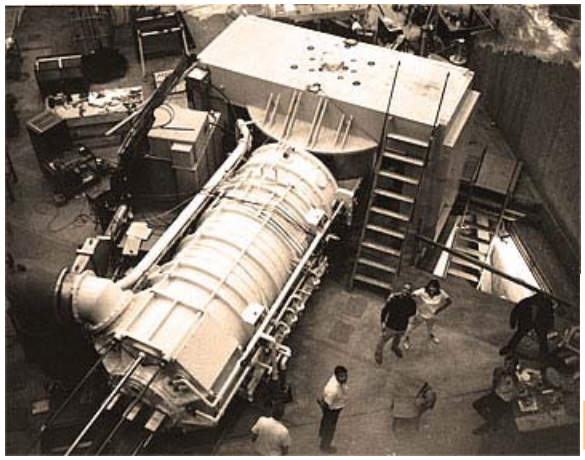
Decadal trends in observed analytical uncertainties for a long series of IMPROVE elemental data

Krystyna Trzepla-Nabaglo and Warren White

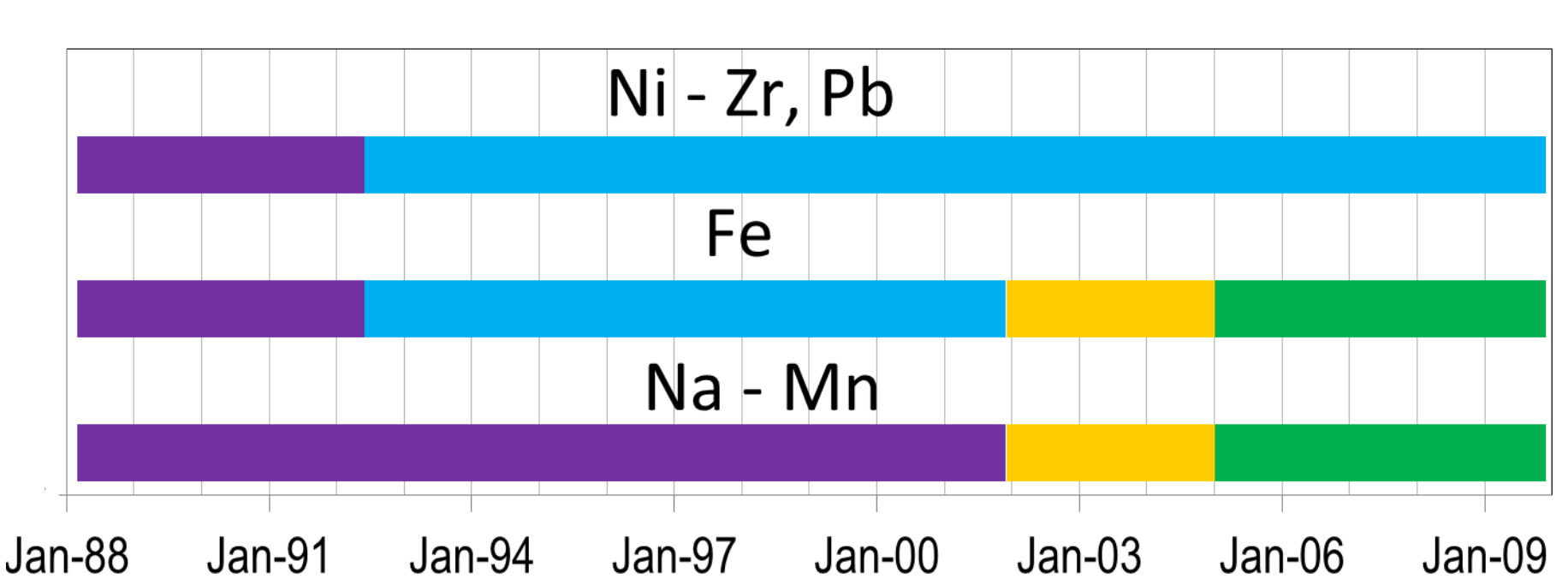
Work supported by United States National Park Service Contract C2350-04-0050 to UC Davis

May 2011

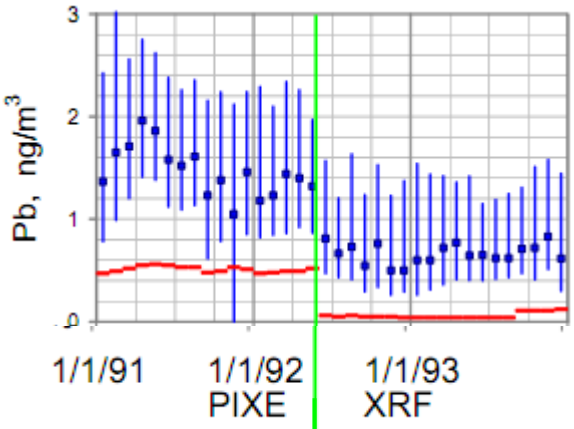


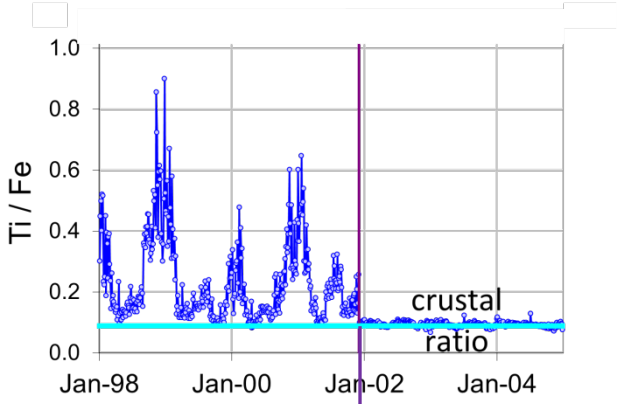
Crocker Nuclear Laboratory

Measurement methods evolve:

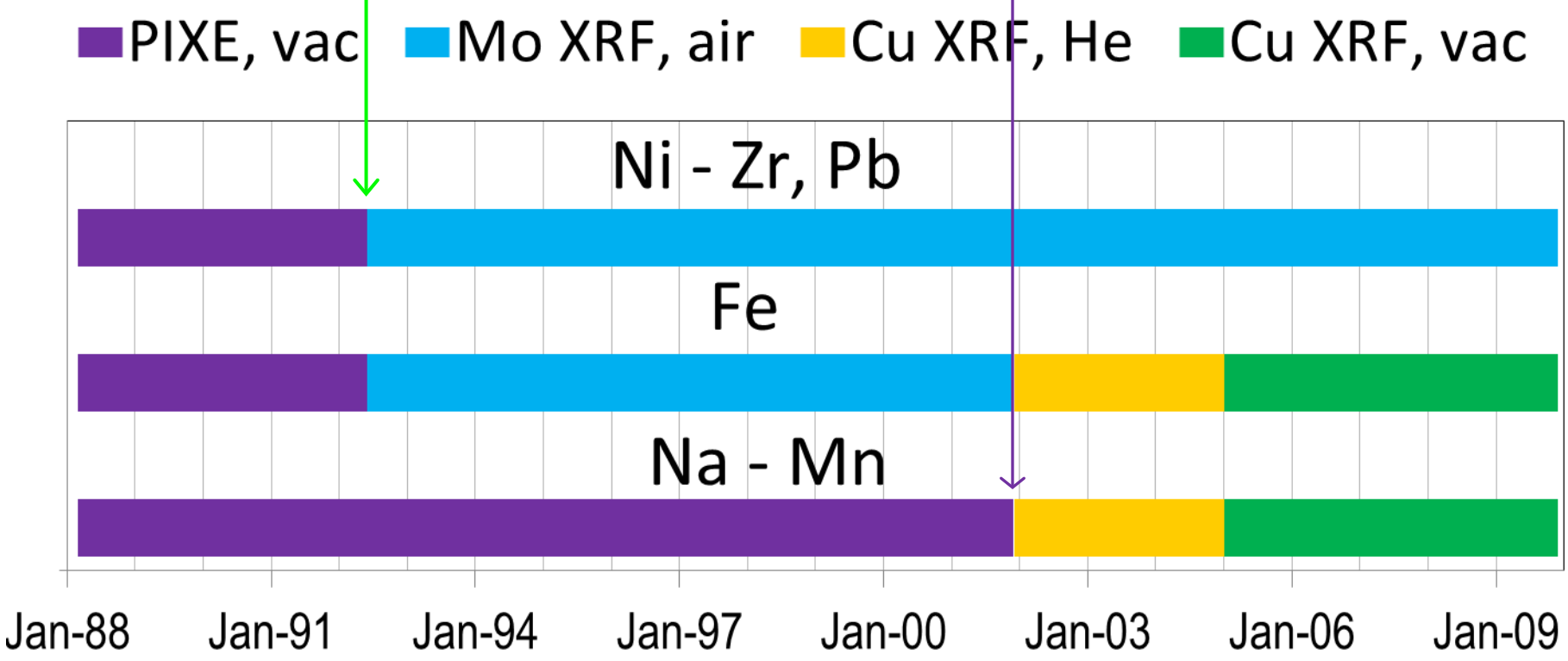


http://vista.cira.colostate.edu/improve/Data/QA_QC/Advisory.htm



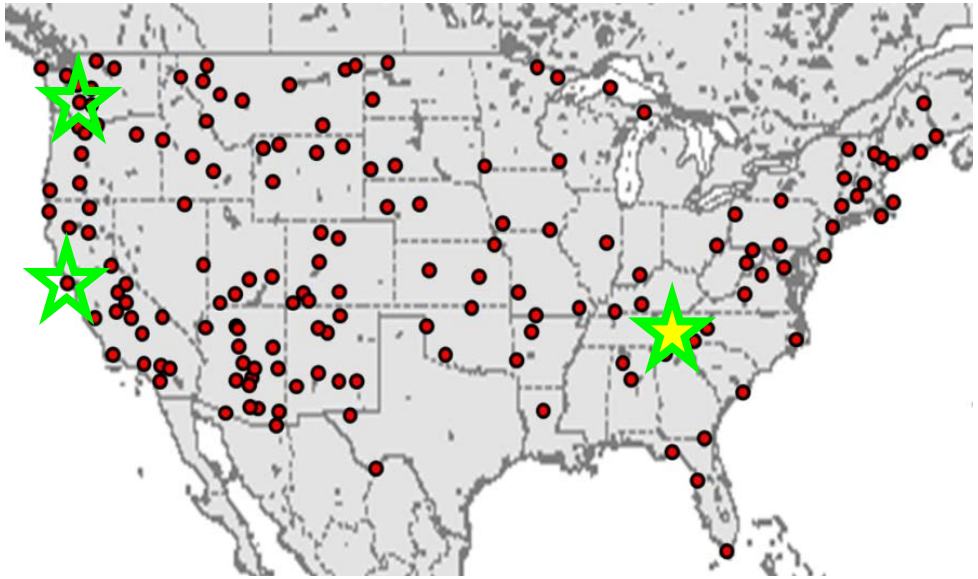


Samples of specific advisories posted at data portal



The IMPROVE network has always used the same size selective inlets and Teflon filters to collect 24h $PM_{2.5}$ samples for elemental analyses. All original sample filters collected since 1995 are archived at UC Davis.

Because the past analytical methods were all non-destructive, the archived filters can be reanalyzed with the current analytical protocol. For any one site, the historical series can be processed in a single analytical batch to generate a homogeneous data set.



Sites selected for reanalysis:

Great Smoky Mtns (completed)
Mount Rainier
Point Reyes

Frequency of robust detection in Great Smoky Mountains samples with both analyses valid.

samples	434	324	513	samples	1271
era	6/95 - 11/01	12/01 - 12/04	1/05 - 11/09	era	6/95 - 11/09
method	PIXE in vacuo	Cu XRF in He	Cu XRF in vacuo	method	Mo XRF in air
both analyses > 3 × mdl					
Na	**31%**	**6%**	**27%**	Ni	**12%**
Mg	**0%**	**0%**	**2%**	Cu	92%
Al	**35%**	**26%**	**67%**	Zn	100%
Si	97%	86%	95%	As	**13%**
P	**0%**	**0%**	**0%**	Se	98%
S	100%	100%	100%	Br	100%
Cl	**0%**	**0%**	**0%**	Rb	**10%**
K	100%	100%	100%	Sr	**26%**
Ca	95%	99%	100%	**Zr**	**0%**
Ti	**60%**	96%	99%	Pb	99%
V	**3%**	**68%**	82%		
Cr	**2%**	**23%**	**42%**		
Mn	**8%**	93%	99%	**coding:**	
Fe	100%	100%	100%	**< 10%**	**< 80%**

Culled detection rates at Great Smoky Mountains: yellow highlighting retained in subsequent slides

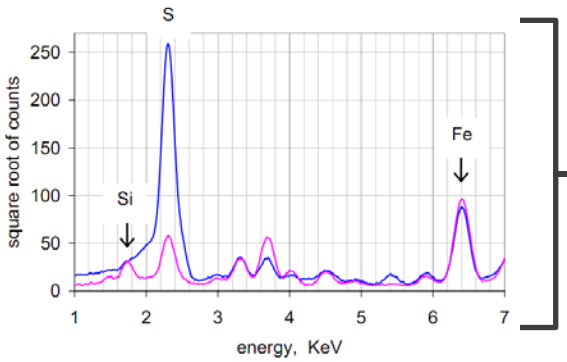
samples	434	324	513	samples	1271
era	6/95 - 11/01	12/01 - 12/04	1/05 - 11/09	era	6/95 - 11/09
method	PIXE in vacuo	Cu XRF in He	Cu XRF in vacuo	method	Mo XRF in air
both analyses > 3 × mdl					
Na	31%	6%	27%	Ni	12%
Al	35%	26%	67%	Cu	92%
Si	97%	86%	95%	Zn	100%
S	100%	100%	100%	As	13%
K	100%	100%	100%	Se	98%
Ca	95%	99%	100%	Br	100%
Ti	60%	96%	99%	Rb	10%
V	3%	68%	82%	Sr	26%
Cr	2%	23%	42%	Pb	99%
Mn	8%	93%	99%		
Fe	100%	100%	100%	**coding:**	**< 80%**

Correlation: $r([c]_{orig}, [c]_{rean})$

samples	434	324	513	samples	1271
era	6/95 - 11/01	12/01 - 12/04	1/05 - 11/09	era	6/95 - 11/09
method	PIXE in vacuo	Cu XRF in He	Cu XRF in vacuo	method	Mo XRF in air
correlation between analyses					
Na	0.31	0.07	0.32	Ni	0.97
Al	0.83	0.37	0.87	Cu	**0.90**
Si	**0.94**	**0.93**	**0.92**	Zn	**0.99**
S	**1.00**	**0.98**	**1.00**	As	0.76
K	**0.98**	**0.98**	**1.00**	Se	**0.97**
Ca	**0.98**	**0.98**	**1.00**	Br	**0.94**
Ti	0.62	**0.99**	**0.98**	Rb	0.39
V	0.12	0.87	**0.94**	Sr	0.86
Cr	0.68	0.55	0.88	Pb	0.89
Mn	0.24	**0.93**	**0.99**		
Fe	**1.00**	**0.99**	**1.00**	**coding:**	**> 0.9**

All Great Smoky Mountains samples with both analyses valid; non-detects are evaluated as ½MDL.

Long-term precision: $\frac{var([c]_{orig}-[c]_{rean})^{1/2}}{mean([c]_{rean})}$

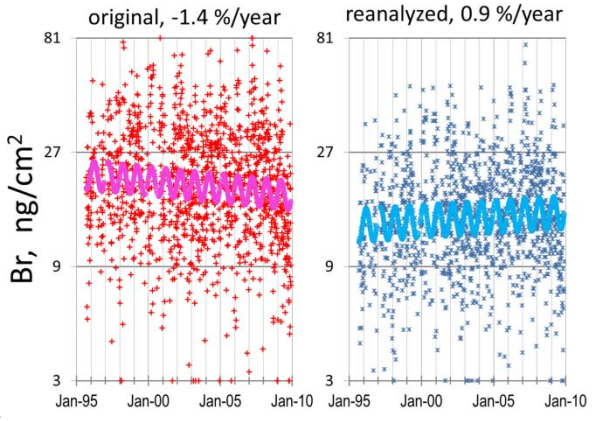


samples	434	324	513	samples	1271
era	6/95 - 11/01	12/01 - 12/04	1/05 - 11/09	era	6/95 - 11/09
method	PIXE in vacuo	Cu XRF in He	Cu XRF in vacuo	method	Mo XRF in air
long-term precision					
Na	123%	218%	124%	Ni	688%
Al	68%	154%	54%	Cu	45%
Si	34%	43%	34%	Zn	**10%**
S	**6%**	**12%**	**6%**	As	63%
K	**10%**	**12%**	**3%**	Se	**18%**
Ca	**17%**	**16%**	**5%**	Br	31%
Ti	256%	26%	21%	Rb	89%
V	357%	51%	27%	Sr	51%
Cr	669%	77%	41%	Pb	26%
Mn	145%	32%	**11%**		
Fe	**9%**	21%	**4%**	**coding:**	**< 20%**

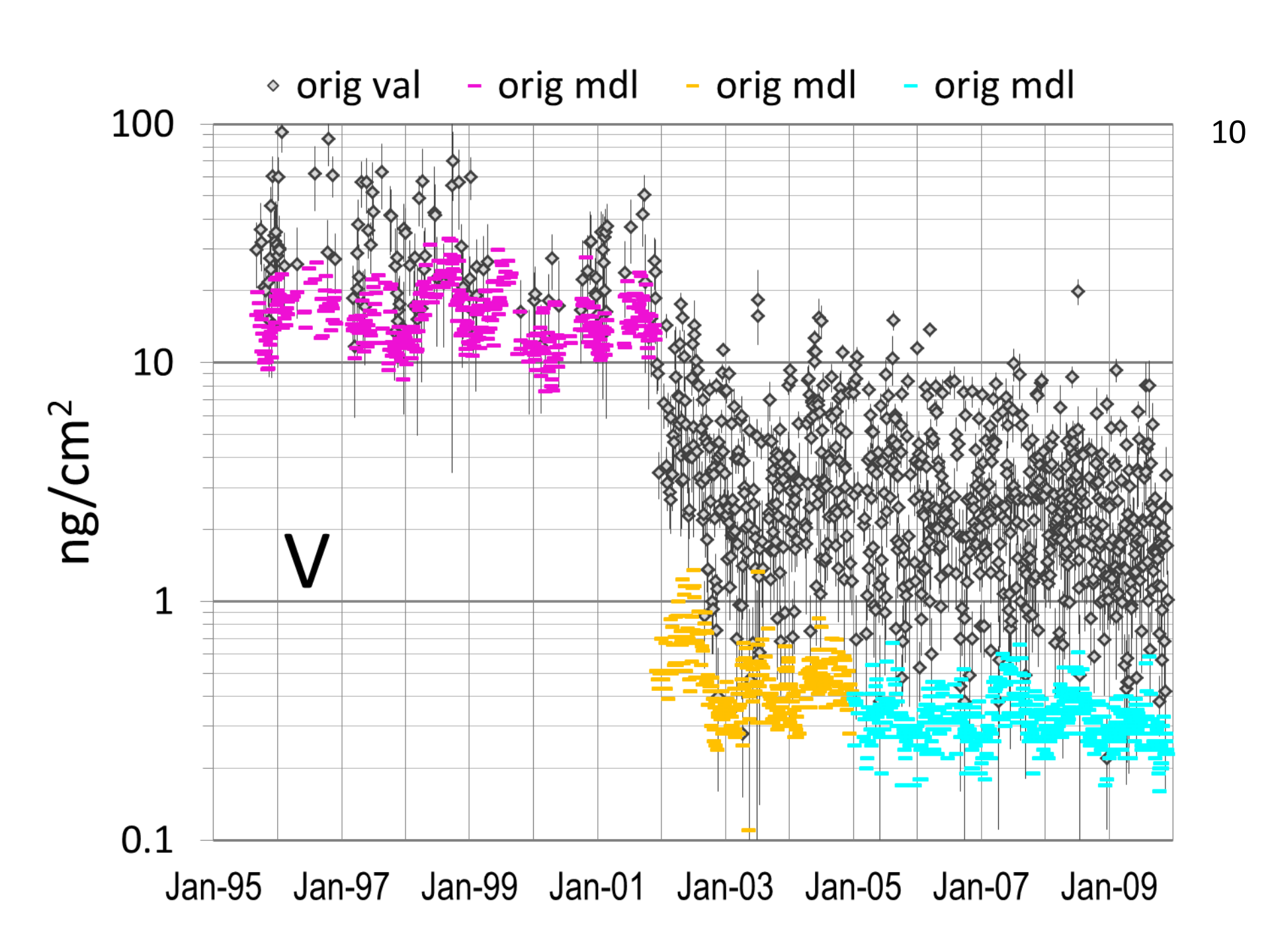
All Great Smoky Mountains samples with both analyses valid; non-detects are evaluated as ½MDL.

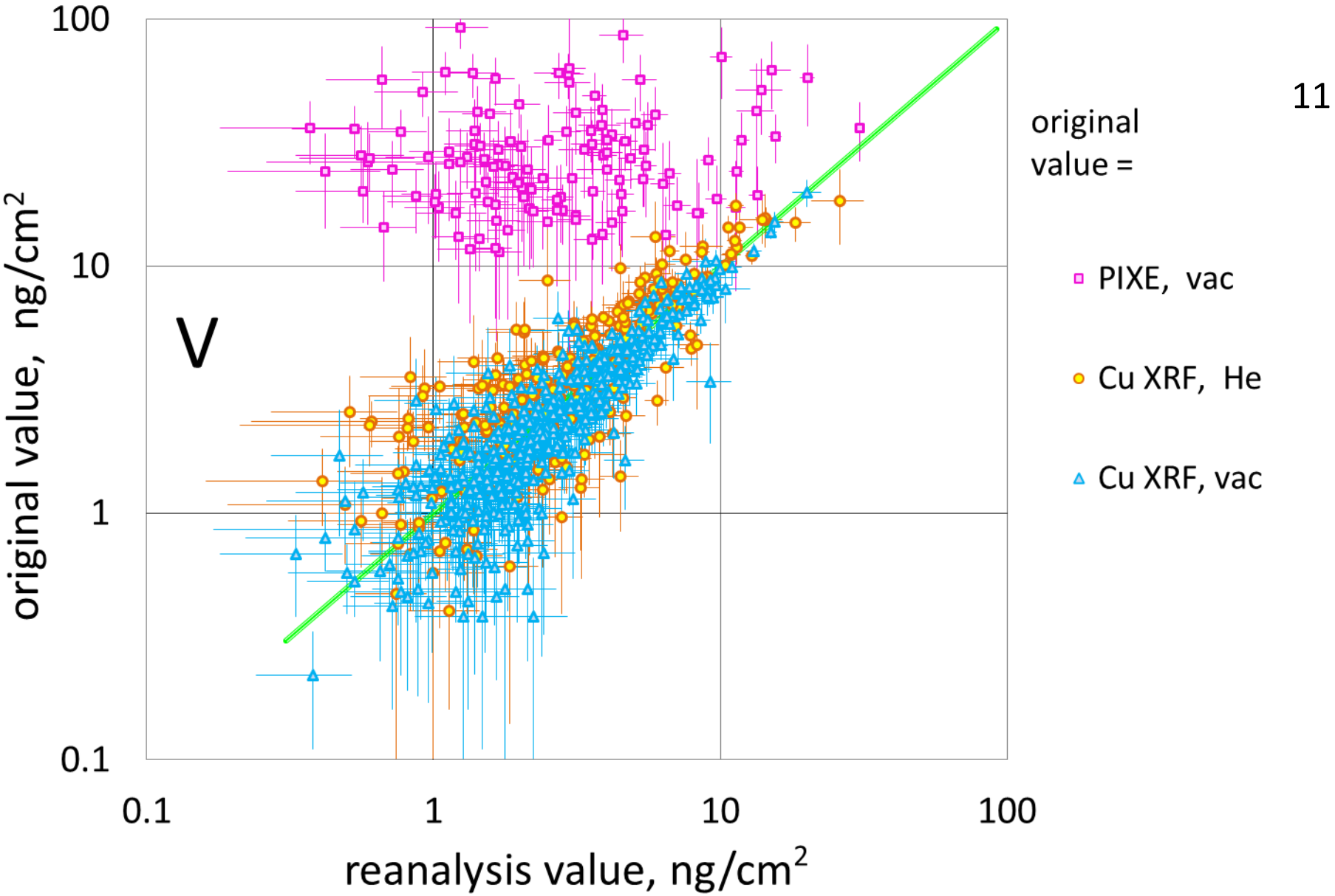
Relative bias: $\frac{mean([c]_{orig} - [c]_{rean})}{mean([c]_{reanal})}$

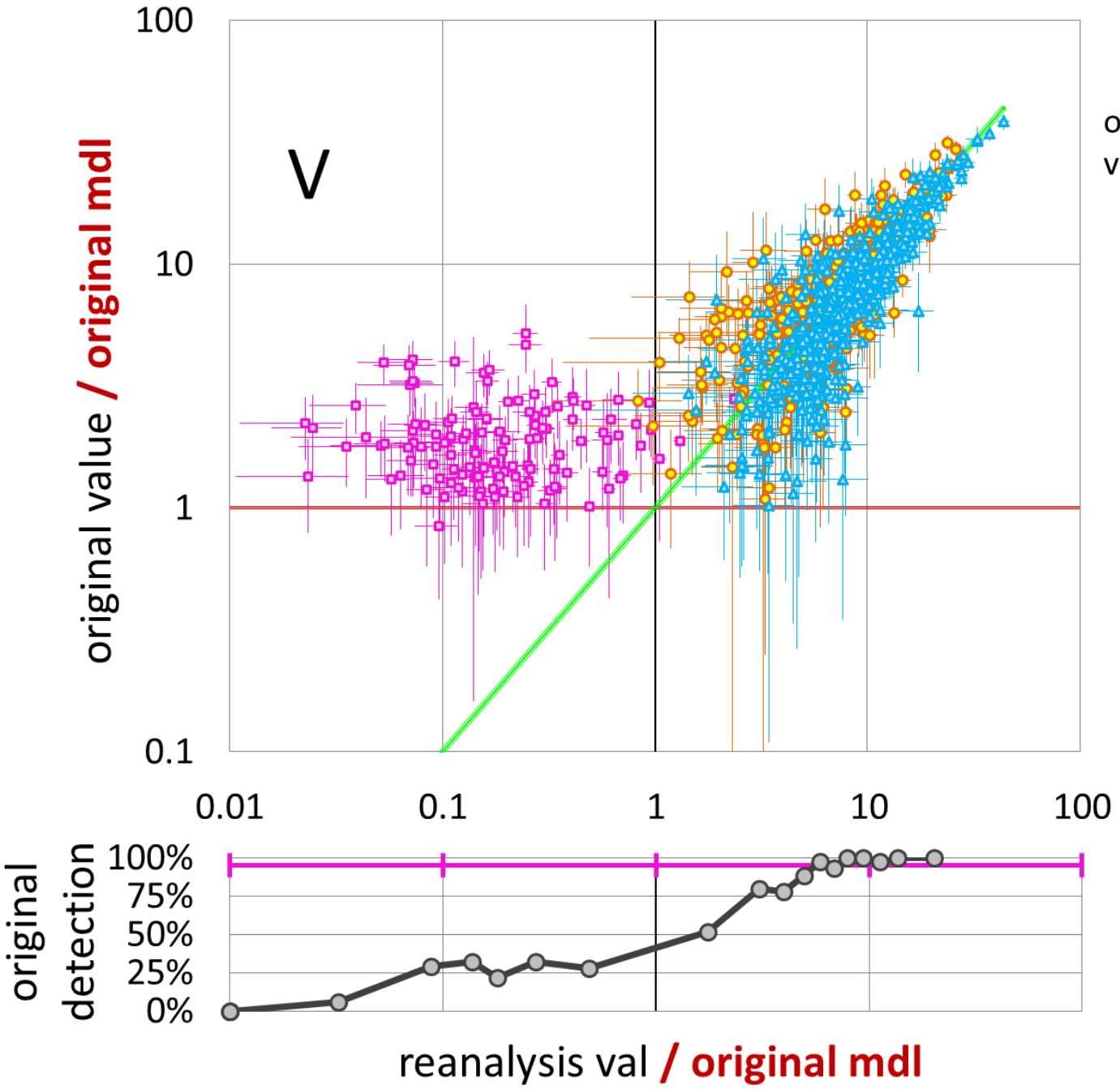
samples	434	324	513	samples	1271
era	6/95 - 11/01	12/01 - 12/04	1/05 - 11/09	era	6/95 - 11/09
method	PIXE in vacuo	Cu XRF in He	Cu XRF in vacuo	method	Mo XRF in air
relative bias					
Na	-43%	29%	-50%	Ni	-14%
Al	-42%	-45%	-32%	Cu	**-3%**
Si	-32%	-13%	-21%	Zn	**-5%**
S	**-1%**	**-2%**	**2%**	As	10%
K	**5%**	**0%**	**1%**	Se	**7%**
Ca	**7%**	**-7%**	**-1%**	Br	38%
Ti	212%	**-1%**	**2%**	Rb	4%
V	287%	9%	**-8%**	Sr	-9%
Cr	716%	-31%	-25%	Pb	**-6%**
Mn	65%	**-9%**	**-4%**		
Fe	**0%**	**-5%**	**1%**	**coding:**	**< 10%**

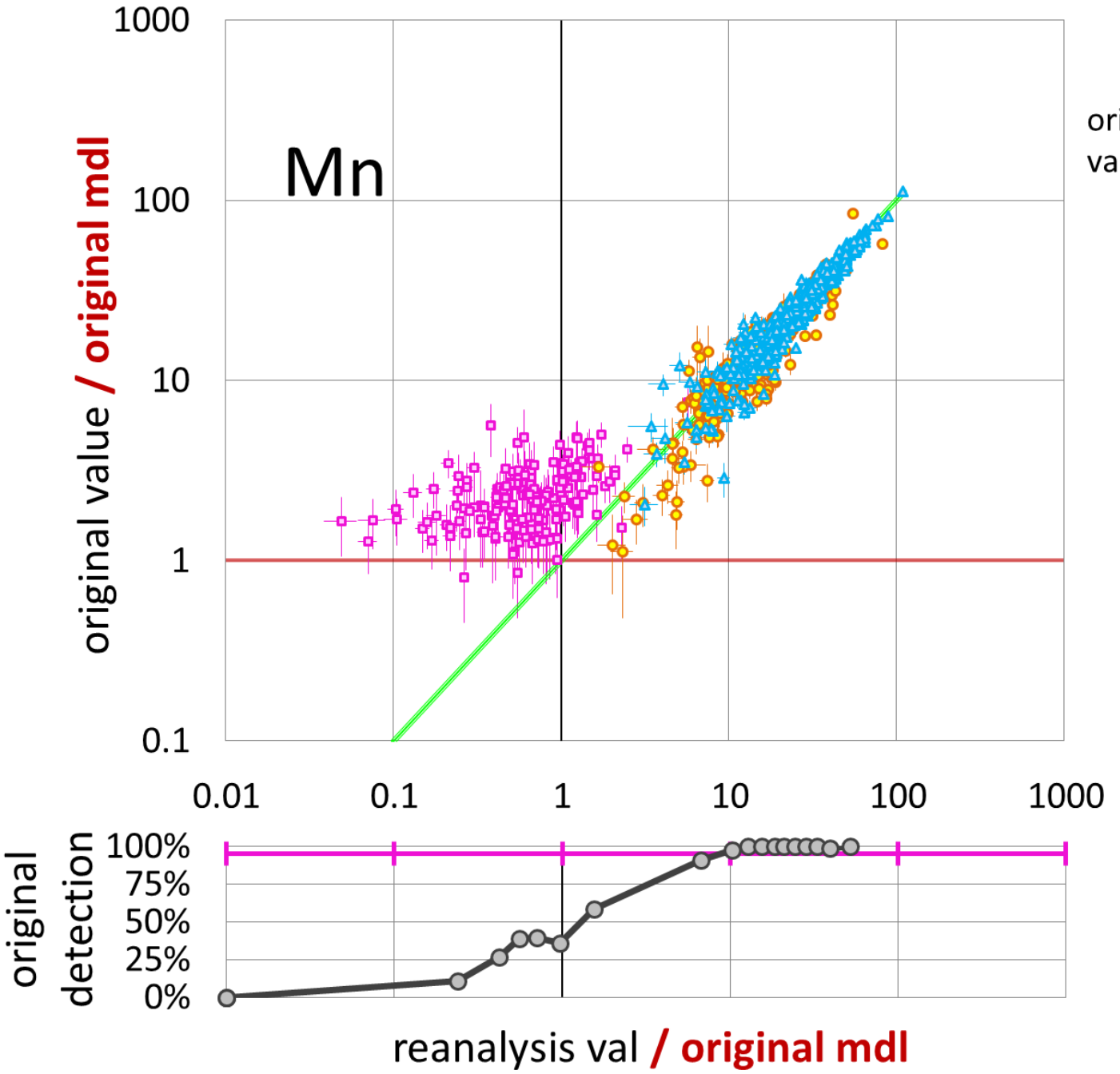


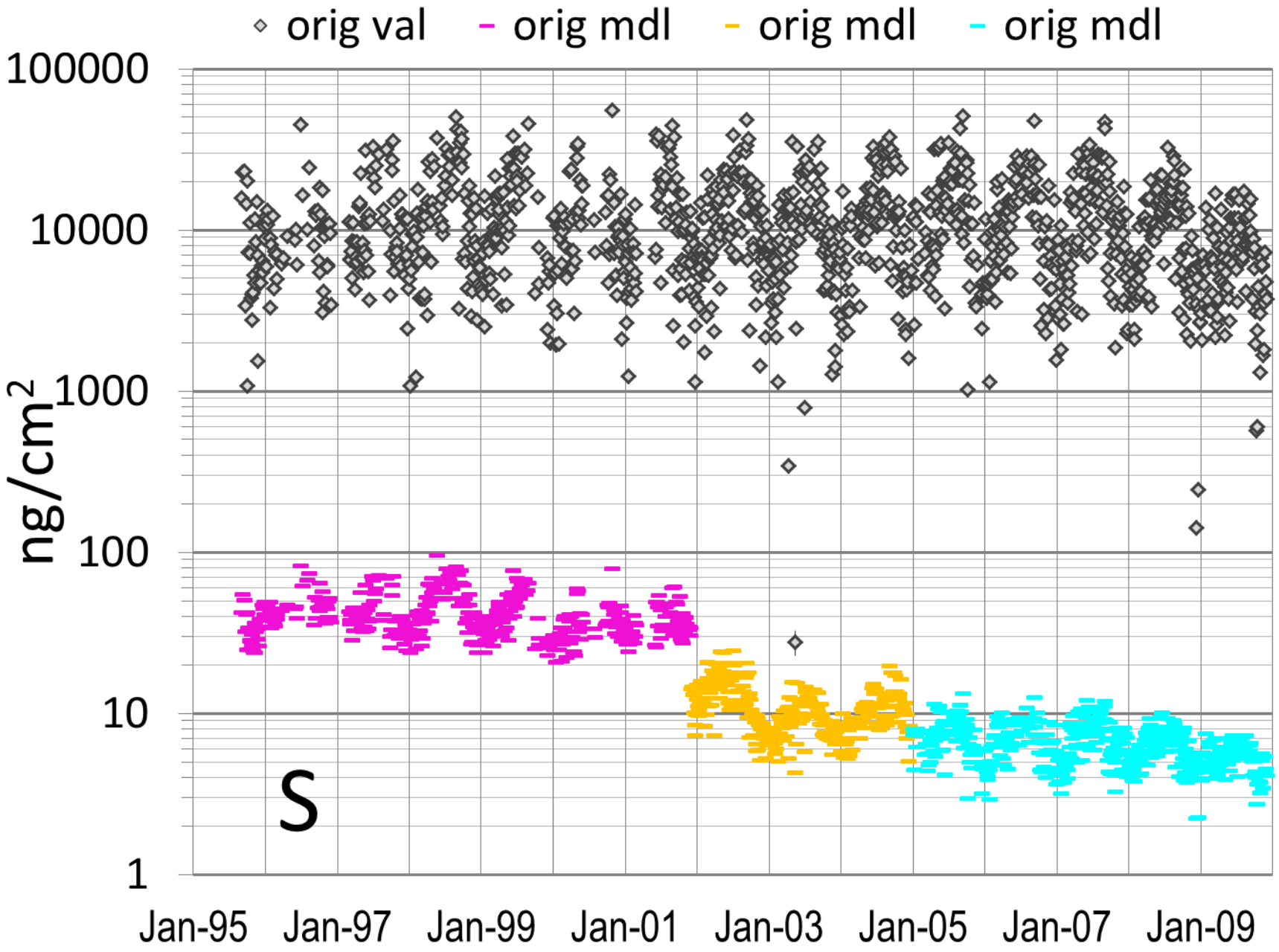
All Great Smoky Mountains samples with both analyses valid; non-detects are evaluated as ½MDL.

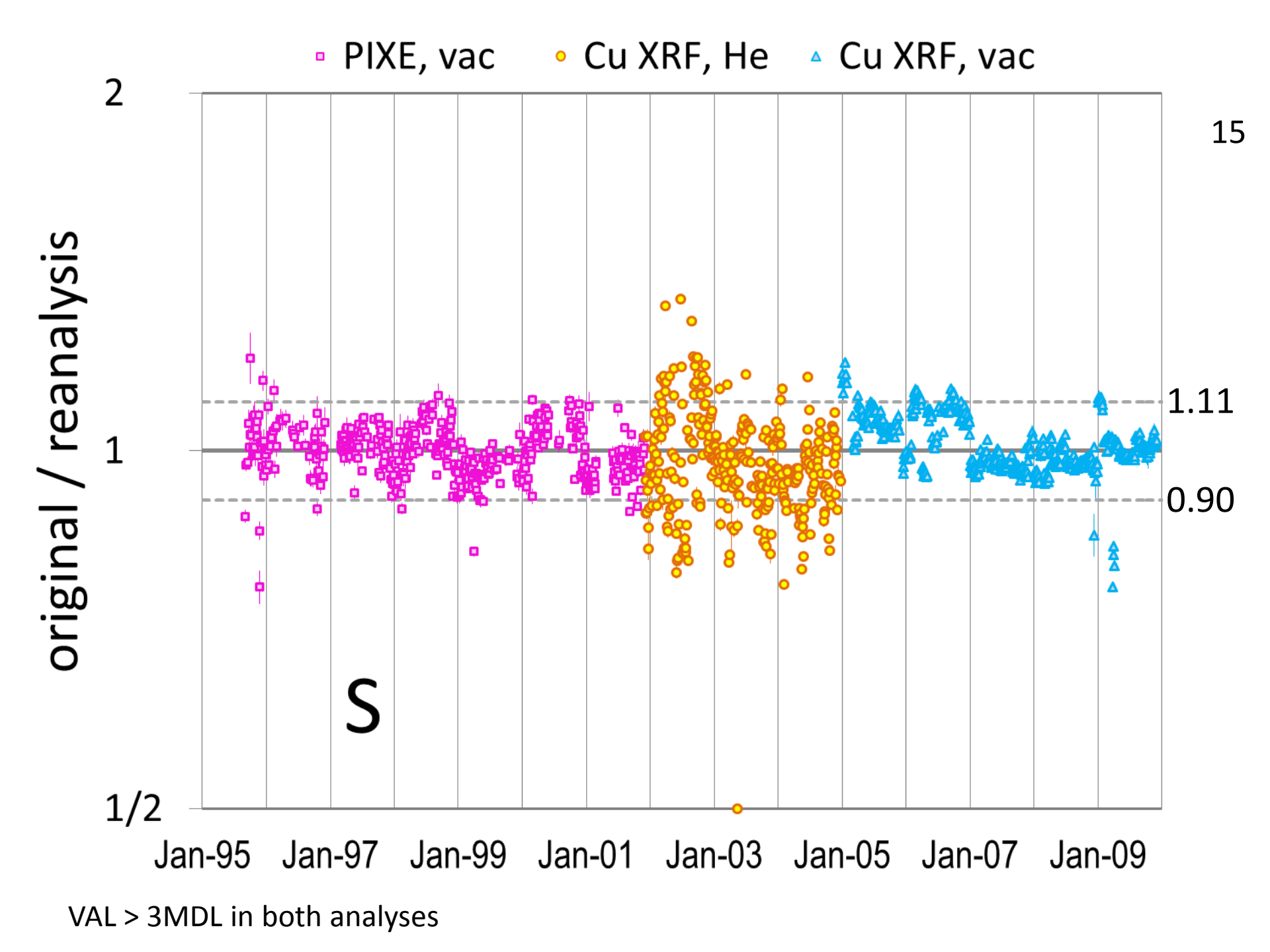

orig val
orig mdl
orig mdl
orig mdl
100
10
1
0.1
ng/cm2
V
Jan-95
Jan-97
Jan-99
Jan-01
Jan-03
Jan-05
Jan-07
Jan-09


V
original value, ng/cm²
reanalysis value, ng/cm²
100
10
1
0.1
0.1
1
10
100
original value =
PIXE, vac
Cu XRF, He
Cu XRF, vac


V
100
10
1
0.1
0.01
0.1
1
10
100
original value / original mdl
original
value =
PIXE, vac
Cu XRF, He
Cu XRF, vac
original
detection
100%
75%
50%
25%
0%
reanalysis val / original mdl


Mn
original value / original mdl
1000
100
10
1
0.1
0.01
0.1
1
10
100
1000
original value =
PIXE, vac
Cu XRF, He
Cu XRF, vac
original detection
100%
75%
50%
25%
0%
reanalysis val / original mdl

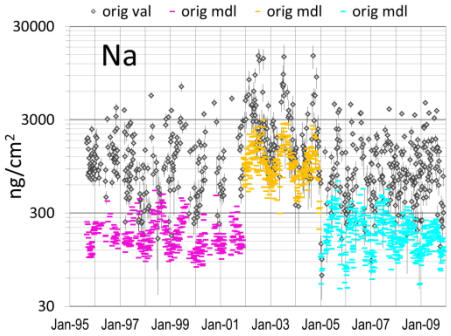

orig val
orig mdl
orig mdl
orig mdl
100000
10000
1000
100
10
1
ng/cm2
S
Jan-95
Jan-97
Jan-99
Jan-01
Jan-03
Jan-05
Jan-07
Jan-09



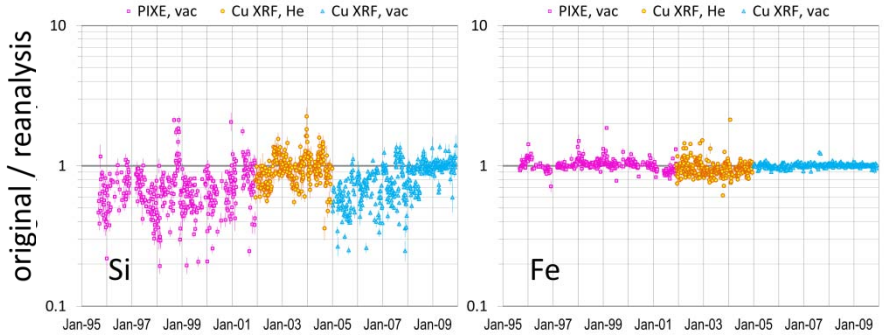
VAL > 3MDL in both analyses

Advice for the analyst:

1. Don't play near the mdl,



2. Focus on the best-determined species you can employ for your purpose,



3. Expect serial correlation in your errors even with consistent methods,

and

4. Mind the transitions!