

# Differences between heavy metal concentrations in sediments analysed by two methods

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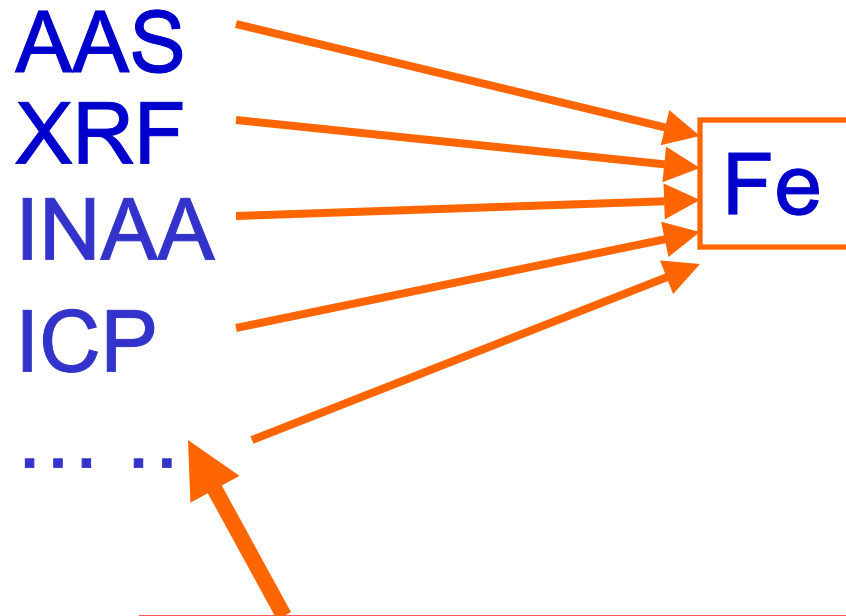
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# 1. Introduction

- ✓ Geochemical databases constructed
- ✓ More than 1 method for an element



**Results consistent?**

# 1. Introduction

- ✓ Quality control

Errors < 10% (reference values)

TRUE?



# 1. Introduction

Objective:

Evaluate data quality

by comparing values from  
two measurements  
of an existing database

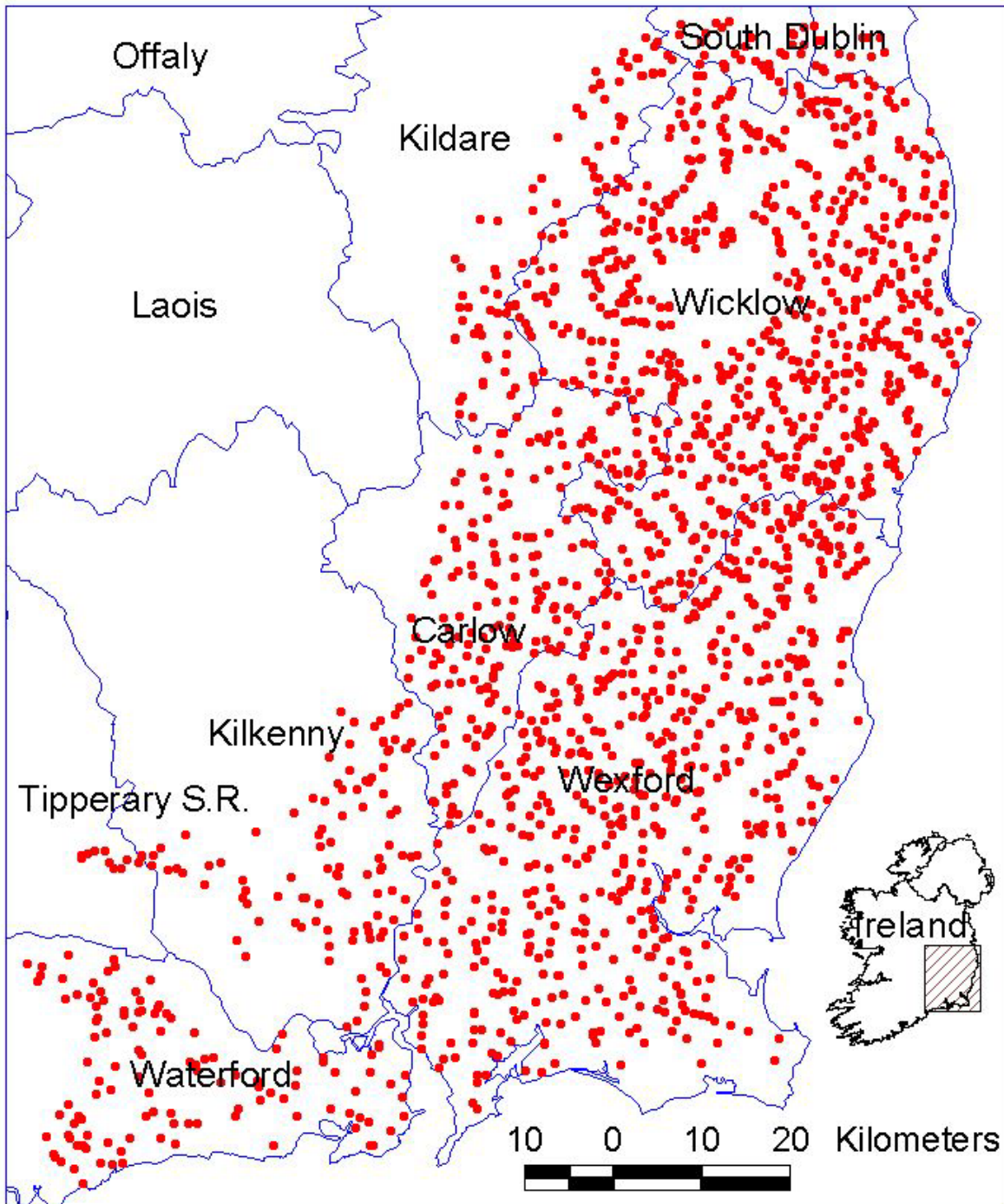
Easy

Objective

## 2. Methods

### Sampling





## Sediments Leinster Area

N=1,884

NAA  
AAS

## 2. Methods

### Lab analyses

➤ NAA

38 elements, 26 selected  
Including Co, Cr, Fe, Ni, Zn

➤ AAS

Co, Cr, Fe, Ni, Zn

Comparison



## 2. Methods

### Detection limits (DL)

Detection limits reported by laboratories (in mg/kg)

	Co	Cr	Fe	Ni	Zn
NAA	5	20	0.2%	20	100
AAS	1	1	5	1	1

$\frac{1}{2}$  DL used for those <DL





## 2. Methods

### Methods for comparison:

- **Basic statistics**

Descriptive

Hypothesis tests

Means

- **Graphics**

Scatter plots

Relationship

- **Maps**

GIS

Spatial

- **Multivariate analyses**

PCA, Cluster

Effects



# 3. Results and discussions

## ➤ Descriptive

**NAA < AAS**

	CoNAA	CoAAS	CrNAA	CrAAS	FeNAA	FeAAS	NiNAA	NiAAS	ZnNAA	ZnAAS
Min	3	1	10	9	0.4	0.3	5	2	50	23
5%	6	4	10	20	1.2	1.0	10	9	50	59
10%	8	7	34	29	1.6	1.3	10	13	50	69
0.25	14	12	65	51	2.7	2.2	10	23	120	93
<b>Median</b>	<b>24</b>	<b>20</b>	<b>90</b>	<b>69</b>	<b>4.1</b>	<b>3.3</b>	<b>30</b>	<b>36</b>	<b>160</b>	<b>126</b>
0.75	36	30	120	86	5.1	4.1	42	48	210	167
0.9	52	42	150	103	6.0	4.8	55	62	280	240
0.95	71	55	170	115	6.6	5.2	65	72	340	307
Max	400	326	1500	1100	18.0	12.4	170	179	86600	99262
Avg	29.8	24.3	96.0	69.8	4.0	3.2	31.3	37.4	244.6	225.9
Stdev	28.9	22.0	72.1	41.6	1.7	1.4	20.1	21.3	2143.8	2410.9
Skew	5.1	5.2	8.0	10.7	0.6	0.3	1.4	1.5	36.4	38.1
Kurt	44.2	50.0	118.0	237.1	3.0	1.0	4.3	5.1	1421.7	1529.5

**NAA > AAS**



# 3. Results and discussions

## Degree of differences

Differences:  $\text{Abs}((\text{AAS}-\text{NAA})/\text{NAA}) \times 100$  (all values in %)

	Co	Cr	Fe	Ni	Zn
Minimum	0.0	0.0	0.0	0.0	0.0
25%	13.8	15.1	11.0	12.5	14.8
<b>Median</b>	<b>24.8</b>	<b>30.0</b>	<b>19.7</b>	<b>29.1</b>	<b>28.0</b>
75%	38.1	47.9	29.3	63.3	46.8
95%	76.8	82.4	45.2	260.0	120.0
Maximum	700.0	1082.8	237.5	1620.0	948.0
<b>Average</b>	<b>32.0</b>	<b>38.0</b>	<b>21.4</b>	<b>68.2</b>	<b>39.0</b>

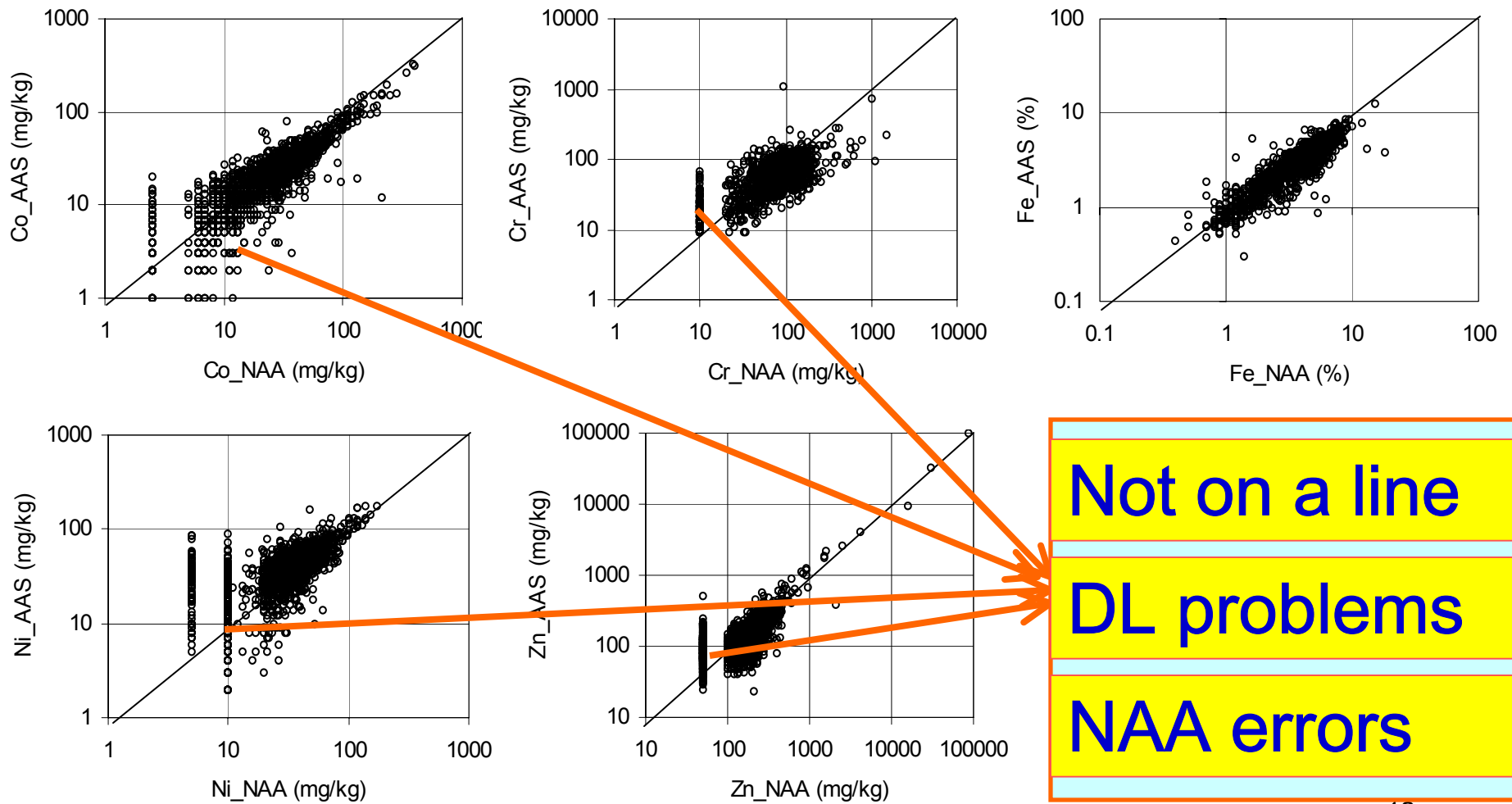
20-30%

>> 10%



# 3. Results and discussions

## ➤ Scatter plots



Not on a line

DL problems

NAA errors

### 3. Results and discussions

#### ➤ Statistical tests

	Co	Cr	Fe	Ni	Zn
n(AAS > NAA)	468	453	199	1221	622
n(AAS < NAA)	1308	1407	1678	598	1251
n(AAS = NAA)	108	24	7	65	11
Z(sign test)	-19.91	-22.10	-34.12	-14.58	-14.51
p(sign test)	.000	.000	.000	.000	.000
Z(Wilcoxon signed rank)	-22.55	-25.57	-34.01	-17.91	-16.05
p(Wilcoxon signed rank)	.000	.000	.000	.000	.000



Significance level  $p < 0.001$



### 3. Results and

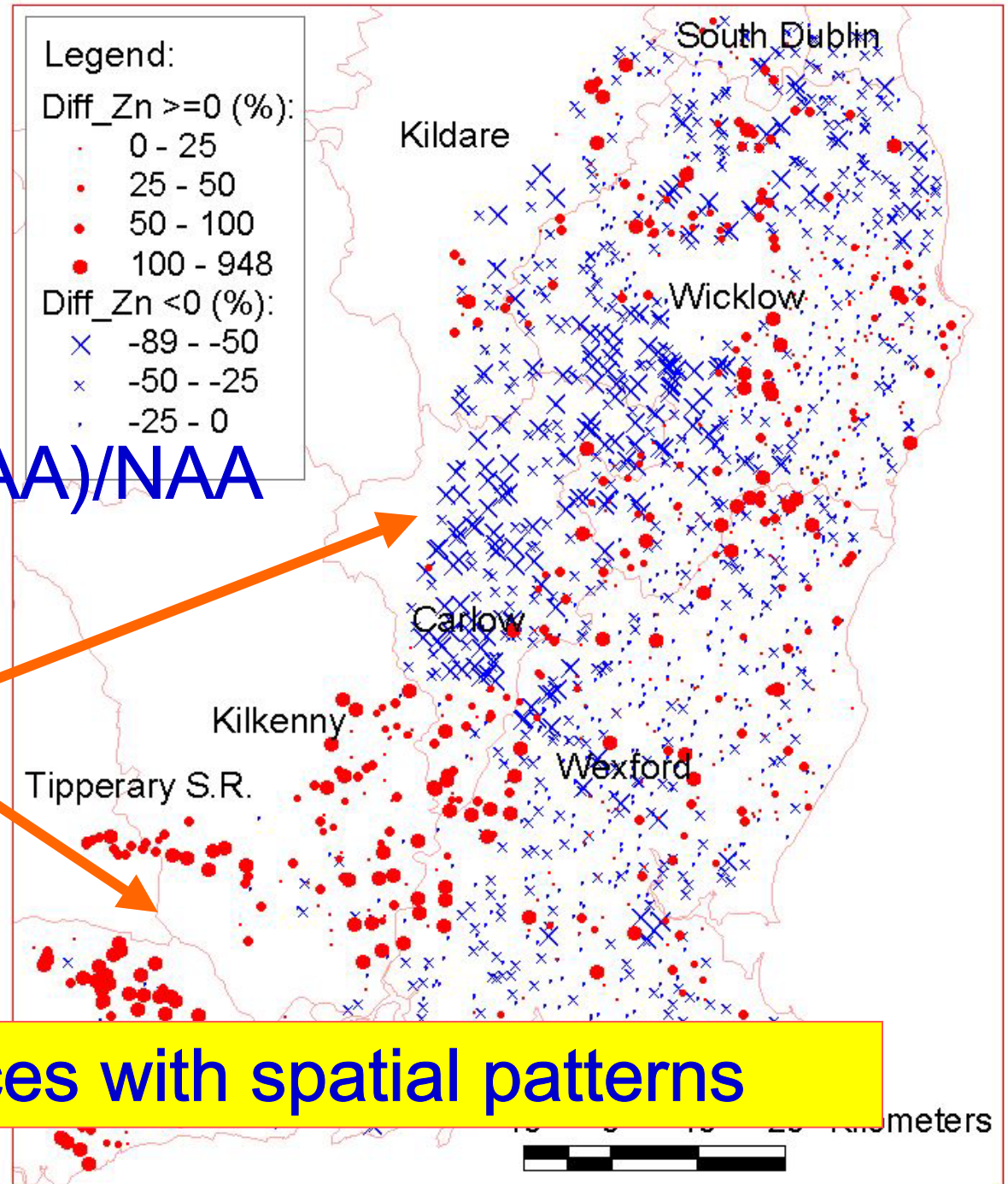
➤ GIS maps

e.g.: Zn

$$\text{Diff} = (\text{AAS} - \text{NAA}) / \text{NAA}$$

AAS < NAA

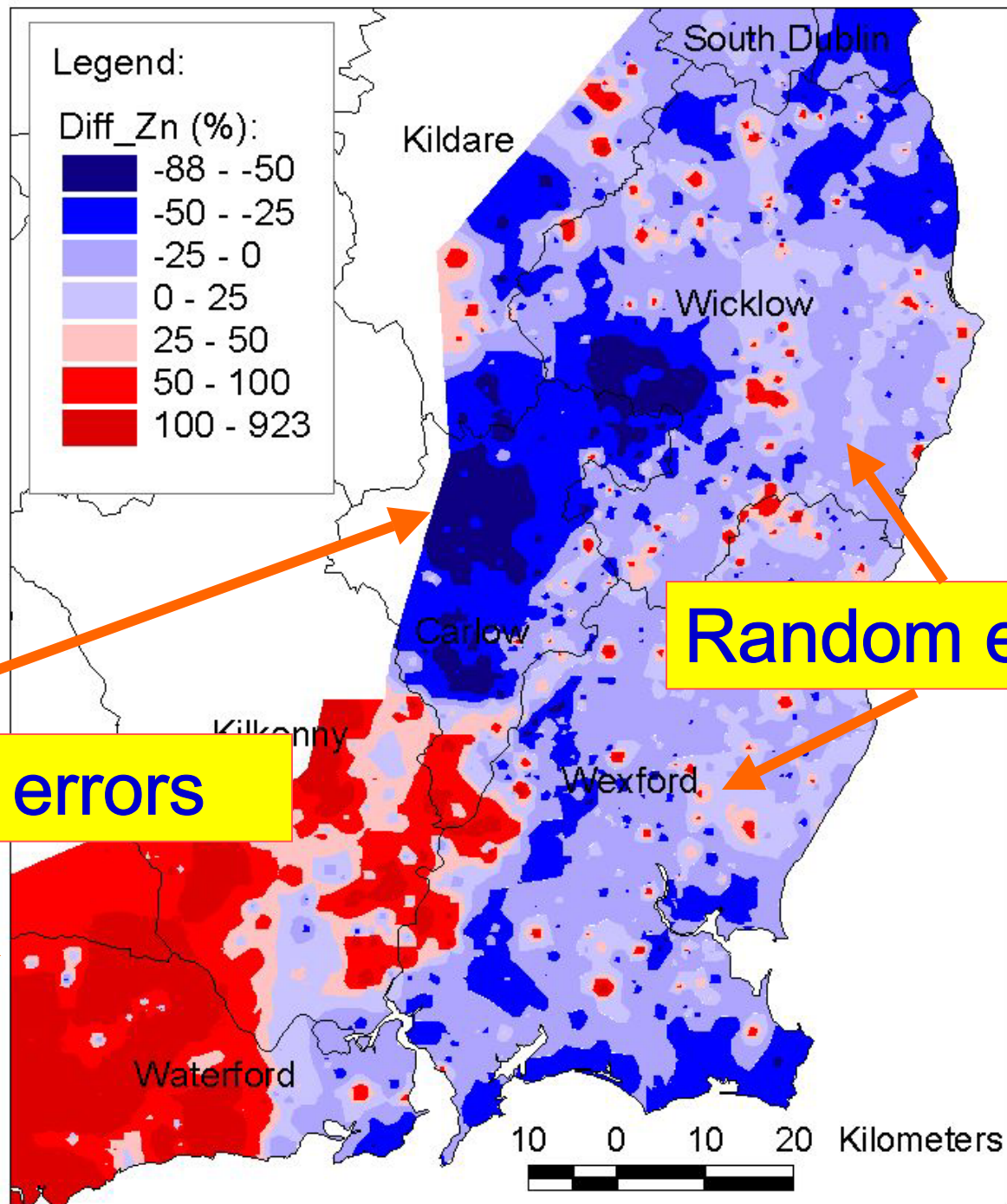
AAS > NAA



Differences with spatial patterns

# 3. Results

IDW

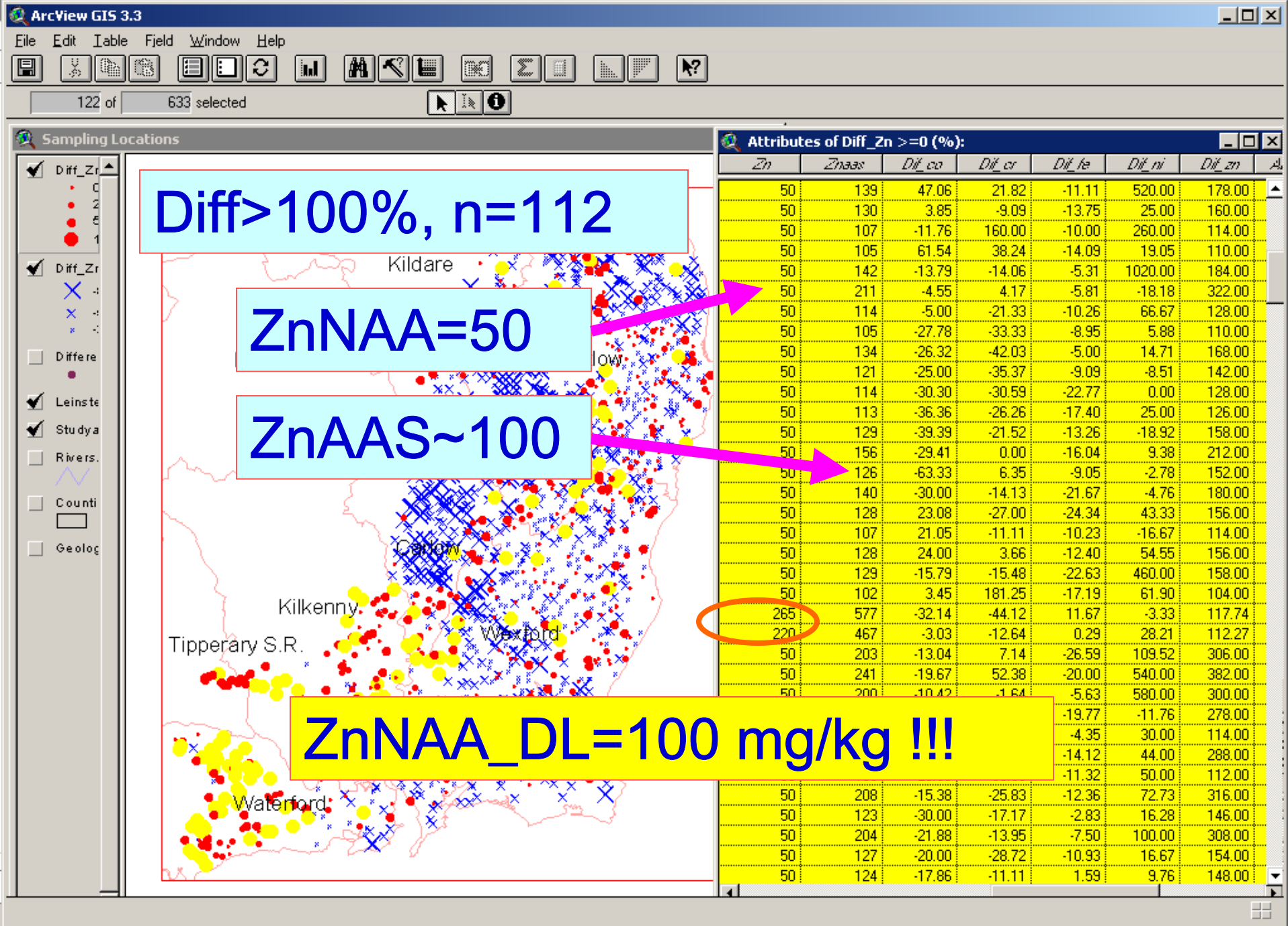


Random errors

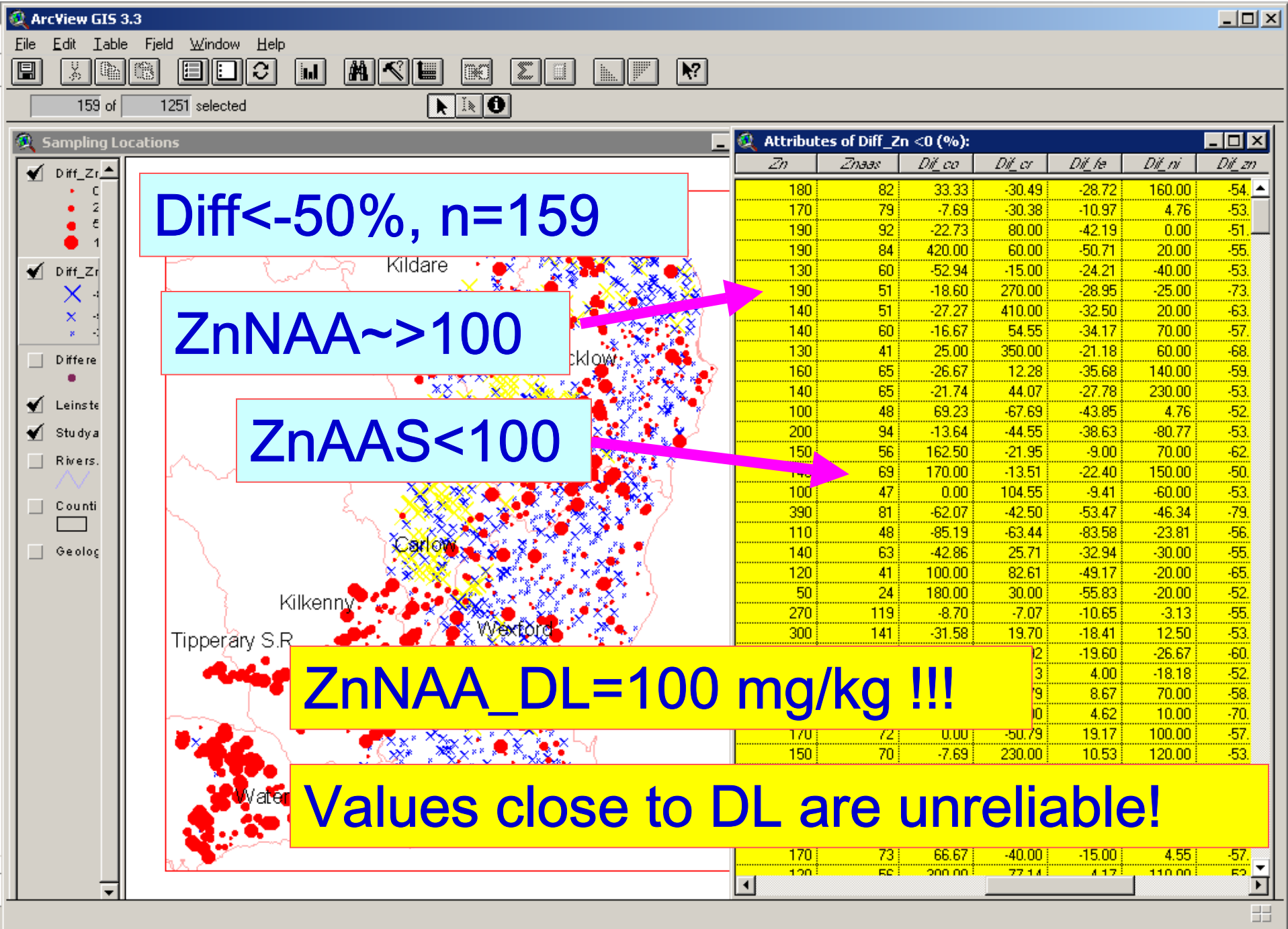
Systematic errors

Why???









**Diff < -50%, n=159**

**ZnNAA > 100**

**ZnAAS < 100**

**ZnNAA\_DL = 100 mg/kg !!!**

**Values close to DL are unreliable!**

Zn	Zn_aas	Dif_co	Dif_cr	Dif_fe	Dif_ni	Dif_zn
180	82	33.33	-30.49	-28.72	160.00	-54
170	79	-7.69	-30.38	-10.97	4.76	-53
190	92	-22.73	80.00	-42.19	0.00	-51
190	84	420.00	60.00	-50.71	20.00	-55
130	60	-52.94	-15.00	-24.21	-40.00	-53
190	51	-18.60	270.00	-28.95	-25.00	-73
140	51	-27.27	410.00	-32.50	20.00	-63
140	60	-16.67	54.55	-34.17	70.00	-57
130	41	25.00	350.00	-21.18	60.00	-68
160	65	-26.67	12.28	-35.68	140.00	-59
140	65	-21.74	44.07	-27.78	230.00	-53
100	48	69.23	-67.69	-43.85	4.76	-52
200	94	-13.64	-44.55	-38.63	-80.77	-53
150	56	162.50	-21.95	-9.00	70.00	-62
140	69	170.00	-13.51	-22.40	150.00	-50
100	47	0.00	104.55	-9.41	-60.00	-53
390	81	-62.07	-42.50	-53.47	-46.34	-79
110	48	-85.19	-63.44	-83.58	-23.81	-56
140	63	-42.86	25.71	-32.94	-30.00	-55
120	41	100.00	82.61	-49.17	-20.00	-65
50	24	180.00	30.00	-55.83	-20.00	-52
270	119	-8.70	-7.07	-10.65	-3.13	-55
300	141	-31.58	19.70	-18.41	12.50	-53
2		-19.60	-26.67			-60
3		4.00	-18.18			-52
9		8.67	70.00			-58
10		4.62	10.00			-70
170	72	0.00	-50.79	19.17	100.00	-57
150	70	-7.69	230.00	10.53	120.00	-53
170	73	66.67	-40.00	-15.00	4.55	-57
120	55	200.00	77.14	4.17	110.00	-52

# 3. Results and discussions

## ➤ Multivariate analyses

- ✓ PCA

- ✓ Cluster



# PCA

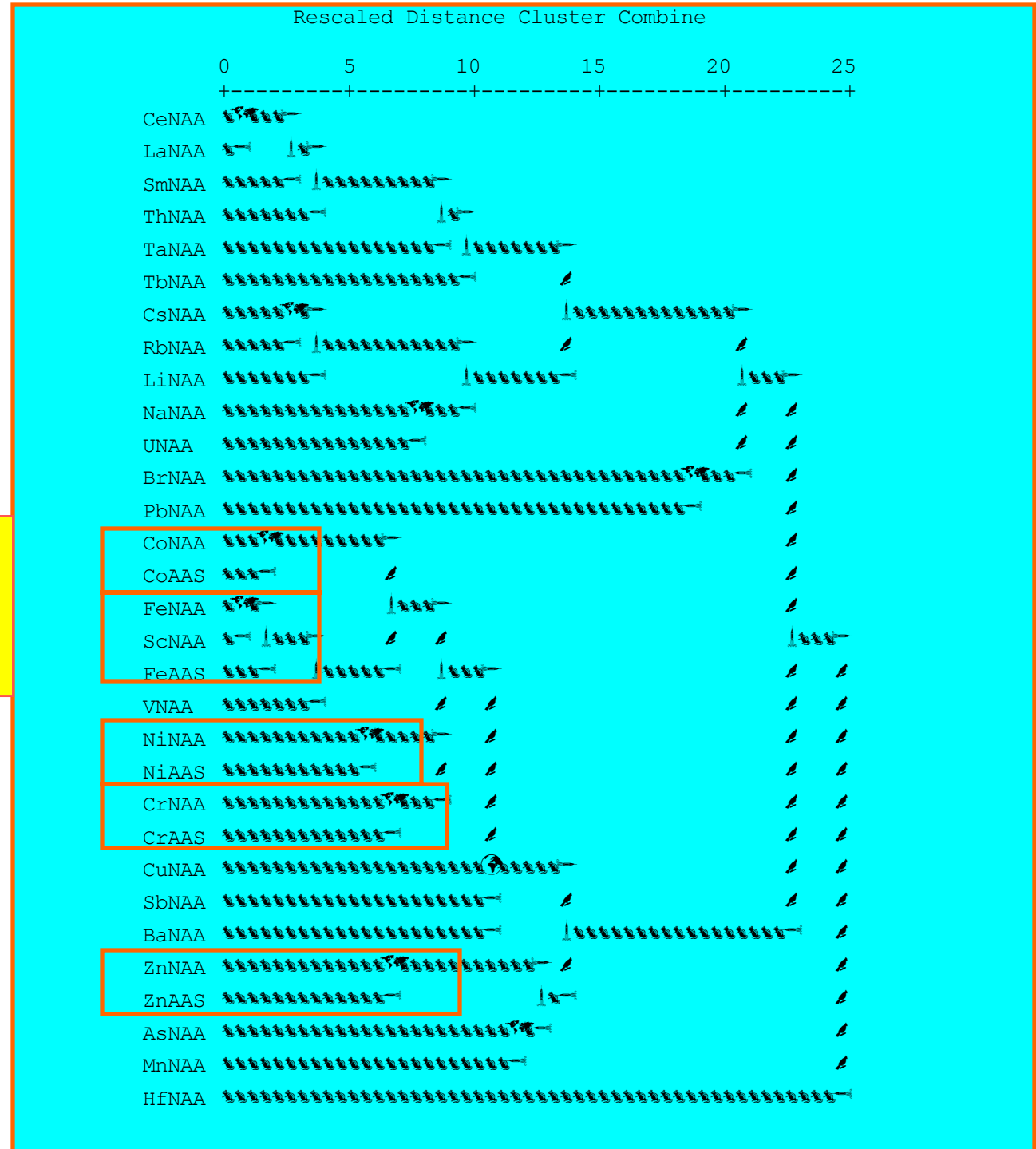
Minor differences

	PC1	PC2	PC3	PC4	PC5
AsNAA	0.42		0.39		0.59
BaNAA	0.63				
BrNAA					0.77
CeNAA		0.90			
CoNAA	0.83				0.29
CoAAS	0.76				0.26
CrNAA	0.60		-0.52		
CrAAS	0.77				-0.28
CsNAA		0.32	0.80		
CuNAA	0.62			0.46	
FeNAA	0.91				
FeAAS	0.88				
HTNAA			-0.78		
LaNAA		0.91			
LiNAA		0.35	0.81		
MnNAA	0.53			0.31	0.41
NaNAA	-0.47	0.47	0.35		
NiNAA	0.73				
NiAAS	0.82				
PbNAA				0.75	
RbNAA		0.47	0.78		
SbNAA	0.60		-0.28	0.42	
ScNAA	0.90				
SmNAA		0.86			
TaNAA		0.66	0.45		
TbNAA	0.54	0.65			
ThNAA		0.90			
UNAA	-0.41	0.58	0.38		
VNAA	0.83				
ZnNAA	0.28			0.61	
ZnAAS	0.59			0.54	0.32
Var. explained	32.1%	21.7%	9.8%	4.6%	3.7%



# Cluster analysis

Almost no differences



## 4. Conclusions

- Results from NAA and AAS for the 5 element were **different** at  $p < 0.001$
- **Average** differences were between 20-30%
- The **largest differences and systematic errors** were caused by the high DLs of NAA



## 4. Conclusions

- Fortunately, the differences have only caused **minor problems** in multivariate relationships
- **GIS** is a useful tool



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