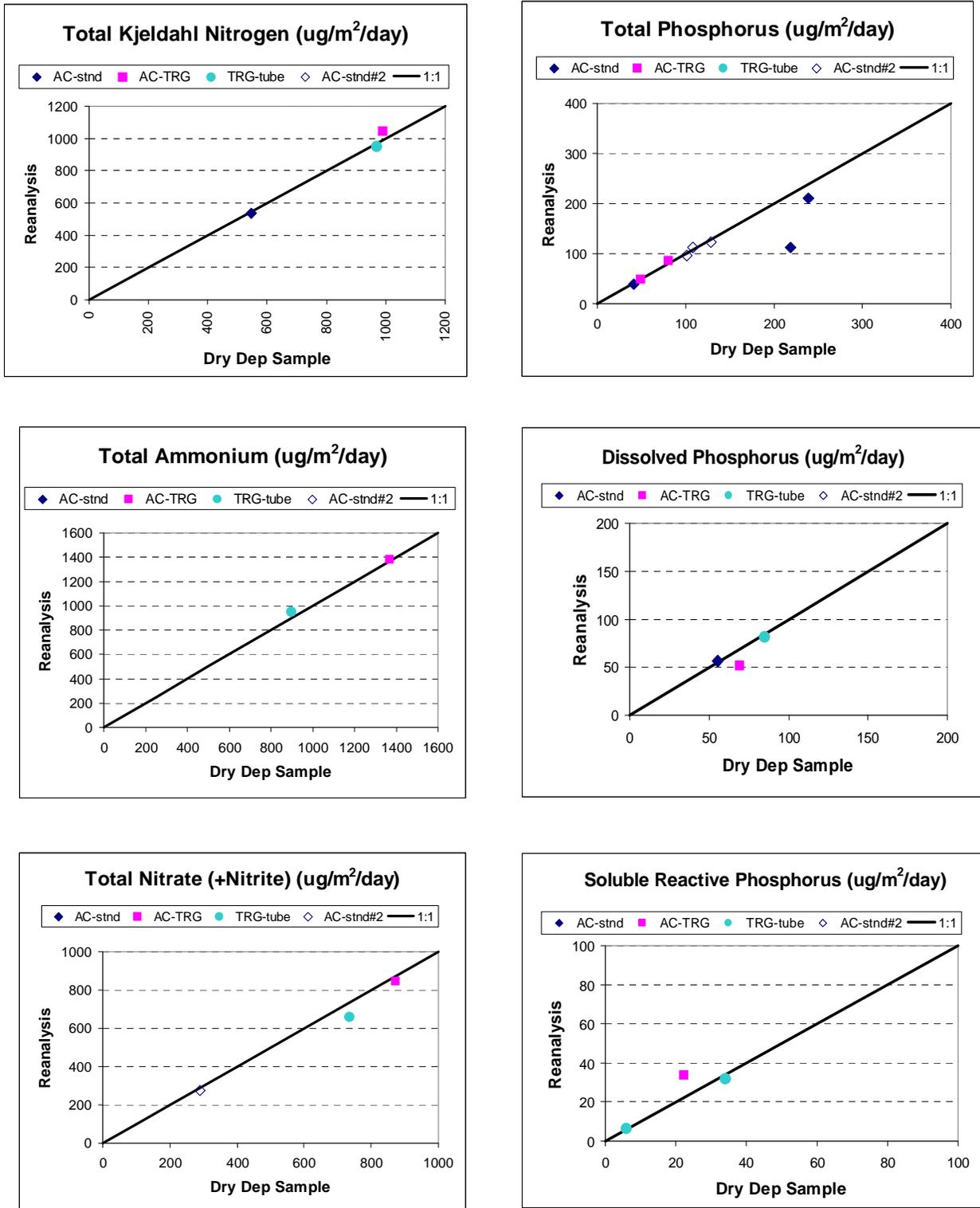
**Figure A-1.** Samplers used in the dry deposition method comparison study on the rooftop of ARB’s Monitoring & Laboratory Division offices in Sacramento.



**Figure A-2.** Close-up views of Water Surface Sampler and TRG-“dry” deposition bucket.



**Figure A-3.** Scatter plots of laboratory replicate analytical results in  $\mu\text{g}/\text{m}^2/\text{day}$ .



**Figure A-4.** Scatter plots of field duplicate analytical results in  $\mu\text{g}/\text{m}^2/\text{day}$ .

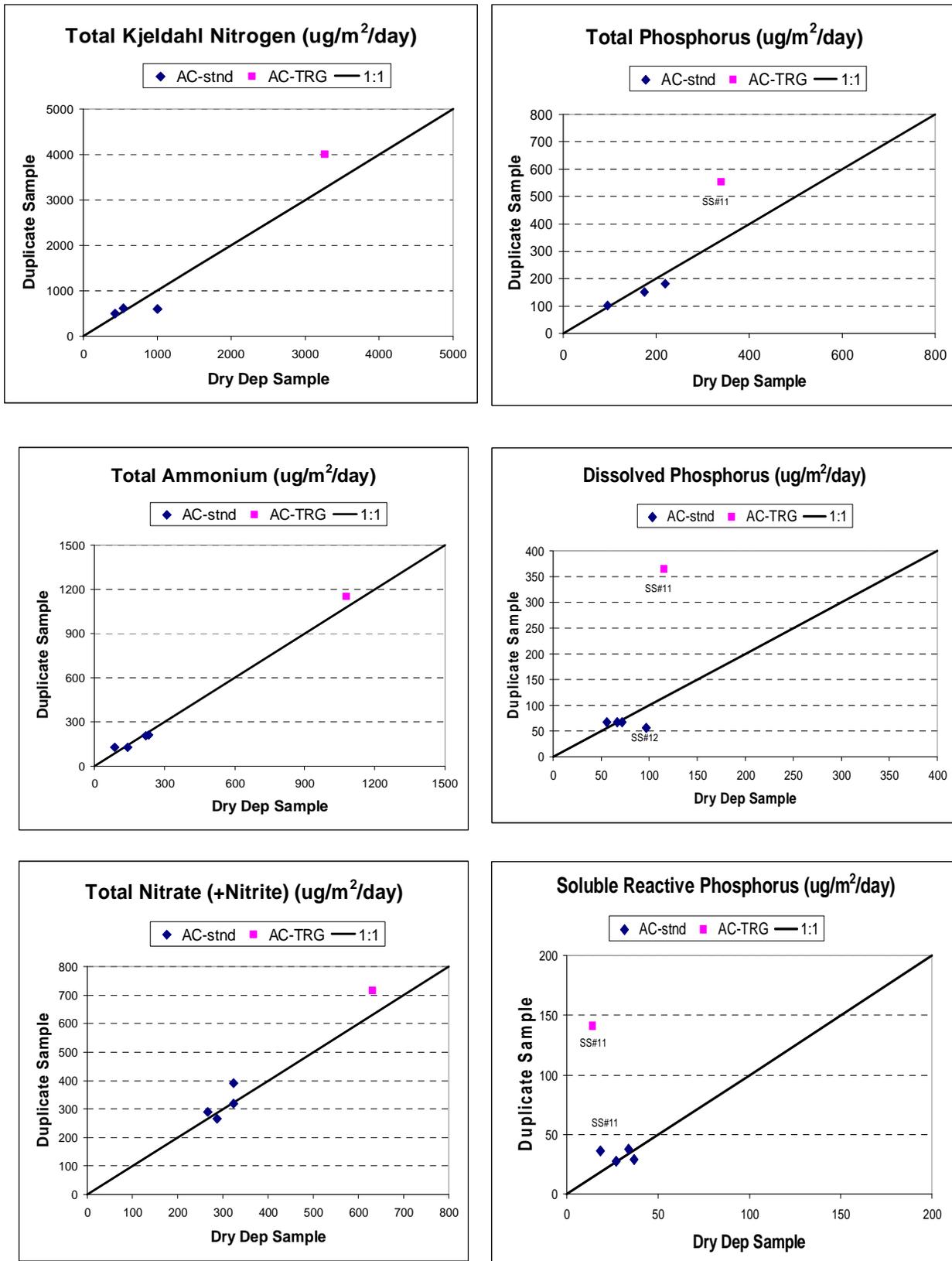


Figure A-5. Scatter plots of Total Kjeldahl Nitrogen results in  $\mu\text{g}/\text{m}^2/\text{day}$ .

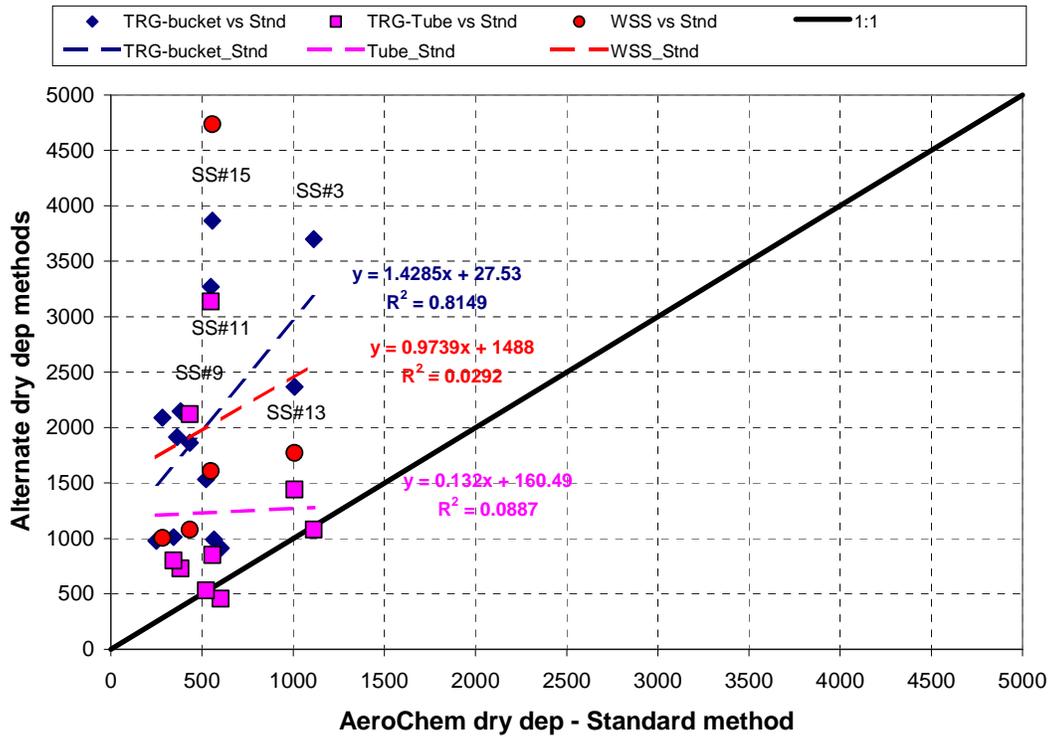
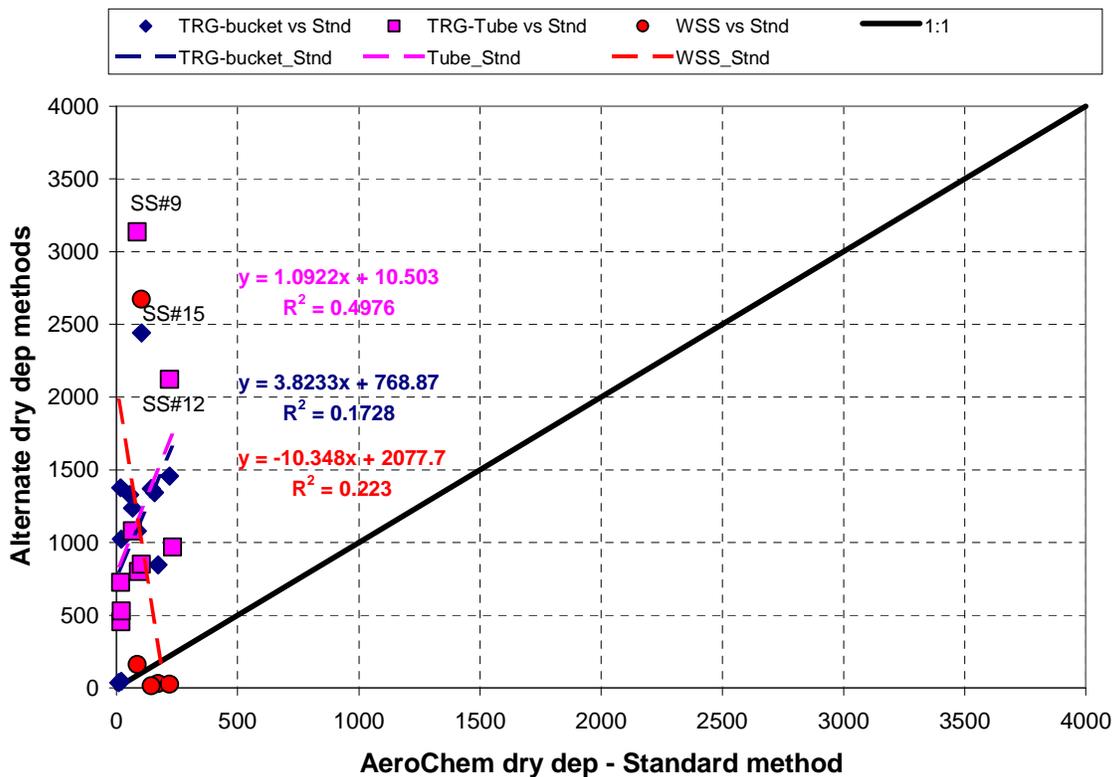
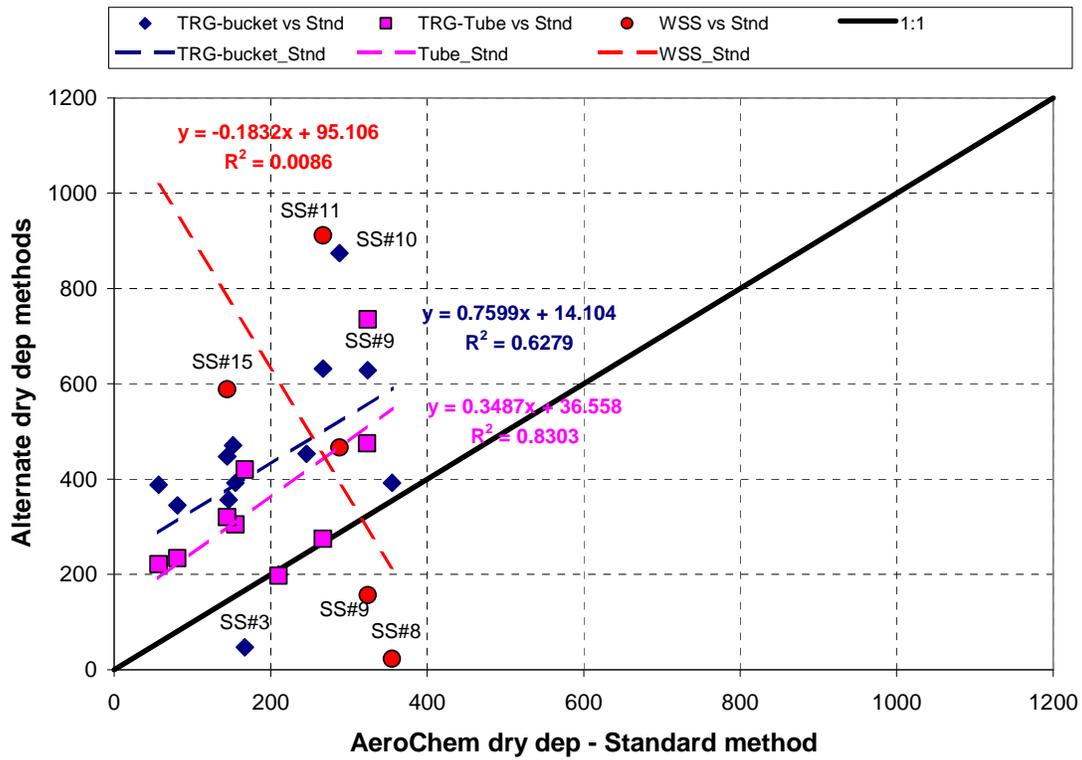


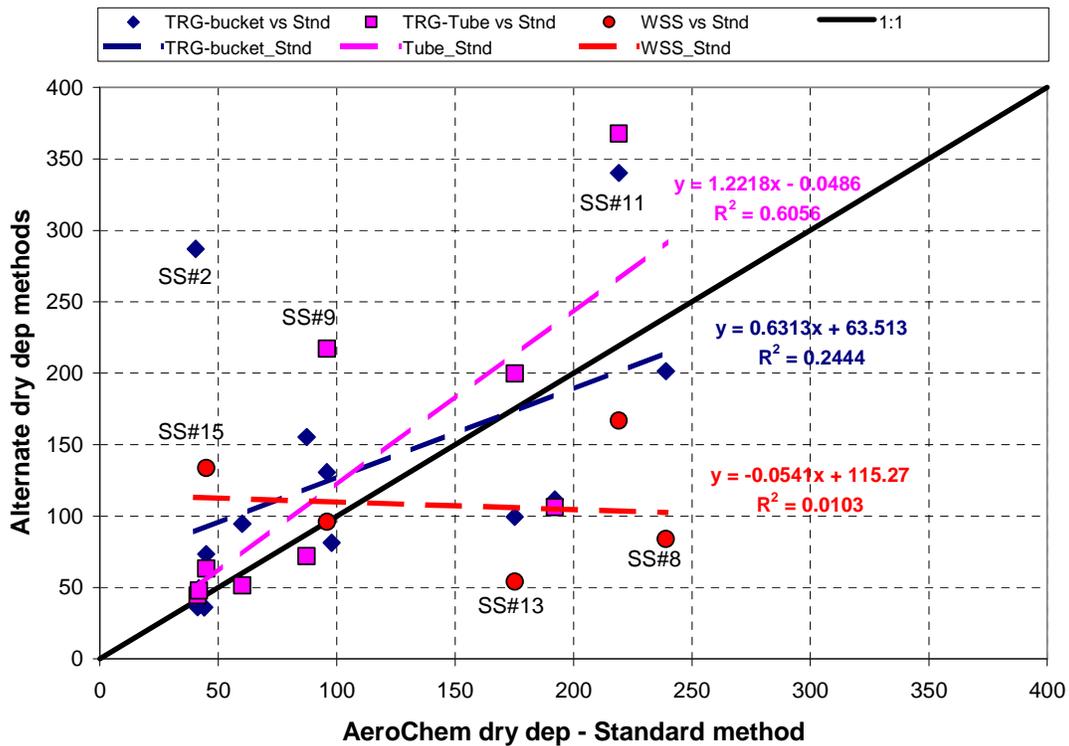
Figure A-6. Scatter plots of Ammonium results in  $\mu\text{g}/\text{m}^2/\text{day}$ .



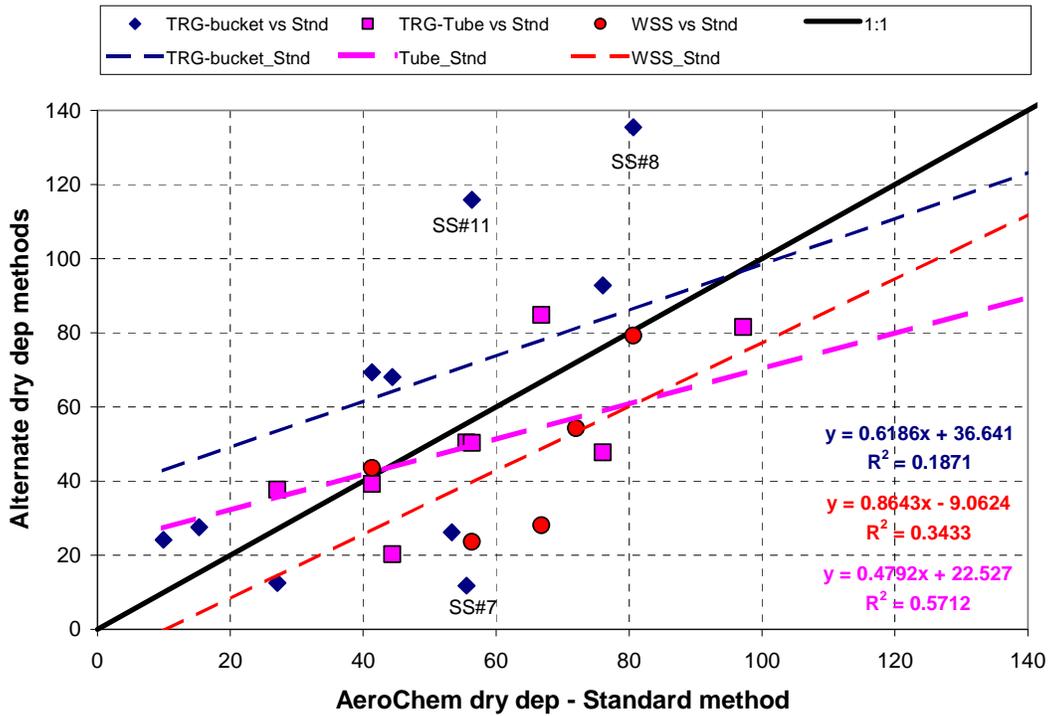
**Figure A-7.** Scatter plots of Nitrite + Nitrate results (as nitrate) in  $\mu\text{g}/\text{m}^2/\text{day}$ .



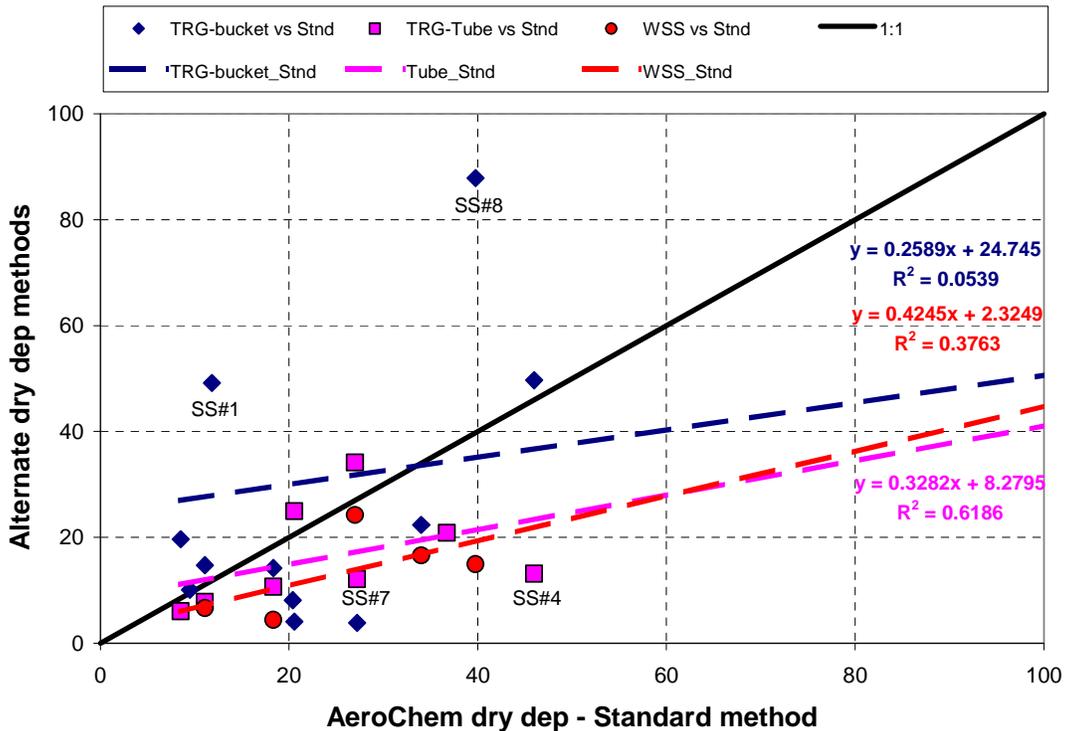
**Figure A-8.** Scatter plots of Total Phosphorus results in  $\mu\text{g}/\text{m}^2/\text{day}$ .



**Figure A-9.** Scatter plots of Dissolved Phosphorus results in  $\mu\text{g}/\text{m}^2/\text{day}$ .



**Figure A-10.** Scatter plots of Soluble Reactive Phosphorus results in  $\mu\text{g}/\text{m}^2/\text{day}$ .



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