Ambient Particle Sampling and Analysis in Support of the Columbia River Gorge Scenic Area Air Quality Study

Submitted to:

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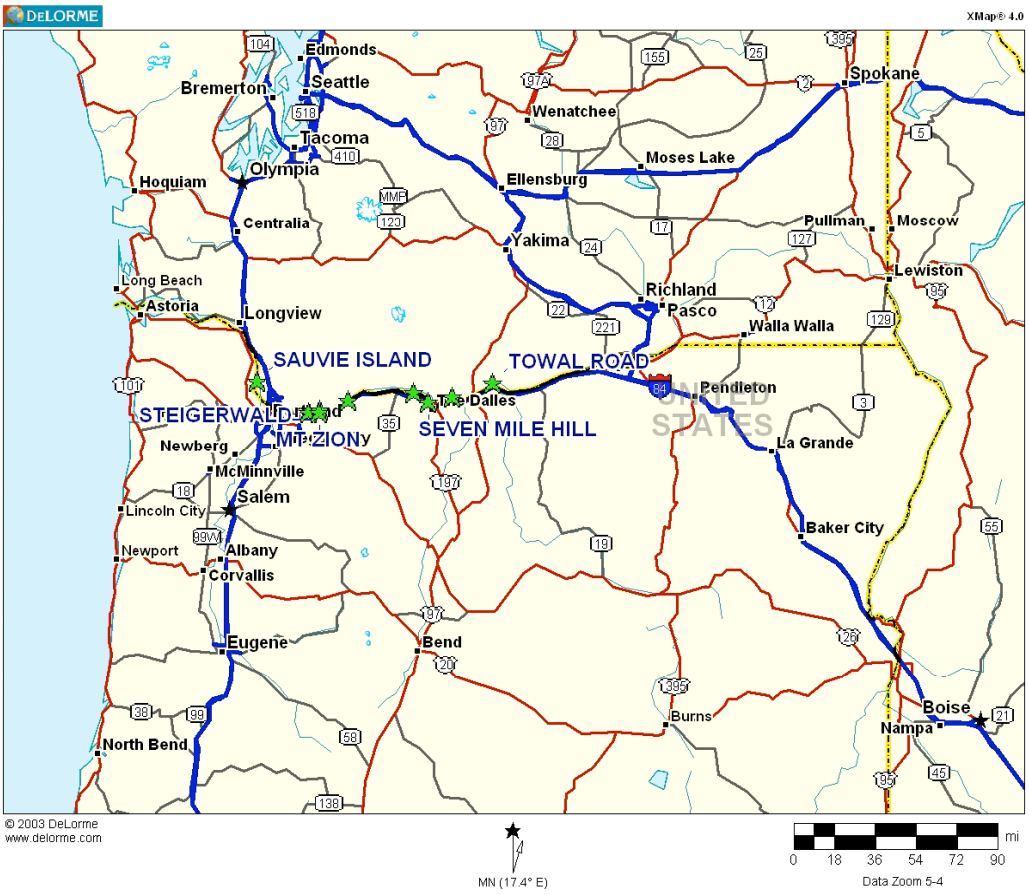
Background

The Columbia River Gorge Scenic Area Air Quality field experiments provided data for the Columbia River Gorge Haze Gradient Study (Green et. al, 2006) and the Causes of Haze in the Gorge (CoHaGo; Green et al., 2006) study. The CoHaGo study (described elsewhere) is a "data analysis effort intended to add to the understanding of the source areas and source types contributing significantly to haze in the Columbia River Gorge in the States of Washington and Oregon". As part of this effort we collected and analyzed aerosol samples in the Columbia River Gorge at several sites and periods from December 2003 through February 2005. This report provides a summary of the sampling we conducted and presents the Quality Assurance report associated with our sampling and analysis campaign.

Sampling Sites

Field sampling during the periods encompassing Winter 2003-2004, Summer 2004, Fall 2004, and Winter 2004-2005 was conducted at six locations. They are: Sauvie Island, Mt. Zion, Bonneville Dam (2 locations), Wishram, and Towal Road. Filter samplers were deployed at Sauvie Island and Towal Road. Impaction based samplers were located at Mt. Zion and Wishram and both filter and impaction sampling occurred at the two Bonneville Dam locations (Note: the Bonneville Dam locations were in sequential, not simultaneous operation). A map below provides an overview of the area encompassing the Columbia River Gorge sampling range (Map courtesy Green et al. 2006).



Sampling Instrumentation

Particulate sampling for the Columbia River Gorge Scenic Area Air Quality study included sampling with two different types of instrumentation for subsequent laboratory analysis of samples. All samples derived from this study have been archived following the non-destructive analyses. Samples were collected using an 8-stage Rotating DRUM Impactor (8-DRUM) sampler alongside an International Aerosol (IMPROVE like) Sampler (IAS). The Interagency Monitoring of Protected Visual Environments (IMPROVE) program (*Malm et al*., 1994) samples at the Wishram and Mt. Zion sites as part of a nationwide program to monitor visual quality in Class 1 (National Parks and Monuments) scenic areas.

The IAS unit collects discrete (time-integrated) aerosol samples in the $PM_{2.5}$ mode on three independent channels for analysis of mass, elemental, ion, and elemental/organic carbon fraction. The IAS collected samples 1 day in 3 to match IMPROVE sampling dates during the Columbia River Gorge Study. Unlike the IMPROVE "module" which contains 3 unique $PM_{2.5}$ samplers, the IAS uses the IMPROVE cyclone to effect a $PM_{2.5}$ cutpoint and traps the particles on 3 independent filters for analysis. Thus, the flow rate (23 liters/minute) and cyclone, cassette and filter media are identical to the IMPROVE units, but 1/3 the flow through each filter (and non-independent channels) is resulted.

The 8-Stage Rotating DRUM Impactor Sampler (8-RDI) is a cascade impactor based on the basic design of *Lundgren* (1967), and evolved from the original DRUM impactor as described by *Raabe et al*. (1988). The RDI sampler used in the CRG study operated at 16.7 liters per minute allowing it to couple to a 10 μm cutpoint ("PM_{10}") inlet (URG Corp.). The aerosol sample for each stage is deposited onto a rotating drum faced with a removable greased Mylar impaction surface. As the drum rotates a continuous aerosol sample is laid down along the direction of rotation with density varying along the length of the Mylar strip in proportion to the aerosol collected as the substrate rotates. By replacing the circular jets of the original DRUM with slits, the aerosol deposit is made uniform crosswise to the direction of rotation and the total deposit is spread over a known area per unit time (*Bench et al*., 2002). With the drums for all stages of the impactor geared together, coincident samples are collected on all eight stages. Analysis using a narrow beam technique (i.e. s-XRF, described below) for elements produces data with time resolution proportional to the ratio of drum surface speed divided by the beam width. Proposed sampling allows 42-day continuous record in 8 size bins (10-5, 5-2.5, 2.5-1.15, 1.15-0.75, 0.75-0.56, 0.56-0.34, 0.34-0.26, 0.26-0.09 micrometers aerodynamic diameter) analyzable in 3-hr time steps. A subset of 6 of the 42-day sampling periods were chosen for analysis.

Analysis

MASS

All Teflon filter samples were weighed prior to exposure (pre-weighed) using a Cahn 33 Microbalance under ambient conditions. Following exposure, the filter post-weight was conducted and recorded. Each sample was collected for 24-hours at a constant flow rate from midnight to midnight local time. Thus a 24-hour average PM2.5 concentration is the result of the

quotient of the post- and pre-weight difference and the total collected air. In a few cases multiple day exposures occurred and were recorded (i.e. 48-hour, etc.).

SYNCHROTRON X-RAY FLUORESCENCE (S-XRF)

Samples were analyzed by synchrotron X-ray fluorescence (s-XRF) [*Knochel*, 1989] using a broad-spectrum X-ray beam generated on beamline 10.3.1 at the Advanced Light Source (ALS) Lawrence Berkeley National Laboratory. The ALS s-XRF system is capable of high sensitivity detection of elements from Na to U (*Perry et al*., 2004). The s-XRF analysis provides quantitative elemental data for approximately 28 elements in 8 size modes with 3-hour time resolution on samples collected during the Columbia River Gorge campaign. This represents approximately 30,000 samples during the period spanning the SWCAA CRG project. The ALS is a Department of Energy (DOE) national user facility that generates intense ultraviolet and soft X-ray beams for scientific and technological research. Light from the beamline is collimated prior to entry into the sample chamber and is user selected to match the desired analysis protocol. The beam is plane-polarized thereby greatly reducing the background signal and dramatically improving the signal-to-noise ratio. Quantitative analysis is performed by calibrating the response of the Si(Li) detector to a comprehensive set of 40 single- and multi-element NIST-traceable standards (Micromatter, Inc.). A recent inter-laboratory comparison reveals no significant bias between for major elements (i.e. those significantly above minimum detectable limit) in samples measured at the Desert Research Institute via XRF and the ALS (*Cliff*, 2005). Previous tests have shown that the sample deposit from the RDI sampler is extremely uniform along the non-time axis [*Bench et al*., 2002]. Deconvolution of the raw X-ray spectra is performed using the latest version of WinAXIL (Canberra).

Filter ID	Site	Sample Date	Note
5	Towal Rd	12/17/03	
6	Towal Rd	12/20/03	
7	Towal Rd	12/23/03	
8	Towal Rd	12/26/03	
18	BonnDam	12/17/03	
19	BonnDam	12/20/03	
20	BonnDam	12/23/03	
21	BonnDam	12/26/03	
32	Towal Rd	2/9/04	
33	Towal Rd	2/12/04	
34	Towal Rd	2/15/04	
36	Towal Rd	2/18/04	
44	BonnDam	2/9/04	
45	BonnDam	2/12/04	
Start Second Season of Study			
2-1	BONN2	7/2&5/2004	No post cal data for #1-14
2-2	BONN2	7/8/04	
2-3	BONN2	7/11/04	
2-4	BONN2	7/14/04	
2-5	BONN2	7/17/04	
2-13	BONN2	8/13/04	

Filter ID	Site	Sample Date	Note
2-14	BONN2	8/16/04	
2-18	BONN2	8/31/04	
2-20	BONN2	9/6/04	
2-24	Sauvie Island	7/2/04	
2-25	Sauvie Island	7/5/04	
2-26	Sauvie Island	7/8/04	
2-27	Sauvie Island	7/11/04	
2-28	Sauvie Island	7/14/04	
2-29	Sauvie Island	7/17/04	
2-38	Sauvie Island	8/13/04	
2-39	Sauvie Island	8/16/04	
2-44	Sauvie Island	8/31/04	
2-45	Sauvie Island	9/3/04	Out of filters, ship 9/8
2-50	Sauvie Island	9/24/04	
51	Sauvie Island	9/27/04	
52	Sauvie Island	9/30/04	Missing B channel noted in SSC log book
102	BONN2	9/24/04	
103	BONN2	9/27/04	
104	BONN2	9/30/04	
105	BONN2	10/3/04	
109	BONN2	10/15&18/2004	Ran 10/15 & 10/18
112	BONN2	10/27/04	post-weight confirmed
114	BONN2	11/2/04	
115	Sauvie Island	10/3/04	
119	Sauvie Island	10/15/04	
123	Sauvie Island	10/27/04	masked
125	Sauvie Island	11/2/04	a masked
126	Sauvie Island	11/5/04	masked
127	Sauvie Island	11/8/04	
128	BONN2	11/5&8/2004	
129	BONN2	11/11/04	
130	BONN2	11/14/04	
131	BONN2	11/17/04	
132	BONN2	11/20/04	masked
133	BONN2	11/23&26/2004	
138	Sauvie Island	11/11/04	
139	Sauvie Island	11/14/04	
140	Sauvie Island	11/17/04	
141	Sauvie Island	11/20/04	
142	Sauvie Island	11/23/04	
200	BONN2	12/11/04	
202	BONN2	12/17&20/2004	
203	BONN2	12/23&26/2004	A hole on the filter
205	BONN2	1/1/05	
206	BONN2	1/4/05	
207	BONN2	1/7&10/2005	
208	BONN2	1/13/05	
209	BONN2	1/16/05	
210	BONN2	1/19/05	

Filter ID	Site	Sample Date	Note
211	BONN2	1/22/04	
212	BONN2	1/25/04	
213	BONN2	1/28&31/2004	
214	BONN2	2/3/04	
217	Towal Rd.	12/11/04	
220	Towal Rd.	12/17/04	
222	Towal Rd.	12/26/04	
224	Towal Rd.	1/1/05	
226	Towal Rd.	1/7/05	
227	Towal Rd.	1/4/05	No sample 1/10/04 possible double? Check with JB
228	Towal Rd.	1/13/05	
229	Towal Rd.	1/16/05	
230	Towal Rd.	1/19/05	
231	Towal Rd.	1/22/05	
232	Towal Rd.	1/25/05	
233	Towal Rd.	1/28/05	
234	Towal Rd.	1/31/05	
235	Towal Rd.	2/3/05	
236	BONN2	2/6/04	
237	BONN2	2/9/04	
238	BONN2	2/12/04	
239	BONN2	2/15/04	
240	BONN2	2/18/04	
241	BONN2	2/21/04	
242	No sample		blank
243	Towal Rd.	2/6/05	
244	Towal Rd.	2/9/05	
245	Towal Rd.	2/12/05	
246	Towal Rd.	2/15/05	
247	Towal Rd.	2/18/05	
248	Towal Rd.	2/21/05	
249	No sample		blank

Table 1. Selected subset of International Aerosol Sampler (IAS) filters chosen for analysis. Data are included in appended CD-ROM. Unanalyzed filters are archived. All samples collected were analyzed for gravimetric mass.

7/16/04- 8/17/04	Mt Zion	Bonneville Cascade Is.
9/29/04-11/2/04	Mt Zion	Bonneville Cascade Is.
1/12/05-2/23/05	Wishram	Bonneville Cascade Is.

Table 2. Selected dates for RDI sample analysis. Six sets of samples were analyzed. Each sampling period represents approximately 6-weeks of sampling. The resultant data (3-hour ambient) are equivalent to more than 15,000 individual samples.

Figure Note 1: The following (Figures 1-14) are scatter plots of s-XRF v. DRI concentration data for the ambient samples collected on filters (N=71 samples) of $PM_{2.5}$, PM_{10} and TSP particle size ranges for selected elements. These samples were collected in the Lake Tahoe Basin and generally have total mass less than 10 μg/m^3 for PM2.5 mass. The range in mass and loading for the Tahoe samples represented in these plots is comparable to the CRG samples for the present work.

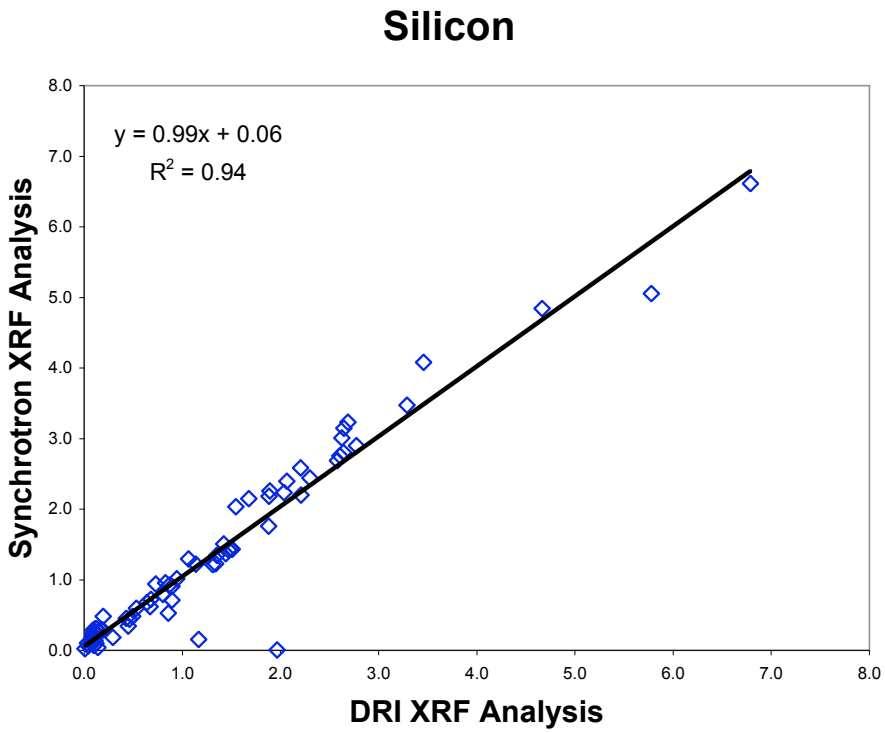


Figure 1. Silicon ALS v. DRI

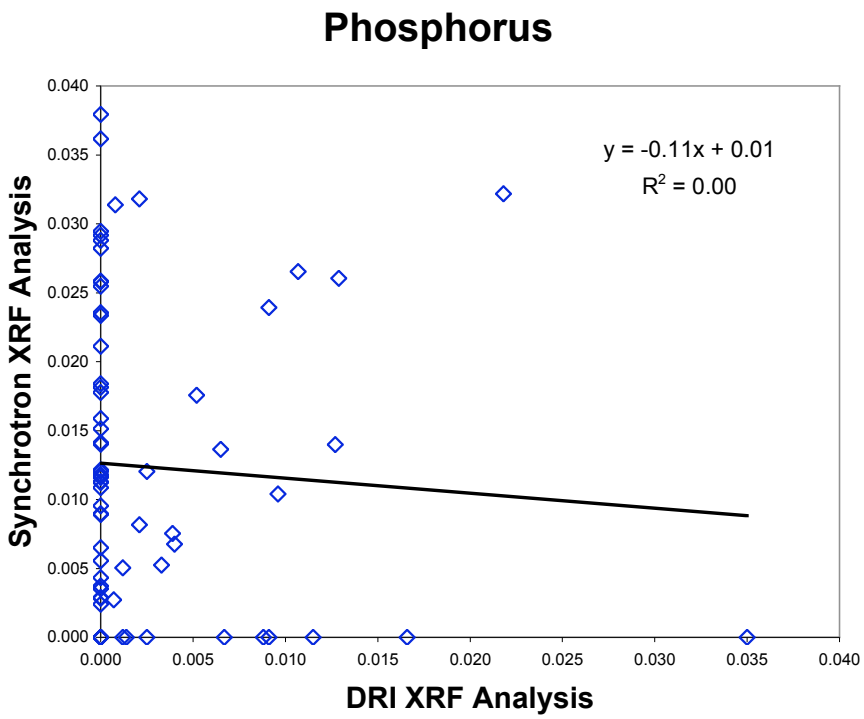


Figure 2. Phosphorous ALS v. DRI

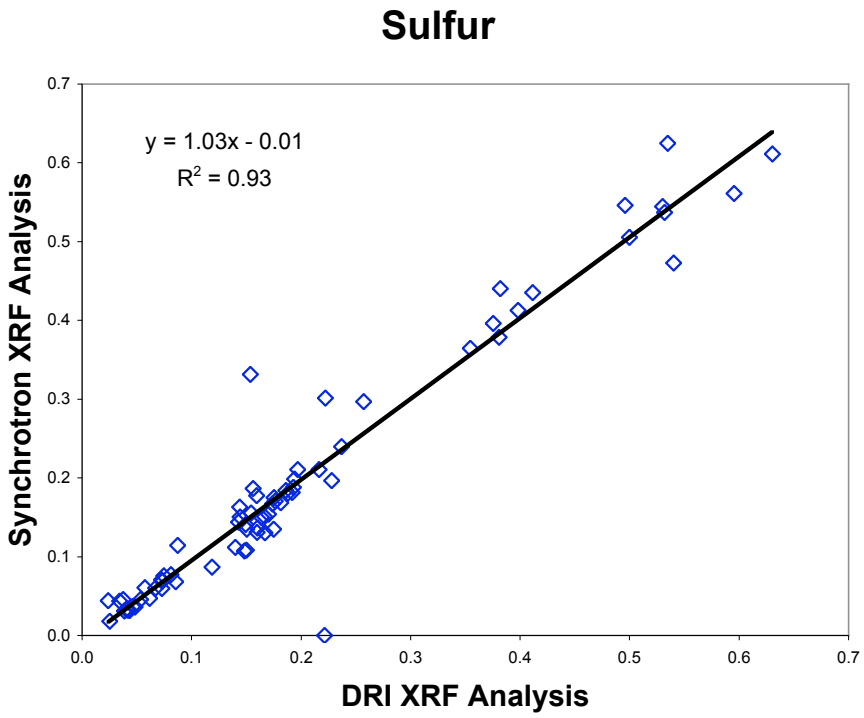


Figure 3. Sulfur ALS v. DRI

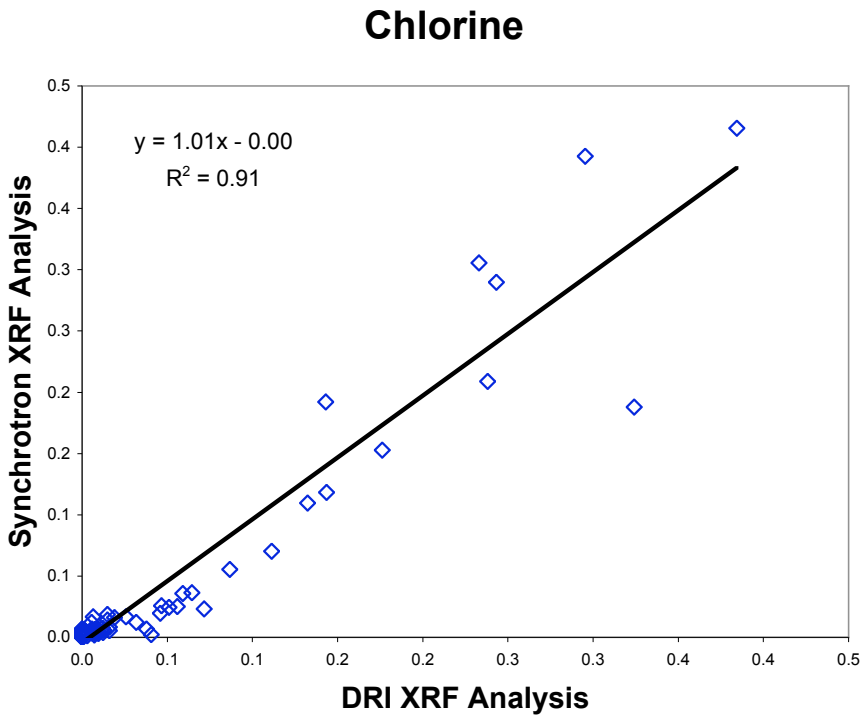


Figure 4. Chlorine ALS v. DRI

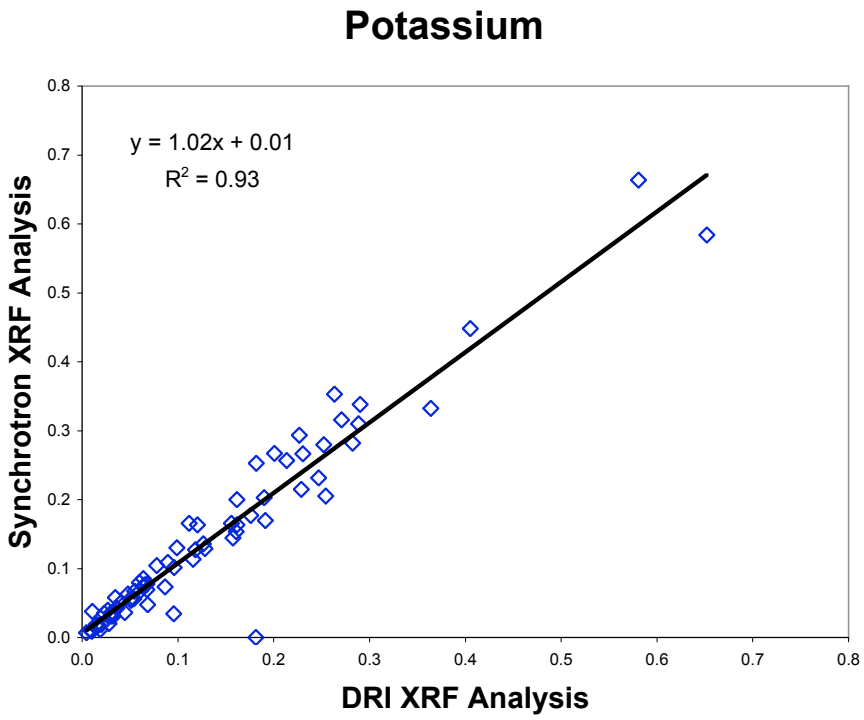


Figure 5. Potassium ALS v. DRI

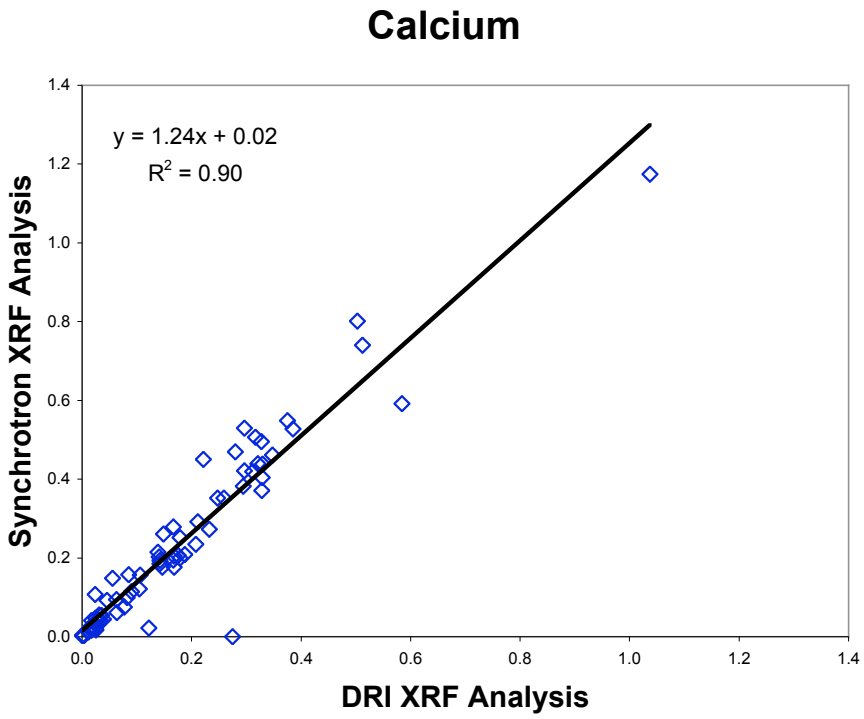


Figure 6. Calcium ALS v. DRI. Note: There is no blank subtraction on s-XRF data for Ca in this plot.

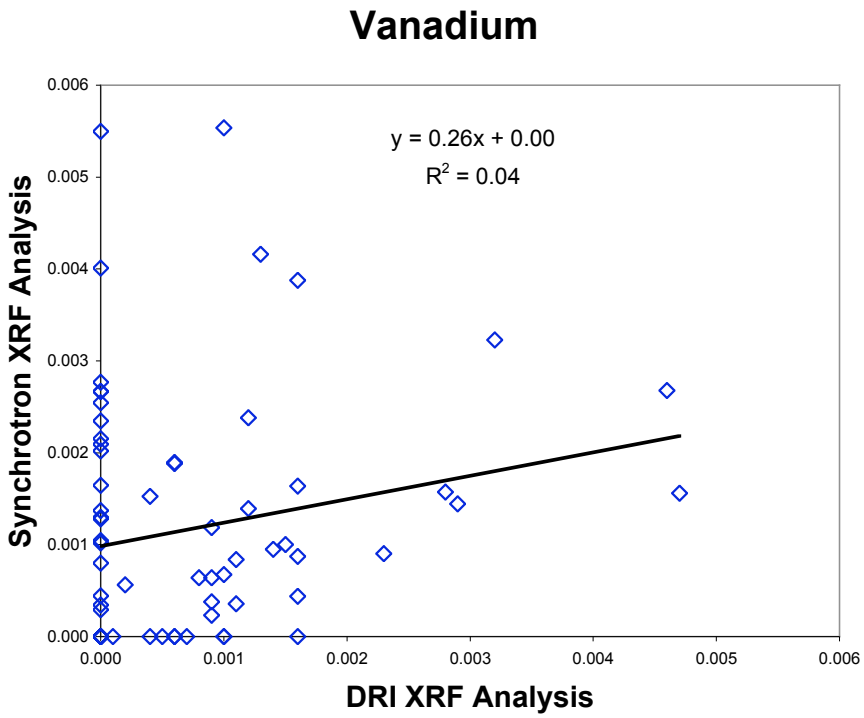


Figure 7. Vanadium ALS v. DRI

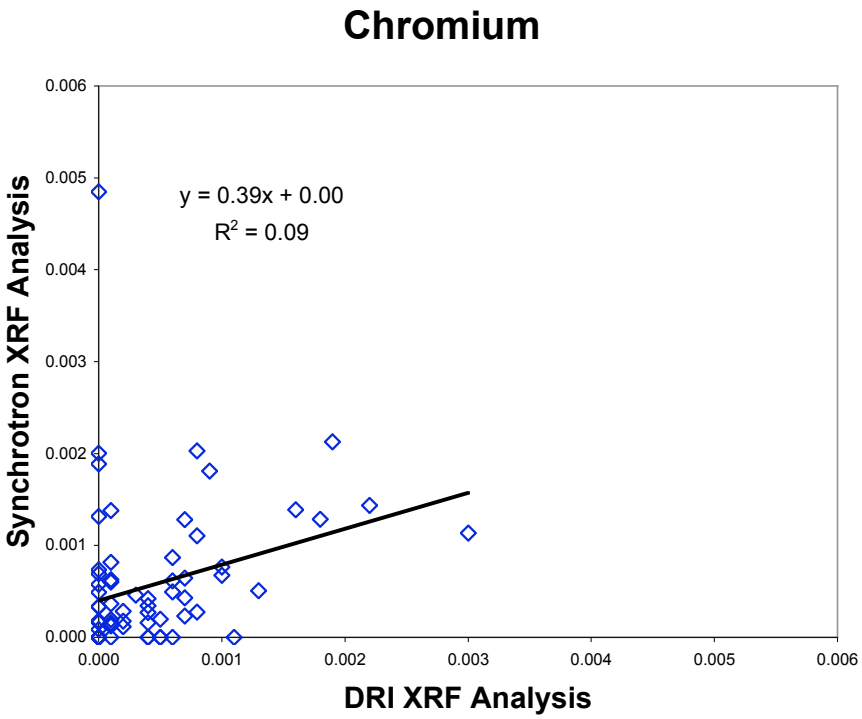


Figure 8. Chromium ALS v. DRI

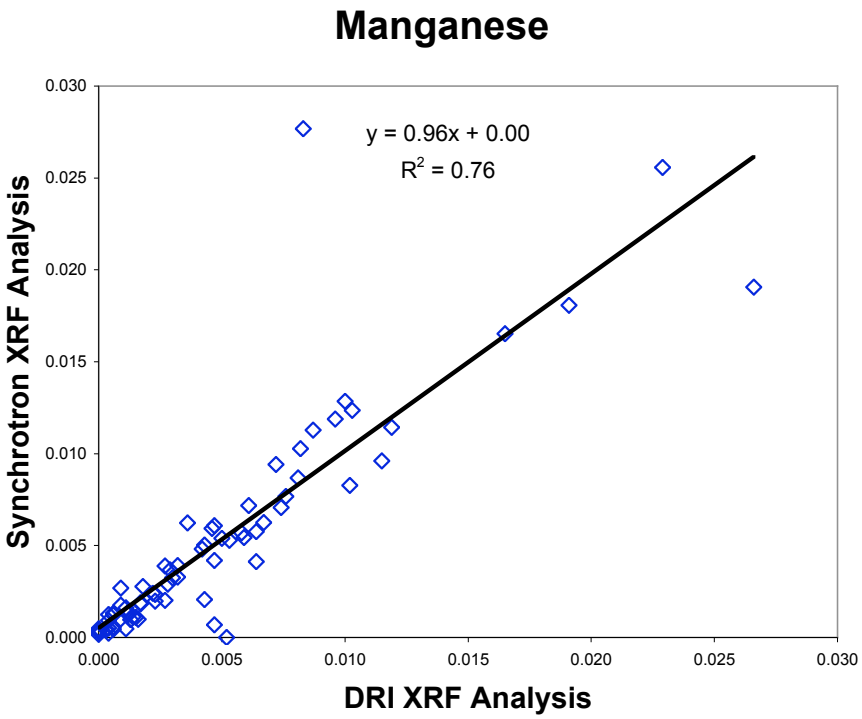


Figure 9. Manganese ALS v. DRI

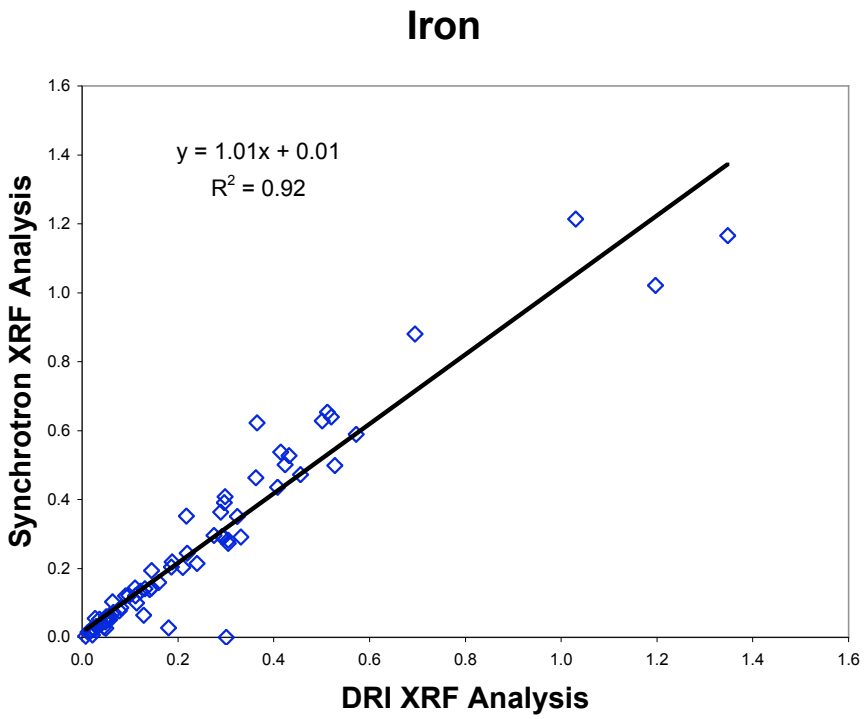


Figure 10. Iron ALS v. DRI

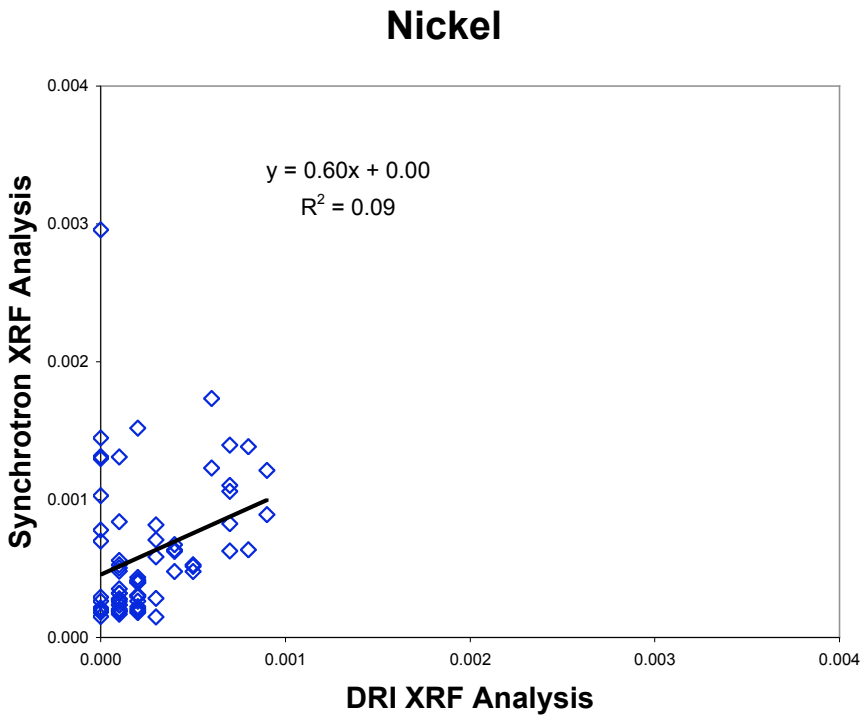


Figure 11. Nickel ALS v. DRI

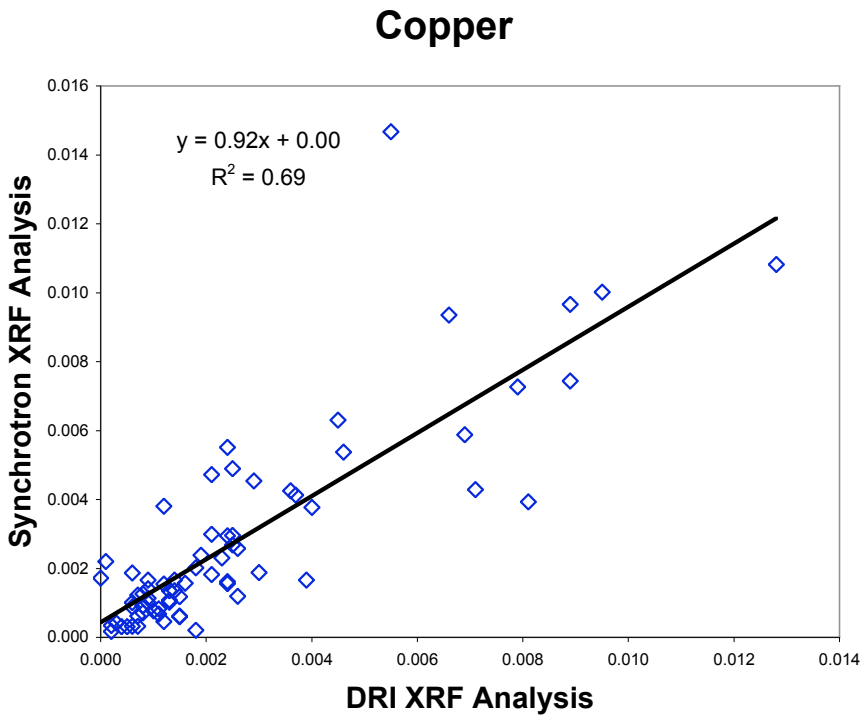


Figure 12. Copper ALS v. DRI

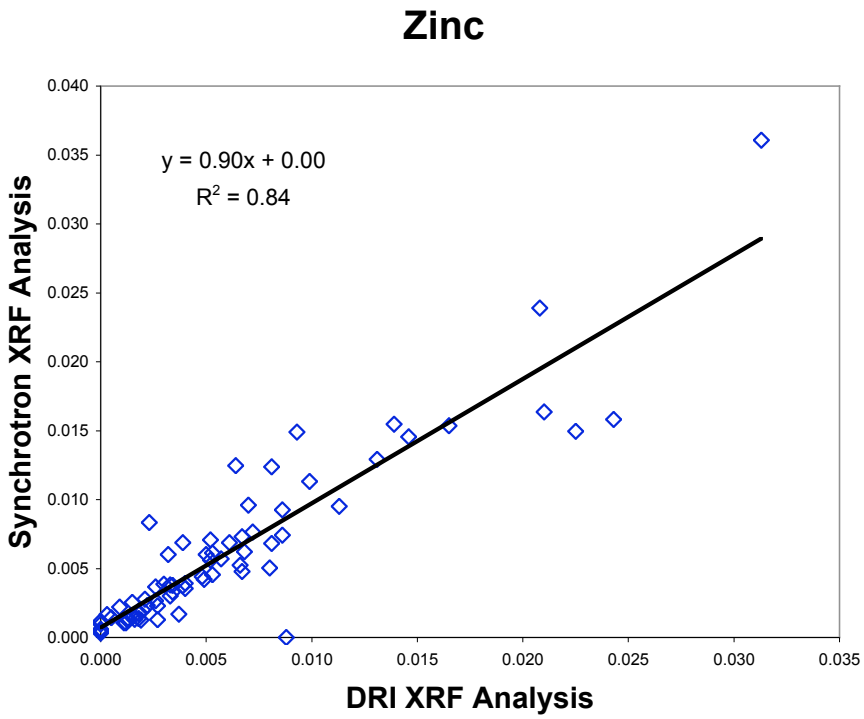


Figure 13. Zinc ALS v. DRI

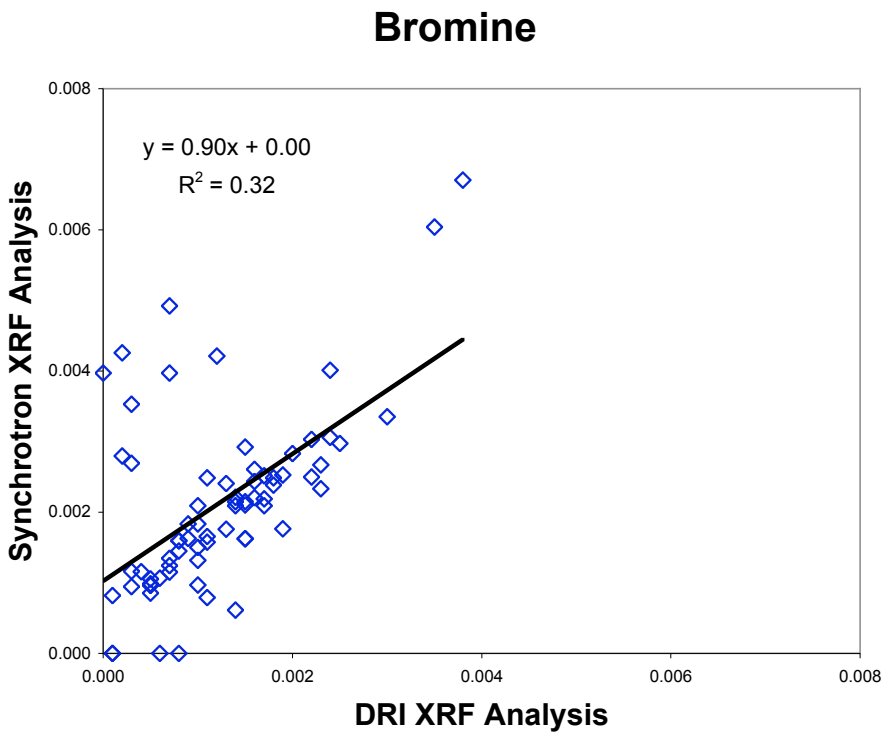


Figure 14. Bromine ALS v. DRI

Comparison of XRF analysis software

In order to effect the best possible results from the XRF analyses, we employed a new peak fitting software package from Canberra Instruments called "WinAXIL." The new software is advertised to use the same least squares peak fitting algorithm as the original AXIL, but is compiled to run on Windows XP and has been updated to provide a more user-friendly interface. We processed approximately 25% of the LTADS ambient filters shown in Figures 1-14 above, using WinAXILBatch (including a blank subtraction). The substantial reduction in uncertainty is an improvement for trace species quantification. The WinAXIL software employed for the present work represents the best possible peak fitting software available for the low density loading on the CRG samples.

Table 3. Elemental concentration comparison of original and new peak fitting x-ray analysis programs. The results indicate that the different software packages do not vary for major elements and blank subtraction has little affect on elements with good comparison with DRI results. Results for P indicate 13% reduction in concentration, on average, based on the reanalysis. These results are derived from reanalysis of approximately 25% of the ambient samples. A significant reduction in the uncertainty is noted for trace elements.

Element	Slope	R^2	Uncertainty Change
Na	1.52	0.73	-87%
Mg	1.25	0.80	-50%
Al	1.01	1.00	0%
Si	1.01	1.00	0%
P	0.87	0.92	-71%
S	1.01	1.00	-1%
Cl	1.03	1.00	+3%
K	1.03	1.00	+3%
Ca	1.02	1.00	+2%
Ti	0.99	1.00	-2%
V	1.47	0.99	-56%
Cr	1.03	0.98	-49%
Mn	1.03	1.00	-1%
Fe	1.00	1.00	0%
Co	0.94	1.00	-38%
Ni	0.87	0.93	-80%
Cu	0.97	1.00	-14%
Zn	0.99	1.00	-9%

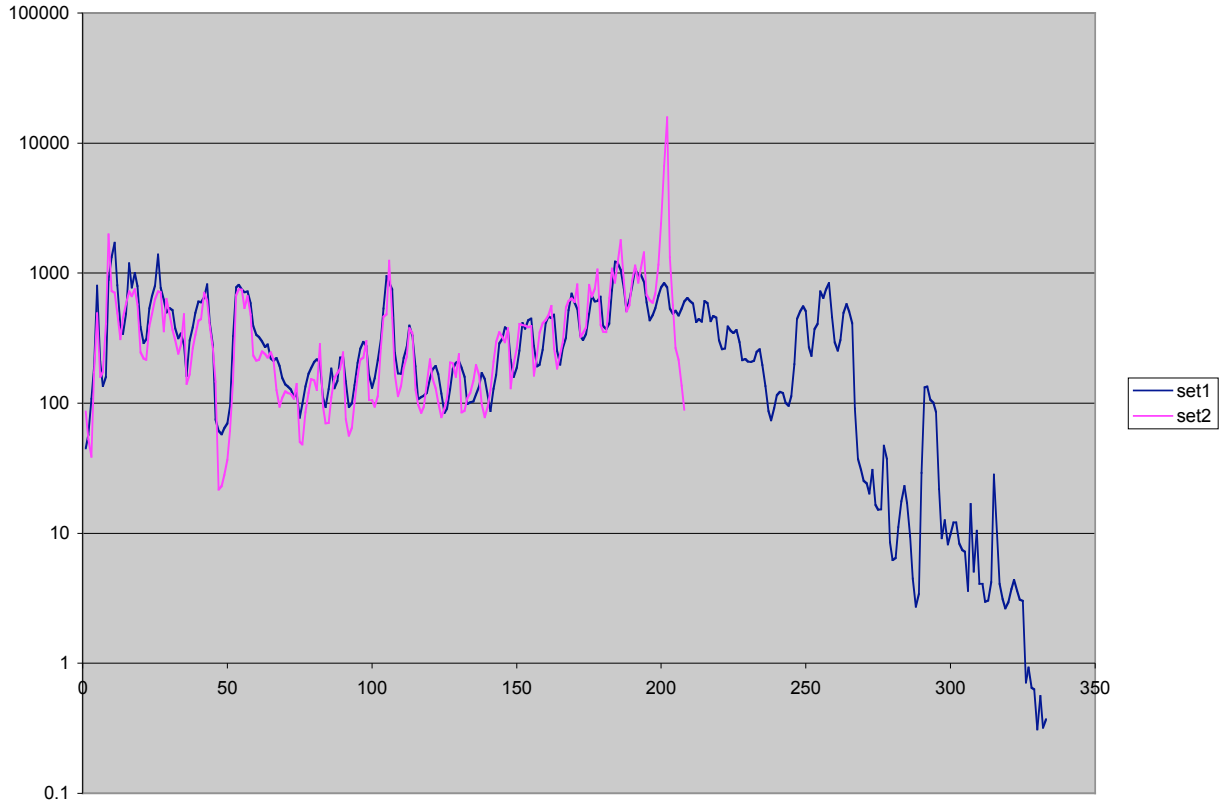


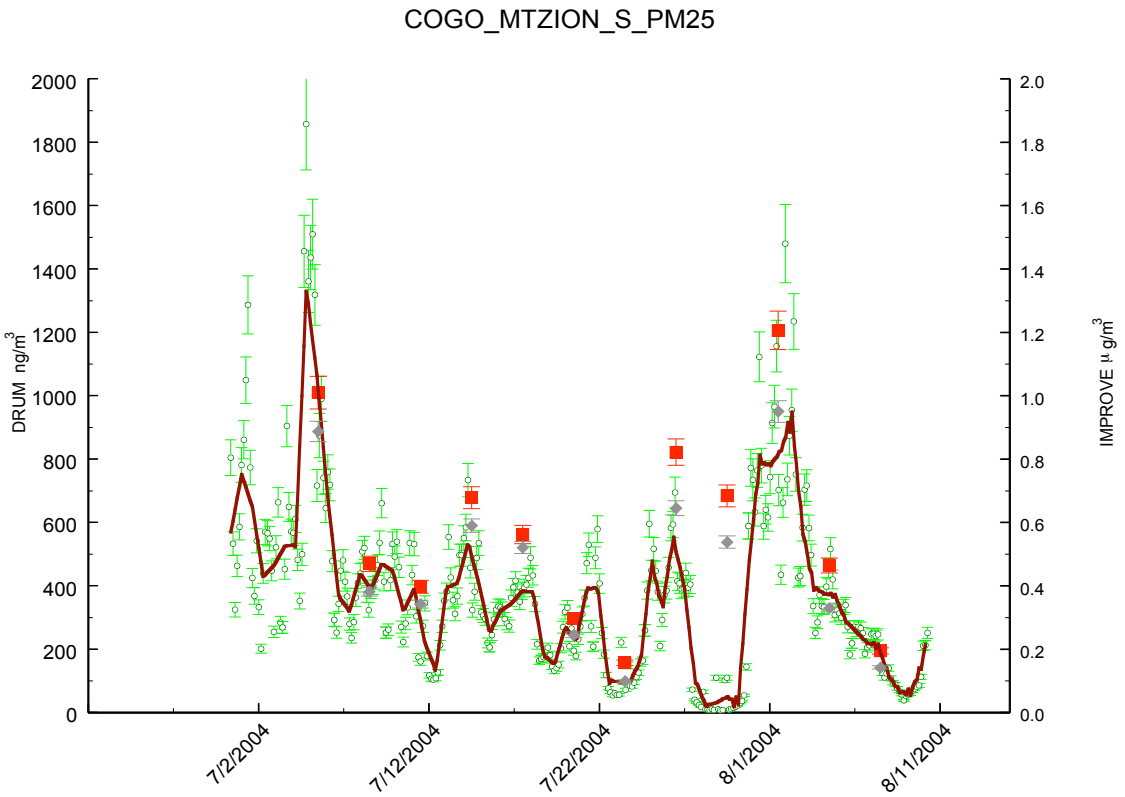
Figure 15. Side-by side comparison PM2.5 combined XRF mass of co-located Rotating DRUM Impactor (RDI) samplers. One sampler was stopped early due to power problems (hence the lack of overlap at the end of the experiment). The sum quantitative XRF results for stages 3-8 of each RDI are compared. An integral blank is show at point 50 and a non-rotating "positive" marker at approximately point 200 occurs only on set 2.

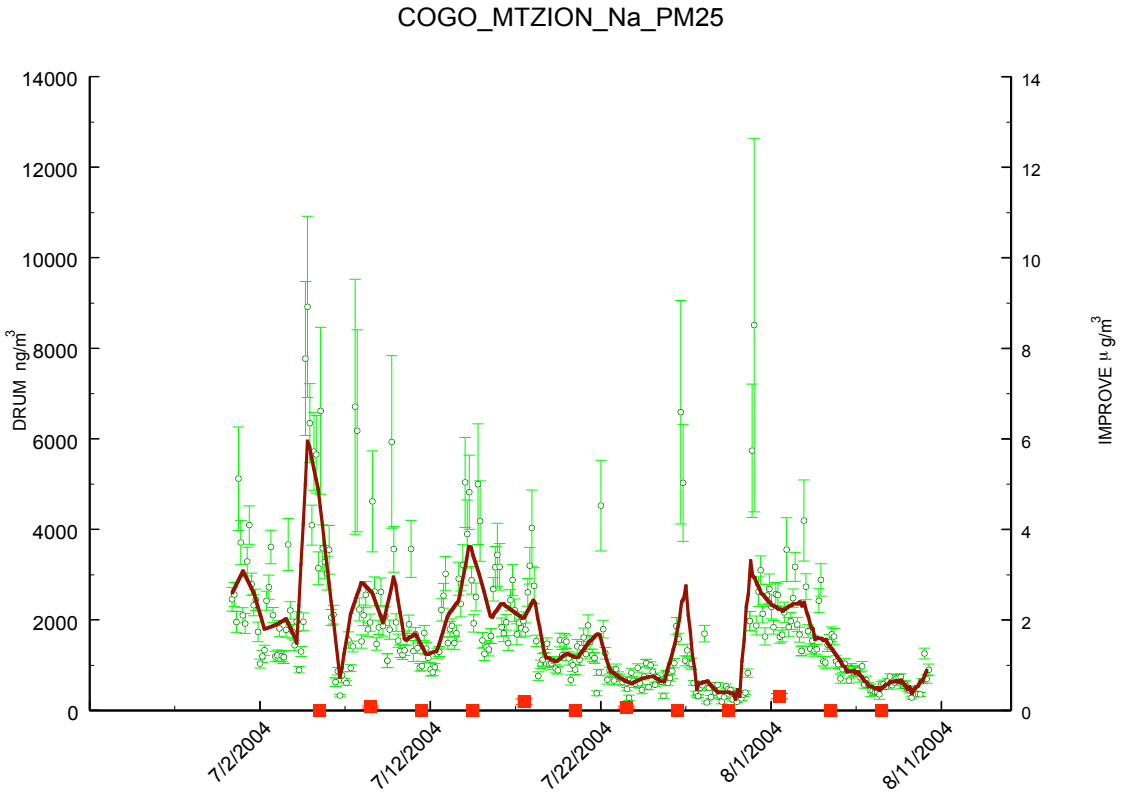
Conclusions

The field component for aerosol sampling provides a comprehensive dataset upon which to understand aerosol dynamics leading to visibility reduction and other detrimental air quality effects. The data available from the present work includes more than 15,000 individual samples analyzed and another 15,000 analyzable samples that have been archived. A detailed description of the complete field program and interpretation of results is given in the "Final CoHaGo Report" (Green et al., 2006). The purpose of this report is to provide a data quality assurance document that supports the use of the filter and impactor results for the CoHaGo report. For the DRUM analysis, the accuracy is approximately 5% (set by the accuracy of the standards and correlation with those). Uncertainty reported in the database incorporates analytical uncertainty, flowrate uncertainty, etc.. The analytical precision is approximately 10% (comparing reruns). In summary, a well quantified database exists that is comparable to or exceeds results from other contract laboratories using highly sensitive analyses and uniquely capable proprietary sampling equipment. Further discussion of comparison of the impactor samples and IMPROVE data is presented in the Appendix.

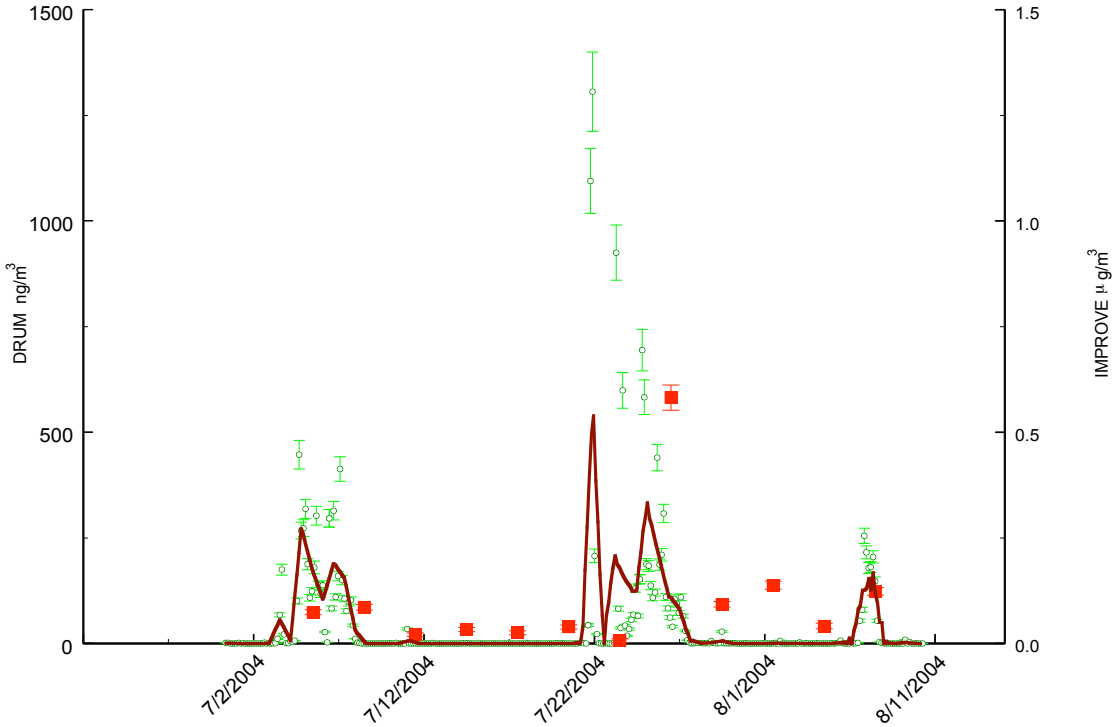
Appendix

Several plots follow showing comparison of the RDI results with the IMPROVE results from the Mt. Zion sampling site. Similar results were seen in data from the Wishram site. The smoothed line in each case represents the 24-hour running average of the RDI data with the circles representing individual RDI data. The red squares are the IMPROVE data for the sample day. Perfect agreement would have the running mean through the red square. For some elements (sulfur for example) there is often good quantitative agreement. For some elements, there is qualitative agreement only (Ca, Si and Fe), and in some cases no agreement is apparent (e.g. Al). It is evident that the influence of timing with respect to the RDI data is an important factor. Because the IMPROVE samples are collected for 24-hours and each 1 day in 3, the high time-resolution influences are important in the comparison. In the case of Al, the IMPROVE data are simply inconceivable. Apparently IMPROVE reported analytical issues that affected Al data during the 2004 time frame that encompasses these samples. It is unclear whether other IMPROVE elements were affected.

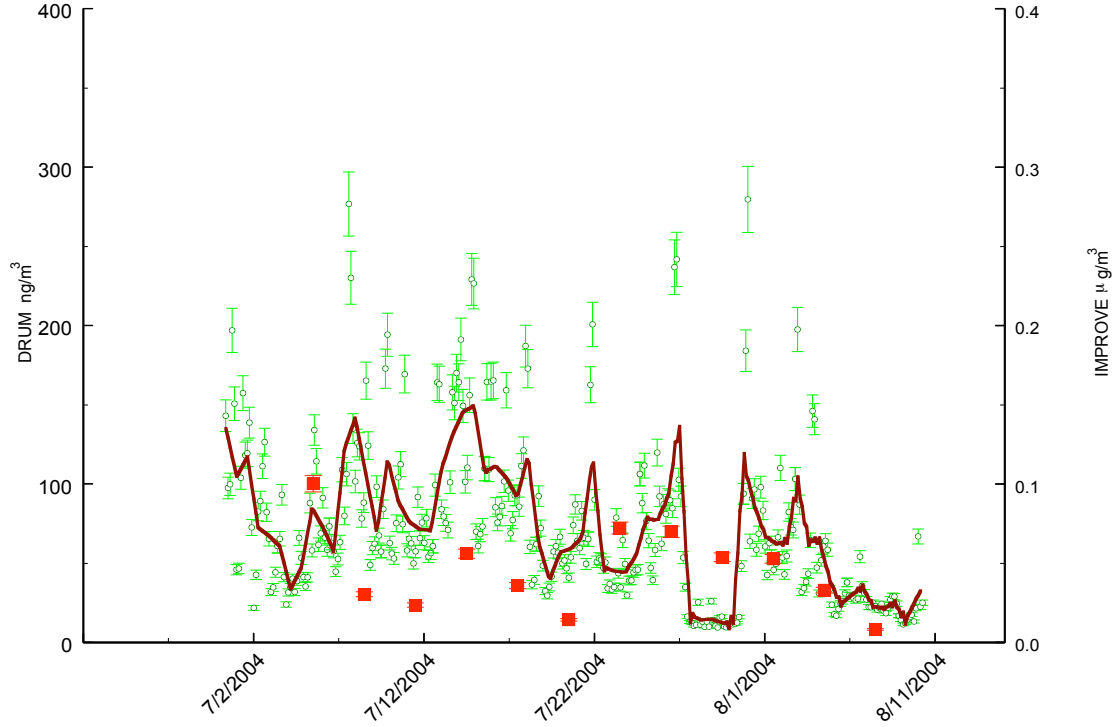

COGO_MTZION_S_PM25
DRUM ng/m3
IMPROVE µ g/m3
2000
1800
1600
1400
1200
1000
800
600
400
200
0
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
7/2/2004
7/12/2004
7/22/2004
8/1/2004
8/11/2004


COGO_MTZION_Na_PM25
DRUM ng/m3
IMPROVE µ g/m3
14000
12000
10000
8000
6000
4000
2000
0
14
12
10
8
6
4
2
0
7/2/2004
7/12/2004
7/22/2004
8/1/2004
8/11/2004

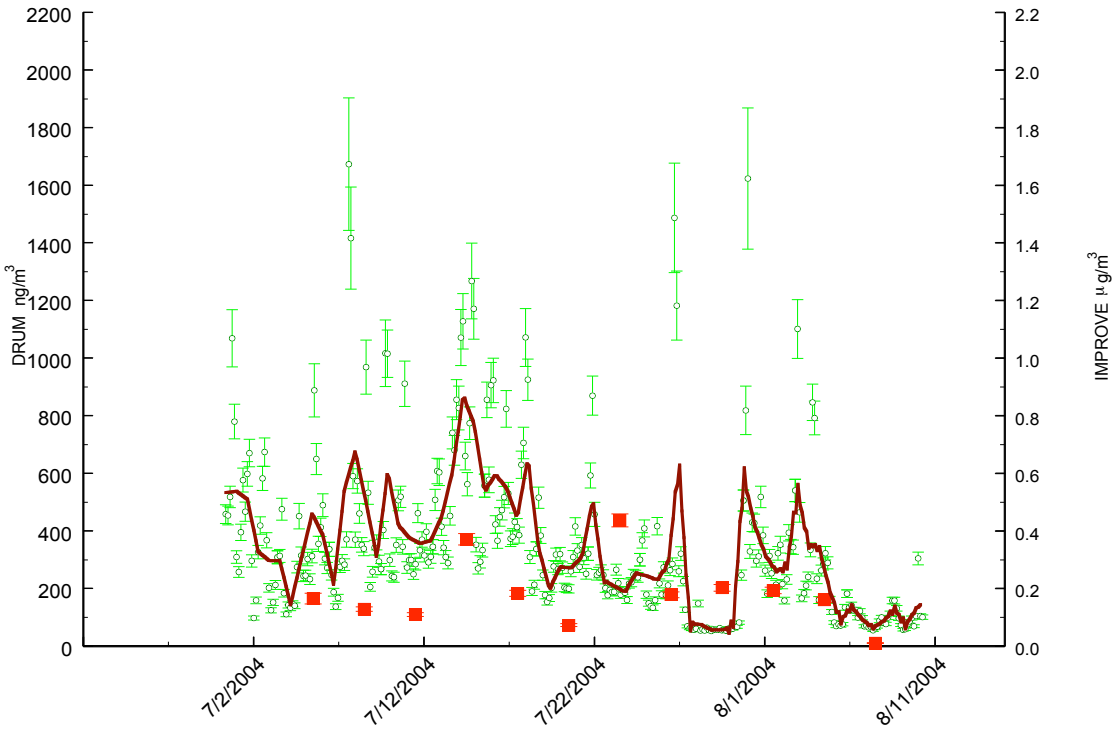
COGO_MTZION_Cl_PM25



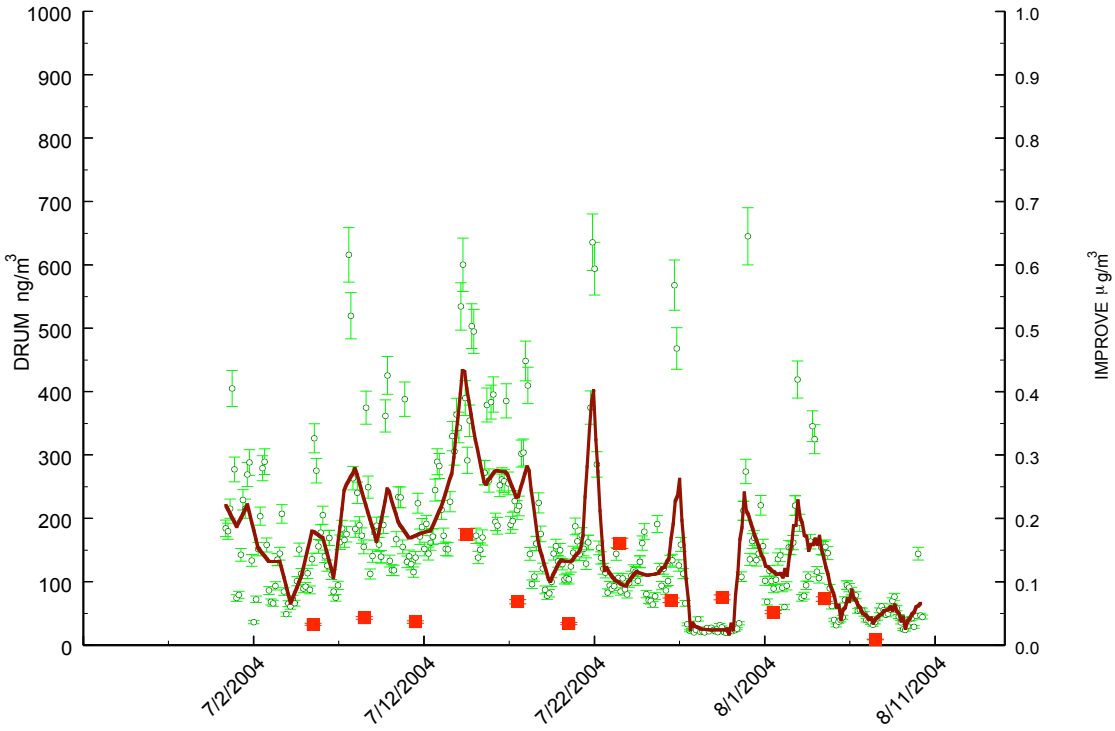
COGO_MTZION_Ca_PM25

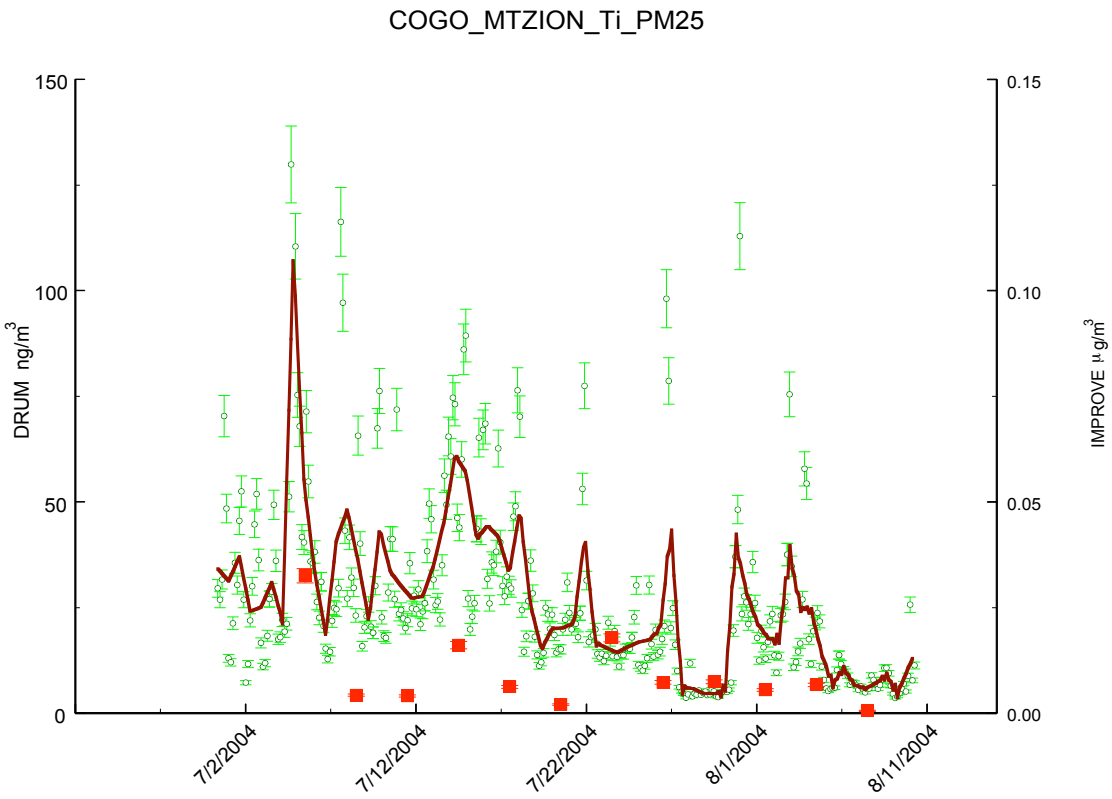


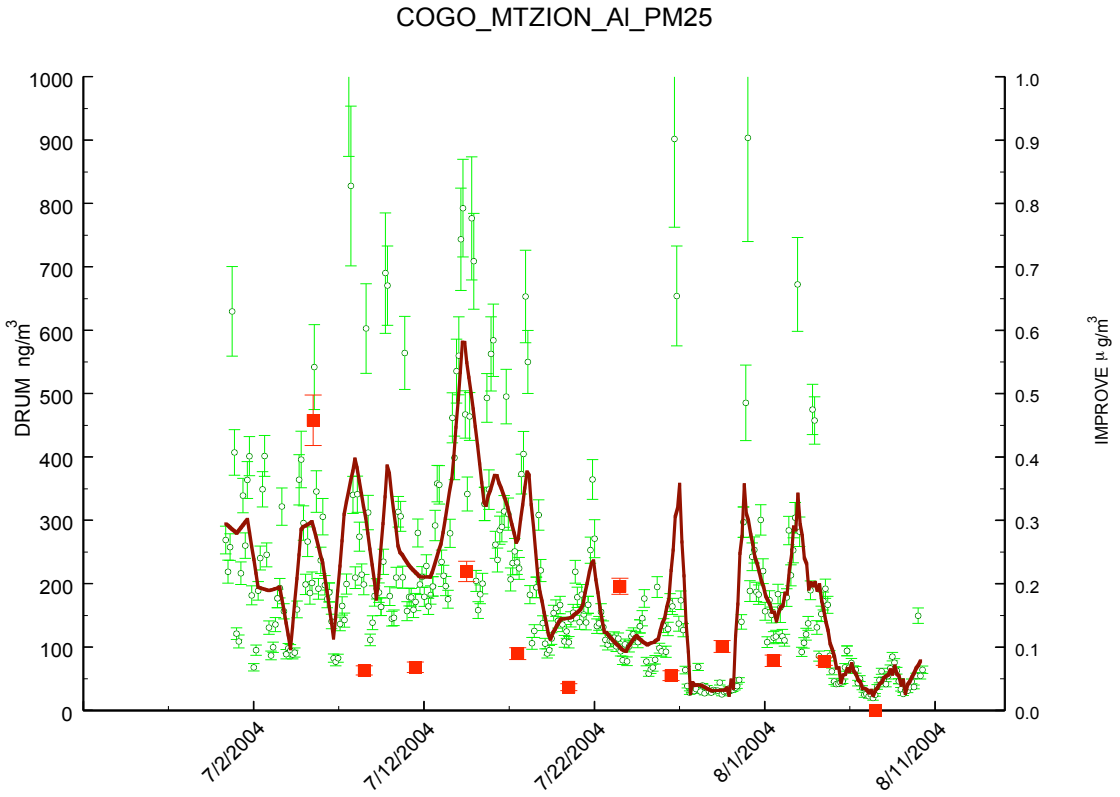
COGO_MTZION_Si_PM25

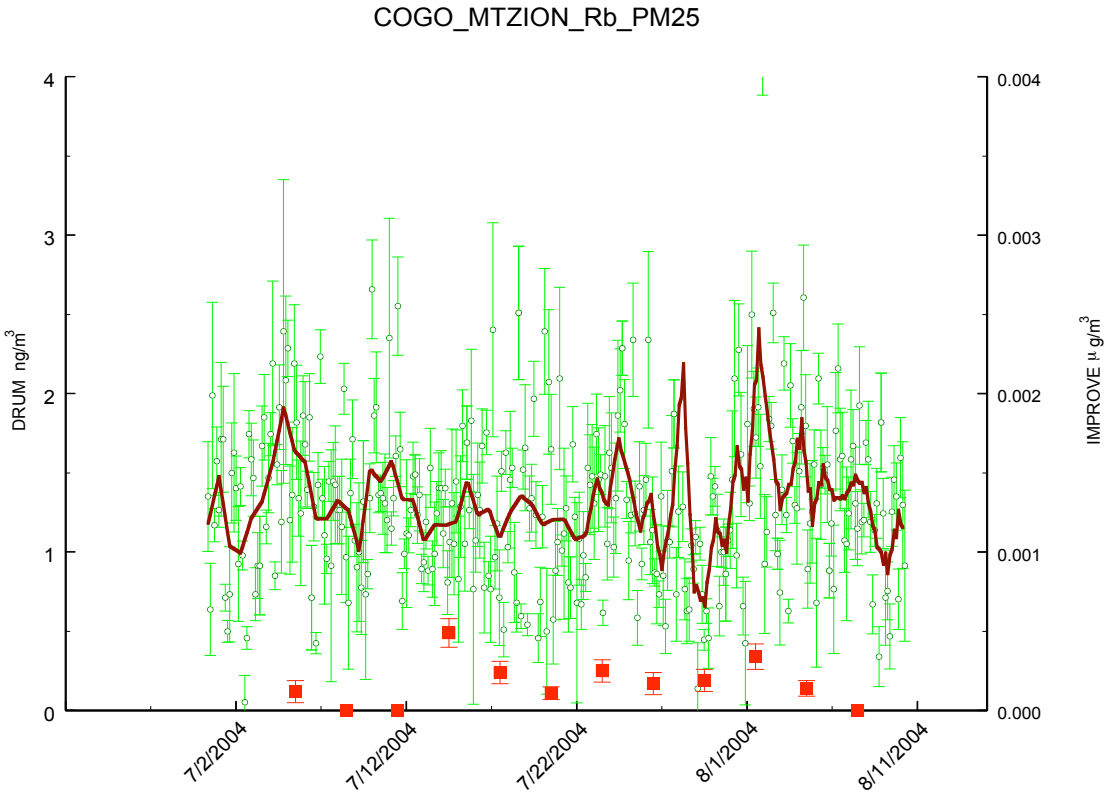


COGO_MTZION_Fe_PM25




COGO_MTZION_Ti_PM25
DRUM ng/m3
IMPROVE µg/m3
150
100
50
0
0.15
0.10
0.05
0.00
7/2/2004
7/12/2004
7/22/2004
8/1/2004
8/11/2004


COGO_MTZION_Al_PM25
DRUM ng/m3
IMPROVE µg/m3
1000
900
800
700
600
500
400
300
200
100
0
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
7/2/2004
7/12/2004
7/22/2004
8/1/2004
8/11/2004


COGO_MTZION_Rb_PM25
DRUM ng/m3
IMPROVE µ g/m3
4
3
2
1
0
0.004
0.003
0.002
0.001
0.000
7/2/2004
7/12/2004
7/22/2004
8/1/2004
8/11/2004

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