Data report for elemental analysis of IMPROVE samples collected during July, August, September 2008
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SUMMARY

This report summarizes the quality assurance performed during elemental analysis of the IMPROVE samples collected in July, August and September of 2008. The elemental analyses include the determination of most elements with atomic numbers from 11 to 26 (Na-Fe) by energy dispersive X-ray fluorescence (XRF) with a Cu-anode system, most elements from 27 to 40 (Ni-Zr) and 82 (Pb) by XRF with a Mo-anode system, and hydrogen by Proton Elastic Scattering Analysis (PESA) with the Crocker cyclotron. The following data assessments and quality controls are obtained for all analyses:

- Concentration calibration and verification (calibration check)
- Energy calibration
- Laboratory replicates (reanalysis)
- Systems comparison
- Field blanks

Analysis details and key events are summarized below.

July, August and September 2008 samples were analyzed on Cu-Vac2. All calibration checks performed on the Cu-Vac2 and Mo systems during the analyses of Jul-Sep 2008 samples met criteria.

Section 1. Overview of Elemental Analysis Systems

The elements Na and Mg (considered qualitative only) and Al to Fe are reported from two XRF systems with a Cu-anode grounded X-ray tube, Cu-Vac1 and Cu-Vac2. Both systems operate under vacuum. Default settings for sample analysis (20 kV, 10 mA for 1000sec/sample) were used for each system.

The elements Ni to Zr and Pb are reported from a similar system with a Mo-anode grounded X-ray tube operating in air. Samples were analyzed for 1000 seconds at 23 mA and 35 kV (default settings for sample analysis).

The PESA system operates under vacuum and uses a proton beam (4.5 MeV H+) from the Crocker cyclotron to quantify the concentration of hydrogen (H). Samples were analyzed for 15 seconds, with an average current value of approximately 50 nA collected on a Faraday cup.

Section 2. General Statistics of July, August and September 2008 data

XRF and PESA analyses were carried out on 1634 samples collected in July 2008, 1832 samples collected in August 2008 and 1671 samples collected in September 2008. All samples were analyzed between 19 November 2008 and 7 February 2009 on the Mo-anode XRF system, between 24 September 2008 and 24 December 2008 on Cu-Vac2, and on 12/9-12/08 (July 2008 samples), 2/2-4/09 (August 2008 samples), and 2/2-4/09, 2/19/09 (September 2008 samples) on the PESA system.

Table 1 summarizes the third quarter 2008 detection rates on the three systems, with rates for June 2008 included for comparison.

PESA					
Z	***element***	***7-2008***	***8-2008***	***9-2008***	***6-2008***
1	H	100%	100%	100%	100%

Cu-anode XRF					
Z	***element***	***7-2008***	***8-2008***	***9-2008***	***6-2008***
11	Na	63%	56%	57%	39%
12	Mg	37%	41%	40%	24%
13	Al	84%	64%	78%	84%
14	Si	99%	98%	98%	98%
15	P	1%	1%	1%	0%
16	S	100%	100%	100%	100%
17	Cl	17%	15%	14%	17%
19	K	100%	100%	100%	100%
20	Ca	100%	100%	100%	100%
22	Ti	100%	100%	99%	98%
23	V	97%	88%	91%	95%
24	Cr	45%	43%	50%	55%
25	Mn	99%	98%	98%	98%
26	Fe	100%	100%	100%	100%

Mo-anode XRF					
Z	***element***	***7-2008***	***8-2008***	***9-2008***	***6-2008***
28	Ni	58%	55%	56%	56%
29	Cu	97%	96%	81%	92%
30	Zn	99%	98%	99%	100%
33	As	66%	63%	42%	38%
34	Se	93%	92%	90%	88%
35	Br	100%	100%	100%	100%
37	Rb	88%	82%	63%	80%
38	Sr	97%	95%	88%	97%
40	Zr	26%	30%	46%	27%
82	Pb	90%	95%	98%	99%

Table 1. Percentage of cases in which the element was detected on each system. June 2008 data included for reference.

Section 3. Quality Control

3.1 Concentration calibration and verification (calibration checks)

Both XRF systems are calibrated with thin (6.3um) film foil standards produced by Micromatter. The standards used for samples from the third quarter of 2008 are listed below in Table 2. Because their concentrations are relatively high, standards are analyzed at reduced X-ray tube current (2.6 mA on XRF-Cu systems and 10mA on XRF-Mo system) to maintain counting live times comparable with those of actual IMPROVE samples.

Standard	Certified Elemental Concentrations +/- 5% (μg/cm^2)	Serial #
NaCl	Na: 19.1, Cl: 29.4	16518
MgF_2	Mg: 20.6	16519
Al	Al: 40.7	16520
SiO	Si: 23.9	16521
GaP*	P: 4.5	16500
CuS_x	S: 12.9 Cu: 37.6	16523
KCl	Cl: 22.5 K: 24.9	16296
CaF_2	Ca: 24.9	16525
Ti	Ti: 13.7	16504
V	V: 12.2	16505
Cr	Cr: 15.8	16507
Mn	Mn: 14.6	16506
Fe	Fe: 14.7	16508
Ni	Ni: 10.5	16509
Cu	Cu: 12.4	16510
ZnTe*	Zn: 5.2	16511
GaAs*	Ga: 8 As: 8.7	16512
Se	Se: 12.9	16513
CsBr	Br: 5.1	16514
RbI	Rb: 5.7	16515
SrF_2	Sr: 10.9	16516
Pb	Pb La: 16 Pb Lb: 16	16517

Table 2. Micromatter standard foils used for all analyses. .Standards (*) with variable stoichiometry.

Spectra from the foil standards are processed and analyzed by the same software used for samples. The performance of all systems (shown in Figures 1-2) is monitored approximately weekly by monitoring the ratios of the system response at each calibration check to the response observed at the last calibration (based on the curve fit). If the ratios lie within the acceptance limits 0.9 – 1.1 for all quantitative elements, then the system is considered stable and the existing calibration factors continue to be used. Deviations beyond 10% trigger an investigation of the problem and possible system recalibration. After a recalibration, all samples analyzed since the last successful calibration verification are reanalyzed with the new calibration factors.

The analysis dates for each sample month are listed in the legends of Figures 1-2. June 2008 samples analysis dates are included for reference.

The XRF-Mo system was not operational for about 2 months due to some construction/ modifications/improvements done in the XRF room. A new system calibration was done on November 18, 2008.

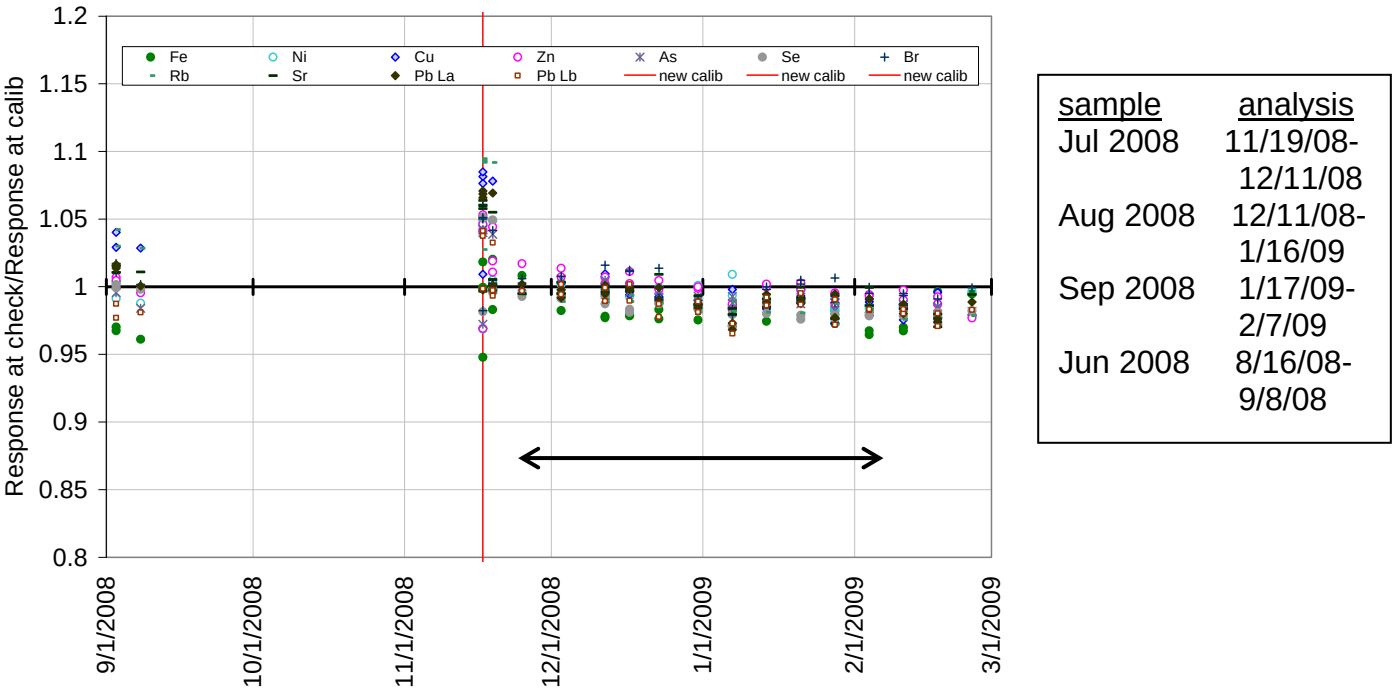

Figure 1. Mo XRF system performance chart referenced to last calibration.

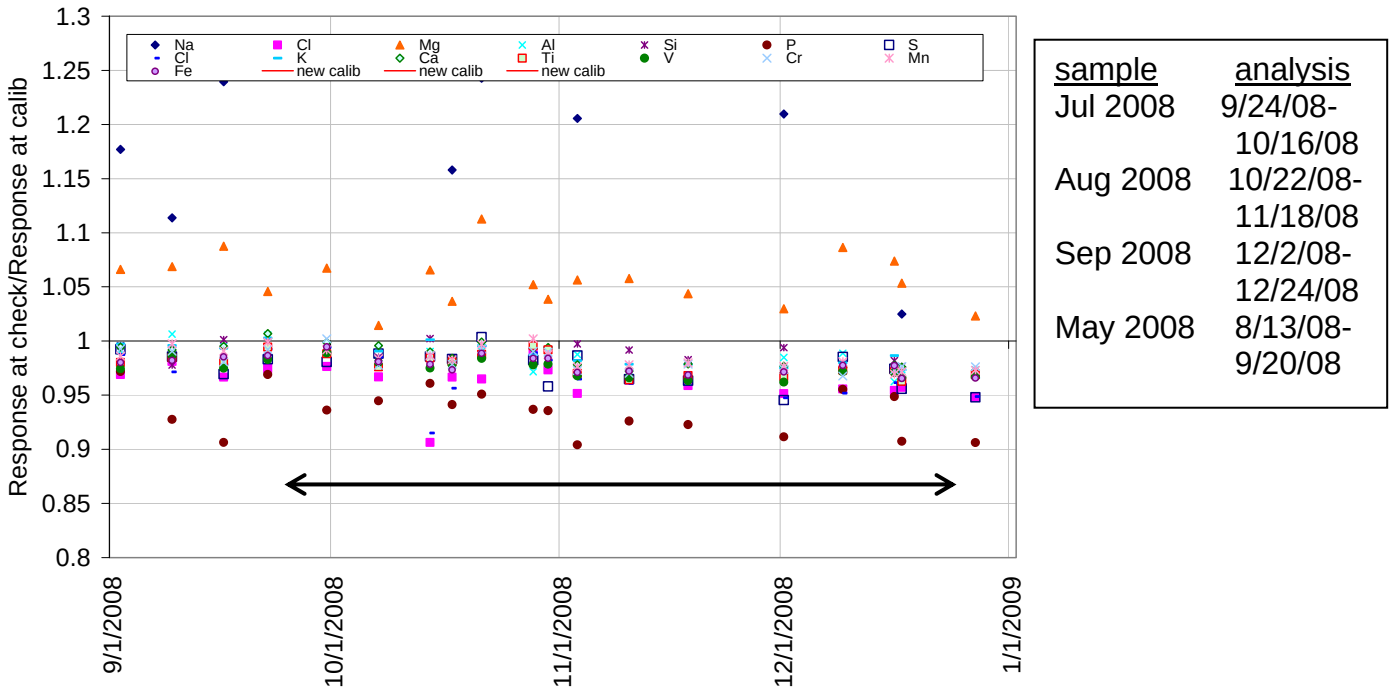

Figure 2. Cu-Vac2 XRF system performance chart referenced to last calibration.

None of the standards ratios exceeded acceptance limits during the analysis of Jul-Sep 2008 samples on the Mo system. All calibration checks were within criteria.

Jul-Sep 2008 samples were analyzed on the XRF Cu-Vac2 system. All weekly calibration checks on the Cu-Vac2 system were within criteria. Ratios approaching 0.9 were observed for P, but remained within criteria.

Eight Mylar foils were used for calibrations and calibration checks of the PESA system. Over the time the foil may become damaged and replaced with a new one. The change is recorded and the calculated H concentration for each of the PESA standards is entered in the table. The current H concentrations are listed below:

PESA Standard	1	2	3	4	5	6	7	8
Calculated H amount (ug/cm2)	20.61	20.61	14.45	14.45	20.28	20.28	34.58	34.58

As with XRF, the calibration factor is based on the average ratio of observed counts for the eight PESA standards to their calculated H concentration.

The PESA system is recalibrated at the beginning of every analytical session and re-tuned during sample analysis, because of variations in the ion source production, amplitude harmonics, and optics. The eight Mylar blanks used as calibration standards are reanalyzed approximately every 100-200 samples to verify the calibration throughout the session. If the ratio of reported to calculated concentrations for these standards drifts outside 5% range during an analysis run., the cyclotron is re-tuned, the system is recalibrated, and the samples are reanalyzed. Figure 3 shows calibration verifications and calibrations during the analysis of the Jul-Sep 2008 samples; the lowest point lies at the limit of 5% low, although the plot makes it appear beyond the limit.

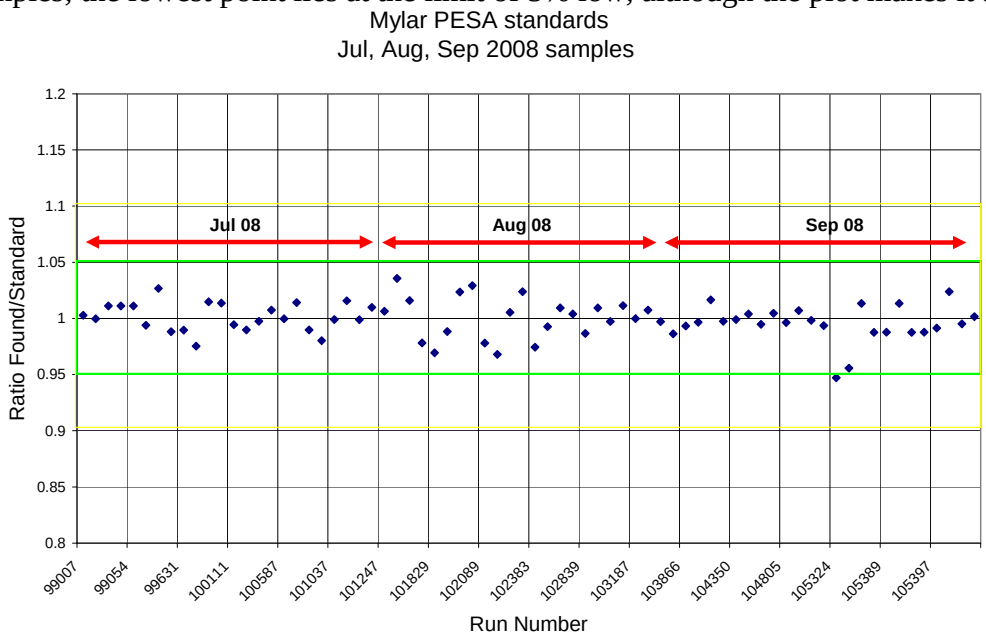

Figure 3. PESA standards for Jul-Sep 2008 samples

3.2 X-ray energy calibration

In addition to the peak counts associated with a known concentration (concentration calibration), the energy channel associated with a known fluorescence line must also be determined; this is the energy calibration. Energy calibrations were performed for the analyses of each sample month on Mo system and whenever determined necessary for Cu systems. The established relationships have a form

*energy = intercept + slope * channel*

The following energy calibration equations (in energy units of KeV) were used for the analysis:

	XRF-Cu1			*change*	XRF-Cu2			*change*	XRF-Mo			*change*
	intercept	slope	full scale	*from Jun05*	intercept	slope	full scale	*from Oct05*	intercept	slope	full scale	*from Jun07*
Jul-08					-4.01E-02	1.71E-02	8.739	*-0.13%*	-7.13E-02	3.70E-02	18.868	*0.32%*
Aug-08					-4.01E-02	1.71E-02	8.739	*-0.13%*	-7.54E-02	3.69E-02	18.820	*0.06%*
Sep-08					-4.01E-02	1.71E-02	8.739	*-0.13%*	-7.98E-02	3.69E-02	18.815	*0.03%*

3.3 Reanalysis

The reproducibility of XRF and PESA data is tracked over time by reanalyzing selected sample filters. Different reanalysis protocols are used for the XRF and PESA reanalyses, reflecting the different impacts of their exciting beams on the Teflon filter substrate, as explained in previous reports.
Filters to be reanalyzed by PESA are selected from the previous quarter's X-module (collocated A-module) samples. During the analysis of Jul 2008 samples, MEVEX, OLYMX and PMRFX filters from Feb 2008 were reanalyzed multiple times. For Aug 2008 samples, MEVEX, OLYMX and PMRFX filters from Mar 2008 were reanalyzed, and multiple reanalyses for Sep 2008 samples were performed on MEVEX, OLYMX and PMRFX filters from Jan 2008. Figure 4 compares the original and repeat analyses.

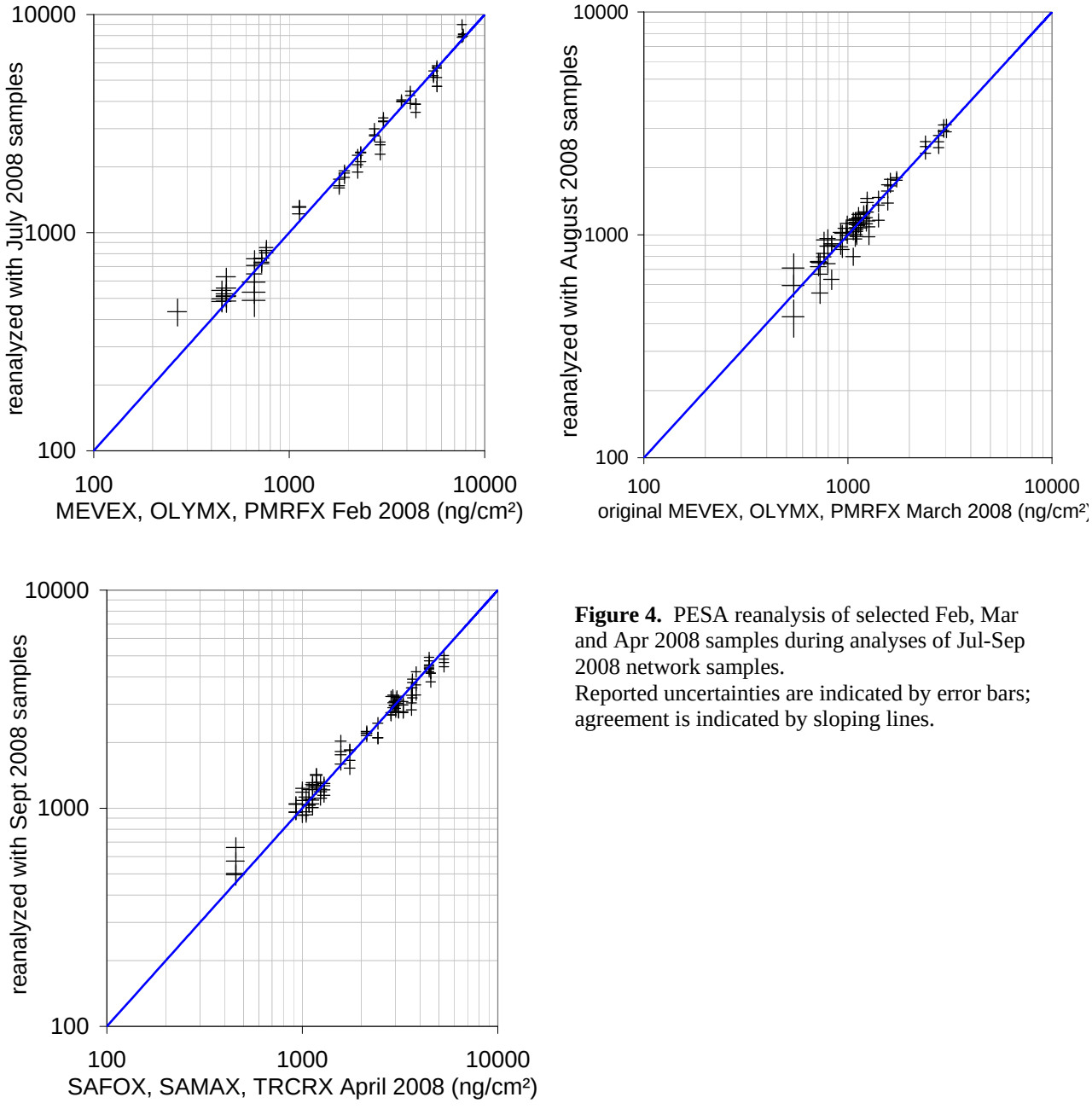

Figure 4. PESA reanalysis of selected Feb, Mar and Apr 2008 samples during analyses of Jul-Sep 2008 network samples.
Reported uncertainties are indicated by error bars; agreement is indicated by sloping lines.

XRF reanalyses are conducted repeatedly on a fixed collection of sample filters referred to as REANAL1 and REANAL2 and described in previous reports. The trays were reanalyzed approximately monthly on the Mo, and Cu-Vac2 systems during analyses of the Jul-Sep 2008 samples. All results are summarized in the Figures 5 and 6 below.

For all the systems, the mean loadings calculated based on approximately 12 consecutive runs (about a year of data during which calibrations have been based on a curve fit approach) are used as a benchmark for comparison. The average ratio of observed deviations from all samples (from the mean) to reported measured uncertainties for each element is calculated and shown on the y-axis. Figures 5-6 highlight the reanalysis results for four elements selected for each system, Fe, Cu, Zn and Br for Mo and Si, S, Ca and Fe for Cu. These major elements serve here as general indicators of system performance and the horizontal continuous and dotted red lines shown are intended to provide proposed action and warning limits, respectively. They are based on historical systems' performance only and may need to be reevaluated if any operational conditions change. The horizontal black arrows indicate the periods of analysis of the third quarter 2008 samples.

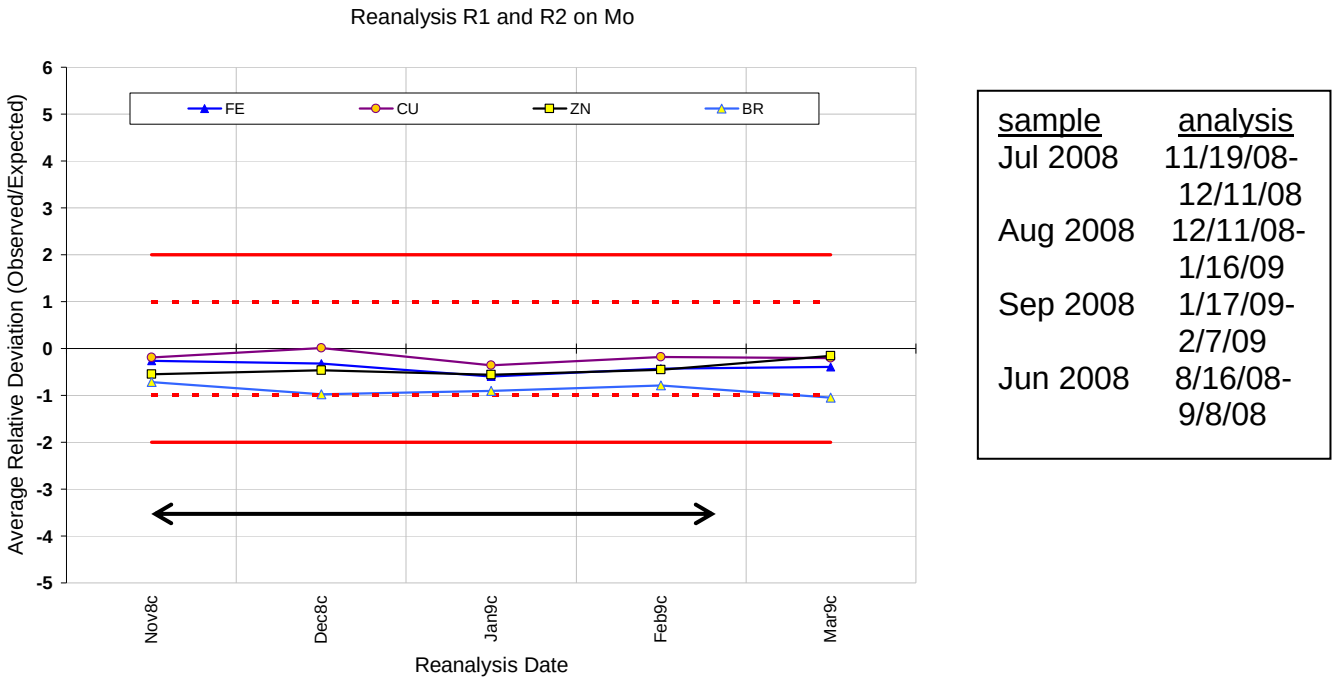

Figure 5. Reanalyses of REANAL1 and REANAL2 samples on XRF-Mo system. Horizontal arrow indicates when Jul-Sep 2008 network samples were analyzed.

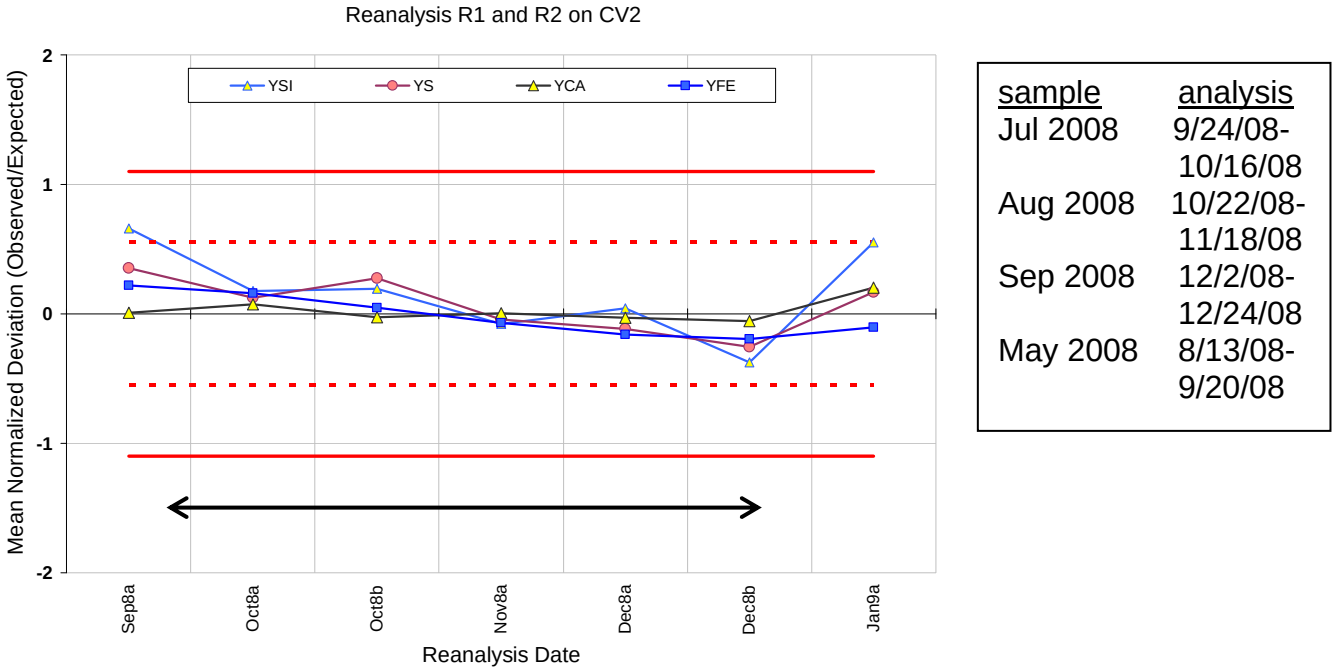

Figure 6. Reanalyses of REANAL1 and REANAL2 samples on XRF-Cu2 system. . Horizontal arrow indicates when Jul-Sep 2008 network samples were analyzed.

System comparison

Additional comparison between selected elements measured independently by the Cu and Mo systems is performed for each data set. The elements Calcium and Iron are reported from the Cu system (Cu-Vac1 or Cu-Vac2) but are also quantified by the Mo system. Figures 7 and 8 compare the two measurements of these two elements for the samples from Jul-Sep 2008. Reported uncertainties are shown as bars for each sample, and reported MDL's are indicated by green and pink points for both systems. The increase in analytical uncertainty closer to the MDL's can be observed for all cases.

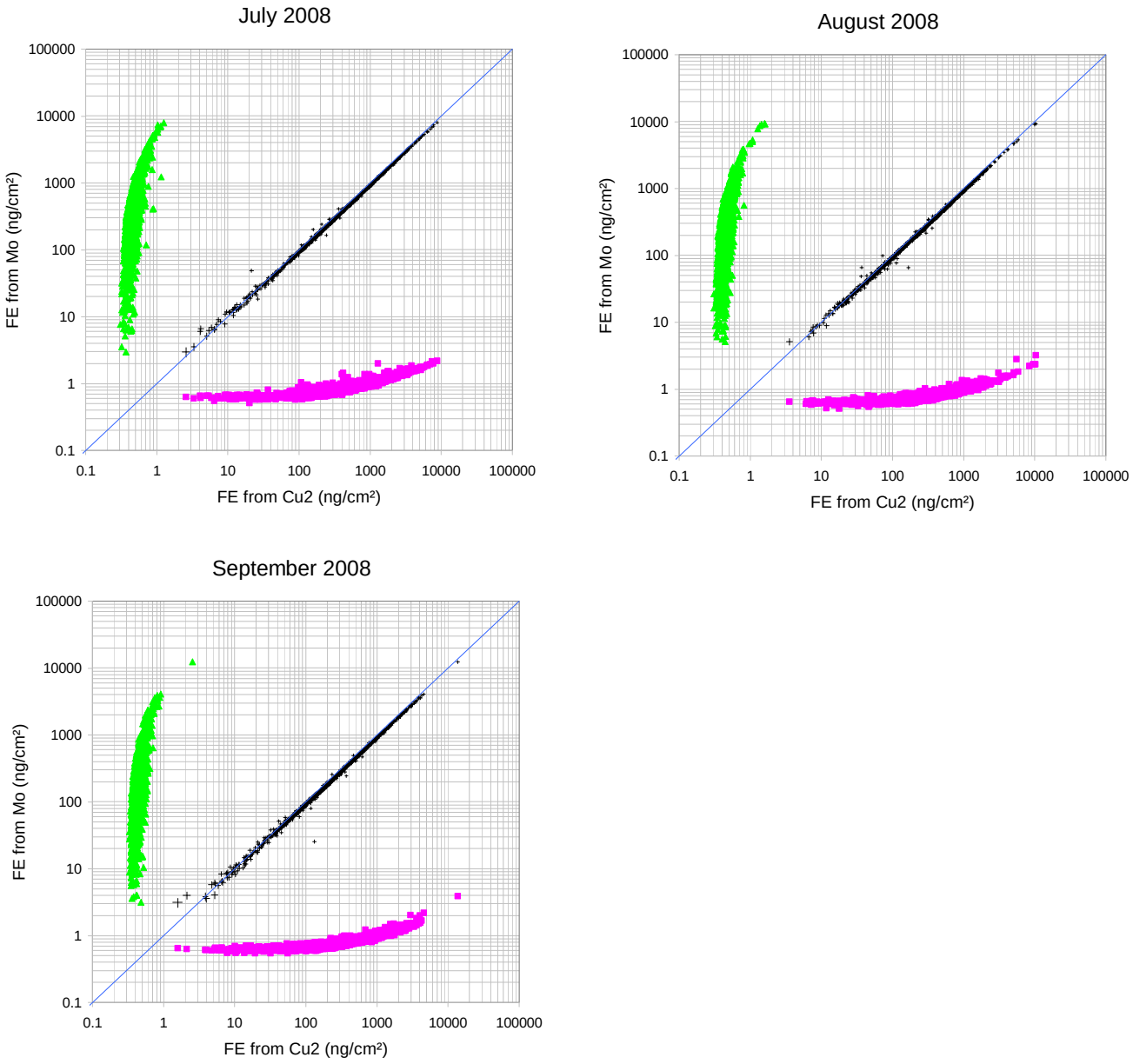

Figure 7. Comparison of Iron data obtained independently from Cu (x-axis) and Mo (y-axis) systems. Cu1 refers to Cu-Vac1 and Cu2 to Cu-Vac2.

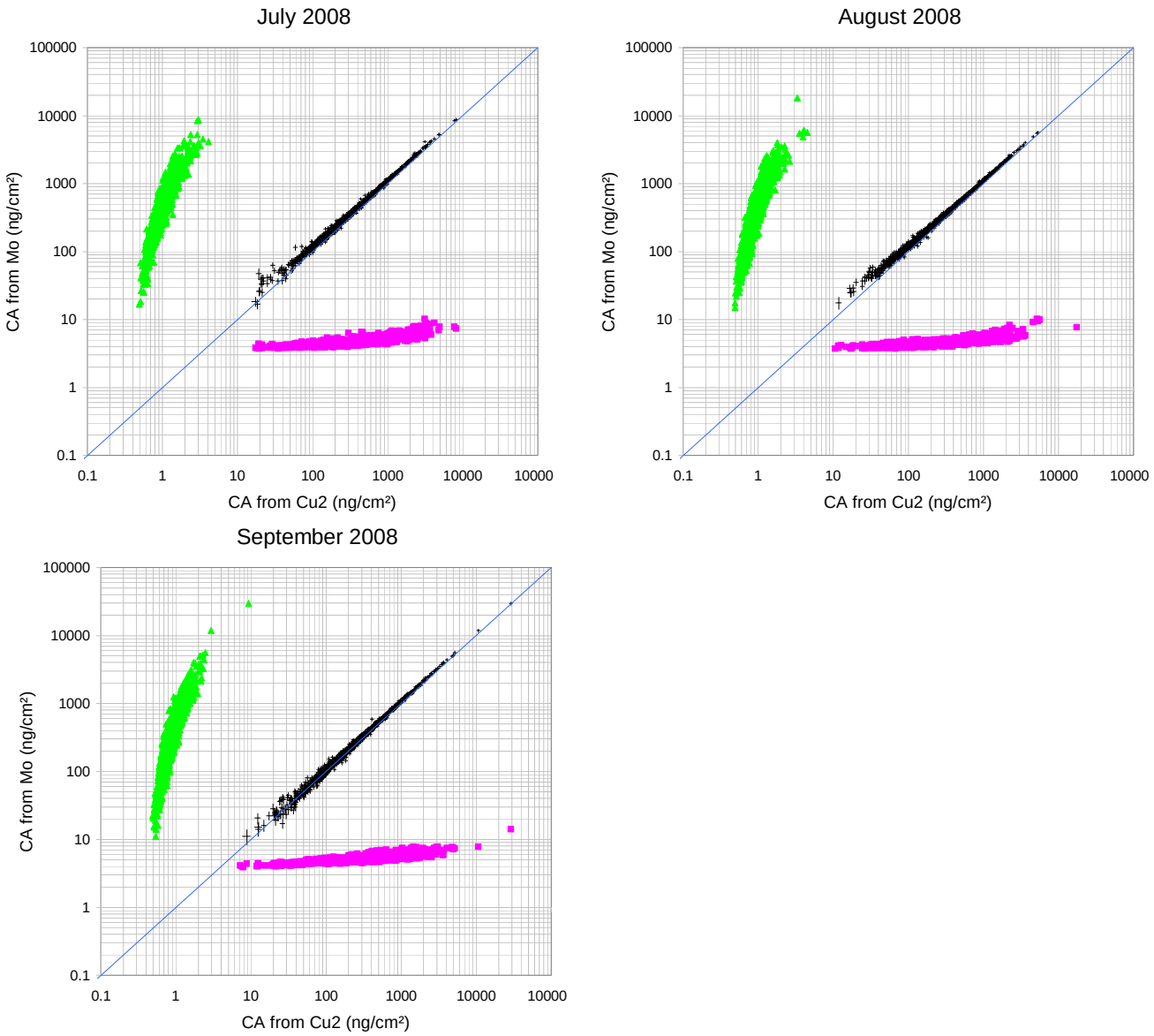

Figure 8. Comparison of Calcium data obtained independently from Cu (x-axis) and Mo (y-axis) systems. Cu1 refers to Cu-Vac1 and Cu2 to Cu-Vac2.

Calcium and iron determinations by the Mo system contain more uncertainty than those from the Cu systems, and are accordingly not used to report concentrations. Their value in these system comparisons is the additional qualitative check they provide on both systems' performance.

3.5 Field blanks

Fifteen field blanks for July 2008, 178 field blanks for August 2008 and 52 field blanks for September 2008 samples were exposed at selected sites on selected sampling events. The field blanks were analyzed on both, XRF-Mo and Cu-Vac2 systems. The Cu-anode system used for analysis of the field blanks was the same system used for the corresponding samples.

As in previous reports, 95th, 90th and 75th percentile field blank loadings are shown for each system in the tables below. They are given as percentiles of well measured network sample loadings during July, August and September 2008. Loadings are considered well measured when their uncertainties are less

than 10%. Thus, the 95th percentile field blank loading for Fe (Sep 2008 samples) was at or above about 5.4% (4% on Mo) of all well measured sample loadings on the Cu system.

Cu anode

Jul 2008	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe
95 %ile	0.0%	0.0%	0.0%	0.9%	0.0%	0.1%	3.2%	1.7%	6.1%	0.9%	0.0%	0.0%	0.0%	3.8%
90 %ile	0.0%	0.0%	0.0%	0.6%	0.0%	0.1%	0.6%	0.6%	3.7%	0.6%	0.0%	0.0%	0.0%	2.8%
75 %ile	0.0%	0.0%	0.0%	0.3%	0.0%	0.0%	0.0%	0.2%	1.1%	0.1%	0.0%	0.0%	0.0%	0.9%
Aug 2008	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**K**	**Ca**	**Ti**	**V**	**Cr**	**Mn**	**Fe**
95 %ile	0.0%	0.0%	0.0%	2.3%	0.0%	0.0%	13.6%	2.9%	6.6%	3.4%	0.0%	0.0%	0.0%	2.2%
90 %ile	0.0%	0.0%	0.0%	0.8%	0.0%	0.0%	7.1%	0.8%	3.2%	0.9%	0.0%	0.0%	0.0%	1.2%
75 %ile	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	2.5%	0.0%	0.6%	0.0%	0.0%	0.0%	0.0%	0.6%
Sep 2008	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**K**	**Ca**	**Ti**	**V**	**Cr**	**Mn**	**Fe**
95 %ile	0.0%	0.0%	0.0%	0.7%	0.0%	0.0%	16.4%	4.4%	4.0%	0.4%	0.0%	0.0%	0.0%	5.4%
90 %ile	0.0%	0.0%	0.0%	0.3%	0.0%	0.0%	14.3%	3.5%	2.7%	0.0%	0.0%	0.0%	0.0%	1.7%
75 %ile	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	4.2%	0.6%	0.5%	0.0%	0.0%	0.0%	0.0%	0.6%

Mo anode

Jul 2008	Fe	Ni	Cu	Zn	As	Pb	Se	Br	Rb	Sr	Zr
95 %ile	4.1%	0.0%	0.0%	27.6%	0.0%	0.2%	0.0%	0.0%	0.0%	0.0%	0.0%
90 %ile	3.0%	0.0%	0.0%	18.9%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
75 %ile	0.5%	0.0%	0.0%	4.7%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Aug 2008	**Fe**	**Ni**	**Cu**	**Zn**	**As**	**Pb**	**Se**	**Br**	**Rb**	**Sr**	**Zr**
95 %ile	2.8%	0.0%	0.0%	43.0%	0.0%	0.2%	0.0%	0.0%	0.0%	0.0%	0.0%
90 %ile	1.1%	0.0%	0.0%	17.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
75 %ile	0.3%	0.0%	0.0%	1.6%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Sep 2008	**Fe**	**Ni**	**Cu**	**Zn**	**As**	**Pb**	**Se**	**Br**	**Rb**	**Sr**	**Zr**
95 %ile	4.0%	0.0%	0.0%	32.5%	0.0%	4.0%	0.0%	0.0%	0.0%	0.0%	0.0%
90 %ile	1.3%	0.0%	0.0%	25.5%	0.0%	2.6%	0.0%	0.0%	0.0%	0.0%	0.0%
75 %ile	0.3%	0.0%	0.0%	5.8%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%

Field blank loadings are negligible compared to samples for all elements except for Cl in Aug and Sep 2008, and for Zn (Jul, Aug and Sep 2008), as observed in previous reports.