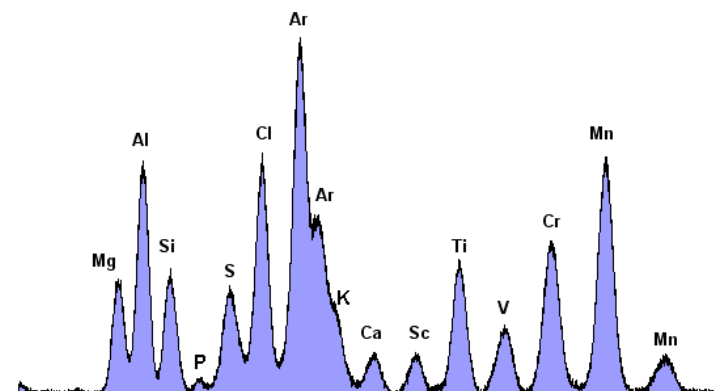


Assessing the performance of four leading-edge pXRF devices for trace metal measurement on contaminated soils in industrial and mining context (Wallonia, South Belgium).



Aubry Vandeuren^a, Eustratios Xyrafis^b, Benoît Pereira^a and Philippe Sonnet^a

^a*Université catholique de Louvain, Earth and Life Institute ;*

^b*University of Thessaly, Vólos, Department of Agriculture Crop Production and Rural Environment*



Soil metal content measurement : Queen Regia

Aqua Regia protocol

- Used for years, well documented
- Comparable to previous soil databases
- Low quantification limits
- Used for most soil norms/guidelines values
- Standardly used in soil and environmental science
-



Soil metal content measurement : Queen Regia



Sampling

[mg/kg]

Soil metal content measurement : Queen Regia



Sampling



Drying

[mg/kg]

Soil metal content measurement : Queen Regia



Sampling



Drying



Sieving 2mm

[mg/kg]

Soil metal content measurement : Queen Regia



Sampling



Drying



Sieving 2mm



3g



Crushing

[mg/kg]

Soil metal content measurement : Queen Regia



Sampling



Drying



Sieving 2mm



3g



Crushing



HCl + HNO₃

[mg/kg]

Soil metal content measurement : Queen Regia



Sampling



Drying



Sieving 2mm



3g



Crushing



HCl + HNO₃

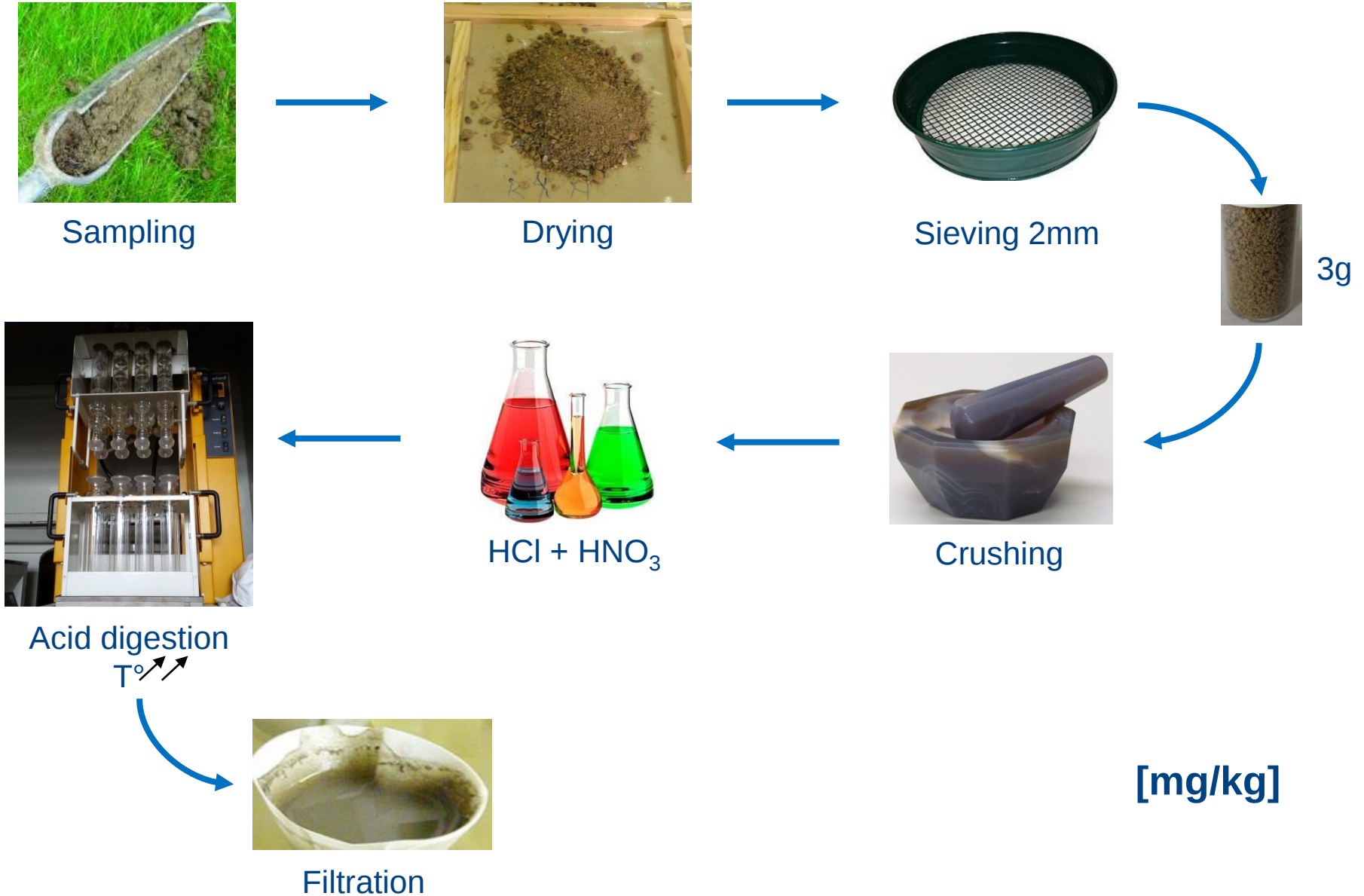


Acid digestion

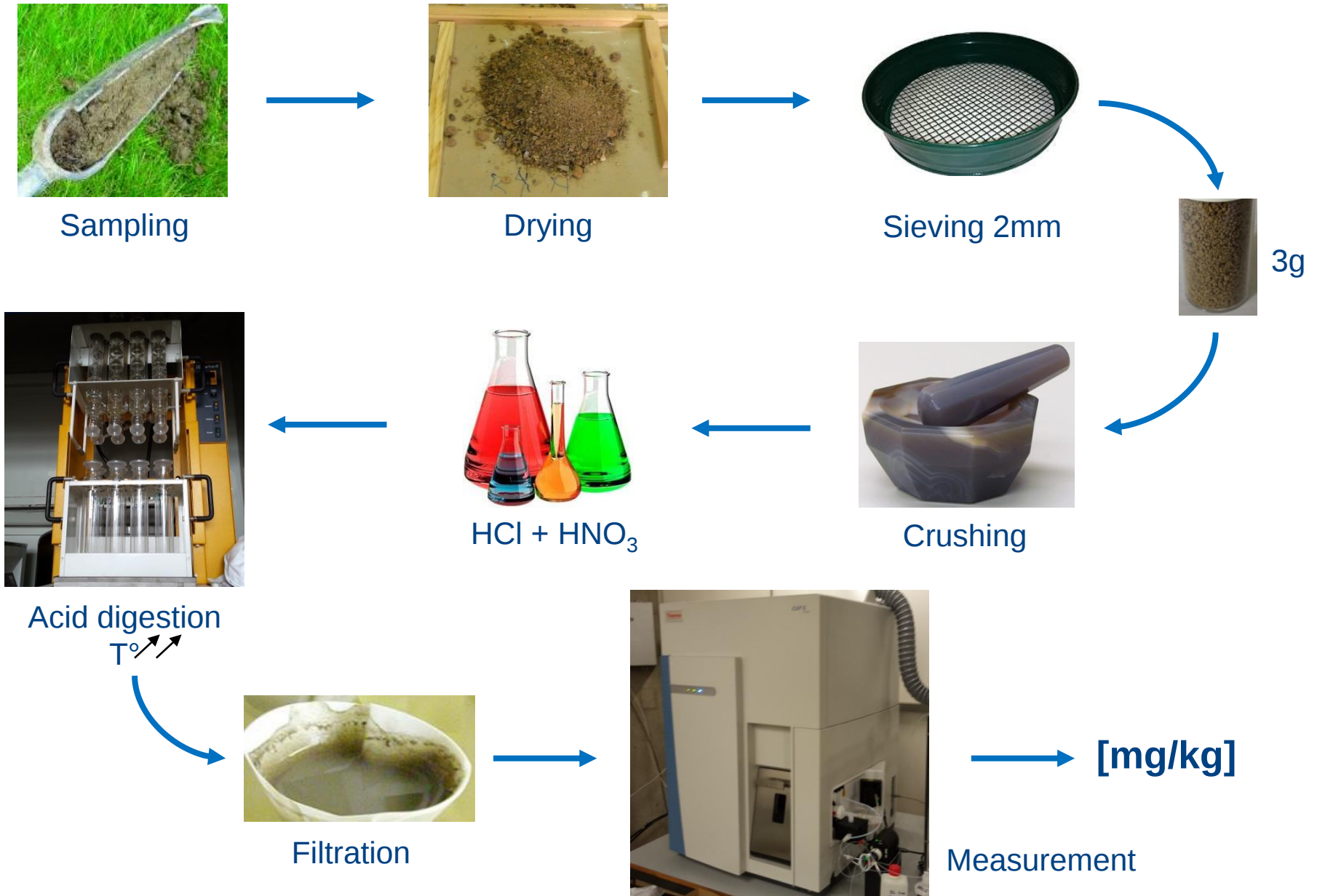
T° ↗ ↗

[mg/kg]

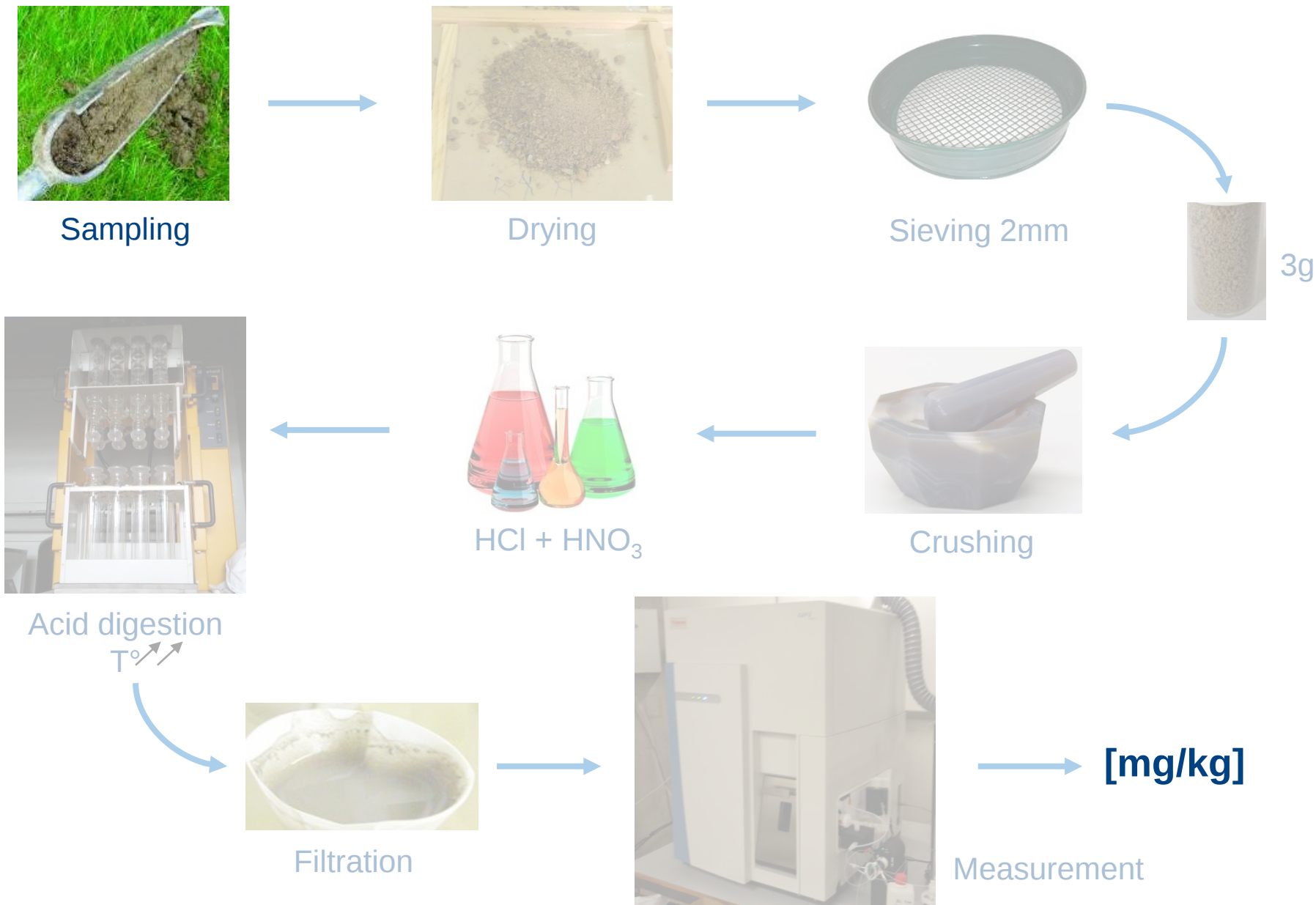
Soil metal content measurement : Queen Regia



Soil metal content measurement : Queen Regia



Soil metal content measurement : Queen Regia



Replacing Aqua Regia by pXRF?



Replacing Aqua Regia by pXRF?



Sampling

- XRF : robust, well-known technology
- miniaturised recently



[mg/kg]

Replacing Aqua Regia by pXRF?



Sampling

- ➔ XRF : robust, well-known technology
- ➔ miniaturised recently

- can be used *in situ*
- non destructive
- quick (~1min)
- uses few (none) reagents
- total analysis
- cost effective
- one step protocol



[mg/kg]

State of the technology : 4 high-end pXRF models

State of the technology : 4 high-end pXRF models



S1 Titan 600
(Bruker)

State of the technology : 4 high-end pXRF models



S1 Titan 600
(Bruker)



X-MET7500
(Oxford Instruments)

State of the technology : 4 high-end pXRF models



S1 Titan 600
(Bruker)



DP-4000
(Olympus Corporation)



X-MET7500
(Oxford Instruments)

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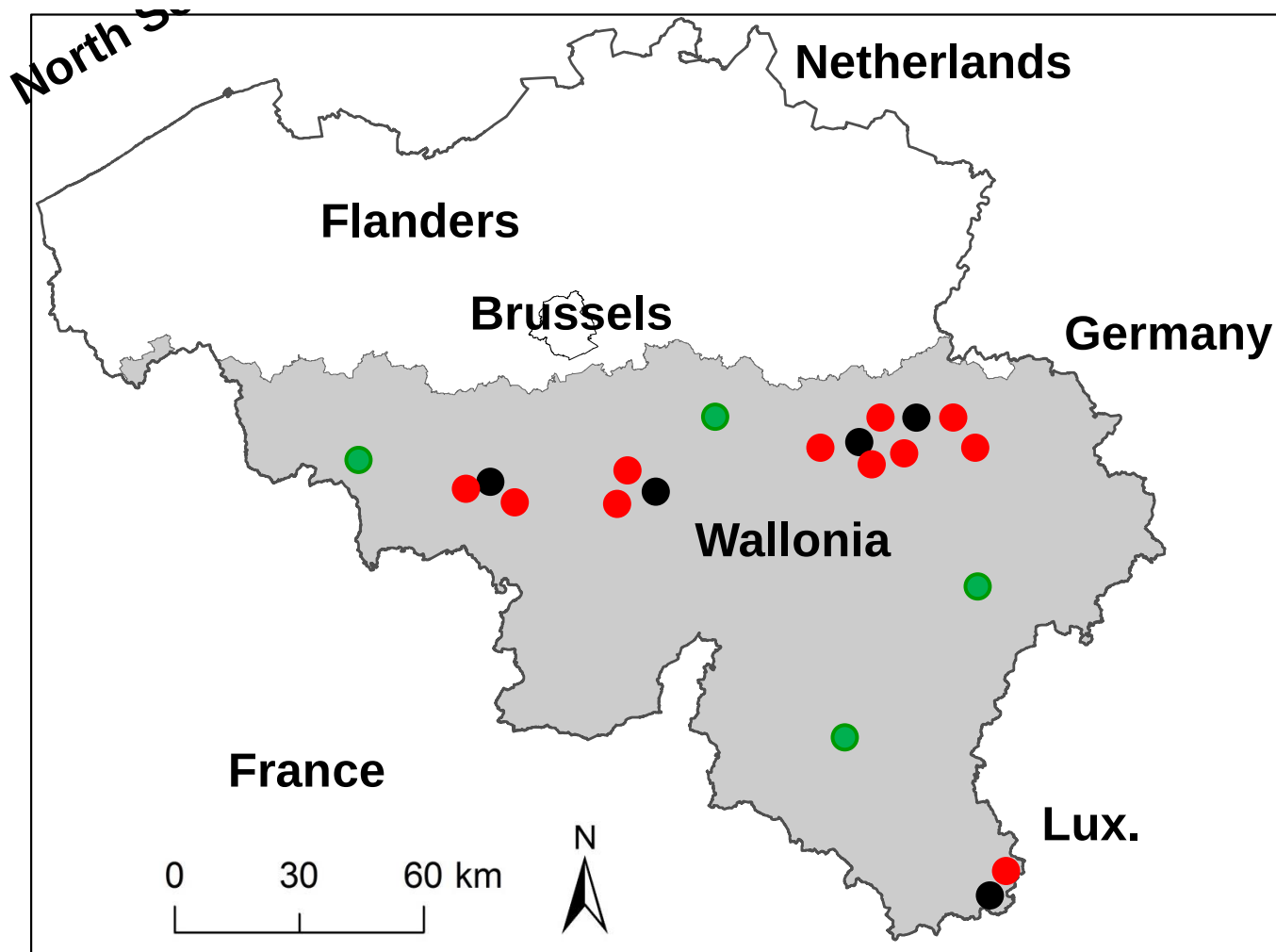


XL3t GOLDD+
(Thermo Fisher Scientific)

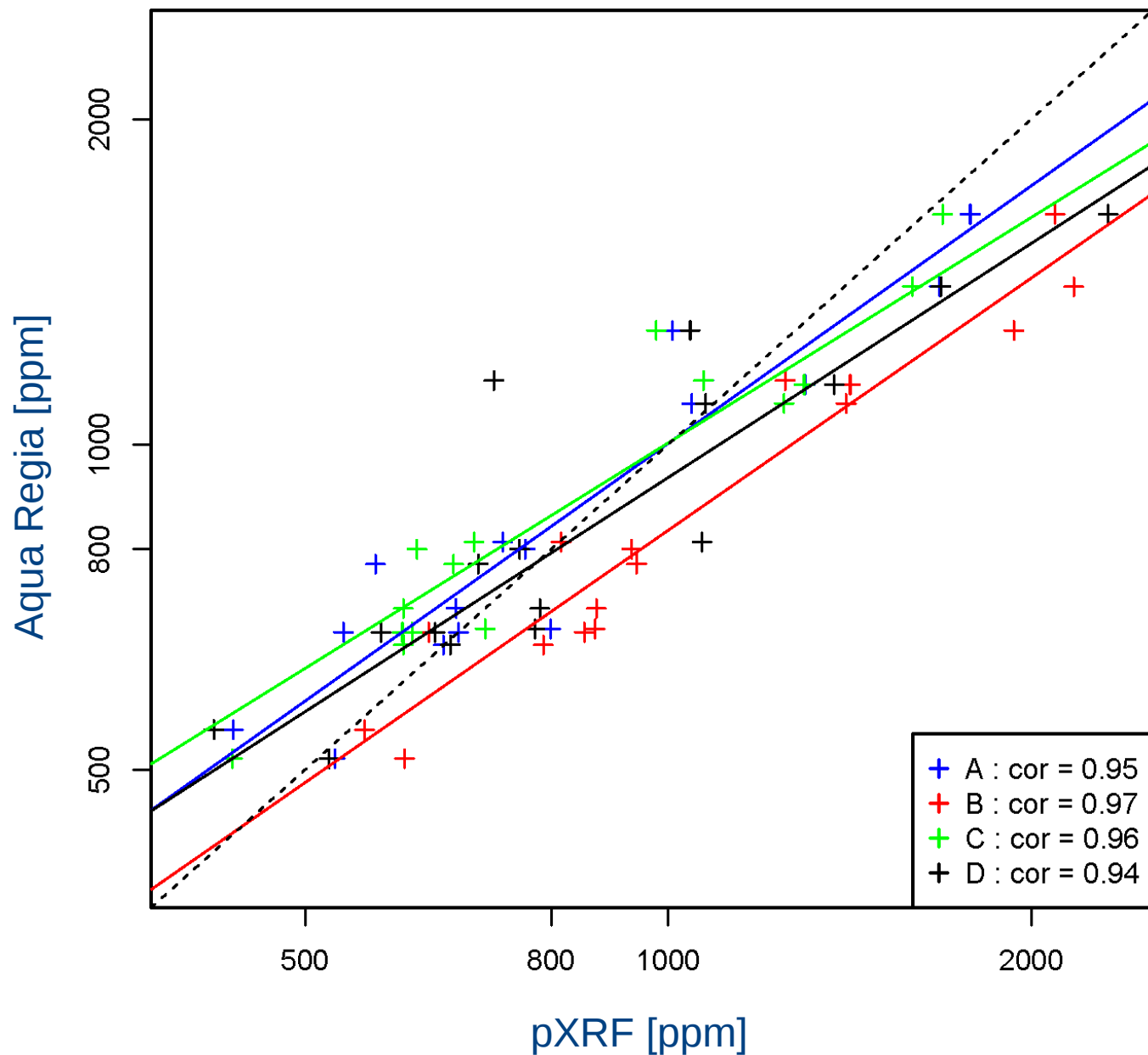
Test on 20 samples measured by Aqua Regia :

4 non contaminated soils (●)

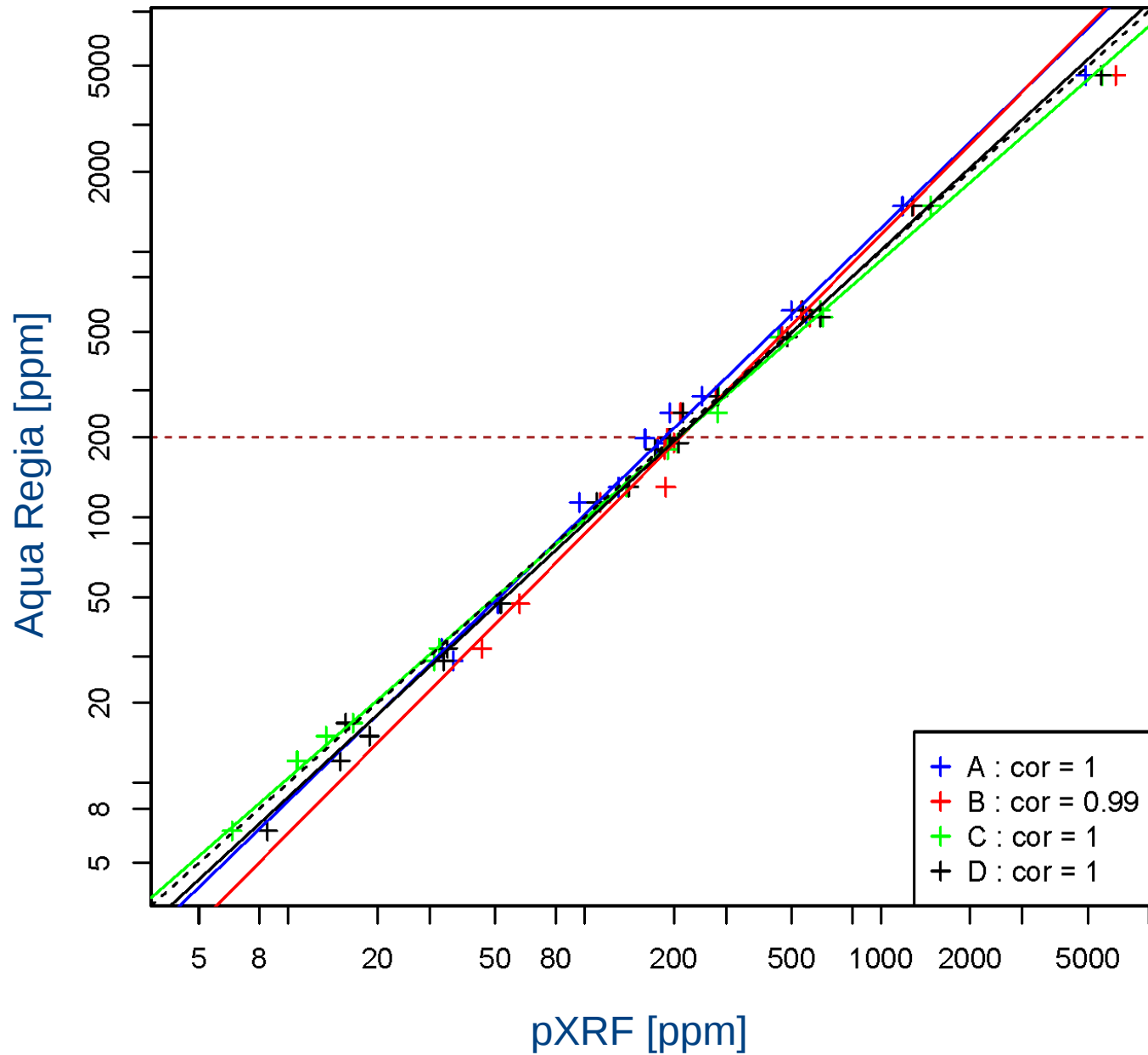
16 contaminated (●) including 5 measured 3 times (●)



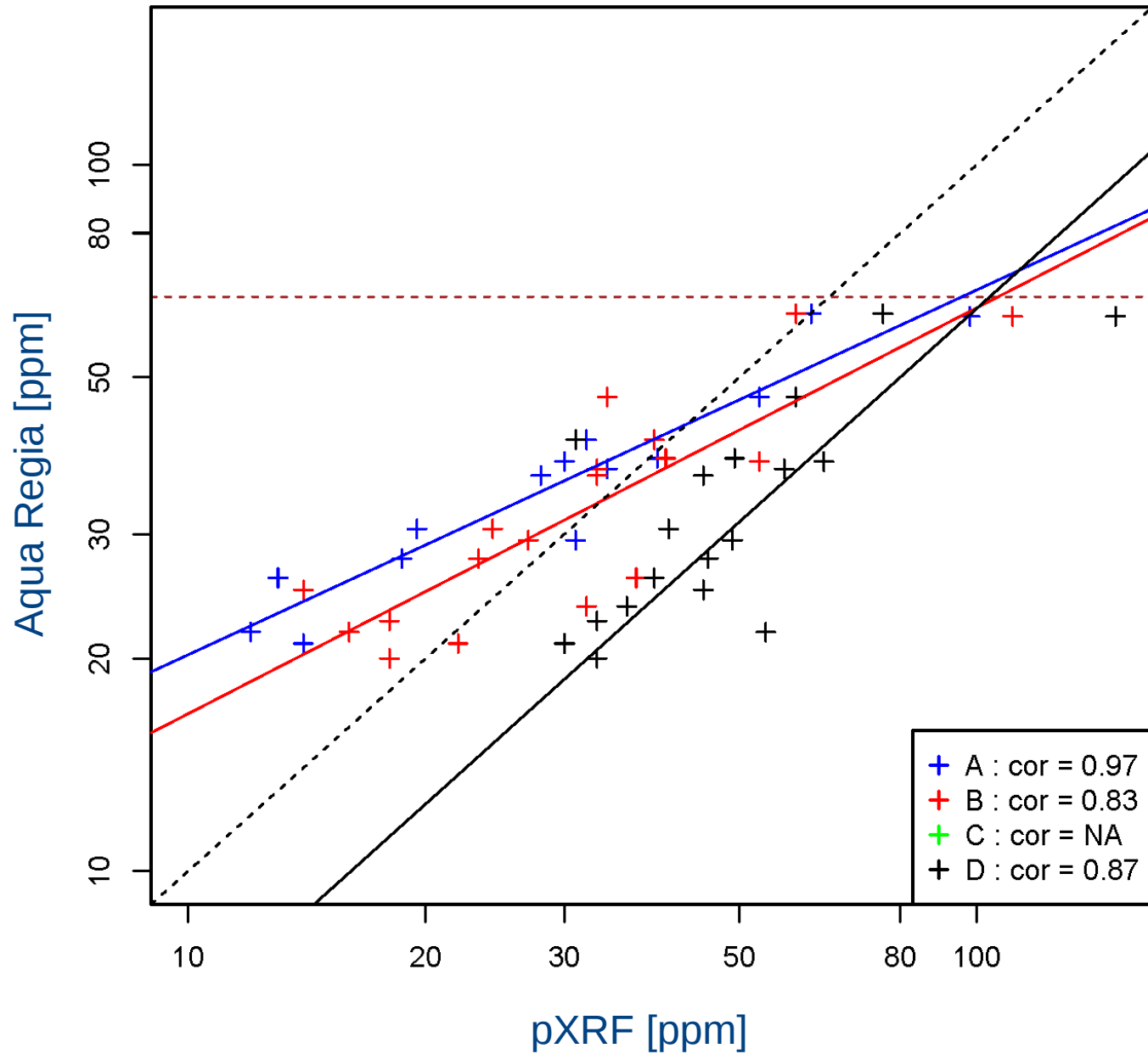
AR – pXRF : Manganese



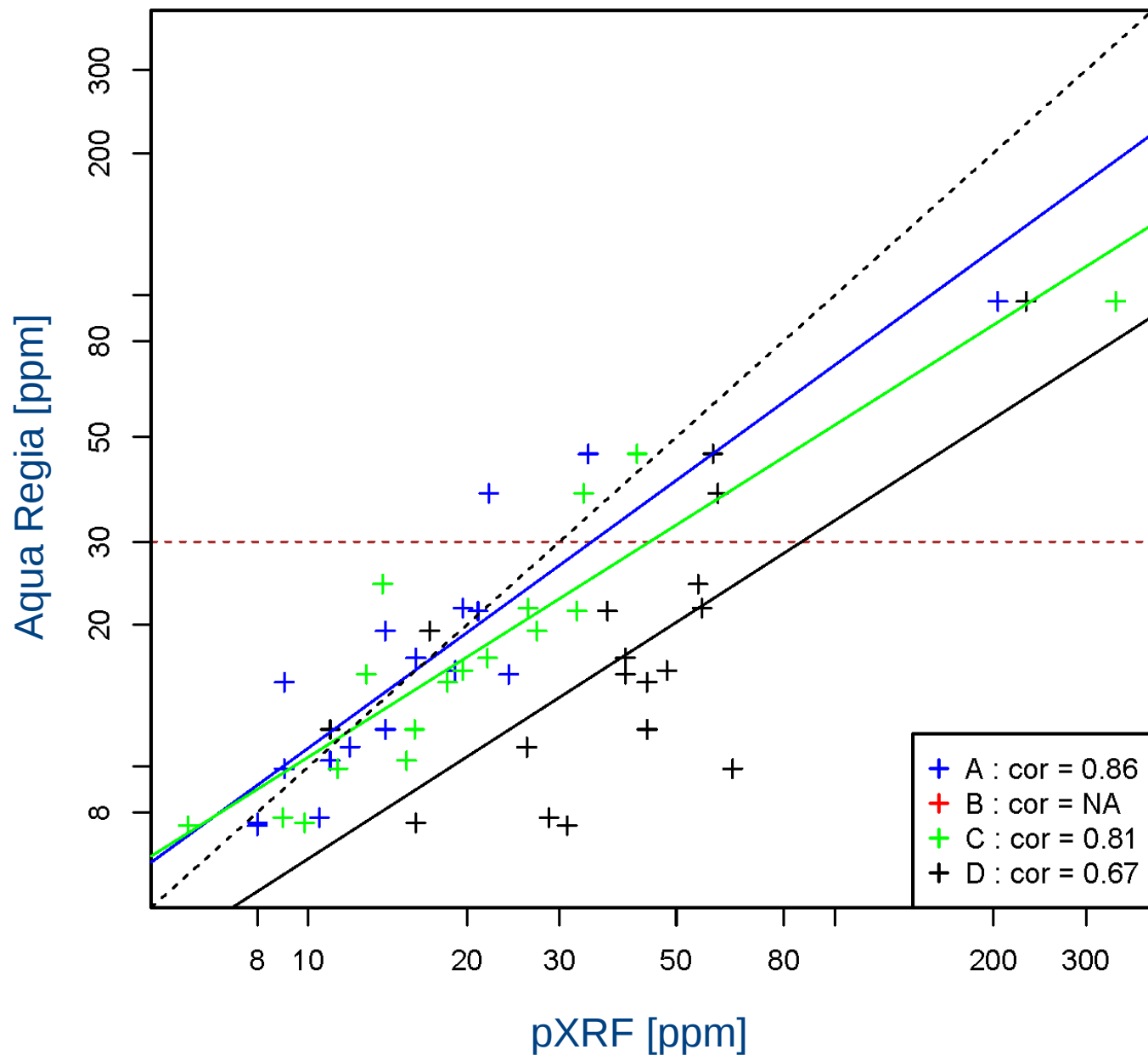
AR – pXRF : Lead



AR – pXRF : Nickel



AR – pXRF : Arsenic



pXRF : Pearson correlation coefficients

Model	Al	Ca	Fe	Mg	Mn	Ba	Mo	Sb	Sn
S1 Titan	-	-	0.93	-	0.95	0.73	-	-	-
X-Met7500	-	0.97	0.95	-	0.97	0.8	-	0.96	0.68
XI3t GOLDD+	0.87	0.99	0.95	0.65	0.96	0.57	0.99	-	0.88
DP-4000	-	0.97	0.88	-	0.94	0.66	0.98	-	-

Model	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn
S1 Titan	0.86	-	-	0.12	0.95	-	0.97	1	1
X-Met7500	-	1	0.83	0.29	0.89	-	0.83	0.99	1
XI3t GOLDD+	0.81	0.96	-	0.8	0.98	-	-	1	1
DP-4000	0.67	-	-	0.58	0.97	-	0.87	1	0.99

AR – pXRF : Pearson correlation coefficients

Model	Al	Ca	Fe	Mg	Mn	Ba	Mo	Sb	Sn
S1 Titan	-	-	0.93	-	0.95	0.73	-	-	-
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DP-4000	0.67	-	-	0.58	0.97	-	0.87	1	0.99

pXRF : 95 % confidence interval [%]

Model	Al	Ca	Fe	Mg	Mn	Ba	Mo	Sb	Sn
S1 Titan	-	-	3	-	17	15	29	28	28
X-Met7500	-	6	6	-	13	20	-	40	37
XI3t GOLDD+	5	7	4	67	29	26	40	34	59
DP-4000	-	7	6	-	11	8	48	21	-
Aqua Regia	19	16	18	22	9	18	163	206	148

Model	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn
S1 Titan	69	-	-	56	29	-	25	28	9
X-Met7500	-	-	78	61	49	-	34	13	15
XI3t GOLDD+	49	26	-	19	37	-	-	34	12
DP-4000	29	-	-	12	16	19	20	21	7
Aqua Regia	15	14	11	16	18	50	13	52	8

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Replacing Aqua Regia by pXRF?



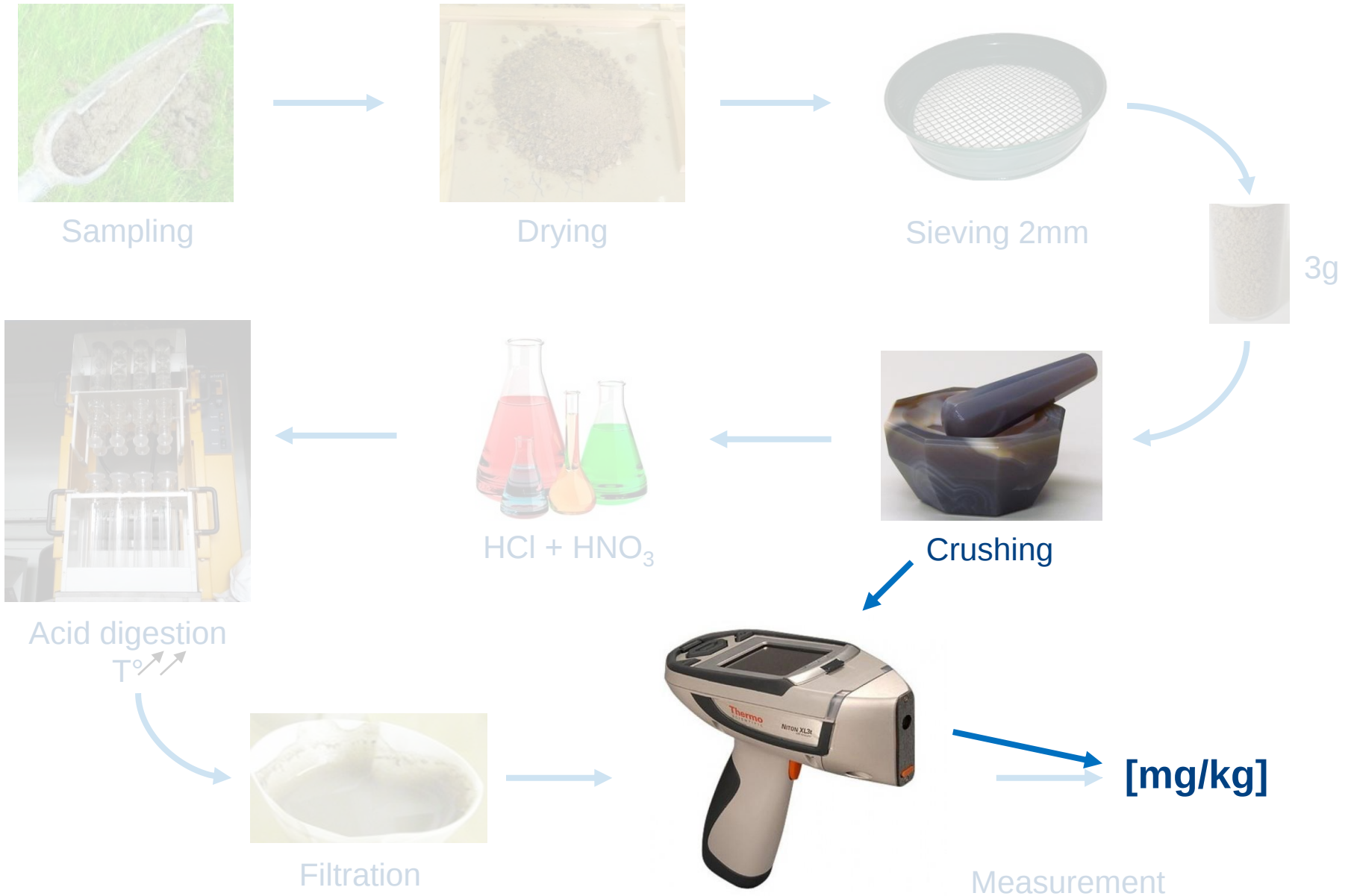
Replacing Aqua Regia by pXRF?



Replacing Aqua Regia by pXRF?



Replacing Aqua Regia by pXRF?



5 sample preparation protocols



1. Fresh in situ



2. Humidity corrected

Fresh / water content



3. In situ prepared

Dried with a pan and sieved 2mm



4. Lab prepared

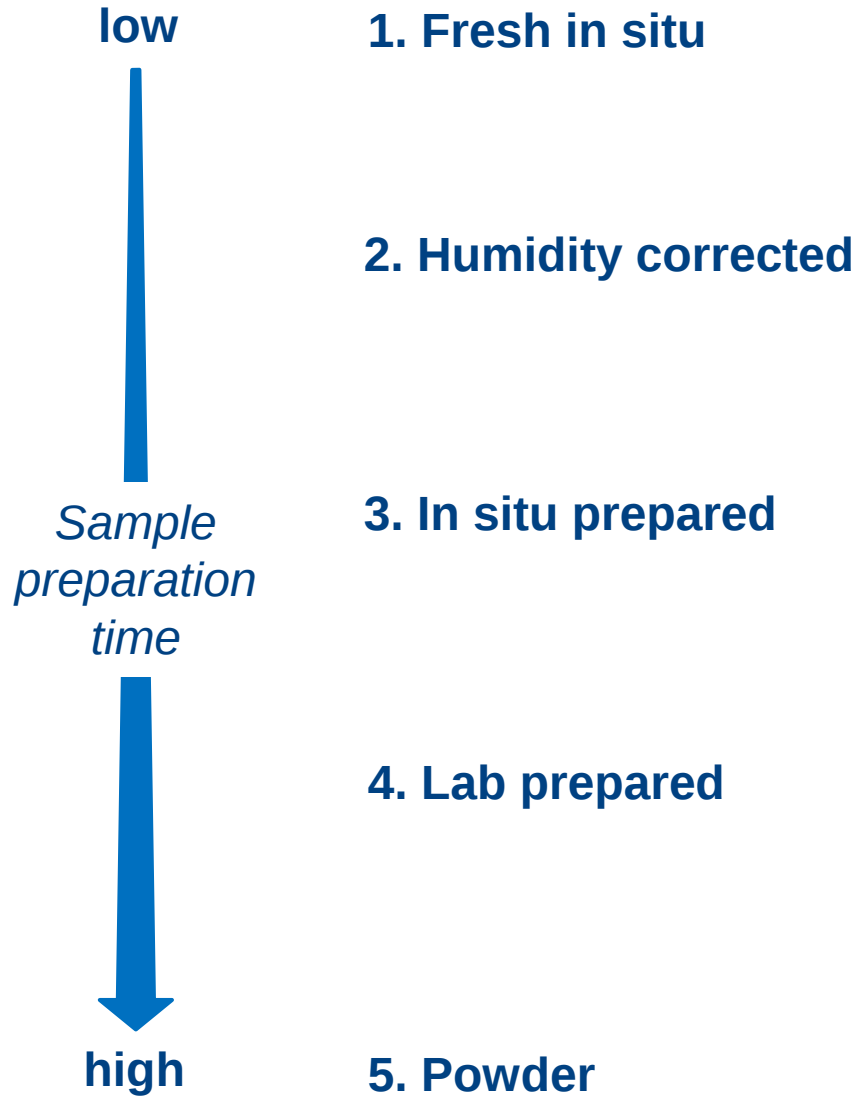
Dried and sieved 2mm

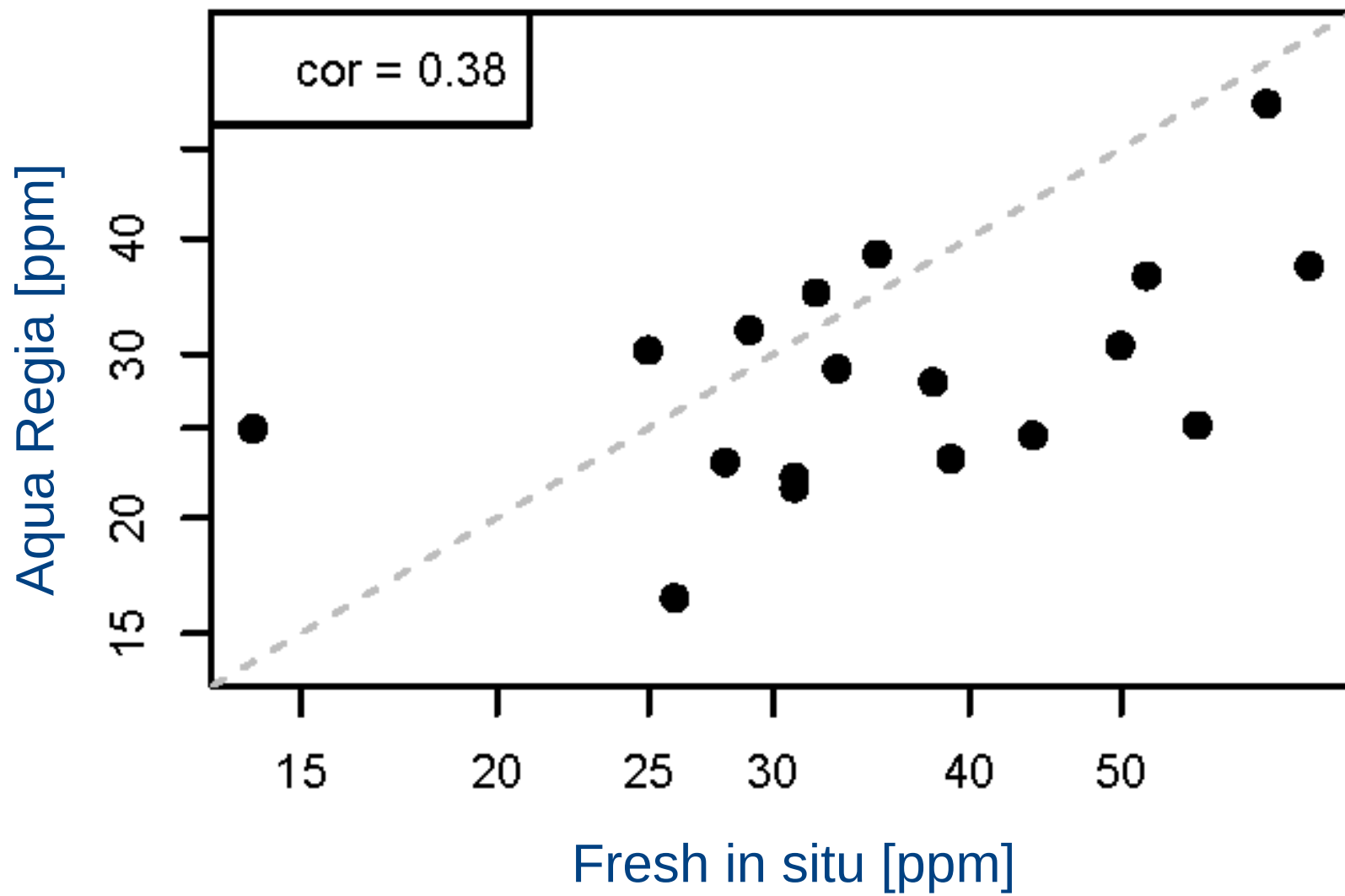


5. Powder



5 sample preparation protocols : Ni





5 sample preparation protocols : Ni



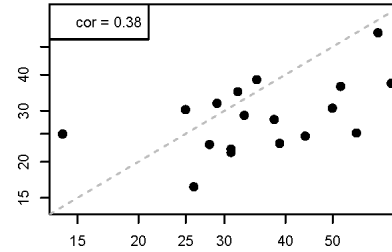
1. Fresh in situ

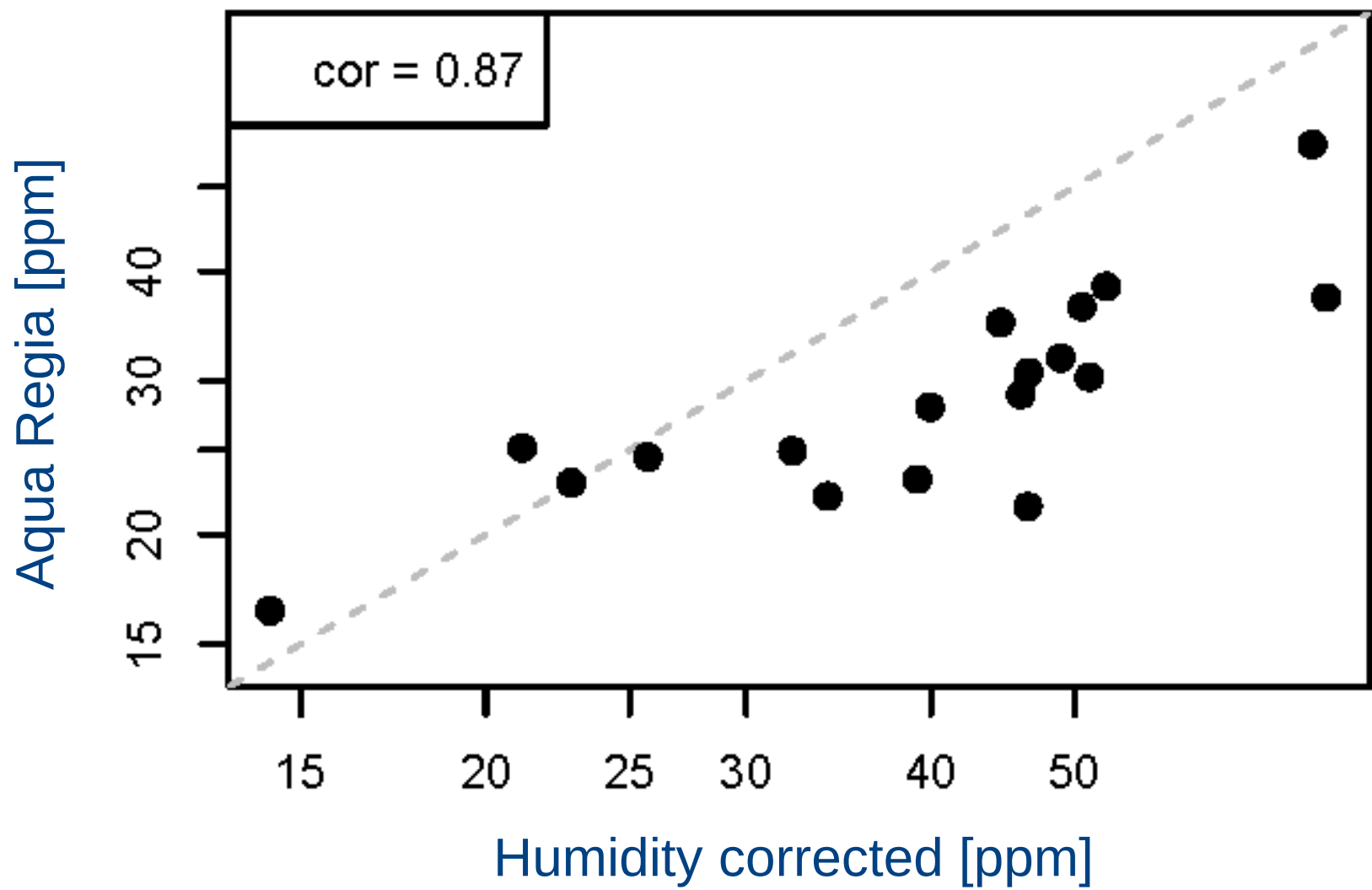
2. Humidity corrected

3. In situ prepared

4. Lab prepared

5. Powder





5 sample preparation protocols : Ni

low

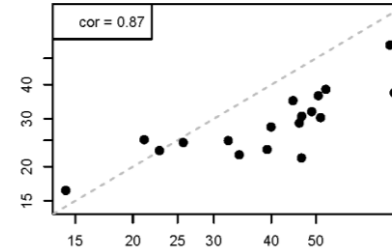
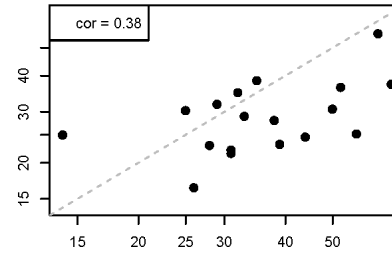
1. Fresh in situ

2. Humidity corrected

3. In situ prepared

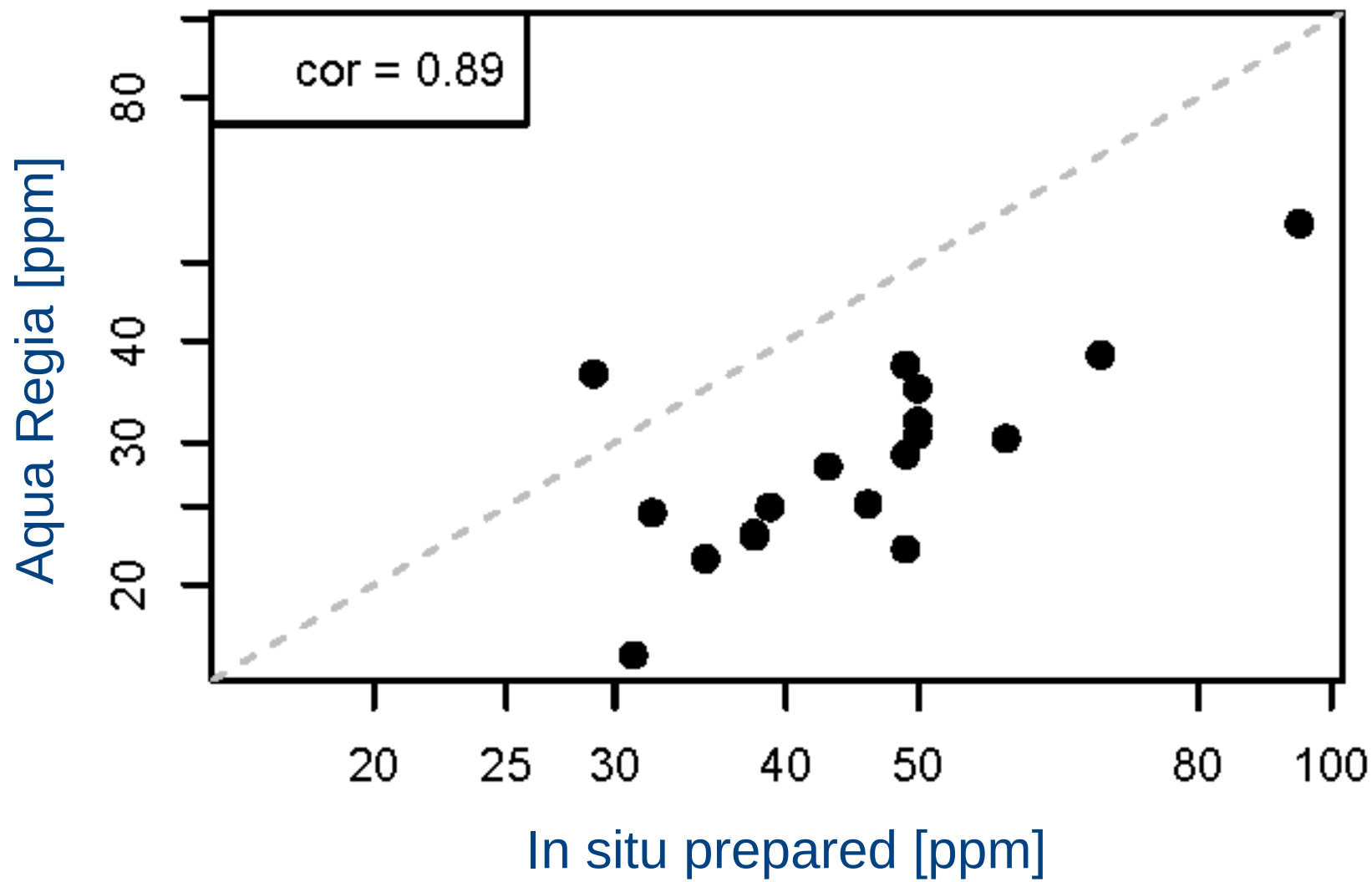
4. Lab prepared

5. Powder



*Sample
preparation
time*

high



5 sample preparation protocols : Ni



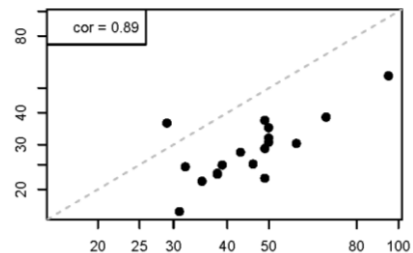
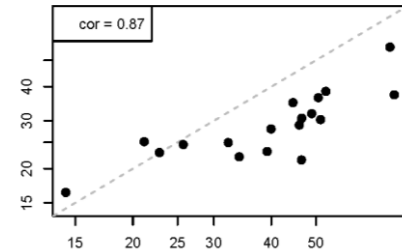
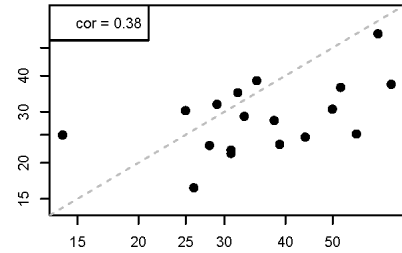
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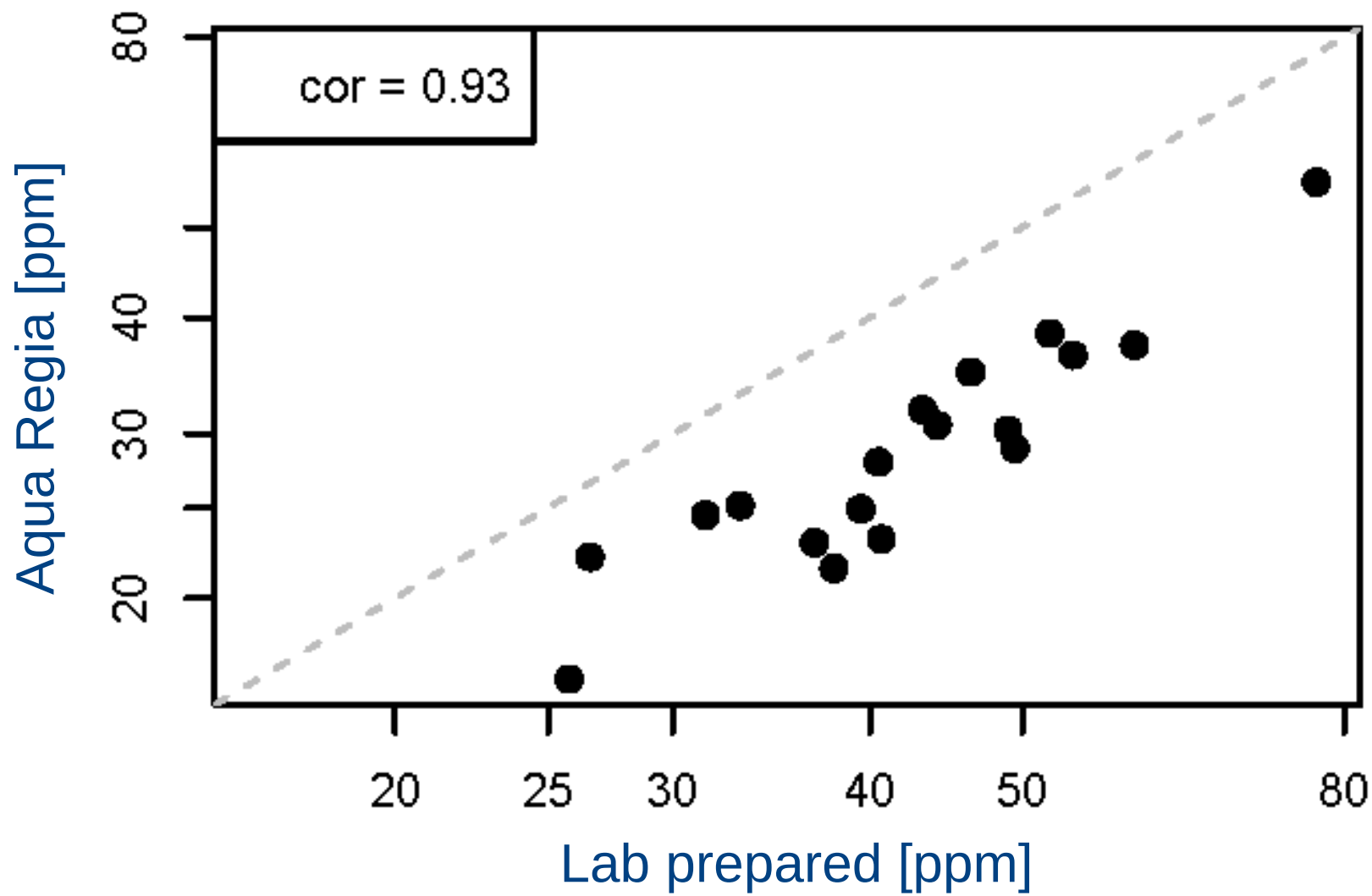
2. Humidity corrected

3. In situ prepared

4. Lab prepared

5. Powder





5 sample preparation protocols : Ni



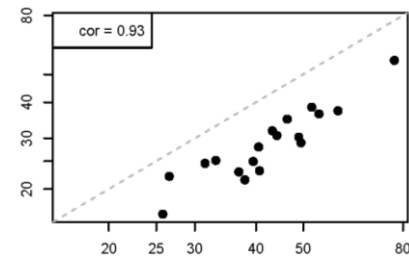
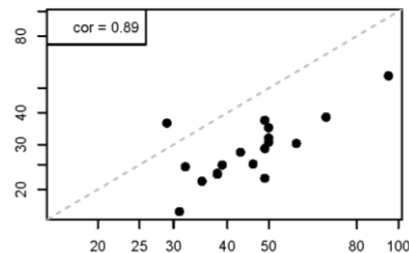
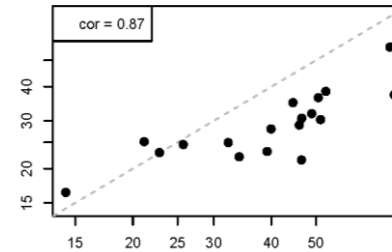
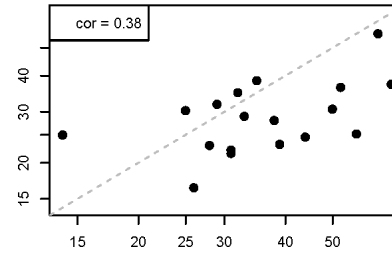
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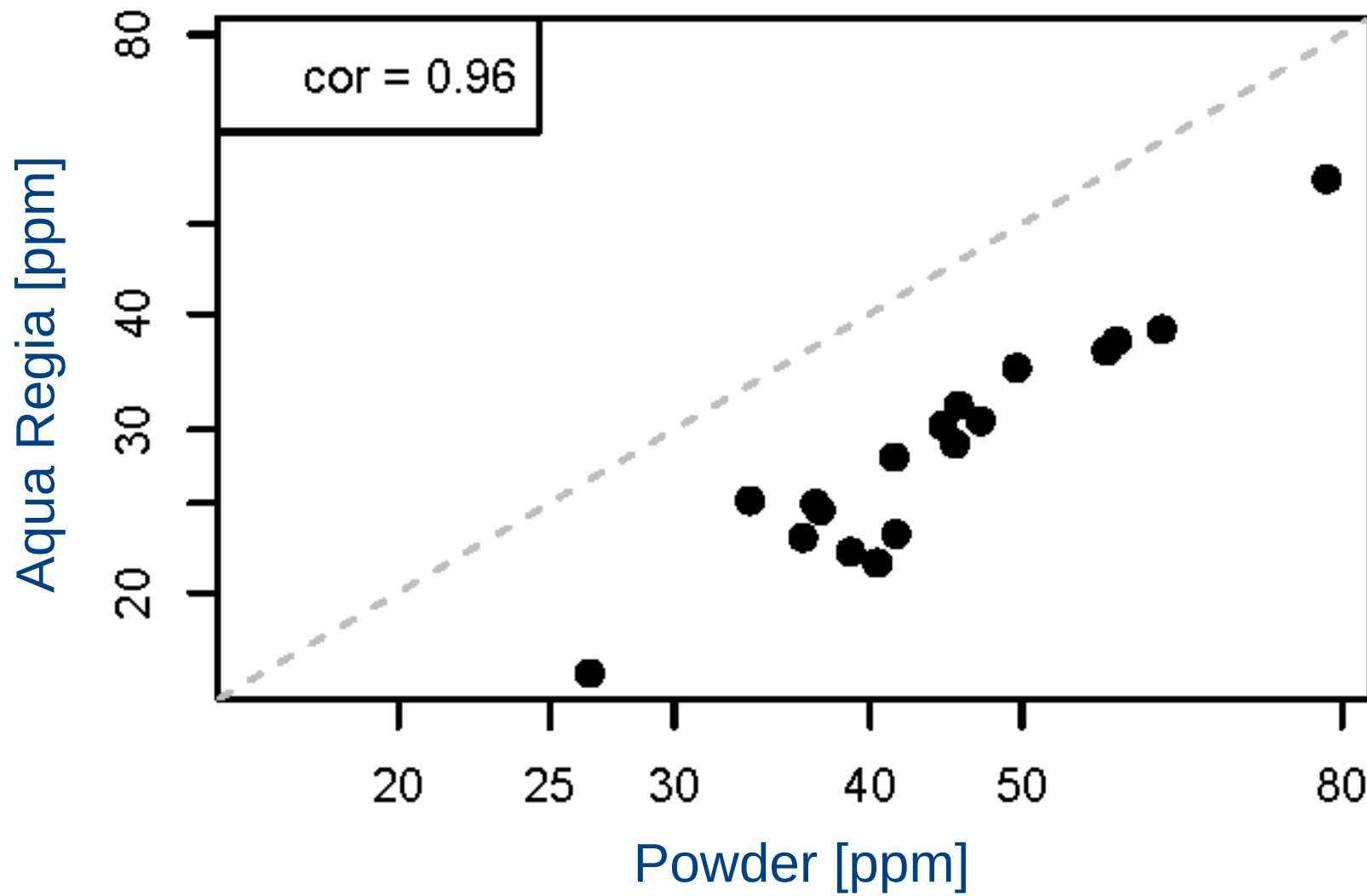
2. Humidity corrected

3. In situ prepared

4. Lab prepared

5. Powder





5 sample preparation protocols : Ni



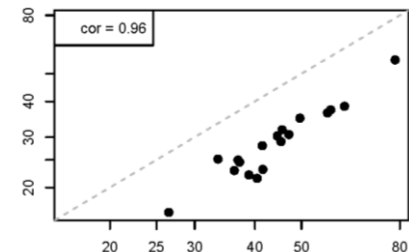
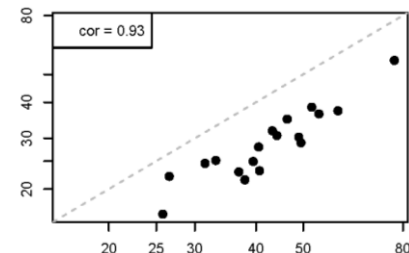
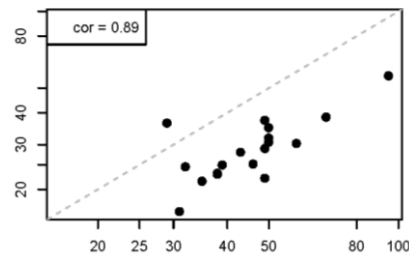
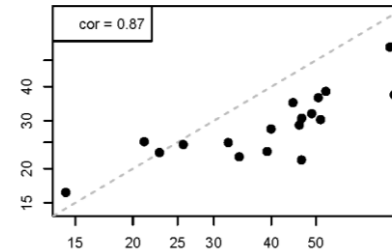
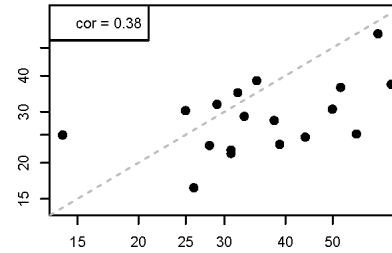
1. Fresh in situ

2. Humidity corrected

3. In situ prepared

4. Lab prepared

5. Powder



Sample preparation protocols : Pearson Correlation

Protocol	As	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Sr	Zn
Fresh in situ	0.16	0.03	0.84	0.74	0.74	0.15	0.38	0.95	0.46	0.77
Humidity corrected	0.27	0.4	0.97	0.88	0.98	-0.84	0.87	0.98	0.65	0.86
Pan in situ	0.19	0.22	0.93	0.92	0.97	0.75	0.89	0.98	0.6	0.92
Sieved 2mm :	0.26	0.69	0.98	0.97	0.98	0.55	0.93	0.99	0.7	0.95
Powder	0.18	0.51	0.99	0.95	0.99	0.5	0.95	1	0.7	0.95

Sample preparation protocols : Pearson Correlation

Protocol	As	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Sr	Zn
Fresh in situ	0.16	0.03	0.84	0.74	0.74	0.15	0.38	0.95	0.46	0.77
Humidity corrected	0.27	0.4	0.97	0.88	0.98	-0.84	0.87	0.98	0.65	0.86
Pan in situ	0.19	0.22	0.93	0.92	0.97	0.75	0.89	0.98	0.6	0.92
Sieved 2mm :	0.26	0.69	0.98	0.97	0.98	0.55	0.93	0.99	0.7	0.95
Powder	0.18	0.51	0.99	0.95	0.99	0.5	0.95	1	0.7	0.95

Sample preparation protocols : Pearson Correlation

Protocol	As	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Sr	Zn
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Sieved 2mm :	0.26	0.69	0.98	0.97	0.98	0.55	0.93	0.99	0.7	0.95
Powder	0.18	0.51	0.99	0.95	0.99	0.5	0.95	1	0.7	0.95

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Protocol	As	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Sr	Zn
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Powder	0.18	0.51	0.99	0.95	0.99	0.5	0.95	1	0.7	0.95

Sample preparation protocols : Pearson Correlation

Protocol	As	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Sr	Zn
Fresh in situ	0.16	0.03	0.84	0.74	0.74	0.15	0.38	0.95	0.46	0.77
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Sieved 2mm :	0.26	0.69	0.98	0.97	0.98	0.55	0.93	0.99	0.7	0.95
Powder	0.18	0.51	0.99	0.95	0.99	0.5	0.95	1	0.7	0.95

Sample preparation protocols : 95 % confidence interval [%]

Protocol	As	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Sr	Zn
Fresh in situ	24	21	26	13	17	/	34	13	9	23
Sieved 2mm :	25	11	18	5	7	47	19	8	5	7
Powder	18	10	25	4	5	35	20	7	5	4
Aqua Regia	15	16	18	18	9	163	13	52	-	8

Sample preparation protocols : 95 % confidence interval [%]

Protocol	As	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Sr	Zn
Fresh in situ	24	21	26	13	17	/	34	13	9	23
Sieved 2mm :	25	11	18	5	7	47	19	8	5	7
Powder	18	10	25	4	5	35	20	7	5	4
Aqua Regia	15	16	18	18	9	163	13	52	-	8

Sample preparation VS quality of measurement

Protocol	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Fresh in situ	</>	HPS	</>	Screening	HPS	Screening	OK	Screening
Pan in situ Humidity Corrected	</>	HPS	</>	OK	HPS	Screening	OK	OK
Sieved 2mm Powder	Screening	HPS	Screening	OK	HPS	Screening	OK	OK

OK

: equivalent to AR or better

Screening

: good proxy to AR

</>

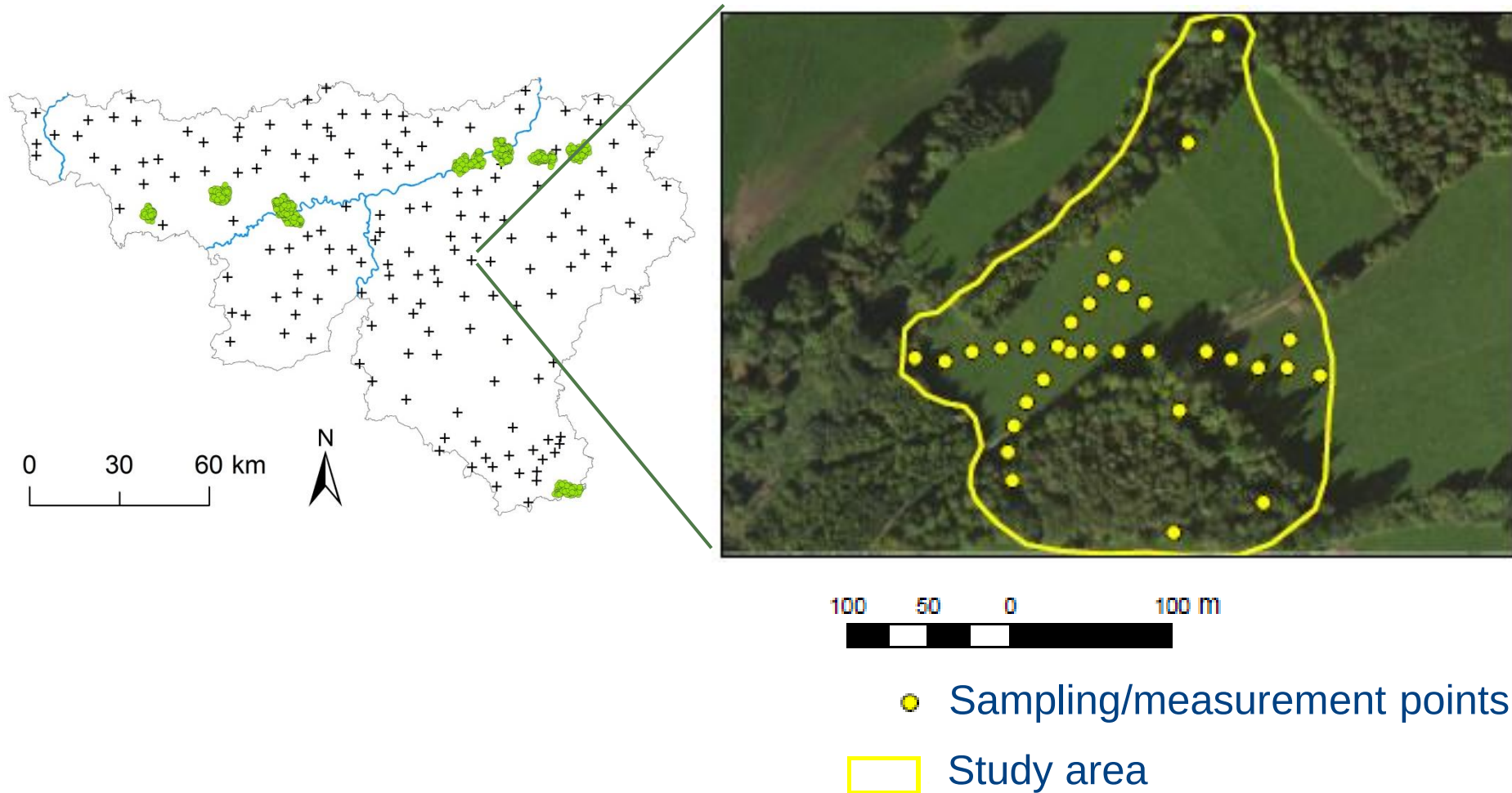
: go/no go

HPS

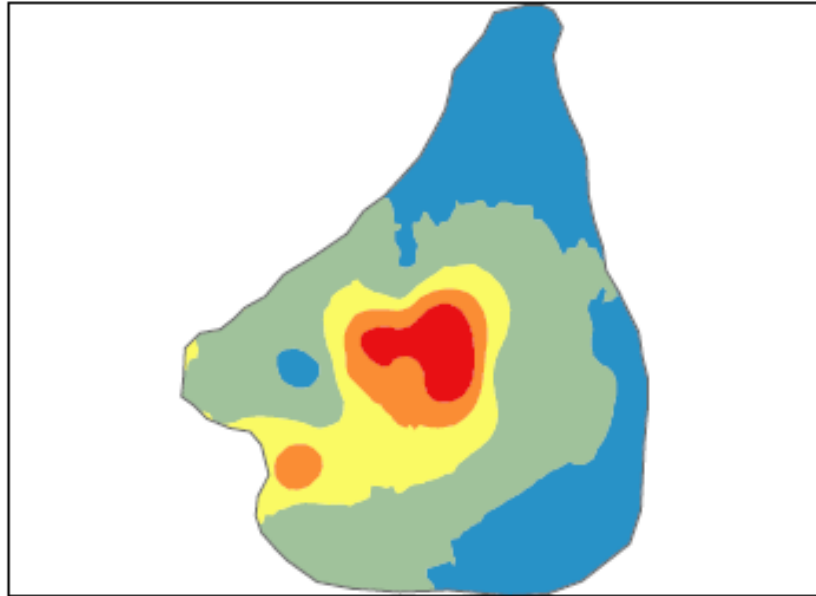
: only for Highly Polluted Sites

Case study : geological anomaly

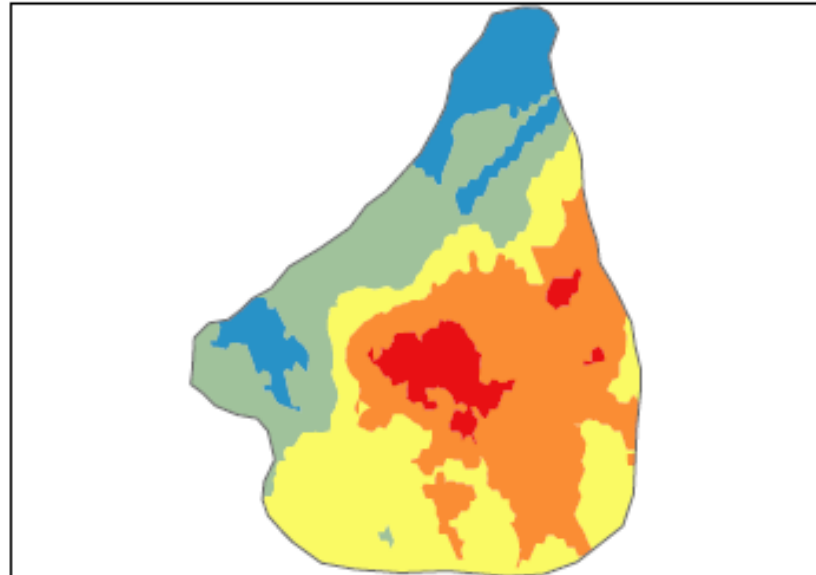
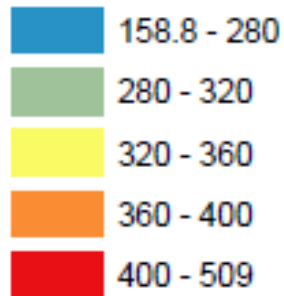
Fresh in situ protocol



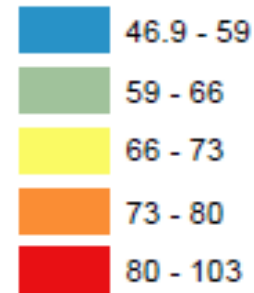
Case study : geological anomaly



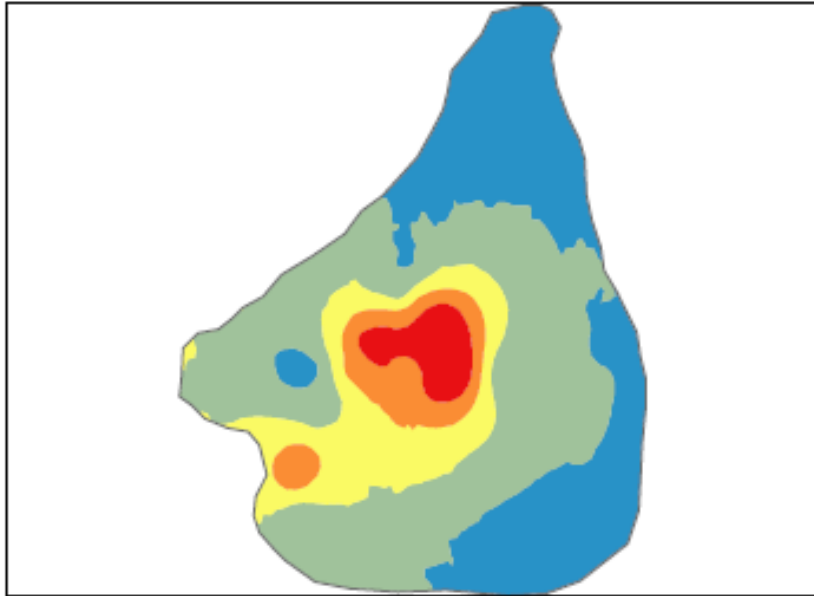
Zn Fresh in situ [ppm]



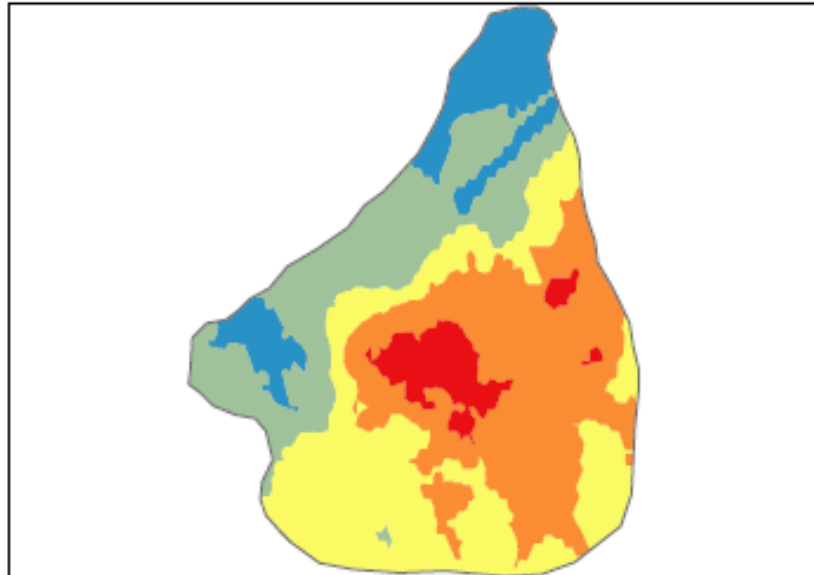
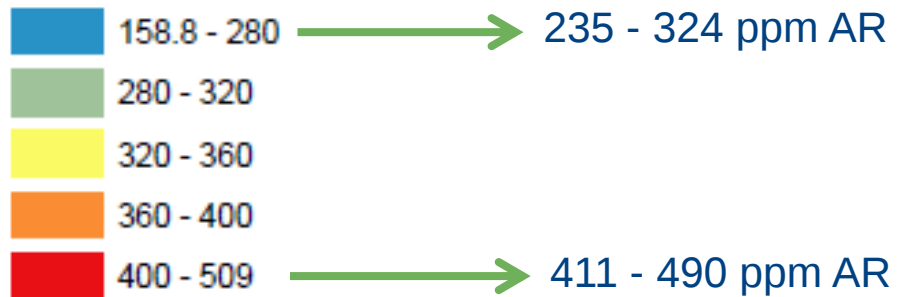
Pb Fresh in situ [ppm]



Case study : geological anomaly



Zn Fresh in situ [ppm]



Pb Fresh in situ [ppm]

