

Interagency Monitoring of Protected Visual Environments (IMPROVE) Data Precision

Nicole P. Hyslop and Warren H. White

IMPROVE Collocated (Duplicate) Measurements

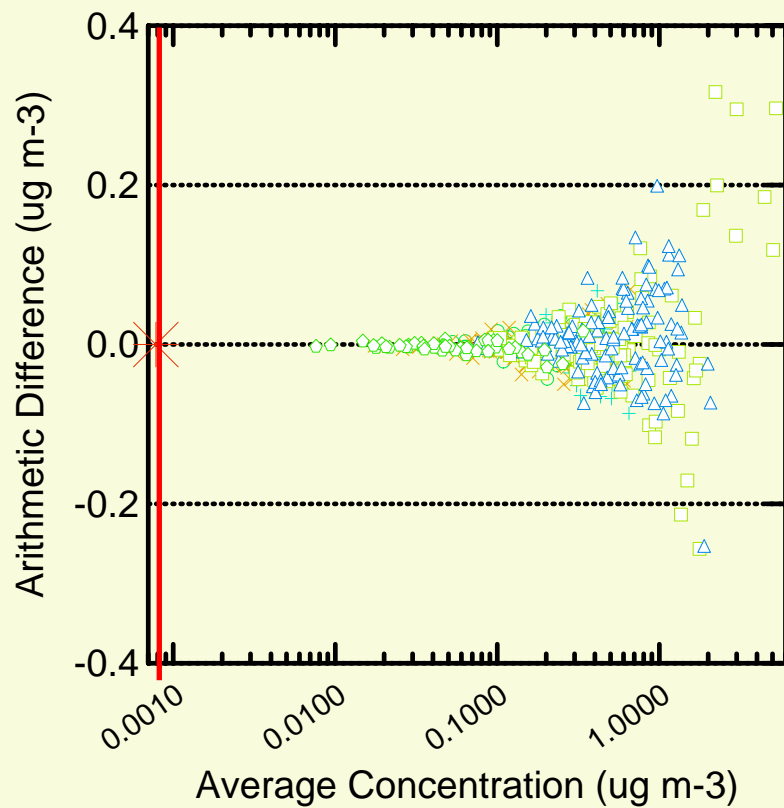
- Established for the first time in 2004.
- Seven collocated modules of each type.
- Two objectives
 - Evaluate precision of measurements and
 - Determine if uncertainty estimates are accurate.
- Captures uncertainty resulting from sample collection, sample analysis, and data processing.
- Does not capture uncertainty resulting from temperature uncertainty or calibration uncertainty.

Module Type	Site Code	Site Name	State	Start Date	Module Type	Site Code	Site Name	State	Start Date
A PM_{2.5} mass & elements	MEVE	Mesa Verde NP	CO	8/13/03	C PM_{2.5} organic & elemental carbon	EVER	Everglades NP	FL	7/11/03
	PMRF	Proctor Maple Research Facility	VT	9/3/03		SENE	Seney NWR	MI	8/10/03
	OLYM	Olympic NP	WA	11/8/03		HOOV	Hoover WA	CA	8/13/03
	PHOE	Phoenix	AZ	3/30/04		MELA	Medicine Lake NWR	MT	9/25/03
	SAFO	Sac and Fox Nation	KS	11/20/03		PHOE	Phoenix	AZ	3/30/04
	TRCR	Trapper Creek	AK	6/22/04		SAWE	Saguaro NP West	AZ	3/25/04
	SAMA	Saint Marks	FL	11/18/04		HEGL	Hercules-Glade WA	MO	9/15/04
B PM_{2.5} anions	LAVO	Lassen Volcanic NP	CA	4/18/03	D PM₁₀ mass	JOSH	Joshua Tree NP	CA	8/7/03
	MACA	Mammoth Cave NP	KY	5/12/03		QURE	Quabbin Reservoir	MA	9/4/03
	BIBE	Big Bend NP	TX	8/30/03		HOUS	Houston	TX	4/4/03
	GAMO	Gates of the Mountains WA	MT	9/23/03		JARB	Jarbridge WA	NV	6/30/04
	FRRE	Frostburg Reservoir	MD	4/15/04		PHOE	Phoenix	AZ	3/30/04
	BLMO	Blue Mounds State Park	MN	9/16/04		WICA	Wind Cave NP	SD	9/17/04
	PHOE	Phoenix	AZ	3/30/04		SWAN	Swanquarter WA	NC	11/9/04

Uncertainty and Precision in this Presentation

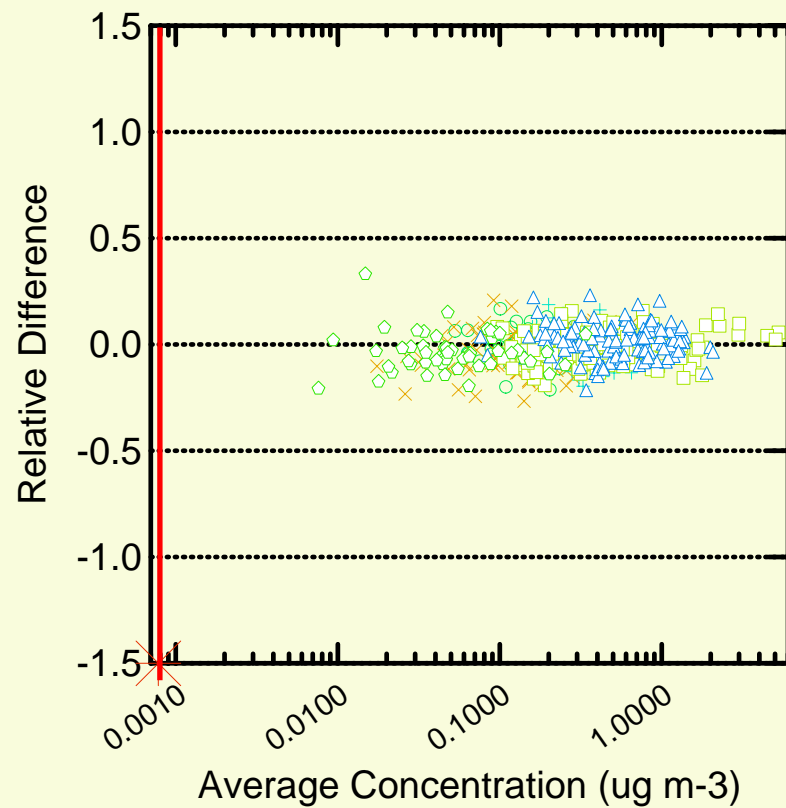
- Uncertainty refers to the expected variance in outcomes of measurements repeated under the same conditions.
- Collocated precision refers to the variance of relative differences between the duplicate measurements.

Collocated Sulfur Data

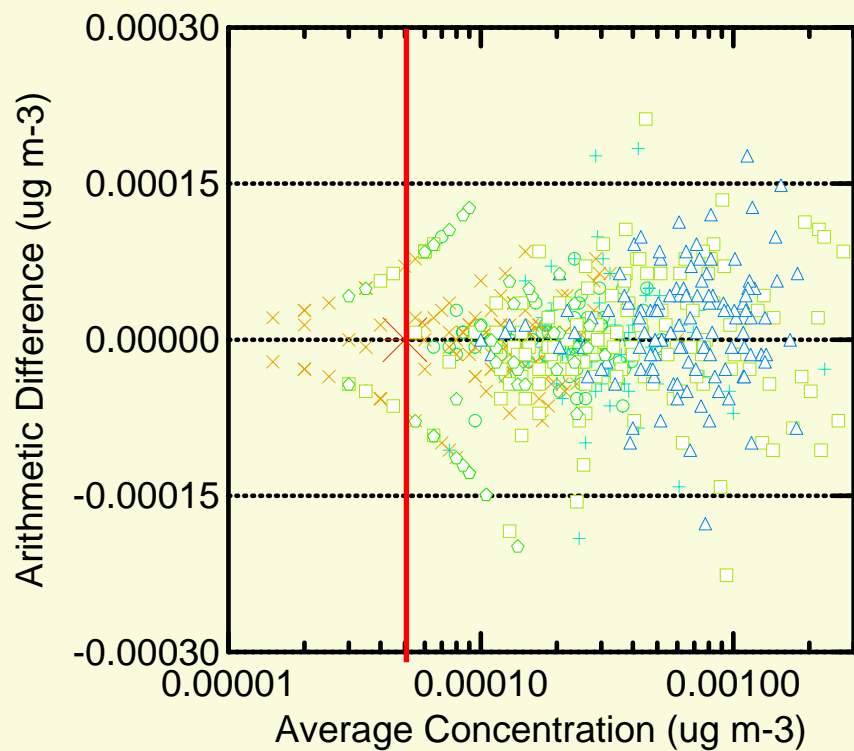


SITES

- * MDL
- MEVE
- × OLYM
- + PHOE
- PMRF
- △ SAFO
- ◇ TRCR

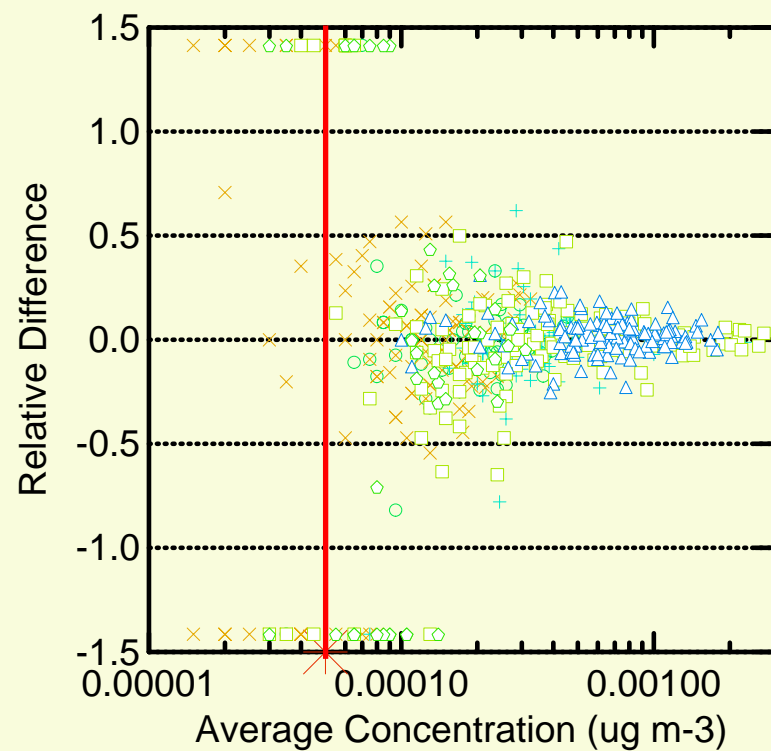


Collocated Selenium Data



SITES

- * MDL
- MEVE
- × OLYM
- + PHOE
- PMRF
- △ SAFO
- ◇ TRCR



Collocated Precision Calculations

$$\text{Collocated Precision} = \sqrt{\frac{1}{n} \sum_{i=1}^n \left(\frac{([Y_i] - [X_i]) / \sqrt{2}}{([Y_i] + [X_i]) / 2} \right)^2} * 100\%$$

$[Y_i]$ denotes routine concentration,

$[X_i]$ denotes collocated concentration,

n is number of sample pairs

- U.S. EPA designated method (FRM, 1997)
- Only use pairs where the average concentration is greater than 3 * MDL.

Estimated Uncertainty for each Concentration

- An uncertainty estimate is reported with every species concentration.
 - Estimates are based on individual sources of measurement uncertainty and propagation of errors.

$$Unc_{[C]} = \sqrt{[C]^2 * (unc_{analytic}^2 + unc_{volume}^2) + (Unc_{constant})^2}$$

where $[C]$ = concentration

$unc_{analytic}$ = proportional analytical uncertainty

unc_{volume} = proportional volume uncertainty

$Unc_{constant}$ = constant analytical uncertainty

Why don't the collocated precisions meet the expectations?

- Analytical issues
 - Analysis area
 - Minimum detectable limits (mdl's)
 - Concentrations always close to mdl
- Sampling discrepancies
 - Cyclone cutpoint differences
 - Non-uniform deposits
 - Deposit area

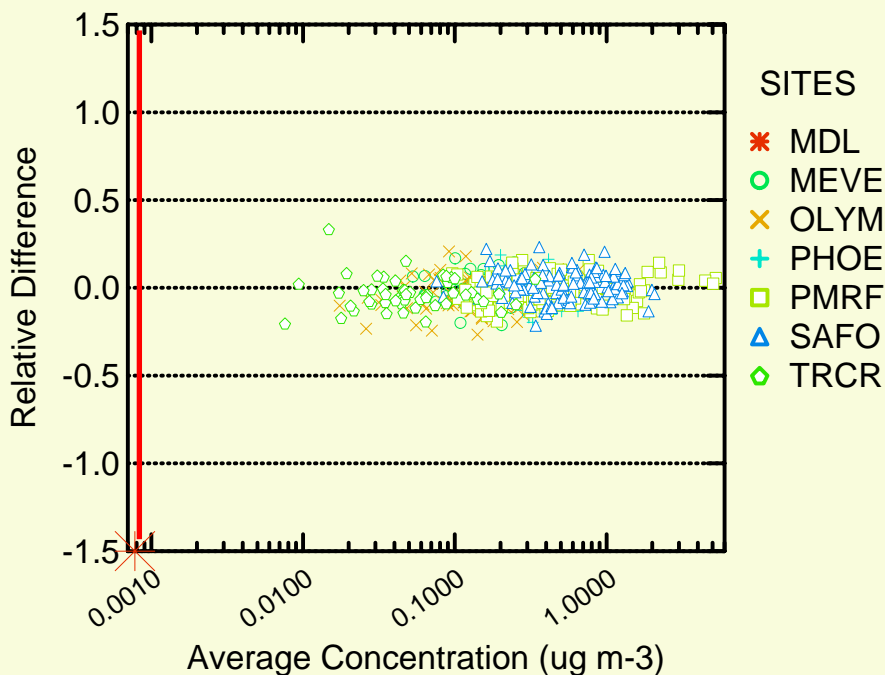
Copper-anode XRF Element Metrics

Species	Count > 3*MDL [†]	Estimated Uncertainty	Collocated Precision	Collocated/ Estimated
Na	15	25%	50%	2.0
Mg	9	n < 10	n < 10	-
Al	257	14%	69%	5.0
Si	533	11%	41%	3.7
P	21	18%	131%	7.3
S	577	5%	8%	1.6
Cl	105	12%	68%	5.6
K	577	6%	13%	2.3
Ca	577	6%	19%	3.0
Ti	528	11%	30%	2.6
V	457	18%	21%	1.2
Cr	108	28%	56%	2.0
Mn	529	12%	24%	2.0
Fe	577	5%	18%	3.3

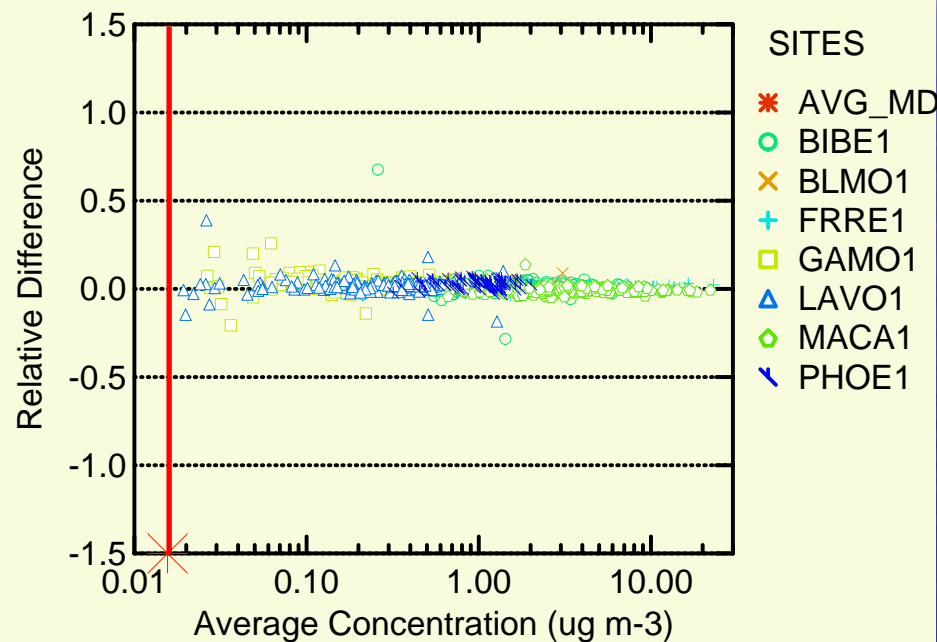
† 577 valid pairs

Sulfur by XRF and Sulfate by IC

Sulfur



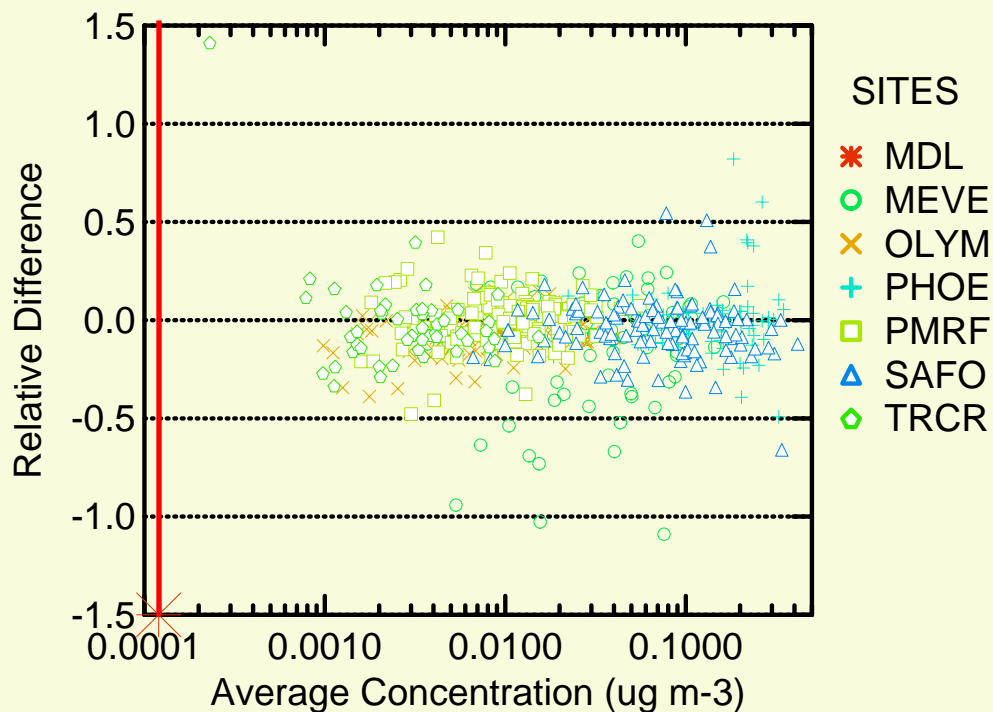
Sulfate



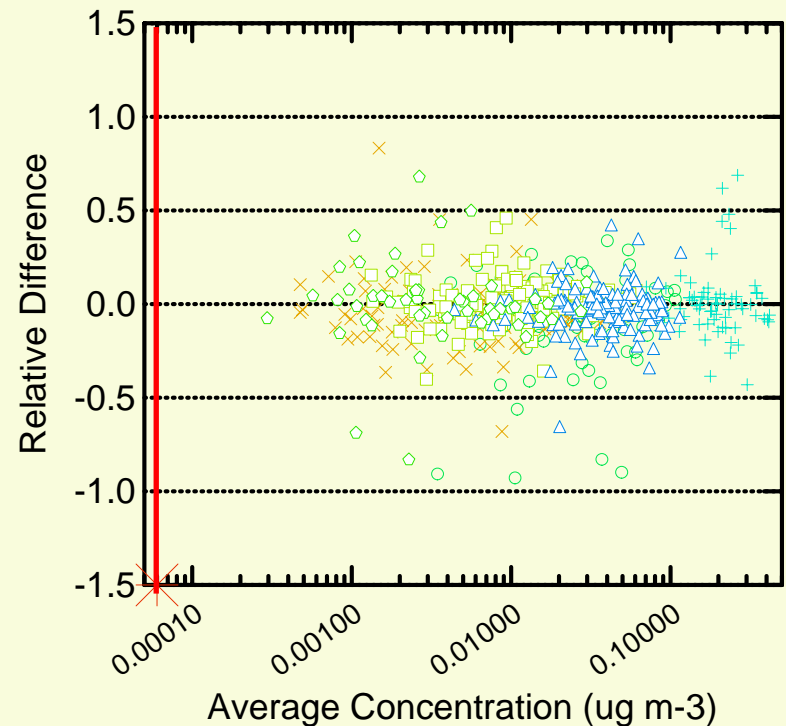
Species	Count > 3*MDL	Estimated Uncertainty	Collocated Precision	Collocated/ Estimated
Sulfur	577/577	5.3%	8.2%	1.56
Sulfate	801/823	4.8%	4.1%	0.86

Soil-derived Elements

Calcium

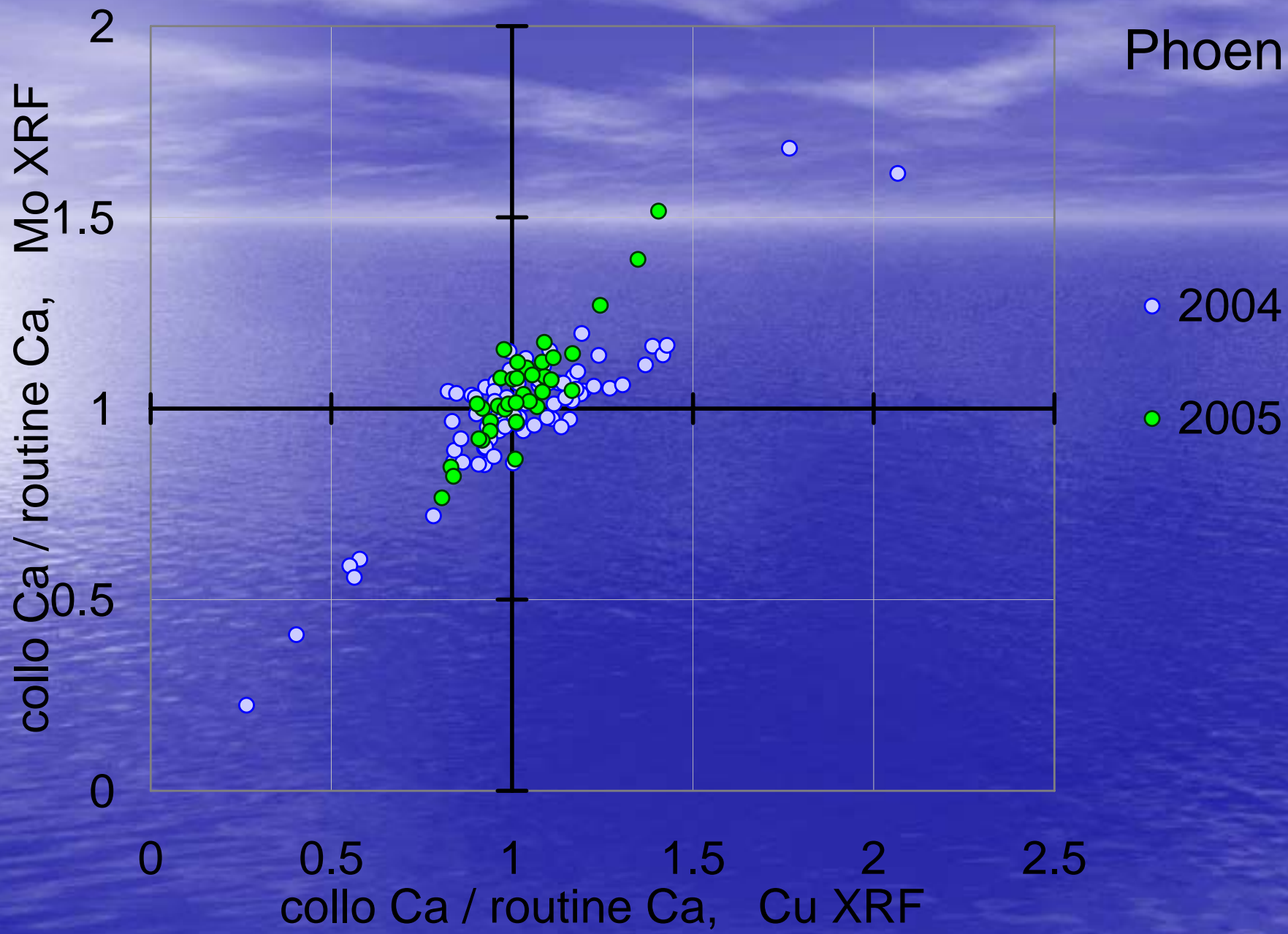


Iron

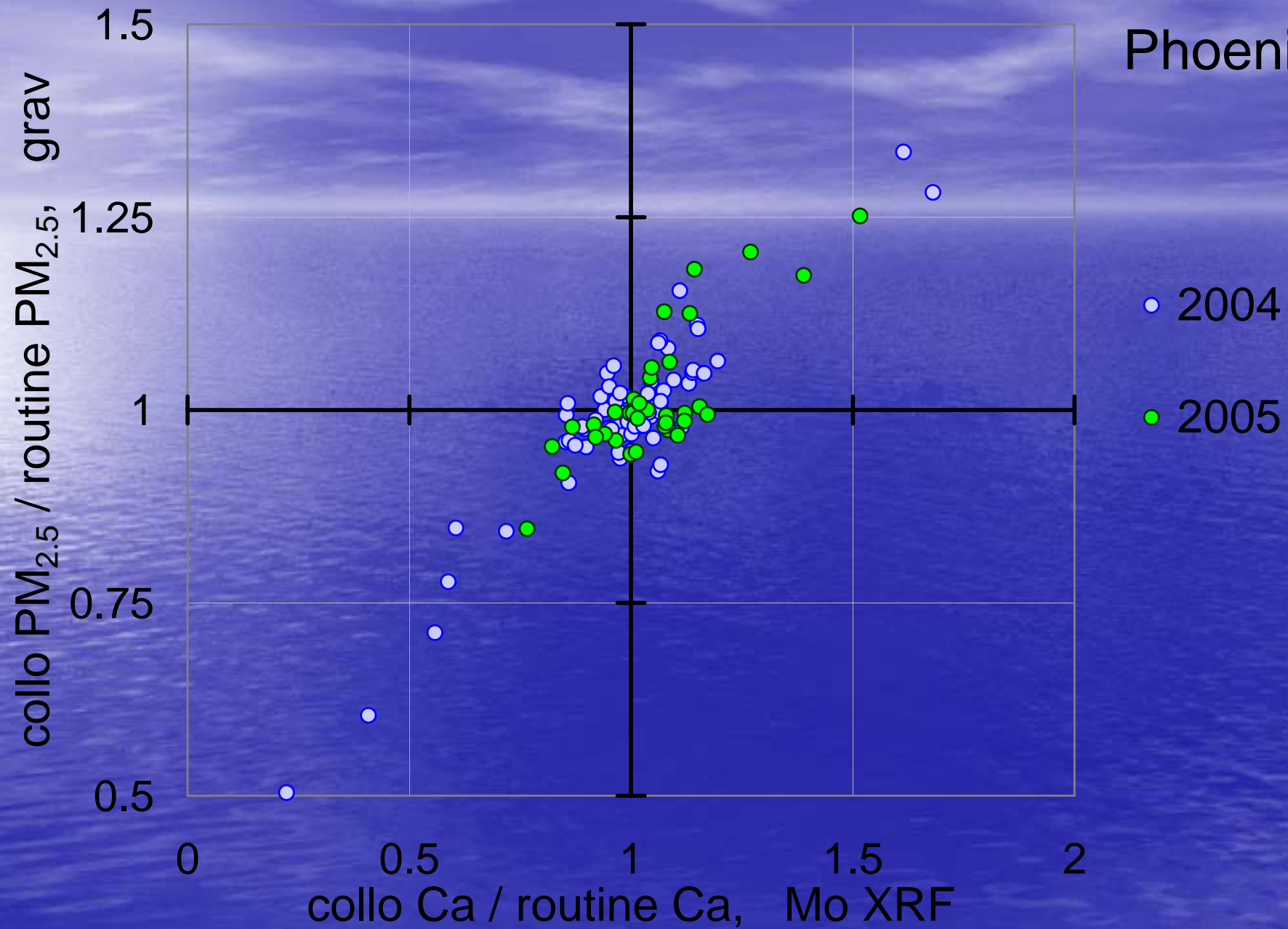


Species	Count > 3*MDL	Estimated Uncertainty	Collocated Precision	Collocated/ Estimated
Ca	577/577	6.2%	18.8%	3.0
Fe	577/577	5.5%	17.9%	3.3

Phoenix

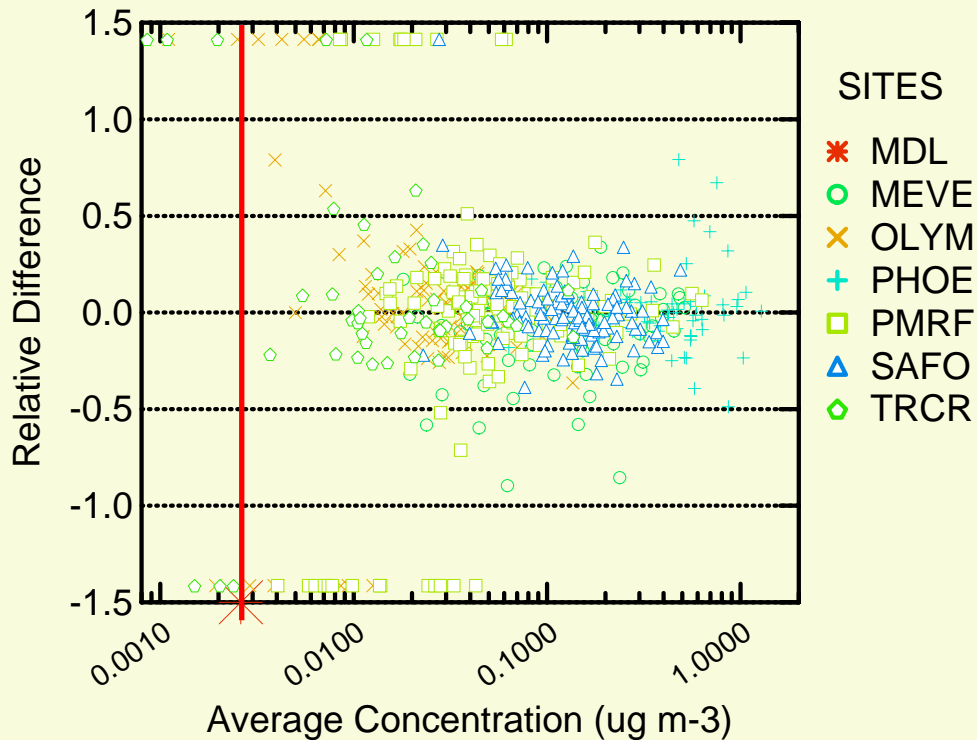


Phoenix

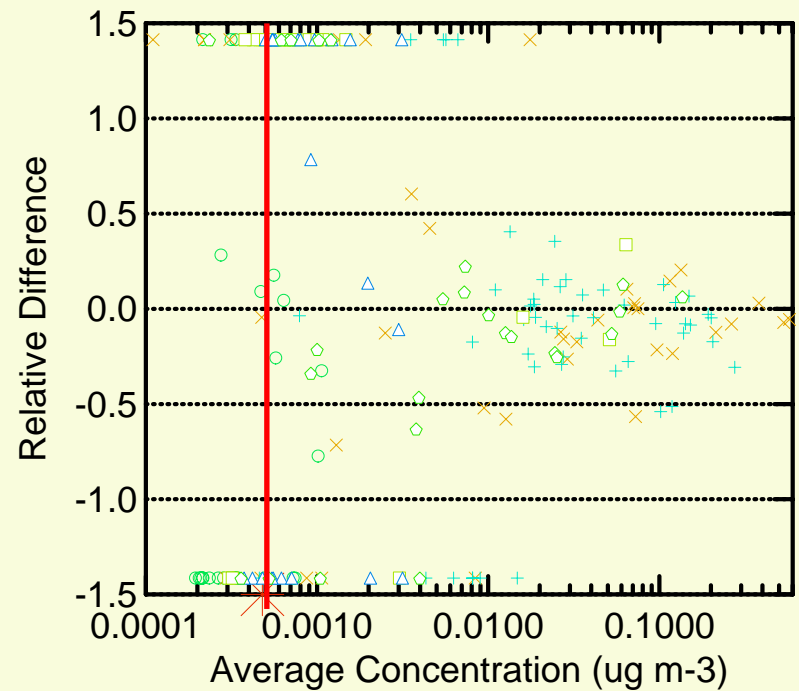


Minimum Detectable Limits (mdl)

Silicon



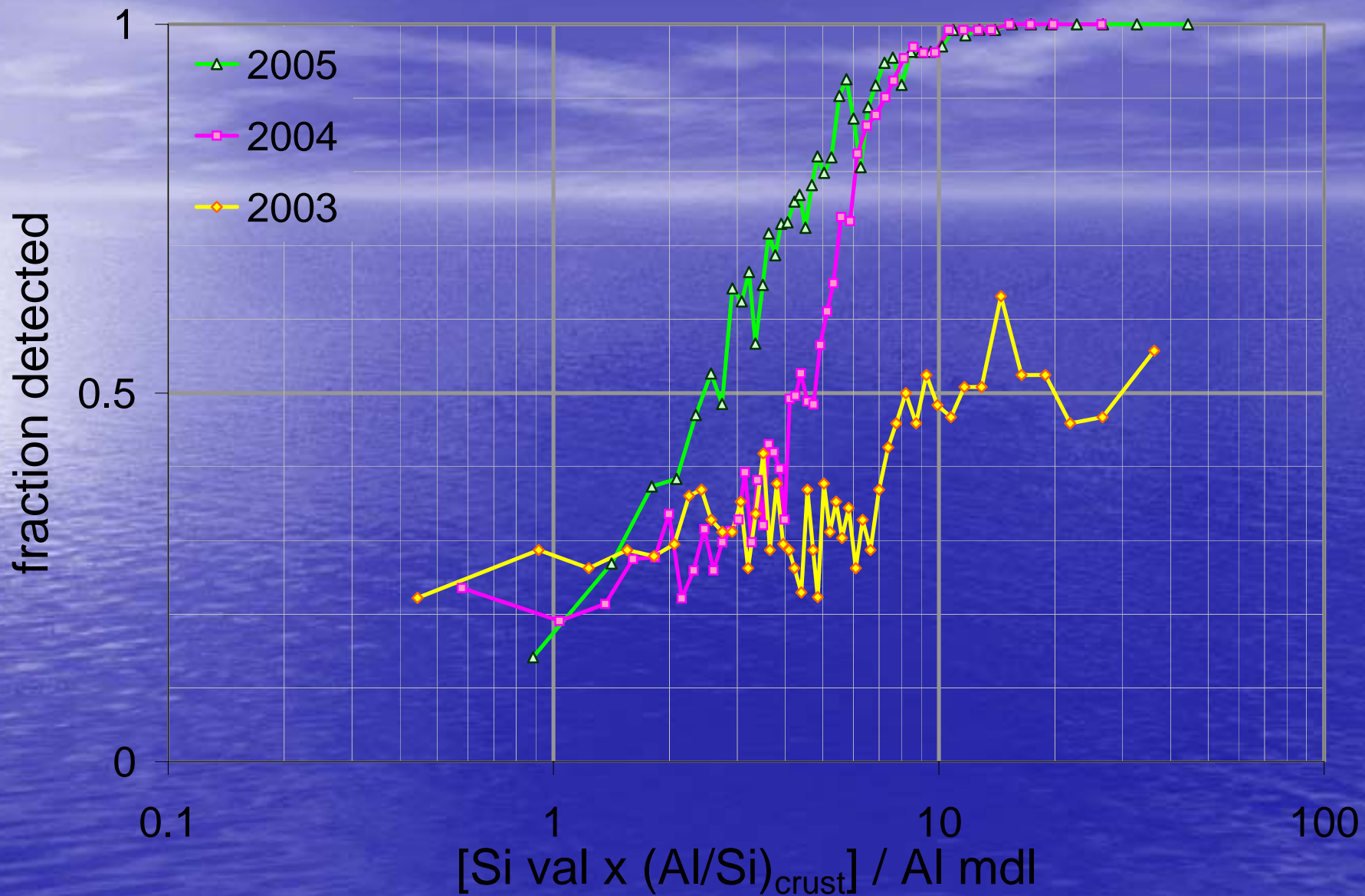
Chlorine



Species	Count > 3*MDL	Estimated Uncertainty	Collocated Precision	Collocated/ Estimated
Si	533/577	10.9%	40.5%	3.7
Cl	105/577	12.1%	68.4%	5.7

Entire network

January - April



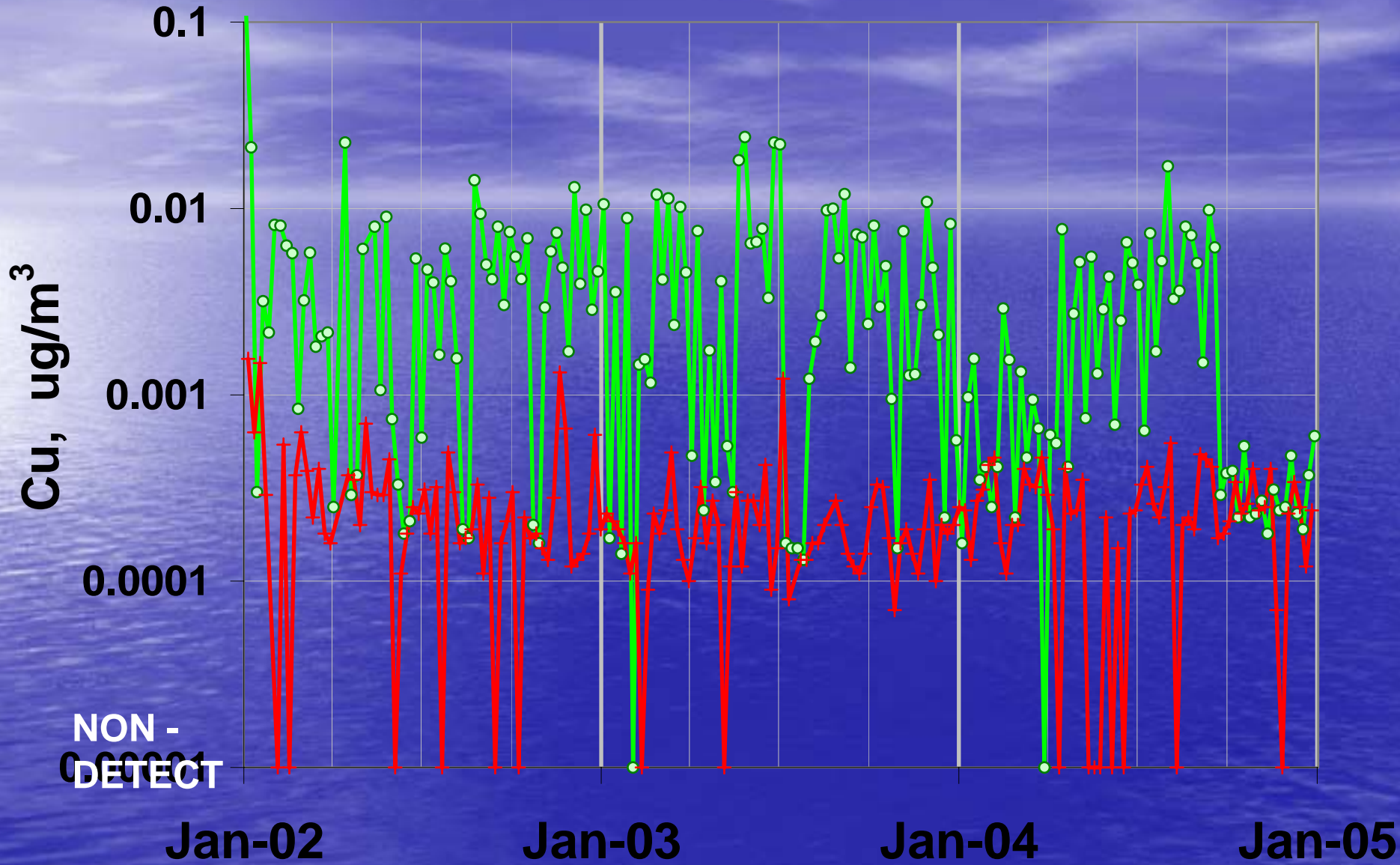
	Original Criteria		Both Detected	
Species	No. Pairs	Collo / Estimated	No. Pairs	Collo / Estimated
Na	15	2.0	71	1.1
Mg	9	-	45	1.0
Al	257	5.0	212	1.7
Si	533	3.7	500	2.0
P	21	7.3	3	-
S	577	1.6	577	1.6
Cl	105	5.6	95	1.4
K	577	2.3	577	2.3
Ca	577	3.0	576	2.9
Ti	528	2.6	520	1.8
V	457	1.2	485	1.0
Cr	108	2.0	195	1.1
Mn	529	2.0	546	1.8
Fe	577	3.3	577	3.3

	Original Criteria		Both Detected	
Species	No. Pairs	Collo / Estimated	No. Pairs	Collo / Estimated
PM _{2.5}	539	1.0	577	0.6
H	577	1.3	577	1.3
Ni	222	2.8	359	1.6
Cu	499	2.5	512	1.8
Zn	575	4.0	571	3.7
As	60	1.1	275	0.9
Se	406	1.1	500	1.1
Br	576	1.2	577	1.2
Rb	64	1.2	256	0.8
Sr	266	2.1	469	1.3
Zr	5	-	21	1.2
Pb	541	1.8	545	1.5

BADL1

—○— even

—+— odd



Carbon Fraction	Analytical Uncertainty, $U_{analytic}$	2004 Replicate Precision	Precision/ Uncertainty
OC1	27%	41%	1.5
OC2	16%	17%	1.1
OC3	11%	19%	1.7
OC4	13%	20%	1.5
OP	27%	50%	1.9
EC1	13%	24%	1.9
EC2	26%	31%	1.2
EC3	40%	66%	1.7
OC	-	11%	-
EC	-	21%	-

Conclusions and Future Work

- Estimated uncertainties are not accurate for most species
 - Additional sampling-related sources of uncertainty must be considered
 - Sample deposit uniformity must be measured
 - Cyclone collection efficiency must be modeled
- Minimum detectable limits (mdl's) are too low for several species
 - Collocated data will be used to evaluate mdl's

Species with Decent Agreement between Precision and Uncertainty

Species	Estimated Uncertainty	Collocated Precision	Collocated/ Estimated
PM _{2.5}	7%	6%	1.0
PM ₁₀	5%	8%	1.6
Na	25%	50%	2.0
S	5%	8%	1.6
V	18%	21%	1.2
Mn	12%	24%	2.0
As	14%	15%	1.1
Pb	12%	22%	1.8
Se	14%	15%	1.1
Br	7%	9%	1.2
Rb	24%	28%	1.2
H	6%	8%	1.3
Nitrate	8%	10%	1.3
Sulfate	5%	4%	0.9
OC1	33%	44%	1.3
OC2	22%	18%	0.8
OC3	17%	24%	1.5
OC4	17%	26%	1.5
OP	29%	45%	1.5
EC1	16%	24%	1.5
EC2	31%	37%	1.2
OC	12%	17%	1.5
EC	12%	22%	1.8
TC	11%	17%	1.5