

**Quality Assurance Analysis of Filter Samples Collected during the Lake
Tahoe Atmospheric Deposition Study using Synchrotron X-Ray Fluorescence
(LTADS-sXRF QA)**

Final Report

Agreement No. 03-344

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Disclaimer

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Abstract

Results for analysis of a subset of 71 Lake Tahoe Atmospheric Deposition Study (LTADS) ambient sample filters via synchrotron sourced x-ray fluorescence (s-XRF) are presented. A rigorous statistical analysis of phosphorous concentration data reveals a lower quantifiable limit of 15 nanograms per cubic meter for the s-XRF analysis results and 30 ng/m³ for DRI analyses for the LTADS ambient filters. Comparison of results for major elements between the s-XRF and DRI technique indicates no significant bias between analytical protocols for ambient samples. Additionally, 21 source samples (7 smoke and 14 roadway) were analyzed via s-XRF. In contrast to the ambient samples, differences were observed when comparing datasets. A non-uniform deposit on the source samples, however, is suggested as being responsible for the observed differences in quantitative results when comparing the s-XRF and DRI data.

Executive Summary

As part of the Lake Tahoe Atmospheric Deposition Study (LTADS) we analyzed 71 ambient filter samples and 21 source filter samples from various collection sites throughout the Lake Tahoe Basin using synchrotron source x-ray fluorescence analysis (s-XRF). The s-XRF analytical technique enhances quantitative elemental sensitivity by use of a more intense, “white” (i.e. poly-chromatic) light source. The primary goal of the present work is to obtain a statistically valid phosphorous concentration in air in the Lake Tahoe Basin. We also compared results for all data returned from analysis via the s-XRF technique and the results from XRF analysis technique employed by the Desert Research Institute.

The s-XRF technique utilizes an intense x-ray beam at beamline 10.3.1 from an electron synchrotron at the Advanced Light Source—Lawrence Berkeley National Laboratory (ALS). The s-XRF technique increases sensitivity through use of a polarized, white intense x-ray beam as the excitation source. A combination of the white (polarized) and extremely bright (about a factor of one million over tube x-ray sources) incident beam increases statistical enhancement during detection thereby reducing the quantifiable detection limit. The lower quantifiable limit (LQL) for phosphorous (P) in the present work was reduced by approximately a factor of two when compared with the traditional x-ray fluorescence analysis.

Comparison of ALS and DRI results from the ambient filters indicates no significant statistical bias between analytical techniques for major elements. Results for phosphorous concentrations confirmed the range of previously obtained values (from non-detectable amounts (< approximately 15 ng/m^3) to almost 40 ng/m^3 P in air at Lake Tahoe), but the measurement uncertainty was better quantified statistically via the s-XRF technique. With its greater sensitivity, the ALS method reported many more P detects in the matched sample set (24 vs. 3 for $[\text{P}] > 0.015 \text{ ng/m}^3$) than did the standard XRF method employed by DRI.

In summary, the results from the generally more sensitive ALS analysis are in excellent agreement for major elements with the DRI results. We believe this finding is applicable to the larger DRI dataset for LTADS results despite a relatively small subset of filters compared by both methods. Phosphorous concentration values from the DRI analyses, while statistically less certain than the ALS results, are nevertheless appropriate as a foundation for deposition calculations in the LTADS work when observed in context of the subset of samples analyzed by both the ALS and DRI methods.

In contrast to the agreement observed in the ambient filter analysis comparison, the source filter samples proved difficult to quantify. We attribute analytical challenges to the non-uniformity in the sample deposit on the source sample filters. Comparison of the ALS and DRI results from source samples indicates general disagreement with occasional, possibly fortuitous, agreement for elemental concentration.

Final Report

Introduction.

As part of the Lake Tahoe Atmospheric Deposition Study (LTADS) we analyzed 71 ambient filter samples from various collection sites throughout the Lake Tahoe Basin (see sample summary below). The sample subset from the large LTADS sample base was selected from those with high reported phosphorous values from other analyses combined with the date-associated samples at corresponding sites. In addition, we analyzed several source and other specialized samples for this project (see sample summary below). Each of these samples was analyzed by the analytical facility at the Desert Research Institute (DRI) and we were given access to the DRI data. Comparisons between DRI reported values and our (UCD) values are shown below. We analyzed these samples using our analytical facility at beamline 10.3.1 at the Advanced Light Source—Lawrence Berkeley National Laboratory (ALS-LBL). While we typically refer to our analysis technique as synchrotron x-ray fluorescence (s-XRF), it is distinguished from traditional XRF (such as that employed by the analytical facility at DRI) by the source of the incident x-rays.

Traditional XRF systems are sometimes referred to as tube-XRF in that they use a metal anode (tube) to generate monochromatic (i.e. single energy or single wavelength) light. The high-energy light interacts with the inner shell electrons (so called K, L, or M shell) producing a characteristic elemental x-ray emission (fluorescence) from the analyte in proportion to the incident beam intensity and concentration of the element in the sample. The analyte x-rays are counted at the detector. The detector records both energy and counts. Careful calibration using standard samples of the detector energy spectrum and counts with respect to incident energy allows precise quantification of the elemental concentration in the sample. Systems such as those used at DRI consist of several anodes (e.g. copper, molybdenum, tungsten, etc.) to produce several monochromatic incident x-ray beams. Synchrotrons, by virtue of circular electron acceleration in a large (e.g. 70 meter diameter) storage ring with a high energy potential, produce a broad spectrum of incident x-rays. Technically, the ALS is a 3rd generation synchrotron which is characterized by many short straight sections followed by rapid deflection by magnets or other electron acceleration inducing schemes (other techniques include wigglers and undulators which are not discussed here). The beamline at 10.3.1 has at its source a “bend-magnet” that accelerates the electron beam around a magnet to produce a plane-polarized fan of “white” (i.e. polychromatic) light. The white light is transmitted to the experiment hutch via a high-vacuum beam pipe (ca. 25 meters in length). A beryllium window at the terminus of the beam pipe transmits x-rays in air before they reach the sample. Air absorbs most x-rays below 4 KeV. The practical upper limit for x-ray energy for beamline 10.3.1 is about 20 KeV. This range of energy, 4-20 KeV, allows more efficient absorption of incident light at the sample, thereby increasing sensitivity. A plane-polarized incident beam, when impinged on a thin film sample, reduces the background (from scattering of the incident beam) by a factor of approximately 1000 at an orthogonally arranged beam-detector arrangement. The peak photon flux occurs at about 8 KeV (near copper). At its peak, the photon flux at ALS is approximately 10⁶ times that of a typical tube x-ray source. Thus the advantage of analysis via s-XRF vs. tube-XRF is threefold: white incident x-ray in the 4-20 KeV range, incident beam polarization, and high x-ray flux.

Materials and Methods.

Sample Summary

We analyzed 99 filters total by S-XRF. These include:

- 29 ambient minivol samples
- 42 ambient Two-Week Sampler (TWS) samples
- 21 source samples (7 wood smoke; 14 roadway)
- 7 blanks

Analytical Protocol

Analysis at ALS beamline 10.3.1 consists of sample exposure from a synchrotron sourced incident beam and fluoresced x-ray collection using a lithium doped silicon crystal, Si(Li), x-ray detector. We employ a Princeton Gamma Tech (PGT) detector with a thin polymer window designed for air or high vacuum application. The PGT detector has an approximately 150 eV peak resolution (FWHM). The peak energy difference between Si-P and P-S x-rays is approximately 300 eV. While we have many potential configurations at 10.3.1 ranging from monoenergetic incident light to exposure in air, we selected “white” light incident beam and fluorescence detection in vacuum. This configuration affords the best possible sensitivity with thin layer (e.g. filter) samples. The sample is placed at 45° to the incident beam and detector. The detector and incident beam are orthogonal (i.e. 90°), which is at the minimum for Compton scattering. The orthogonal detector placement reduces the background from a polarized source by approximately 10^3 . Calibration is accomplished using 60 thin film elemental standards ranging from Na to U (MicroMatter Co., Deer Harbor, WA, USA) with a concentration uncertainty of $\pm 5\%$. In order to avoid modifying the filters, we acquired a vacuum chamber from the Crocker Nuclear Laboratory at UCD (CNL) capable of handling 47mm diameter filters and modified it for use on our experimental end station at beamline 10.3.1. The protocol for the LTADS samples was to collect 10 spectra across each filter. These spectra were then averaged to create a composite spectrum that should average out spatial inhomogeneities on the filter. Five filters were scanned at higher resolutions (ca. 30 points) to quantify the filter non-uniformity. Each spectrum was collected from a 30 second exposure (dwell time). Ten analysis points is double the standard protocol for our filter analysis in order to enhance the results for the LTADS sample analyses.

The resultant spectra (essentially counts vs. bins with approximately 1000 bins representing 0-20 KeV) were analyzed using the International Atomic Energy Agency peak fitting routine AXIL (loosely Analytical X-Ray Analysis by Least Squares Fit). AXIL integrates the peak area with respect to energy and subsequent processing by comparing standard calibration results in quantification. Corrections are applied to the quantitative data to account for sample matrix, particle size, and loading effects on the spectra. In the samples reported here, a standard quartz-like matrix correction and PM_{2.5} particle size correction was applied to all samples regardless of source.

Results and Discussion.

Phosphorous

The entire DRI dataset of TWS and MVS filter samples (>600) is not discussed here but only the subset of such samples provided to UCD for reanalysis at the ALS (<100). The ALS subset included all available samples for periods when the DRI analysis indicated detectable concentrations of phosphorus (some samples were not available due to earlier reanalysis by ICPMS, which is a filter destructive method). An indication of how the phosphorus reanalysis subset represents the total dataset is provided in Figure 1, where the DRI analytical results are shown with the reanalyzed samples being indicated by open circles. Focusing on the number of valid samples with P concentrations greater than or equal to 10 ng/m³, one-third of the samples with the highest P were reanalyzed by UCD. This sampling ratio is almost three times that of a random sampling protocol and thus provides an enhanced characterization of the highest P values during LTADS.

Preliminary (not corrected for filter blank values) results for phosphorous in both the DRI and S-XRF data had values ranging from 0 to almost 40 ng/m³. These data, based on samples from the Two-Week-Sampler (TWS) and Mini-Vol Sampler (MVS) networks, are included in a separate Excel spreadsheet. Unknown by us at the time of our comparison study, the TWS results from DRI had been corrected for filter blank values but the MVS results from DRI had not been corrected for filter blank values. The s-XRF analyses of both the TWS and MVS samples reported P “as is”, i.e., assumed no P was initially present on the sample filters. Thus, if the amount of P on blank filters is significant, the TWS comparison could be skewed. In Figure 2, P concentration versus date for UCD (magenta squares) and DRI (blue diamonds) analyses is plotted. We use the results of Figure 2 to discuss the phosphorous data from the selected samples. Here we present data only from the selected subset of samples which we were given for analysis.

We refer to minimum detectable limit (MDL) as the elemental quantity for which an element can be statistically discerned from background or another value. We typically define this value operationally, if possible. In these samples, we define the interference corrected (i.e. operational MDL) as the average uncertainty for P (or any other element) when a "0" value is reported. Using this methodology, we derive 5 ng/m³ as an MDL (N=16 samples with reported “0” value) for the entire ambient filter set (includes 11@TSP, 2@PM₁₀ and 3@PM_{2.5}) for the s-XRF analyses. The same methodology gives 10 ng/m³ as an MDL for the DRI analyses (N=45 samples with reported “0” value, with 28@TSP, 4@PM₁₀, and 13@PM_{2.5}).

The minimum or lower quantifiable limit (MQL or LQL) is the quantity threshold above which statistically sound data are indicated. The LQL can be thought of as the 2σ or 3σ values above which data have high confidence (within reported uncertainty). Since here we define MDL as the minimum quantity statistically discernable from another quantity, we equate MDL to 1σ. Therefore, using an LQL of 3X the MDL (or 3σ) we calculate 15 ng/m³ for the s-XRF analyses and 30 ng/m³ for the DRI analyses for phosphorous. These values are appropriate, for the ambient sample set analyzed by both laboratories.

While DRI did not provide a project specific (i.e. ambient LTADS) LQL samples because of variability, an assignment of 186 ng/filter for an LQL (with 78 ng/filter MDL) based on replicate

blank analysis. Based on this, DRI would be able to quantify between 4 ng/m^3 and 21 ng/m^3 on the LTADS filters depending on sample area and air collected (sample collection ranges from 9 m^3 - 51 m^3). DRI derives LQL by using 3σ to estimate LQL, which is a standard and statistically valid method. The blank filter analysis (from which the DRI estimate of MDL and LQL are derived) does not account for interferences from ambient concentration of Si and S. Since MDL is related to the signal/noise ratio, an interference corrected MDL (and thus LQL) is more statistically appropriate.

Our uncertainty calculation includes not only the peak fitting uncertainty, but also a propagation of other uncertainties such as standard sample concentration uncertainty and flow rate uncertainty (not project specific, but a standard value of about 5%). Since it appears that our uncertainty calculation is generally conservatively reported, an LQL value of 2-3 times the MDL appears to be statistically valid (representing approximately 95% or 99% confidence limits, respectively). Therefore, 10 to 15 ng/m^3 is a representative value for LQL for P in the LTADS samples analyzed by s-XRF.

With the $10\text{-}15 \text{ ng/m}^3$ LQL threshold in mind, the ambient sample data are better understood. There are 39 samples with values 10 ng/m^3 or greater (5@ $\text{PM}_{2.5}$, 5@ PM_{10} , and 29@TSP) and 24 samples with values 15 ng/m^3 or greater (5@ $\text{PM}_{2.5}$, 3@ PM_{10} , and 16@TSP) in the s-XRF data (out of 71 total). It is interesting to note that if we decrease the LQL threshold to 10 ng/m^3 we include no more $\text{PM}_{2.5}$ and only 2 additional PM_{10} samples. The remaining additional values in the lower LQL (i.e. 10 ng/m^3) represent only TSP samples. This is a good physical result as P has been theorized to be associated, at least in part, with re-suspended road soil. Sample volumes in these categories span the range collected (i.e. $9\text{-}51 \text{ m}^3$).

Figure 2 plots UCD and DRI P concentration values vs. date. Horizontal lines delineating thresholds at 10, 15, 20, and 30 ng/m^3 are indicated (corresponding to 2X MDL-UCD, 3X MDL-UCD, 2X MDL-DRI, and 3X MDL-DRI per our calculations, respectively). Figure 2 indicates that DRI data in this sample subset exceed the 30 ng/m^3 threshold only once, and the 20 ng/m^3 threshold only twice. In fact, even a 10 ng/m^3 threshold (equivalent to 2X the s-XRF MDL) indicates only 8 out of 71 samples for the DRI analyses. Again this is only the subset of data, not all of the LTADS filters analyzed by DRI. If we use 186 ng/filter for LQL (DRI), we find 14 samples above threshold when accounting for flow rate and filter area. The 14 samples above LQL assume that the 186 ng/filter LQL value refers to blanks with 11.92 cm^2 sample area.

The ARB criterion for selecting ambient air filter samples for our re-analysis by s-XRF was to choose the highest P concentration samples based on the DRI results and then to include the date-corresponding samples from the other sites in LTADS. This filter selection provided a wide range of P values and full geographic coverage, which allowed us to examine data from contemporary samples in the context of each other. In both the DRI and UCD analysis, we get high values for some of the mid-lake samples, although not for corresponding analyses (i.e. s-XRF data indicate 0 for the DRI high mid-lake samples and vice-versa). However, the two high value samples on 7/24/03 in the s-XRF data were both mid-lake (i.e. NASA raft) samples. As indicated, the high values for 7/24/03 are identical within uncertainty. Since the mid-lake sites are in relatively close proximity and should see similar meteorological conditions, one would expect to observe similar results when valid data are reported. The elemental concentration correlation for these specific samples is also observed for other elements (e.g. Si, S, etc.).

Finally, although approximately the same peak P concentration value is observed (35 ng/m^3 on 4/30/03 for a mid-lake sample in the DRI data and 38 ng/m^3 on 8/13/03 in the s-XRF data) in both datasets, the peak DRI P value corresponds with a below MDL value in the S-XRF analysis. Two additional shoreline sites with samples on 4/30/03 had “0” values reported in the DRI analysis for P. The second highest P concentration sample in the DRI analysis (@ 22 ng/m^3 on 12/16/03 at SOLA) corresponds to the third highest value in the s-XRF analysis (@ 32 ng/m^3 at SOLA 12/16/03). Thus, while an LQL of 20 ng/m^3 in the DRI data for these samples is statistically appropriate, the peak DRI reported value here (35 ng/m^3) has less confidence using the approach of comparing corresponding sites for that particular sample. A similar data analysis treatment was not completed for other samples in the DRI dataset as these 2 samples were the only ones that exceeded the 20 ng/m^3 lower LQL threshold. Synchrotron-XRF analysis of a larger set of samples would be expected to retrieve additional valid P results. If the present subset of filters selected for analysis were treated as random, approximately half of the total samples would have P concentration values between ca. $10\text{-}40 \text{ ng/m}^3$. However, it is extremely unlikely from these results that an increase in the upper limit for P concentration would be observed if additional sample analysis by s-XRF were undertaken.

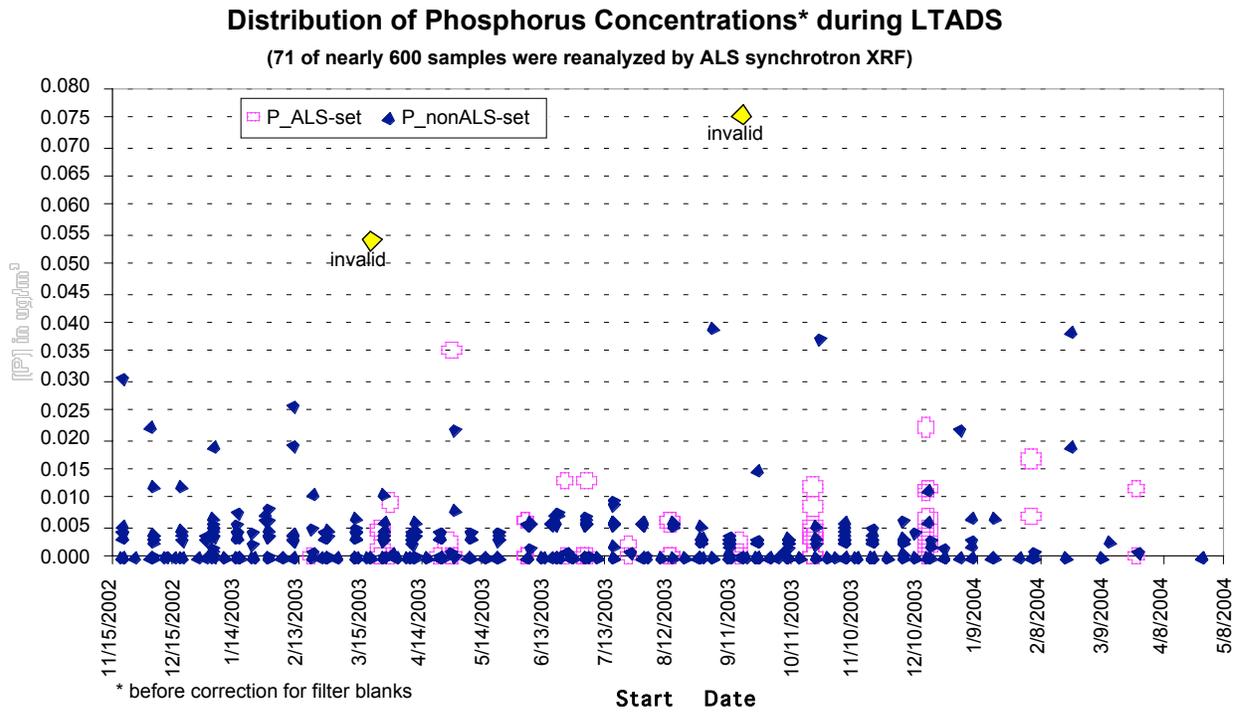


Figure 1. Ambient phosphorus concentrations by the DRI analysis are plotted (neither the TWS not the MVS samples are shown corrected for blank values). The subset of these ambient filter measurements submitted to UCD for reanalysis with the ALS system is indicated with open circles.

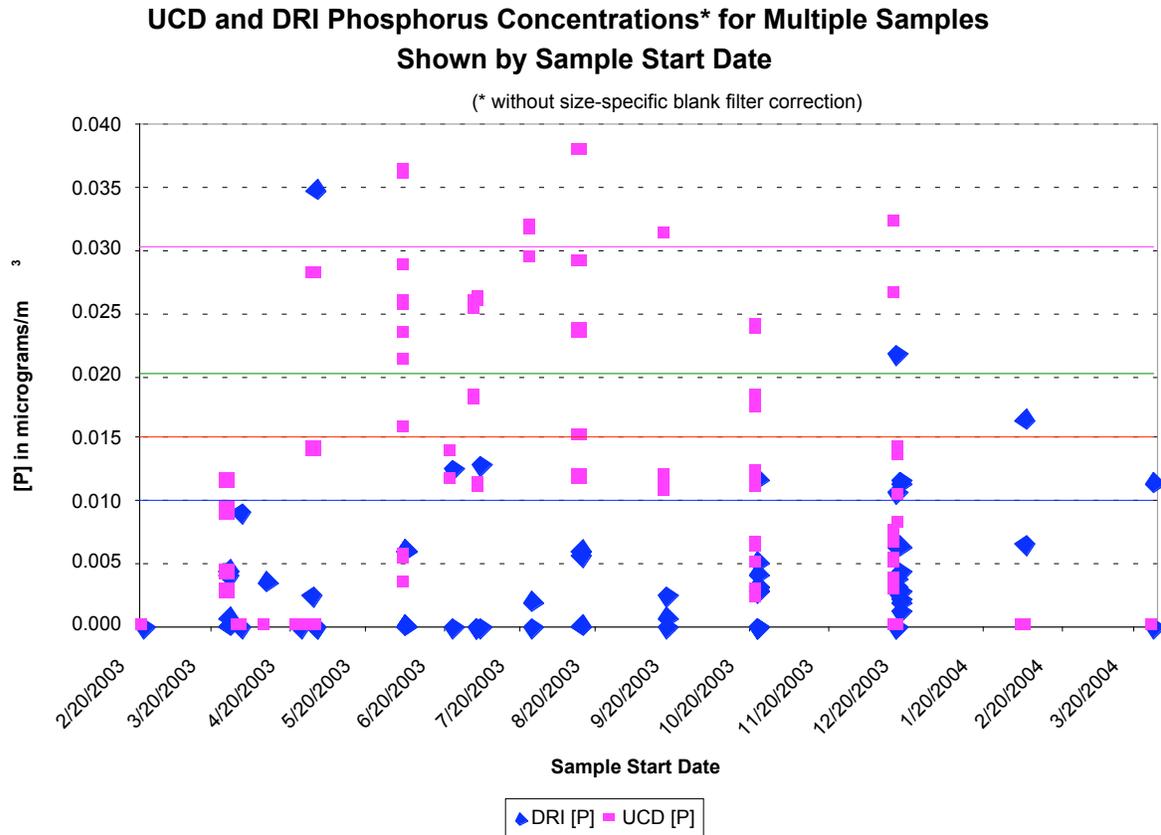


Figure 2. Time series plot of phosphorous concentrations by s-XRF (magenta squares) and DRI (blue diamonds). Horizontal delineation at 10, 15, 20, and 30 ng/m³ represent 2X MDL-UCD, 3X MDL-UCD, 2X MDL-DRI, 3X MDL-DRI, respectively. Average uncertainty of 5 ng/m³ for the s-XRF (squares) and 10 ng/m³ for the DRI (diamonds) is not indicated.

Elemental Comparison UCD/DRI

As a component of the quality assurance for the preliminary analytical dataset provided by DRI, it is instructive to compare the results between the DRI XRF and UCD s-XRF data. Figures 2 through 15 show comparison between results from s-XRF (UCD) and DRI analyses for selected elements (i.e. Si, P, S, Cl, K, Ca, V, Cr, Mn, Fe, Ni, Cu, Zn, and Br). Excellent agreement between analysis methods for e.g. Si, S, Cl, K, Ca, Mn, Fe, Cu, and Zn is observed. The Ca data between methods are highly correlated, but offset by about 25%. This is likely due, in part, to the lack of [Ca] background subtraction in the s-XRF preliminary data. Elemental data for e.g. P, V, Cr, Ni, and Br show substantial scatter between methods with general trending toward unity in most cases. The lack of correlation between analyses in these data is likely due to the low abundance of these elements in the selected samples (as specifically discussed for P above). In other words, concentrations near or below the minimum detectable limit (MDL) or lower quantifiable limit (LQL) are observed in these samples for P, V, Cr, Ni, and Br. The specific determination of the LQL varies widely between laboratories and interpretation. In addition, LQL is an operationally dependent quantity relying on interpretation of results from specific

samples as shown for P above. A better understanding of the data processing for the DRI analyses (e.g. matrix, loading, particle size corrections, and background/blank subtraction calculation) is necessary to understand the discrepancies between results for some elements. The s-XRF data have only a PM_{2.5} particle size correction applied to them. Although a more detailed particle correction may be inappropriate for some of the samples and more important for some elements, no significant bias is observed between reported data from the s-XRF and DRI analyses. A weighted particle size correction would likely suffer from incorrect assumptions about particle characteristics in these samples. Thus, additional bias would result from further particle size correction in these data.

Figure Note 1: The following (Figures 3-16) are scatter plots of s-XRF v. DRI concentration data for the ambient subset (N=71 samples) of PM_{2.5}, PM₁₀ and TSP LTADS filters for selected elements. Note that s-XRF data have applied to them only PM_{2.5} particle size correction for all sizes.

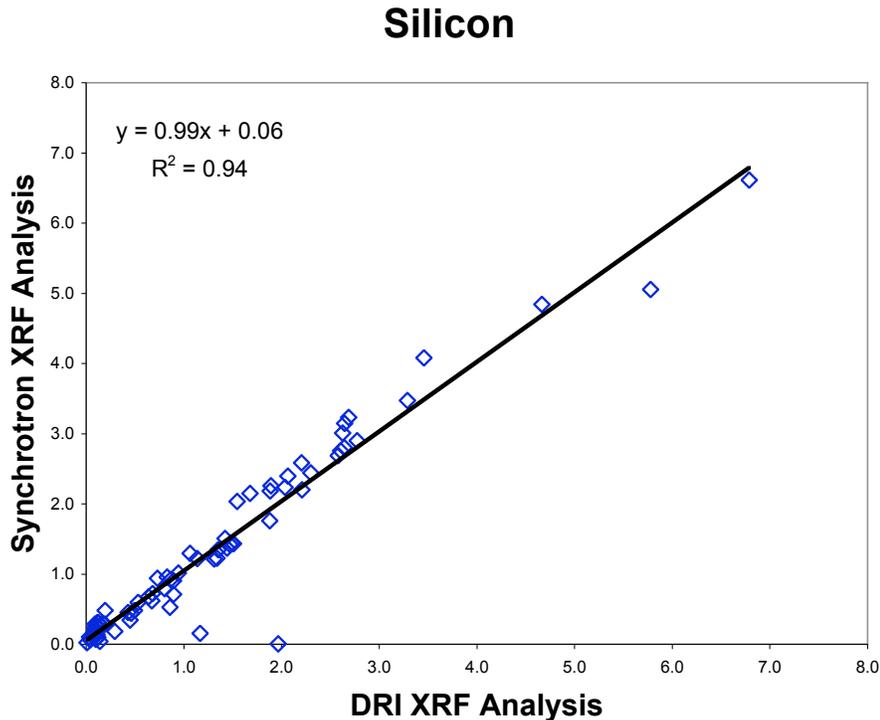


Figure 3. Silicon ALS v. DRI

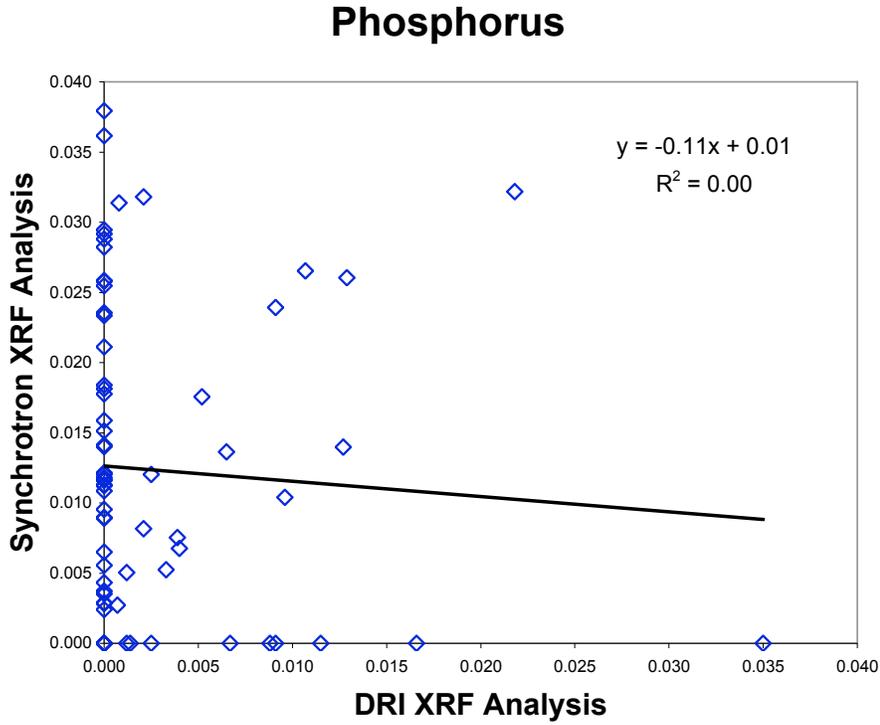


Figure 4. Phosphorous ALS v. DRI

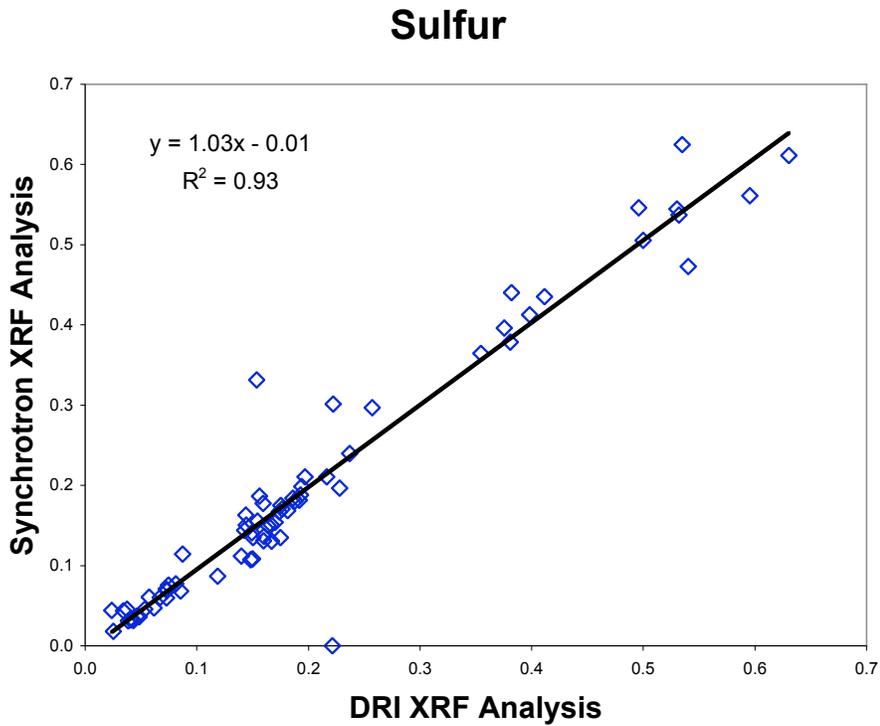


Figure 5. Sulfur ALS v. DRI

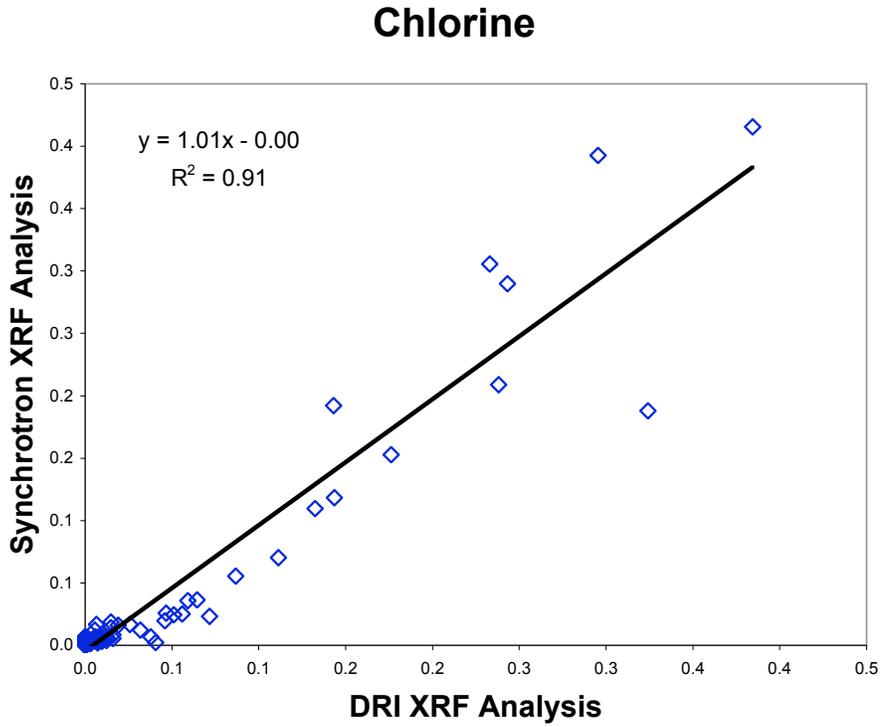


Figure 6. Chlorine ALS v. DRI

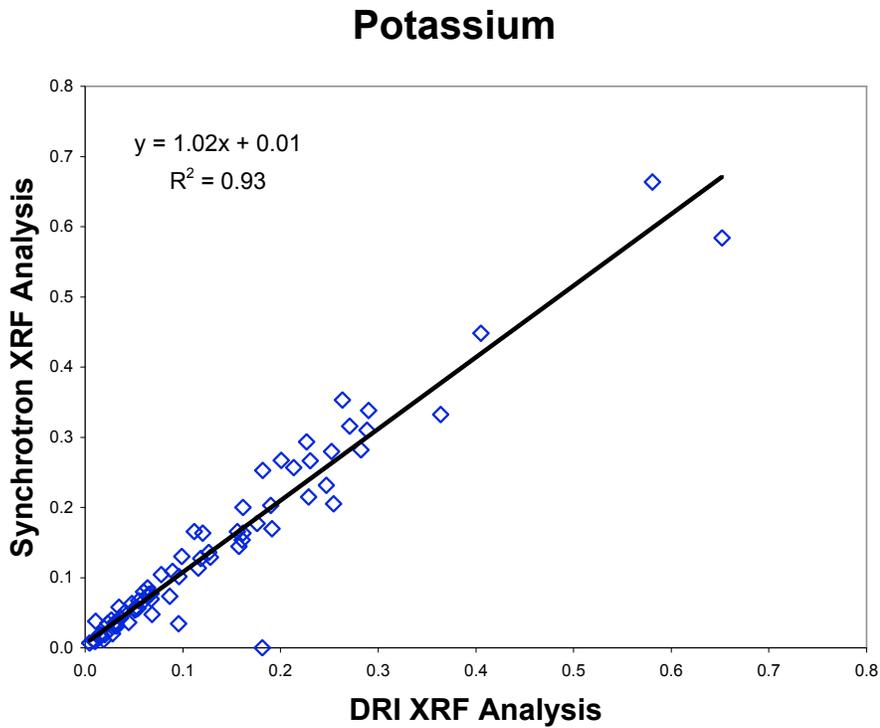


Figure 7. Potassium ALS v. DRI

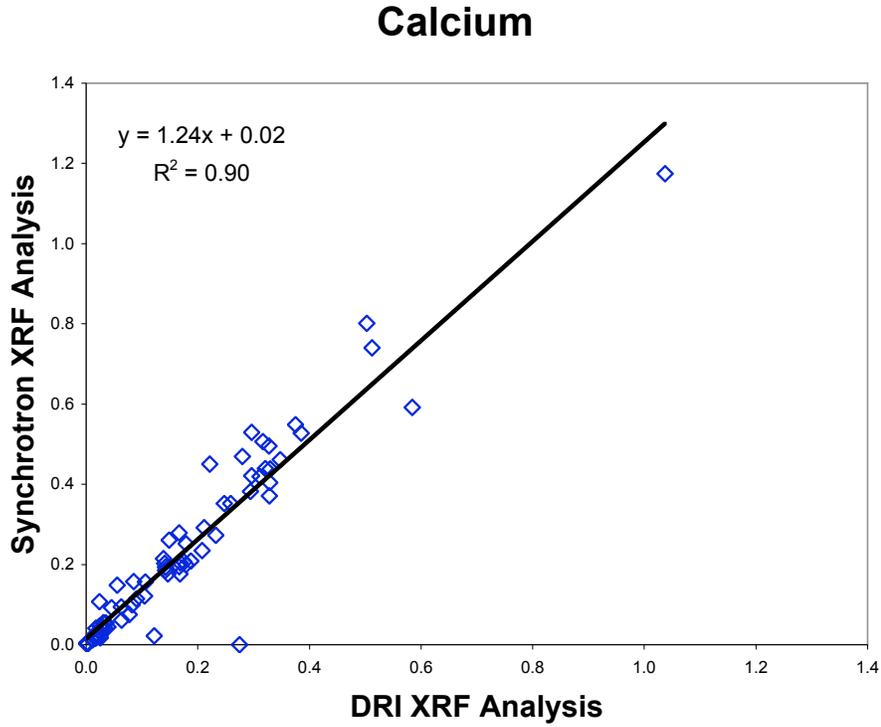


Figure 8. Calcium ALS v. DRI. Note: There is no blank subtraction on s-XRF data for Ca in this plot.

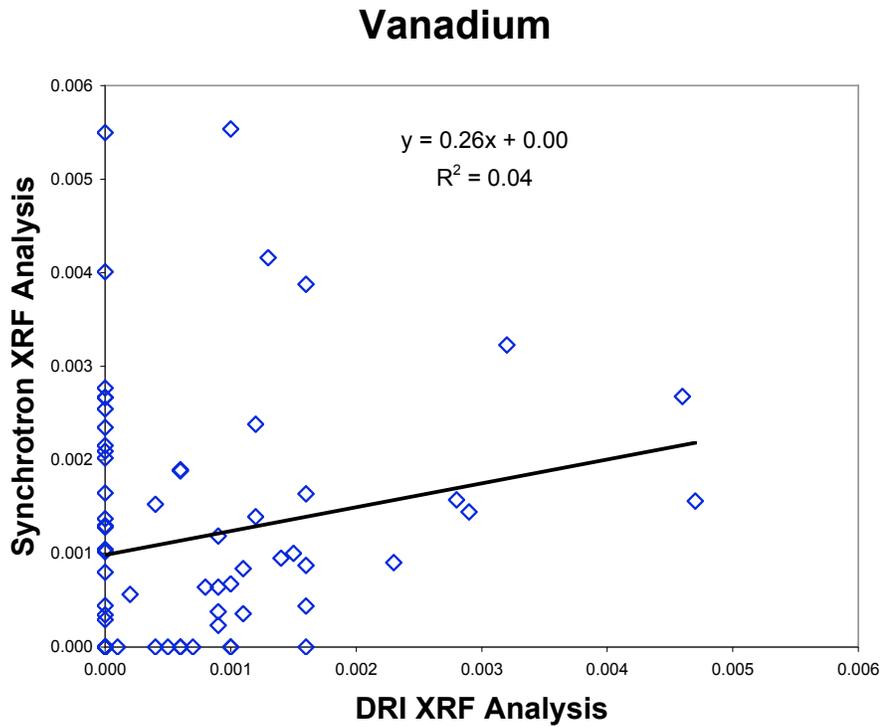


Figure 9. Vanadium ALS v. DRI

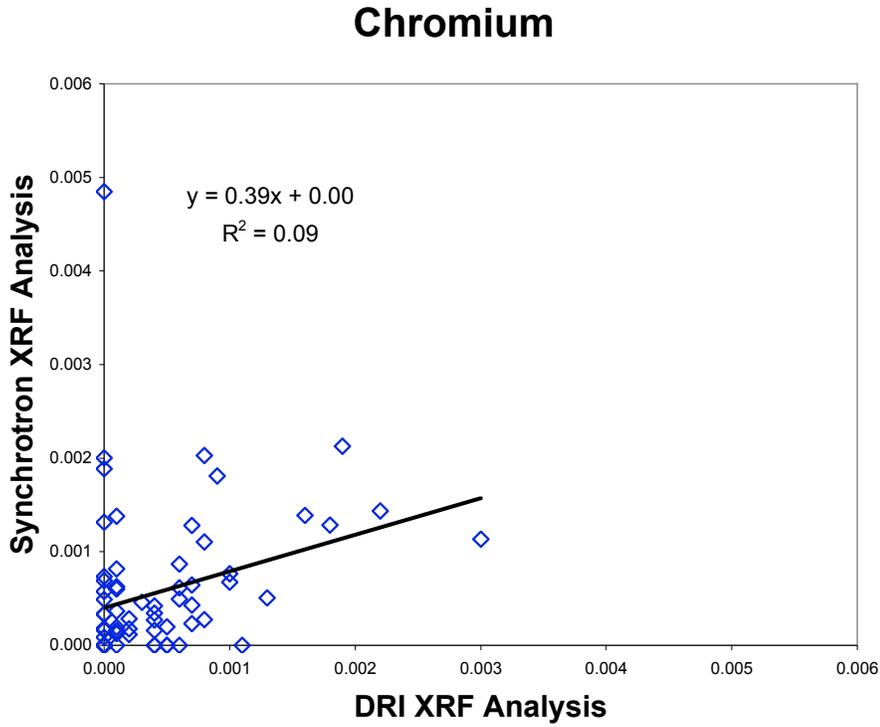


Figure 10. Chromium ALS v. DRI

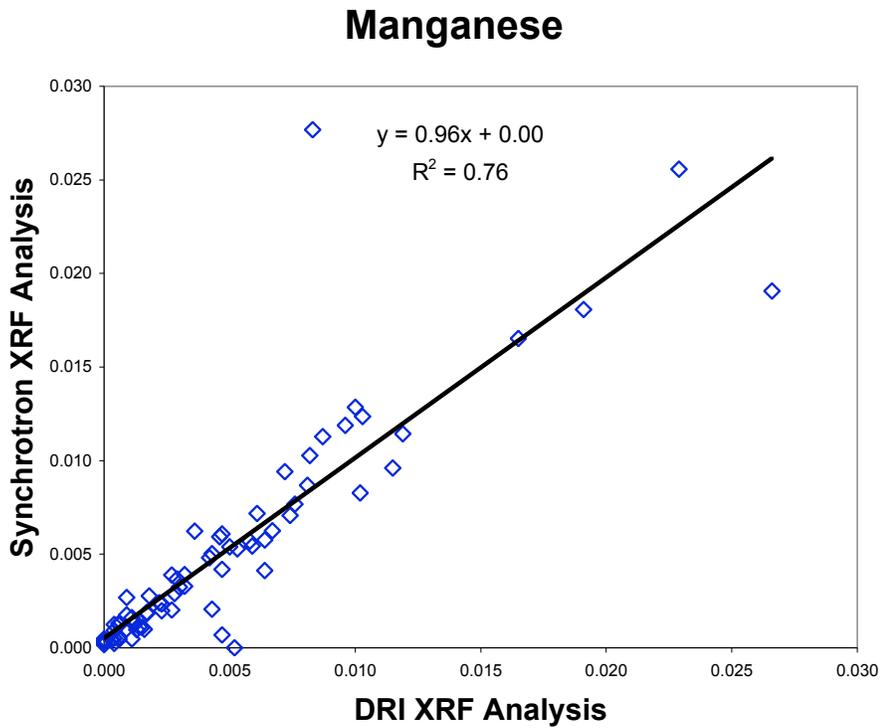


Figure 11. Manganese ALS v. DRI

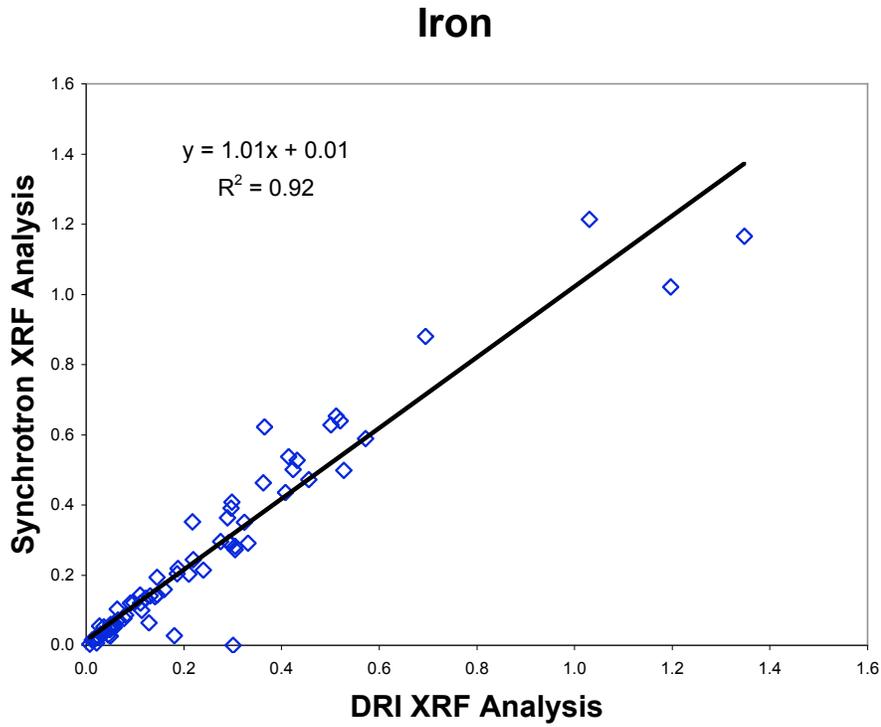


Figure 12. Iron ALS v. DRI

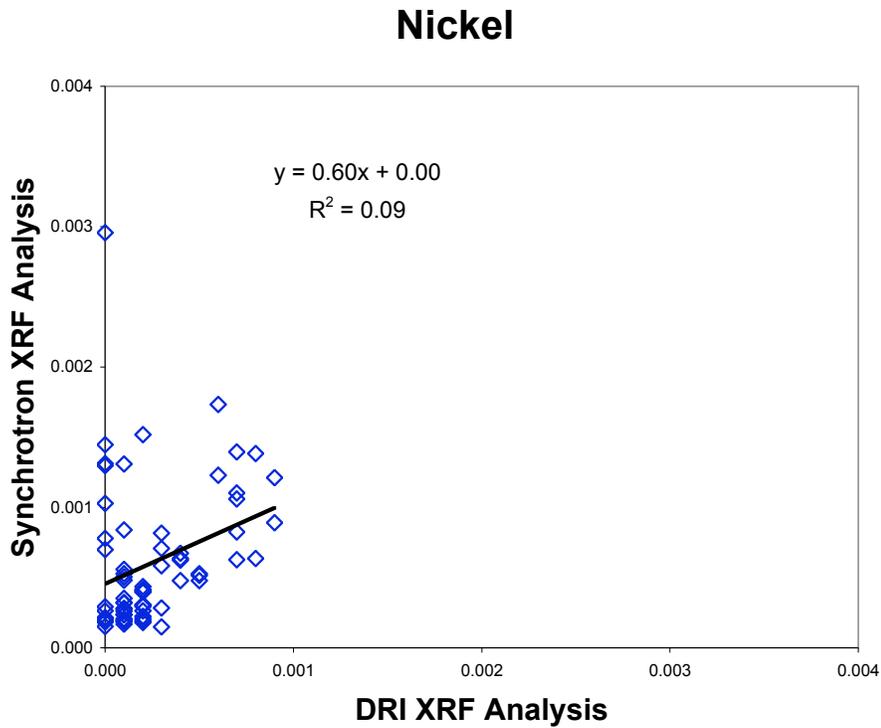


Figure 13. Nickel ALS v. DRI

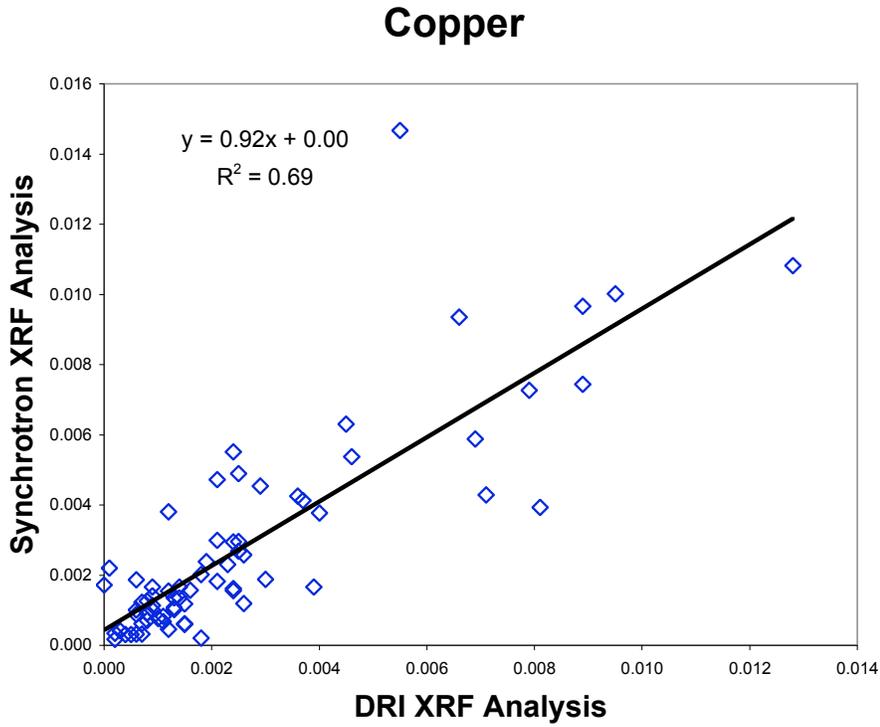


Figure 14. Copper ALS v. DRI

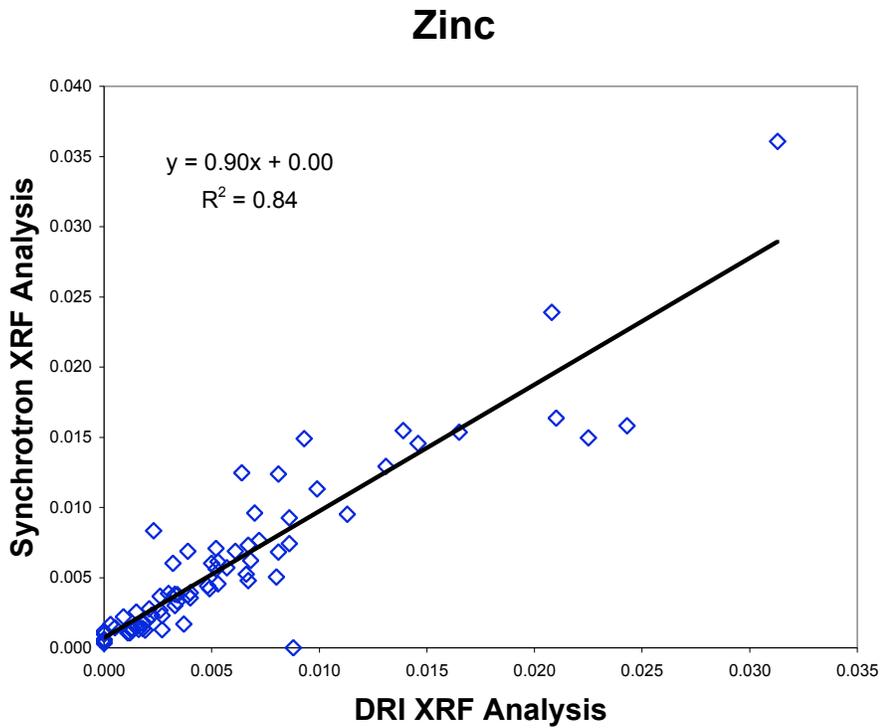


Figure 15. Zinc ALS v. DRI

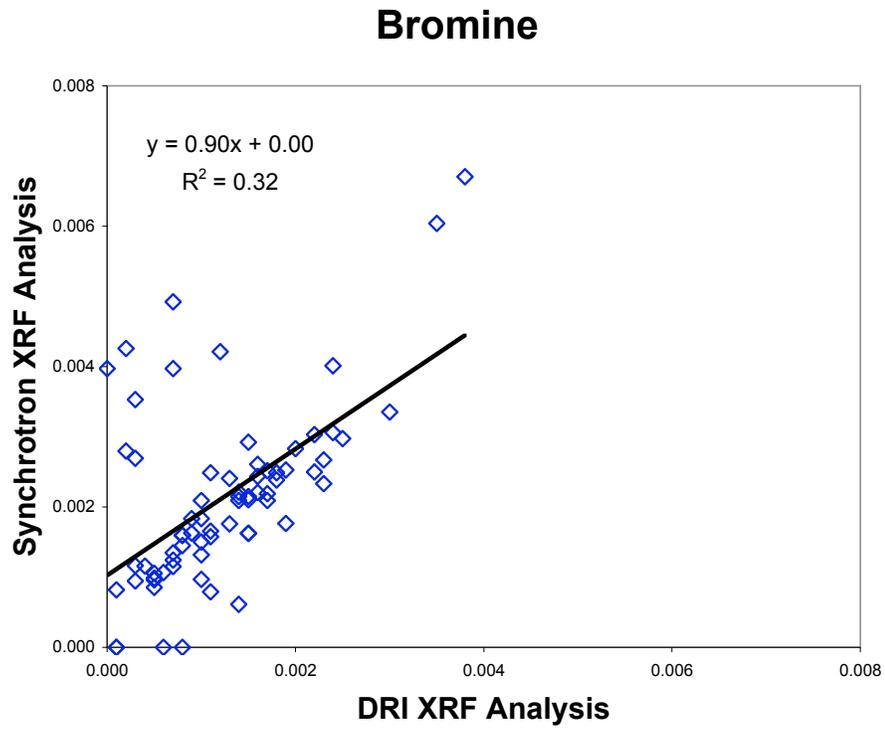


Figure 16. Bromine ALS v. DRI

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 using WinAXILBatch (including a blank subtraction). The comparison of the filters is presented in Table 1. Note that there is a slight (approximately 13%) reduction in average P concentration and that blank subtraction has little affect for major elements. The substantial reduction in uncertainty is an improvement for trace species quantification. However, examination reveals that modifying the results for P is inappropriate based on the statistical analysis of MDL and LQL.

Table 1. 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%

Source Sample Analysis Results

In addition to the 71 ambient filter samples, we analyzed 21 source samples (7 wood smoke and 14 re-suspended road dust; see table below) for quantitative elemental results using the s-XRF technique. Figure 17-21 show the comparison of results from the ALS vs. DRI analyses for several different source samples and elements. Generally, there is a lack of correlation between the quantitative elemental results when the ALS and DRI data are compared. Figures 22-23 plot the individual scans, the average ALS results for iron (arithmetic average of individual points), and DRI data for two different source samples (APL 1628 and APL 1588, respectively). Figure 22 (APL 1628 - smoke in TSP from residential stove/fireplace) reveals a factor of 10 in quantitative results from the individual ALS scans, but with resulting agreement in the average ALS data compared with the DRI data. Figure 23 (APL 1588 - smoke in TSP from prescribed burn) reveals a factor of 7 in quantitative results from the individual ALS scans, but without resulting agreement in the average ALS value compared with the DRI data. It is likely fortuitous that the ALS and DRI results for APL 1628 agree. The extreme non-uniformity on the source samples combined with limited (10 spots per filter) is the primary reason why there is a lack of agreement between ALS and DRI analyses of the source samples.

In light of the excellent agreement for the more lightly loaded, and uniform deposit, ambient samples, further work would need to be undertaken to better quantify these samples. The additional work could include a different analysis protocol (e.g. more analysis points per filter with great spatial representation) or different sampling protocol. This additional work is not practical under the present agreement and therefore was not undertaken. Further, additional work is not expected to change the result of deposition calculations from the ambient sample analysis. Thus, we do not explicitly recommend the additional work for the sake of this LTADS project; however, a better defined protocol for similar samples may benefit future work not related to the present study.

Description of Source Samples

Filter Group Label	# of Samples Reanalyzed	Source Type
LZST	8	smoke from stove/fireplace
APL	7	smoke from prescribed burn
RS	4	road dust
TMTT	1	road dust in PM10
TMFT	1	road dust PM2.5

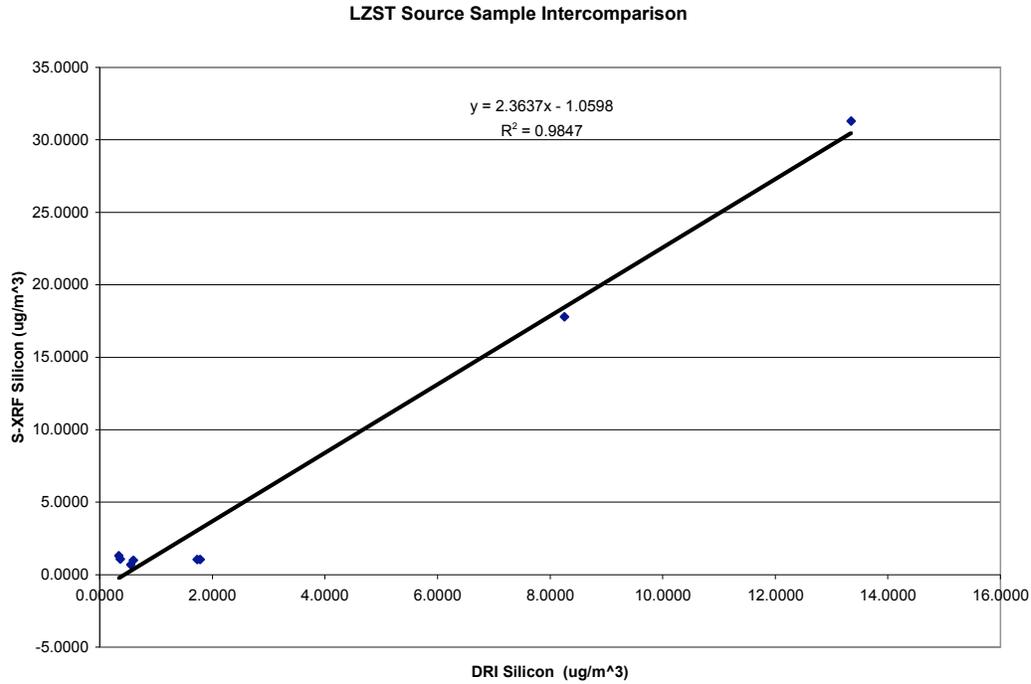


Figure 17. Comparison of ALS vs. DRI silicon results from analysis of the LZST source samples.

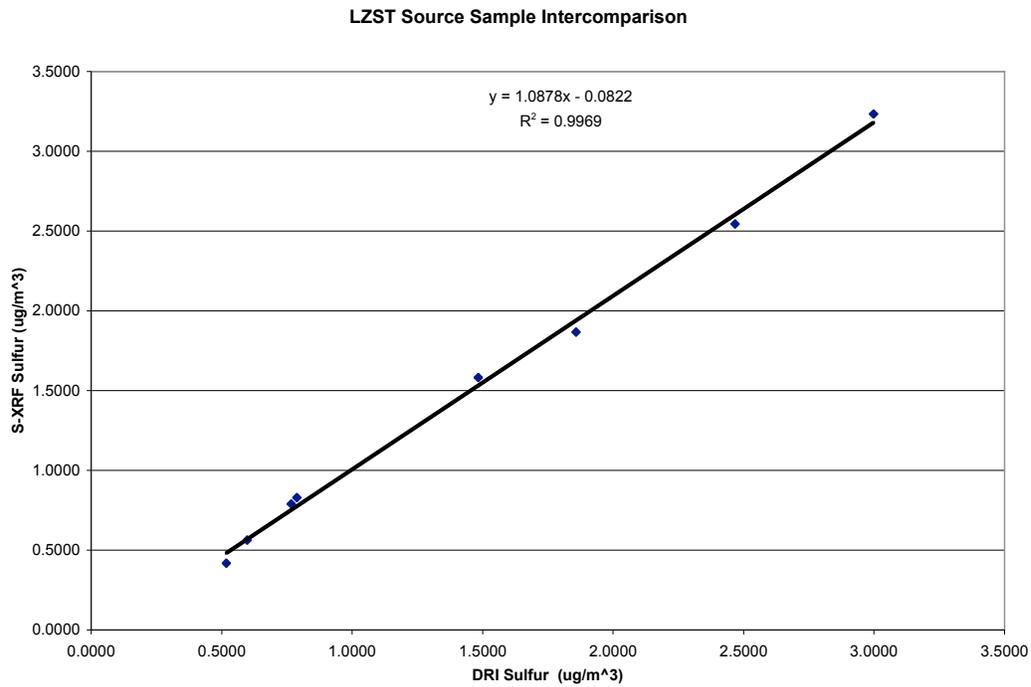


Figure 18. Comparison of sulfur results from ALS vs. DRI analysis of the LZST source samples.

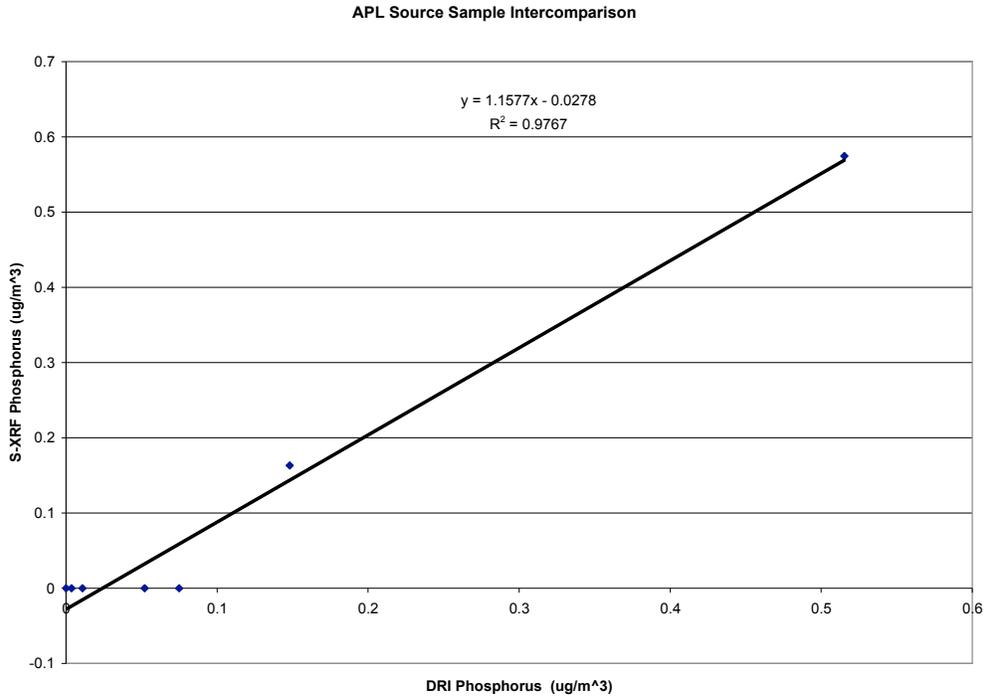


Figure 19. Comparison of phosphorous results from ALS vs. DRI analysis of the APL source samples.

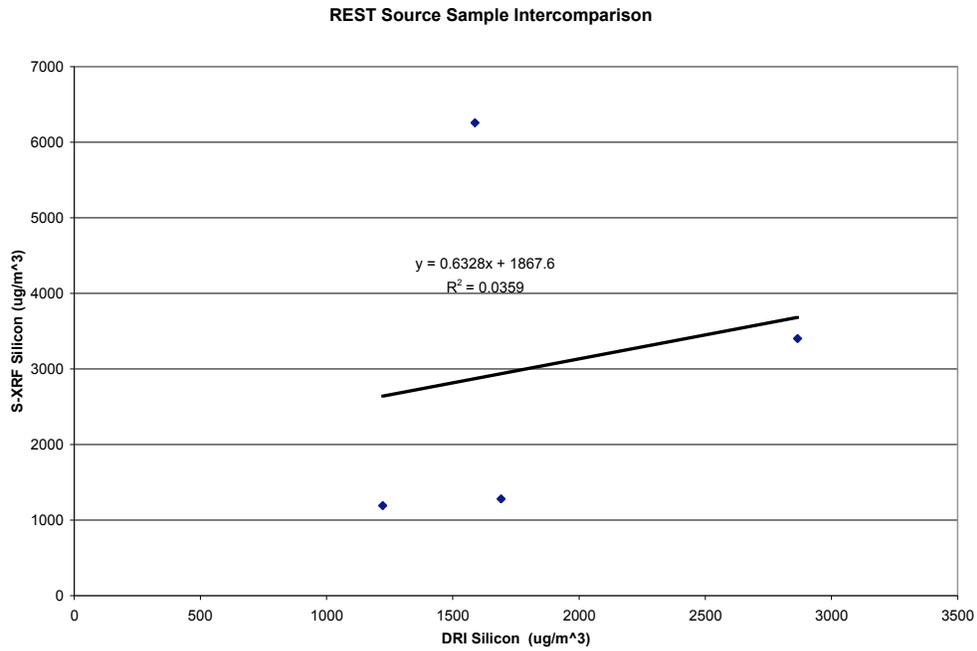


Figure 20. Comparison of ALS vs. DRI silicon results from analysis of the REST source samples.

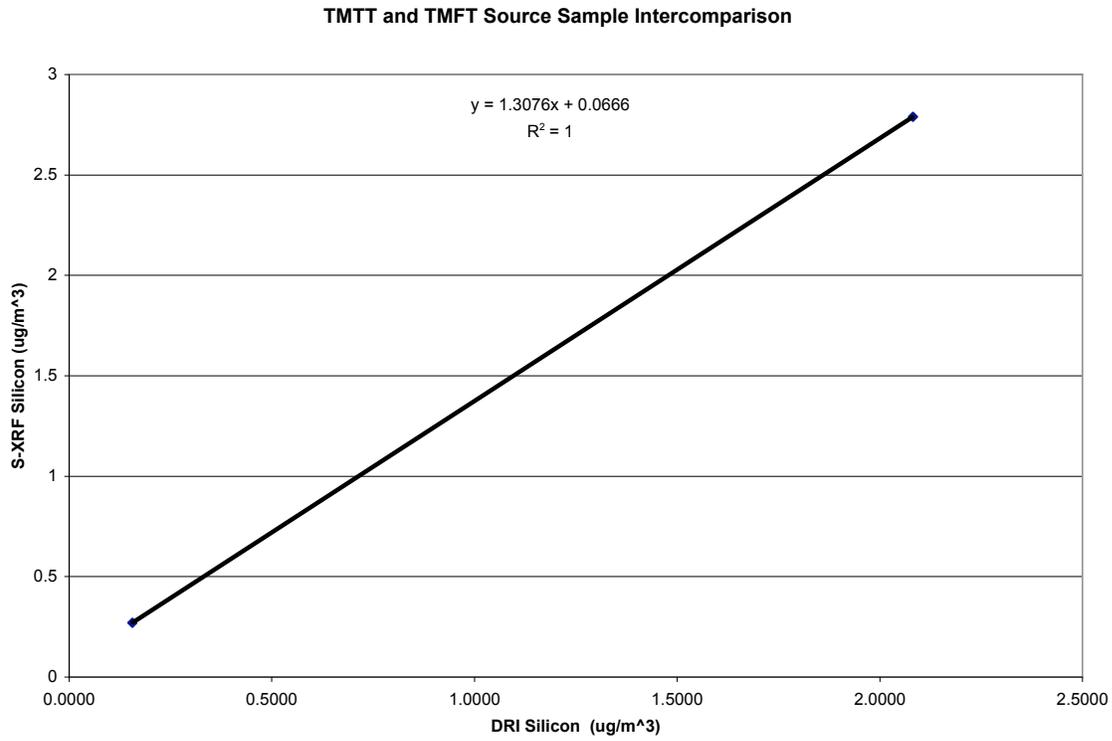


Figure 21. Comparison of the ALS vs. DRI silicon results for analysis of the TMTT and TMFT source samples.

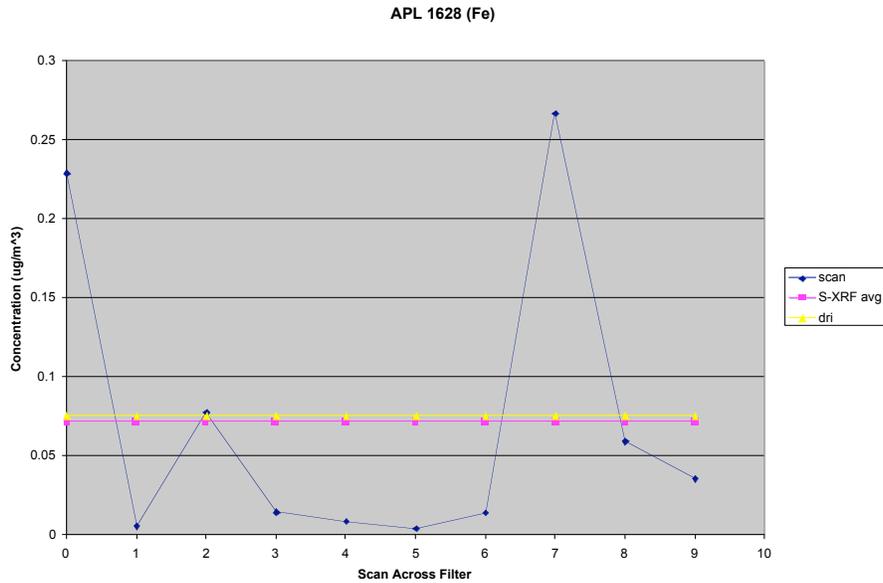


Figure 22. Comparison of point analysis and average analysis results from ALS and DRI for an APL source sample. In this case, the scan across the filter revealed variations greater than a factor of 10 in concentration for iron. Iron was chosen for comparison as results do not suffer significantly from matrix and loading corrections at this x-ray energy. It is likely fortuitous that the average of ALS analyses from this nonuniform sample is in agreement with results obtained by DRI.

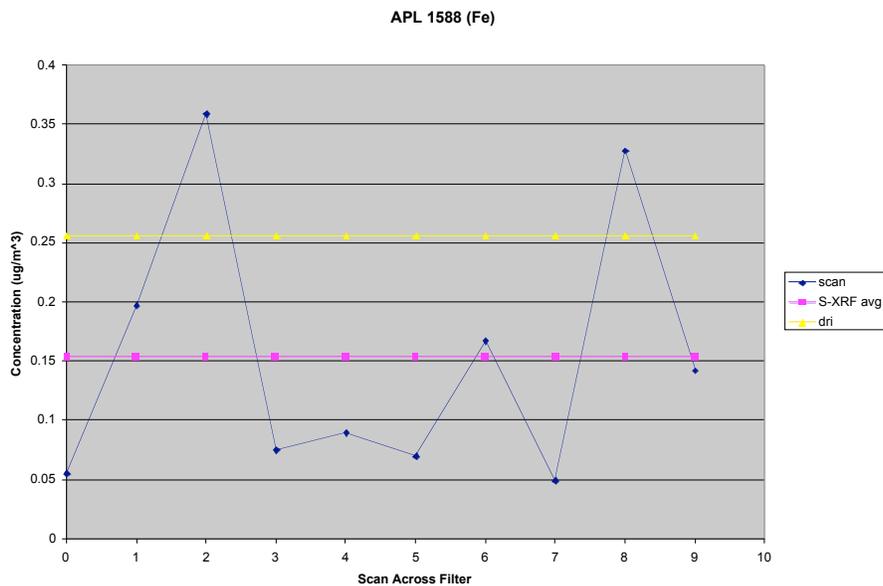


Figure 23. Comparison of point analysis and average analysis results from ALS and DRI for an APL source sample. In this case, the scan across the filter revealed variations by up to a factor of 7. The resulting average of the s-XRF data is significantly different than that obtained by DRI.

Summary and Conclusions.

The primary goals for undertaking the LTADS filter QA study were to 1) determine the range of phosphorous concentration in the Lake Tahoe Basin, and 2) determine the statistical significance of reported phosphorous data from the s-XRF and DRI analyses as an additional quality assurance of the LTADS sampling and analytical program.

Determining the range of phosphorous in the LTADS filter subset requires first understanding the statistical significance of reported [P] values in the XRF analyses. A strong argument for an MDL of 5 ng/m³ and an LQL of between 10-15 ng/m³ can be made from the s-XRF results. In addition, the ca. 30 ng/m³ value for the mid-lake samples on 7/24/03 appear to be valid based on a sample context approach to understanding the s-XRF results. In contrast, using the same statistical and sample context approach examining the DRI data (for samples corresponding to our analyses) results in far fewer above threshold values. The DRI results indicate an MDL value of 10 ng/m³ and an LQL of 20 ng/m³ (2 σ) or 30 ng/m³ (3 σ) for P concentration based on our statistical approach. Therefore a strong case may be made that, at least for the samples analyzed by s-XRF, phosphorous values range between an LQL of 10 ng/m³ and a peak value of 38 ng/m³ in ambient samples. Values between an MDL of 5 ng/m³ and an LQL of 10 ng/m³ would be within uncertainty of MDL (i.e. no value is known better than ± 5 ng/m³). A larger filter analysis set would result in more statistical validity. If the present sample set were treated as random, approximately half of the samples would have P concentration between 10-40 ng/m³. Thus, a larger peak P concentration value is unlikely to be observed from a larger or different sample selection. Although higher peak values are observed in the larger DRI dataset (there are no corresponding s-XRF analyses for these samples), none of these samples met the Standard Operating Procedure (SOP) criteria. Furthermore, because this analysis is based on measurements that have not been corrected for filter blank values, peak ambient P concentrations in the Tahoe basin are extremely unlikely to be greater than 40 ng/m³.

A secondary, yet equally important, result of the present work is comparison of analytical results from the UCD/LBL and DRI laboratories. The observed agreement between the laboratories for major elements indicates no significant bias between methods. A reanalysis of the raw s-XRF spectra using a newly purchased peak fitting application (WinAXIL from Canberra Instruments) allowed reduced uncertainty for minor elements. This reanalysis indicated little change for major elements and reduced the overall average quantity of phosphorous by 13%. The results of the reanalysis provided additional QA for the s-XRF dataset.

Analysis of the 21 source samples revealed inhomogeneities in the distribution of material on the filters and this resulted in statistically poor quantitative results. Occasional (likely fortuitous) agreement between ALS and DRI results for the source samples was observed. The source sample data generally did not show good correlation between ALS and DRI methods in sharp contrast to the excellent agreement observed between analytical methods for the ambient filter samples.

Glossary of Terms, Abbreviations, and Symbols

ALS	Advanced Light Source—Lawrence Berkeley National Laboratory
AXIL (WinAXIL)	x-ray data reduction software
DRI	Desert Research Institute
LBL	Lawrence Berkeley National Laboratory (also ALS)
LQL	lower quantifiable limit
LTADS	Lake Tahoe Atmospheric Deposition Study
MDL	minimum detectable limit
ng/m ³	nanograms (of an element) per cubic meter (of air)
P	phosphorous (other elements presented in similar one or two letter chemical abbreviation)
PM ₁₀	particulate matter less than 10 microns (aerodynamic diameter)
PM _{2.5}	particulate matter less than 2.5 microns (aerodynamic diameter)
QA	quality assurance
s-XRF	synchrotron x-ray fluorescence analysis (at ALS)
TSP	total suspended particulate (in air)
UCD	University of California Davis (operator of ALS facility)
XRF	x-ray fluorescence analysis