



A combined
hydrochemical, isotopic and
multivariate statistics approach
for pollutant source identification
in a regional aquifer

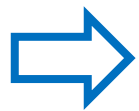
Julie GESELS, Claire JONIAU, Kay KNÖLLER and Serge BROUYÈRE

Good qualitative status for the groundwater resources in the EU by the end of 2015 (European Parliament and Council)

Exemption if

↓ groundwater quality degraded by
natural factors

Groundwater quality objectives and
management plans adapted



*Need to prove that the poor quality status
is caused by natural conditions*

Alluvial aquifer of the Meuse river near Liège (Belgium - Europe)

in a strongly urbanized and industrialized area

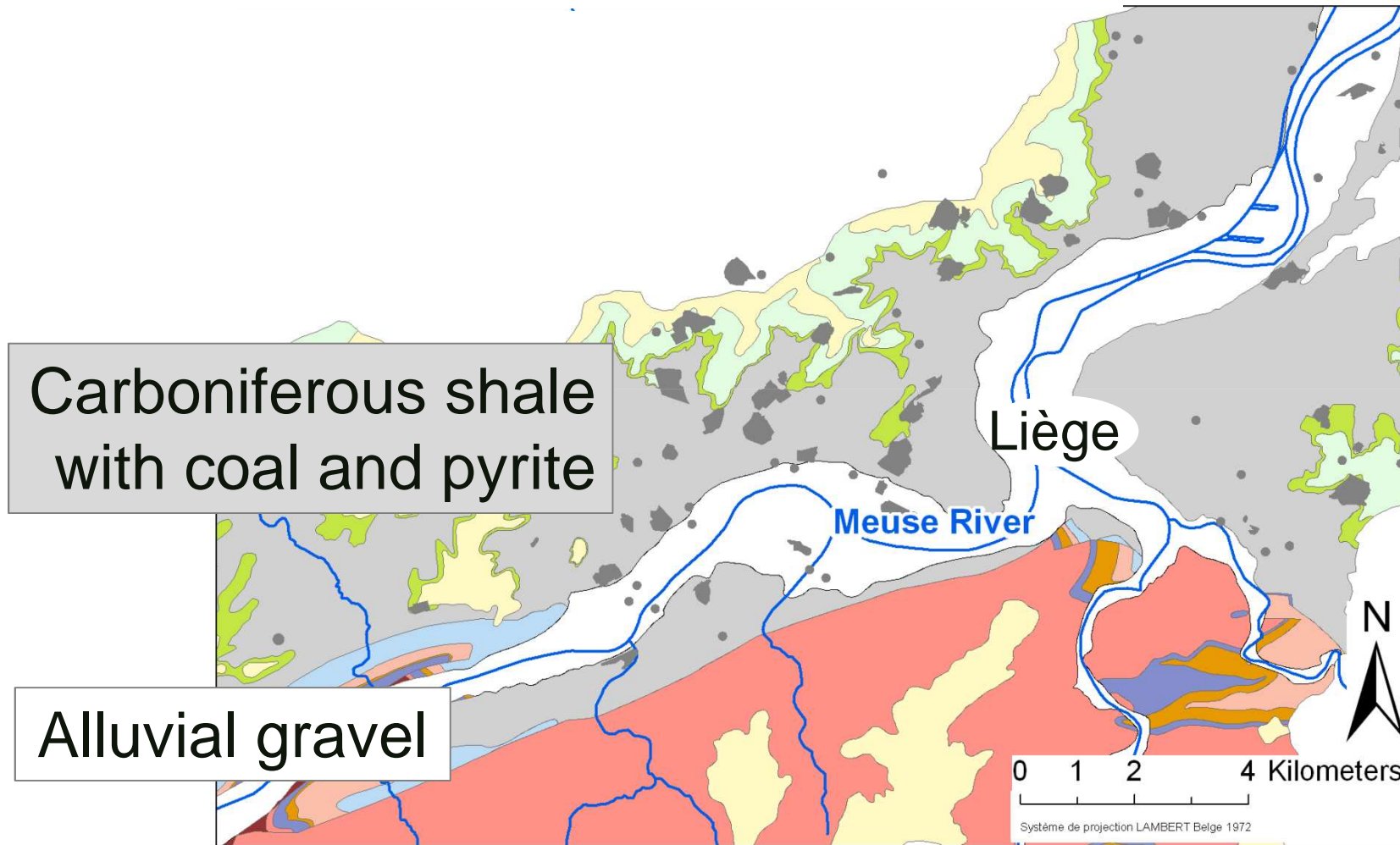
heavily contaminated

at the regional scale

with various types of contaminants

Sources of contamination associated with the
urban and industrial context ?

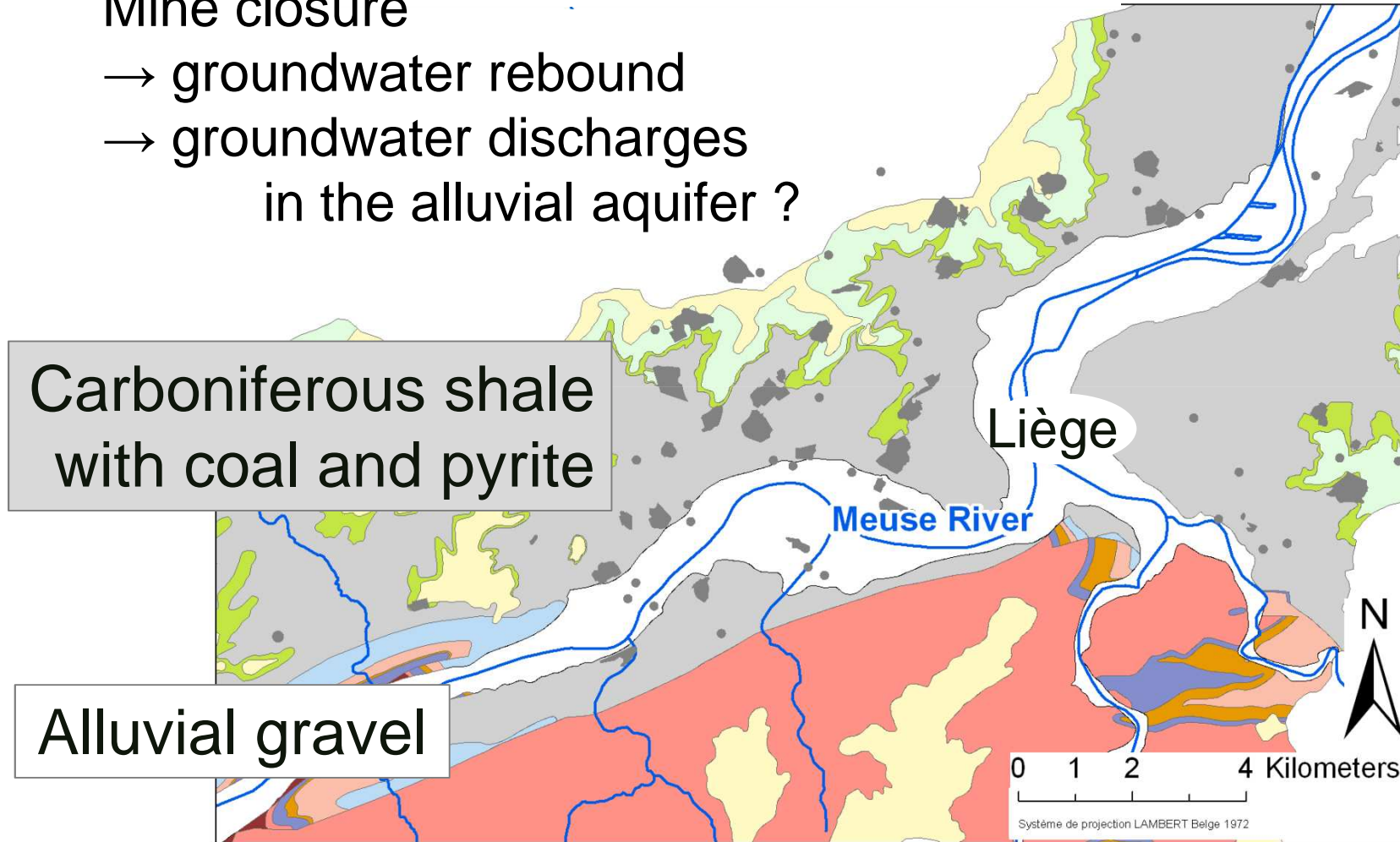
Hydrogeologic context



Hydrogeologic context

Mine closure

- groundwater rebound
- groundwater discharges
in the alluvial aquifer ?



Natural or anthropogenic origin ?

Many sources of contamination contribute to poor quality

- brownfields
- urban waste
- atmospheric deposits related to industrial emissions

Anthropogenic

- subsurface acid drainage from former coal mining activities

'Natural'

Most probably impossible to take measures to reduce the contamination of the alluvial aquifer

How to prove that the poor quality status is caused by natural conditions ?

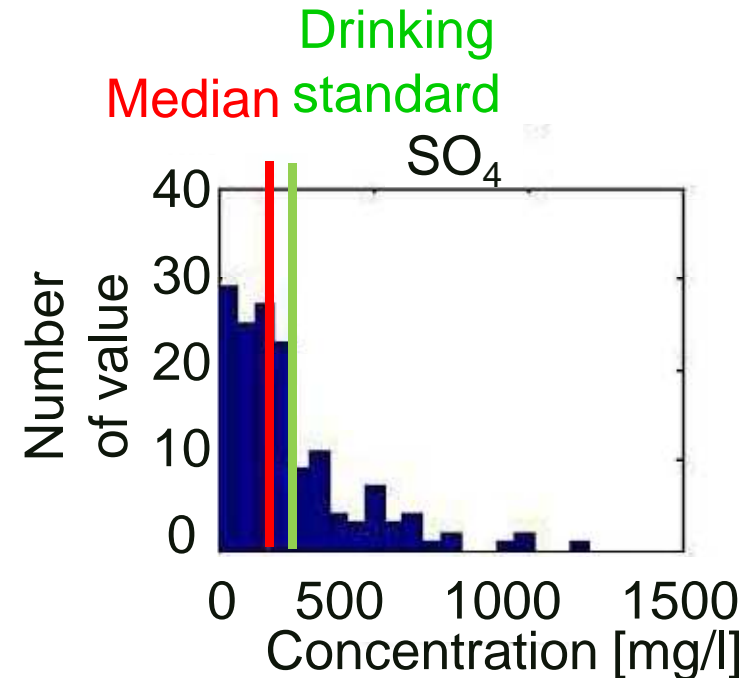
To determine

- the origin of the inorganic contaminations
- the main processes contributing to poor groundwater quality

Hydrogeochemical investigation using different combined approaches

- classical hydrochemistry
- multivariate statistics
- spatial distribution maps
- a first look to isotopic techniques

Sulfate is the main degrading factor

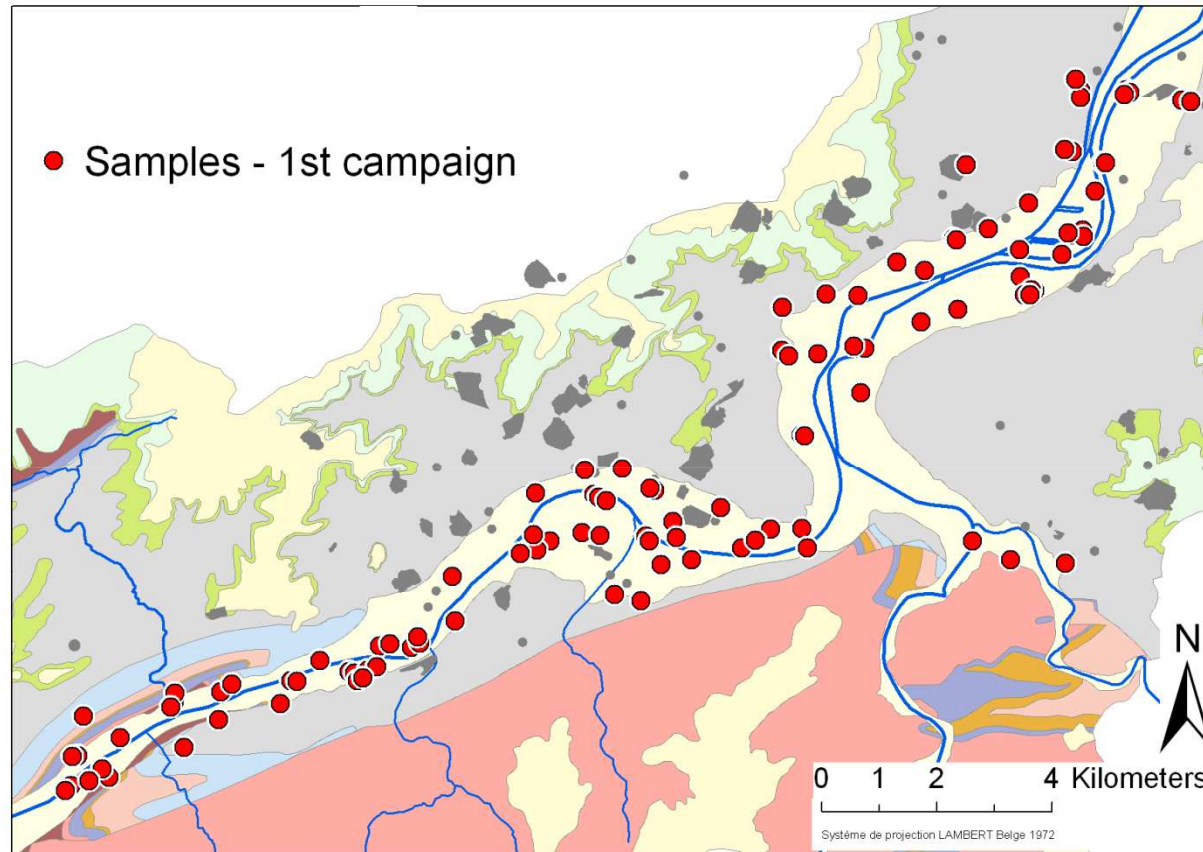


Sulfate is both

- typical pollutant of the aquifer
- tracer of the possible contamination sources

Focus on this compound

1st campaign – 90 groundwater samples

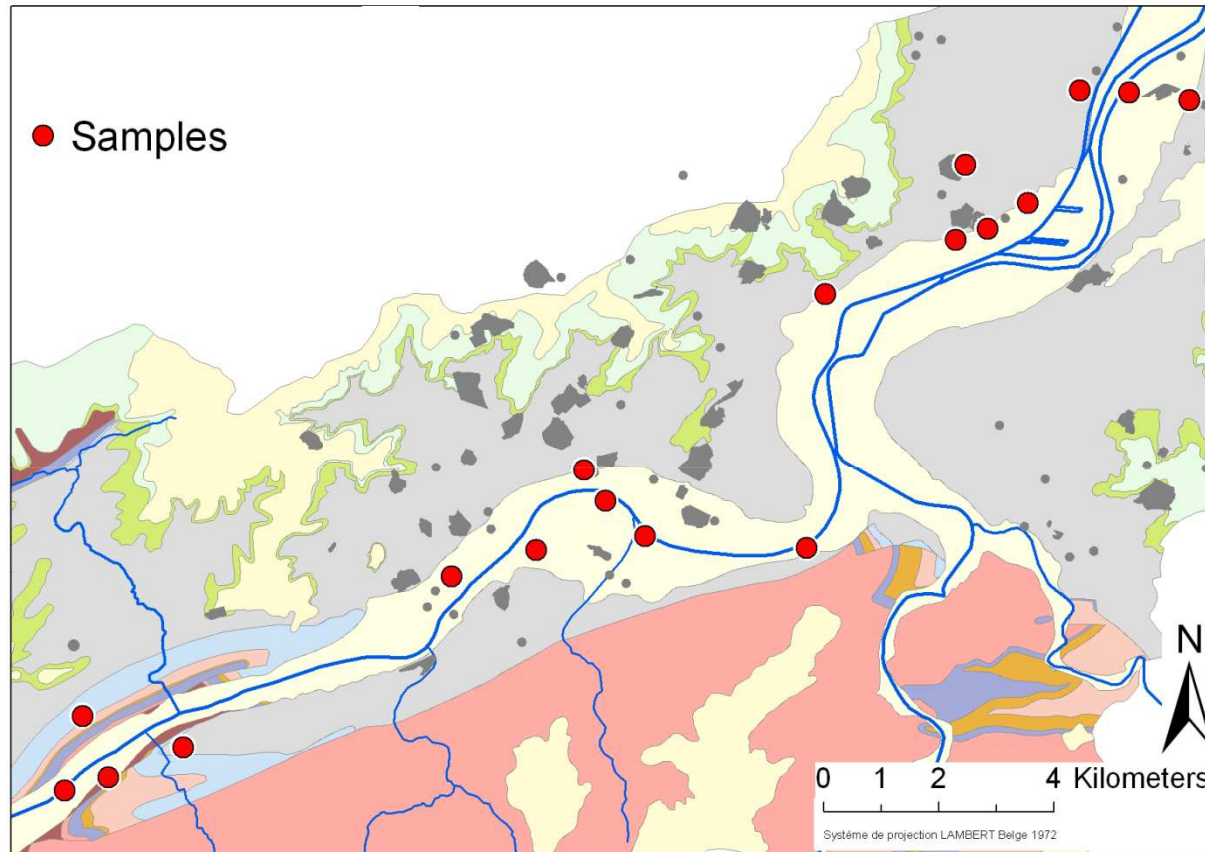


Major and minor compounds

+ organic and inorganic contaminants

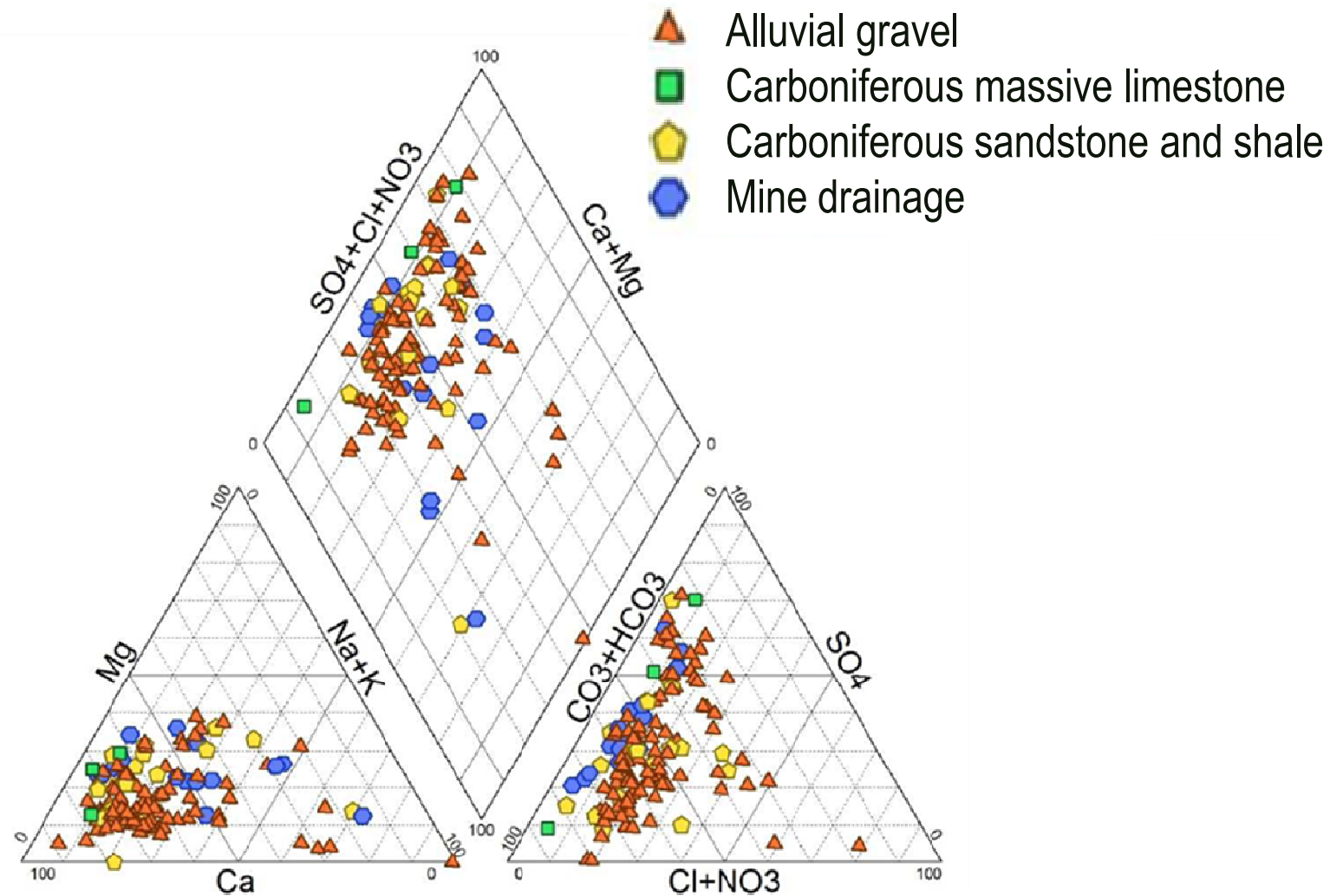
usually observed in such urban environments 8

2nd campaign – 19 groundwater samples

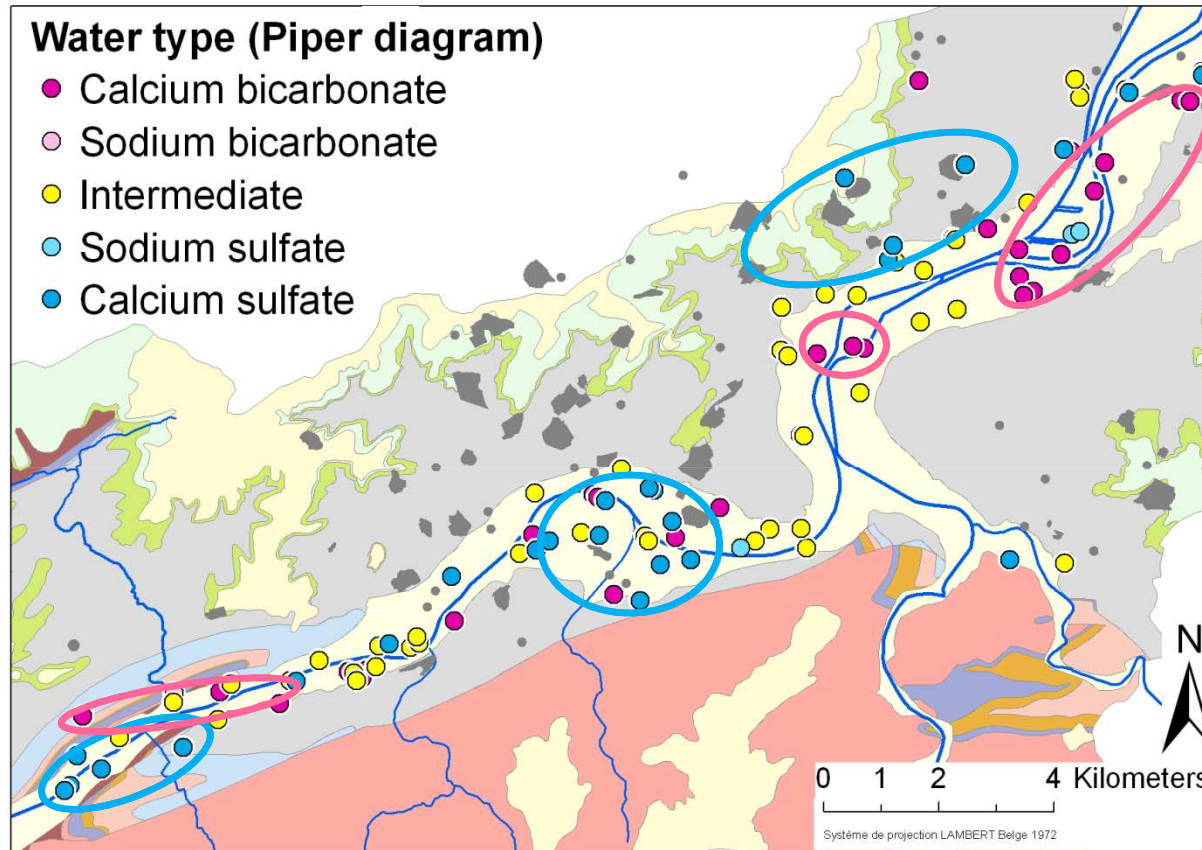


Isotopic analyses ^{34}S and ^{18}O of sulfate
+ Major compounds

Calcium sulfate or calcium bicarbonate types



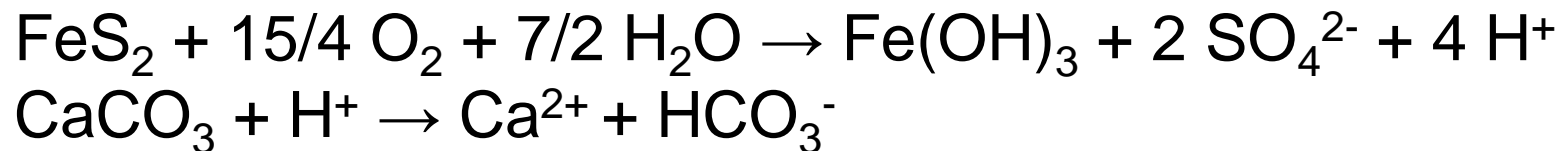
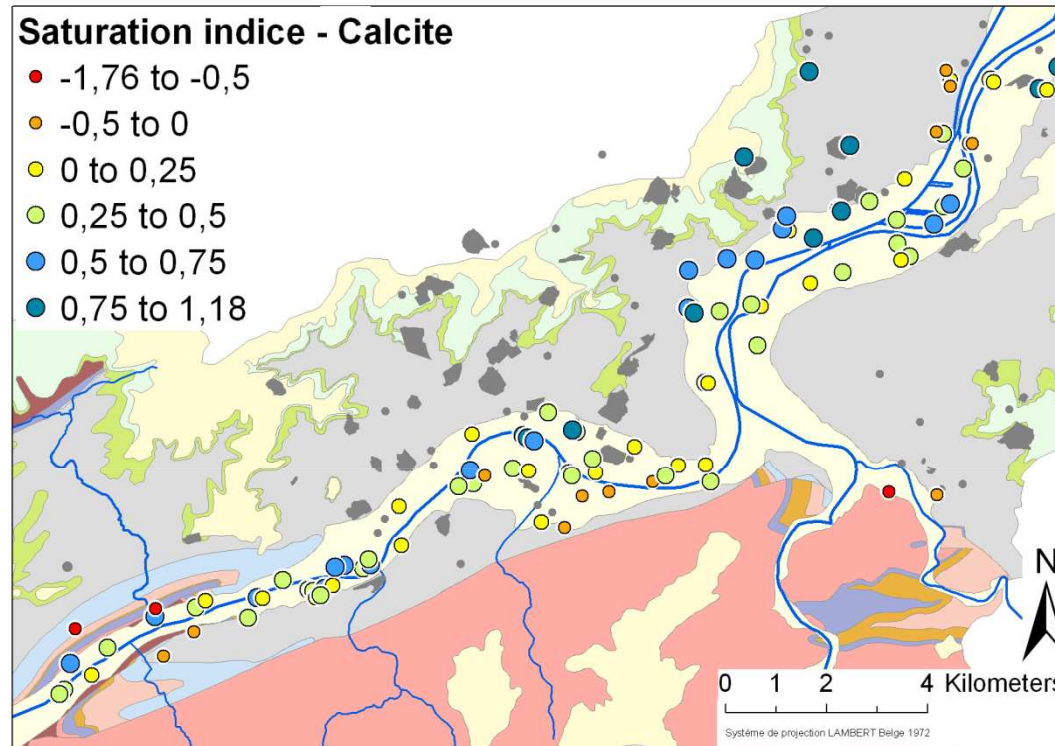
Cartography of the water types (Piper diagram)



3 major areas of calcium sulfate type

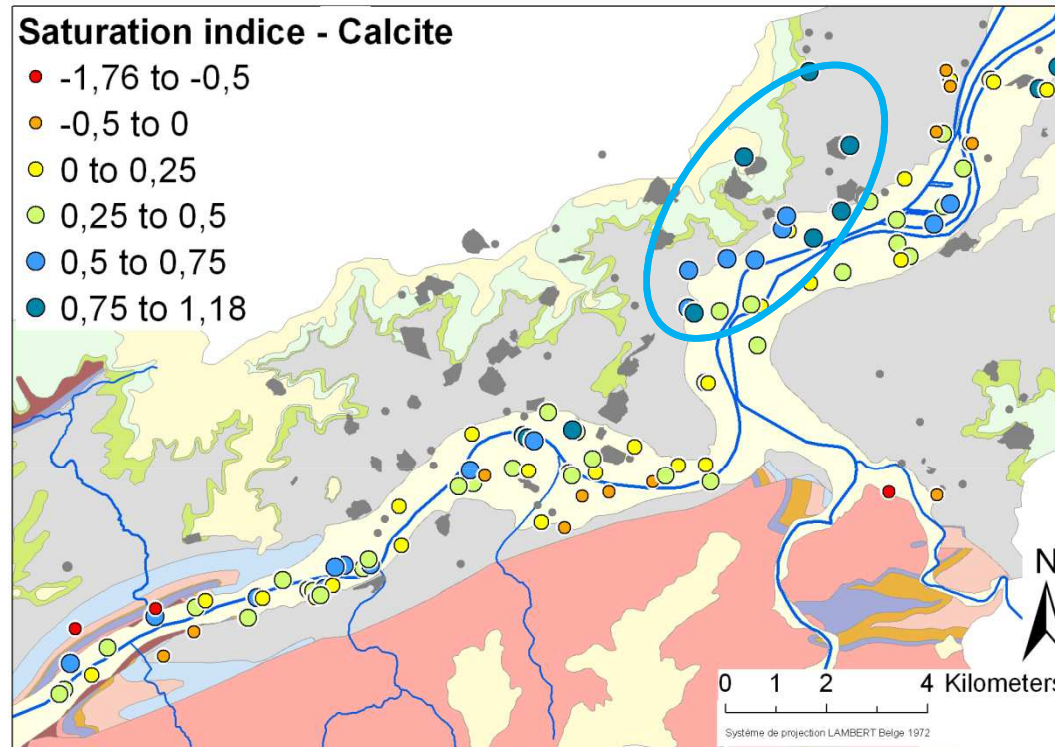
3 major areas of calcium bicarbonate type

Changes in groundwater composition in relation with acid mine drainage

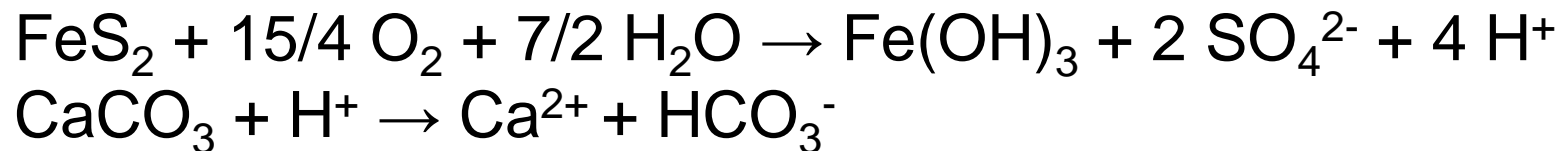
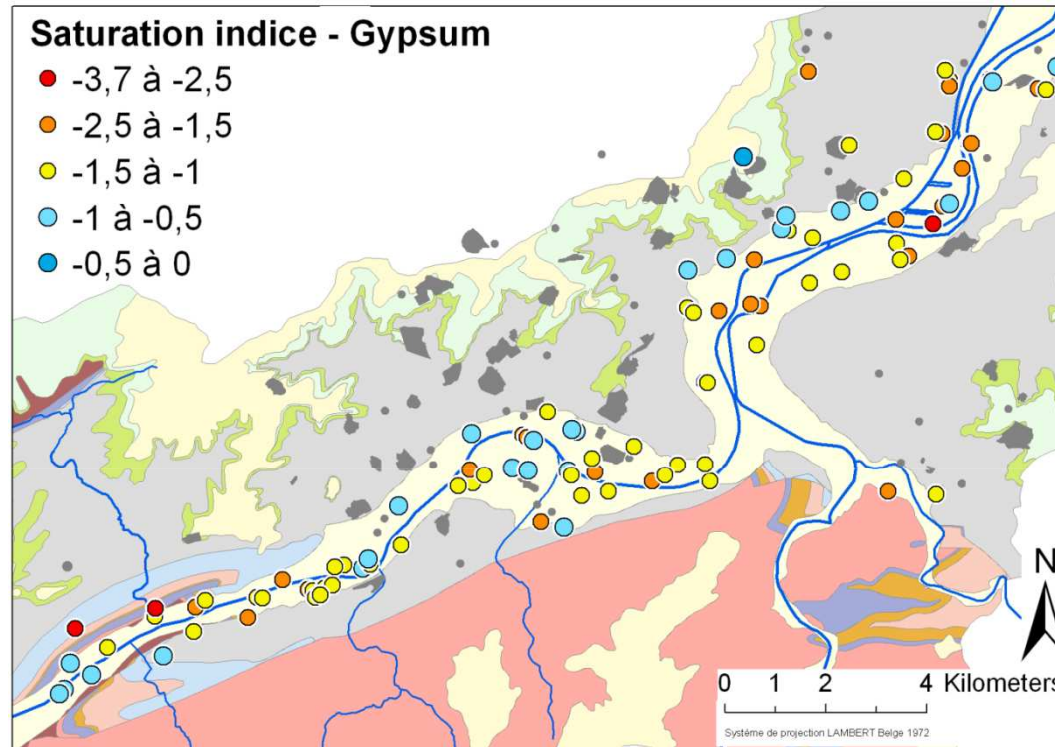


Changes in groundwater composition in relation with acid mine drainage

SI >> 0

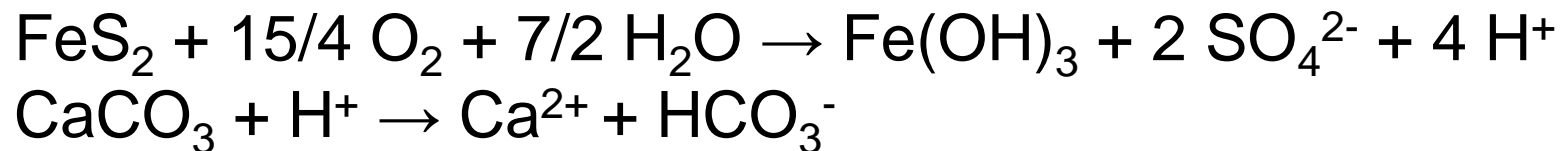
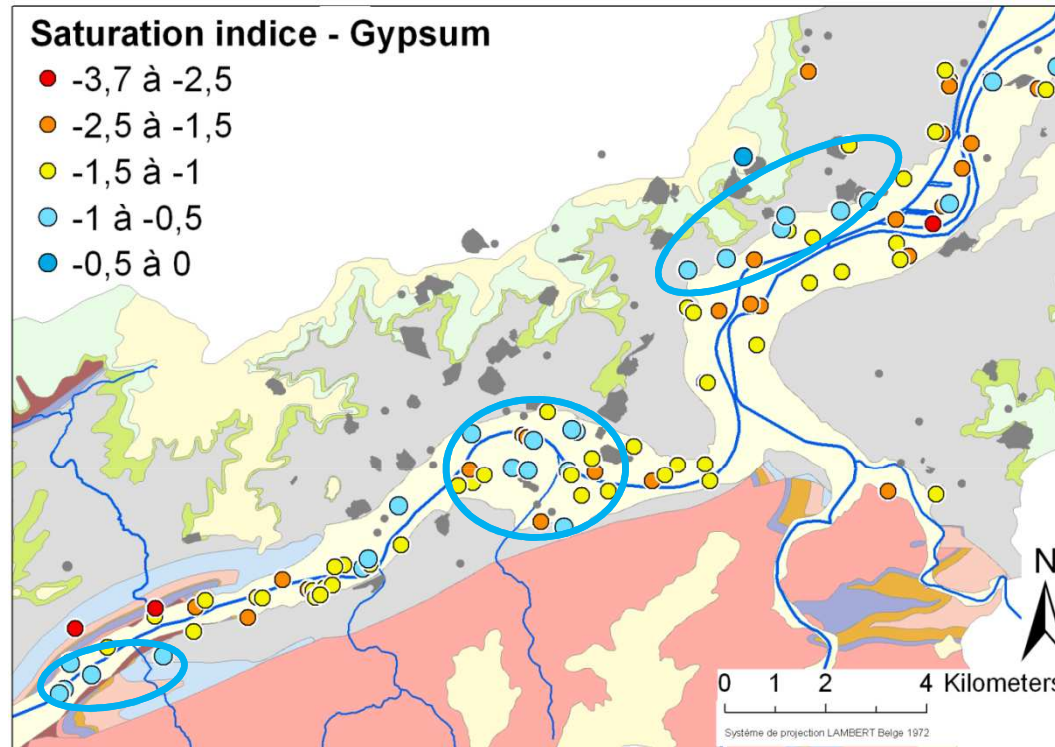


Changes in groundwater composition in relation with acid mine drainage

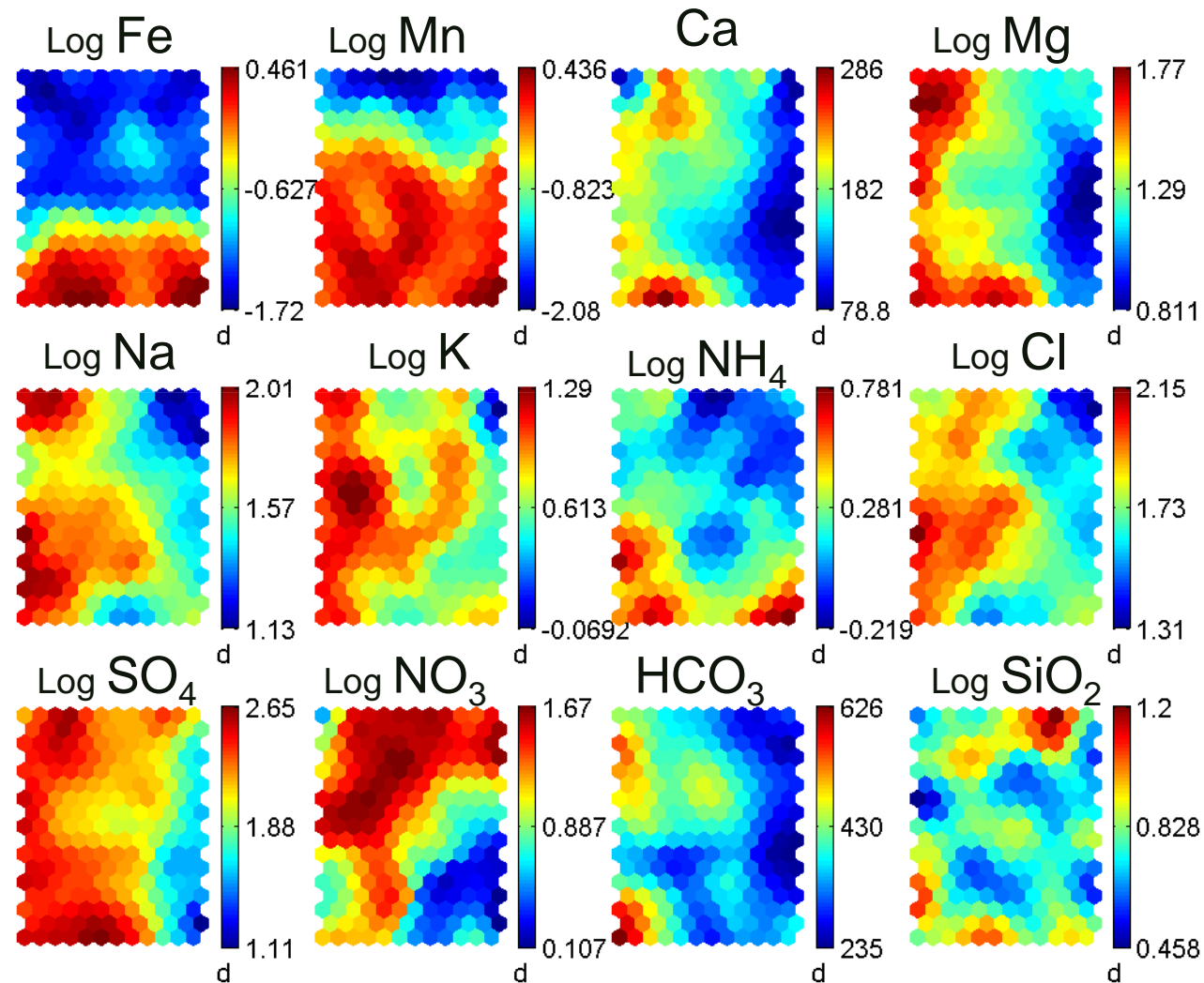


Changes in groundwater composition in relation with acid mine drainage

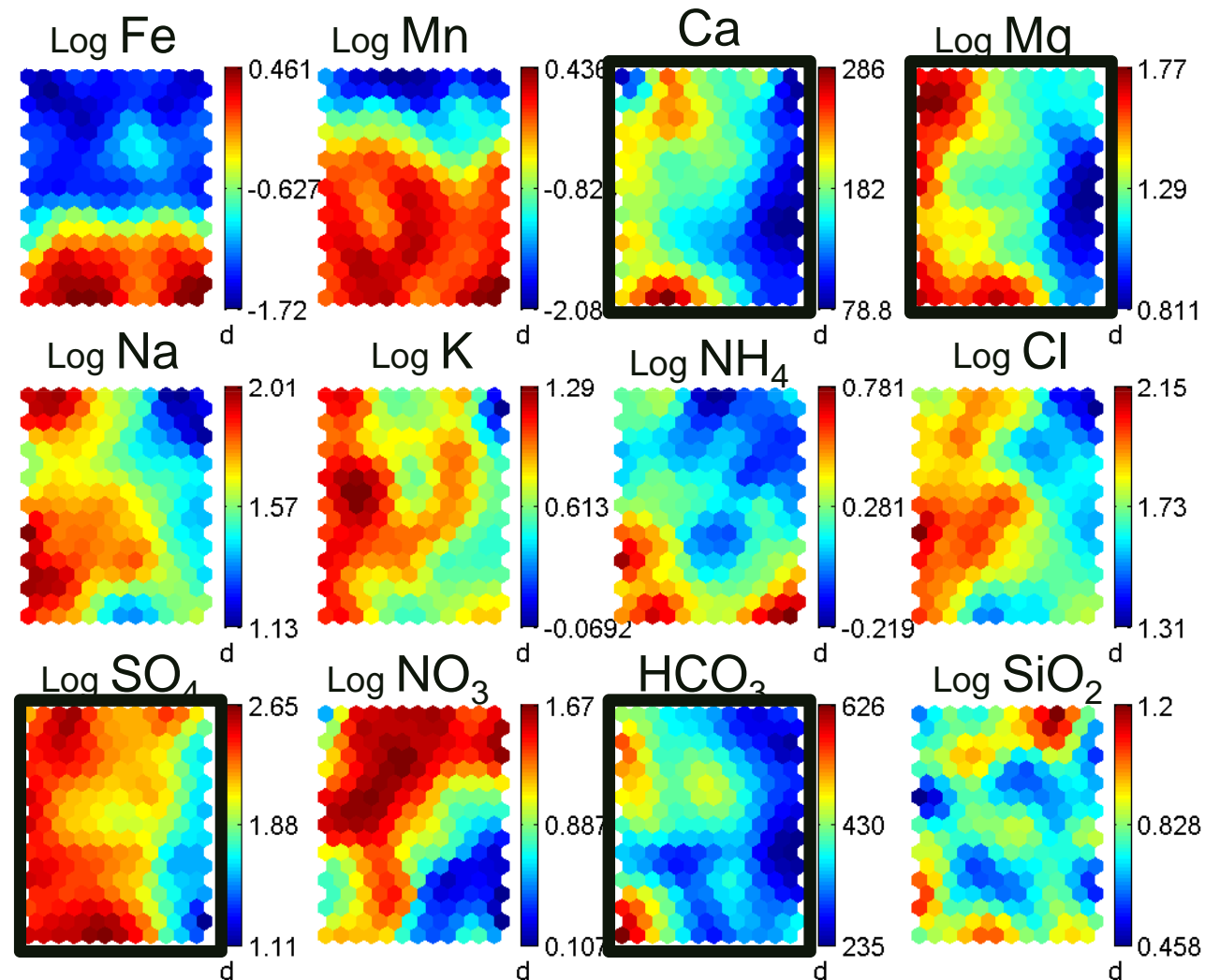
SI \approx 0



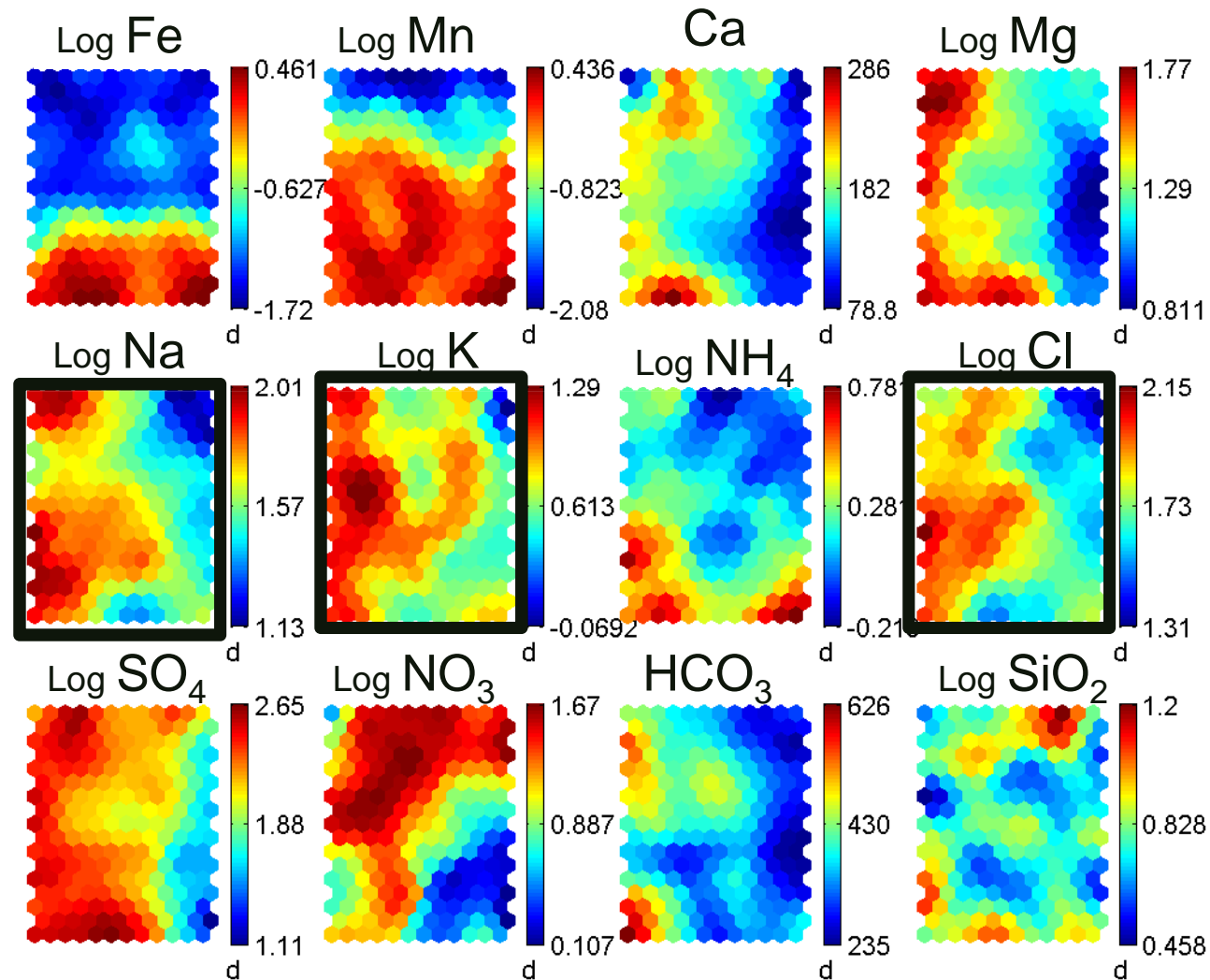
A non-linear multivariate statistical method is applied (Self Organizing Maps)



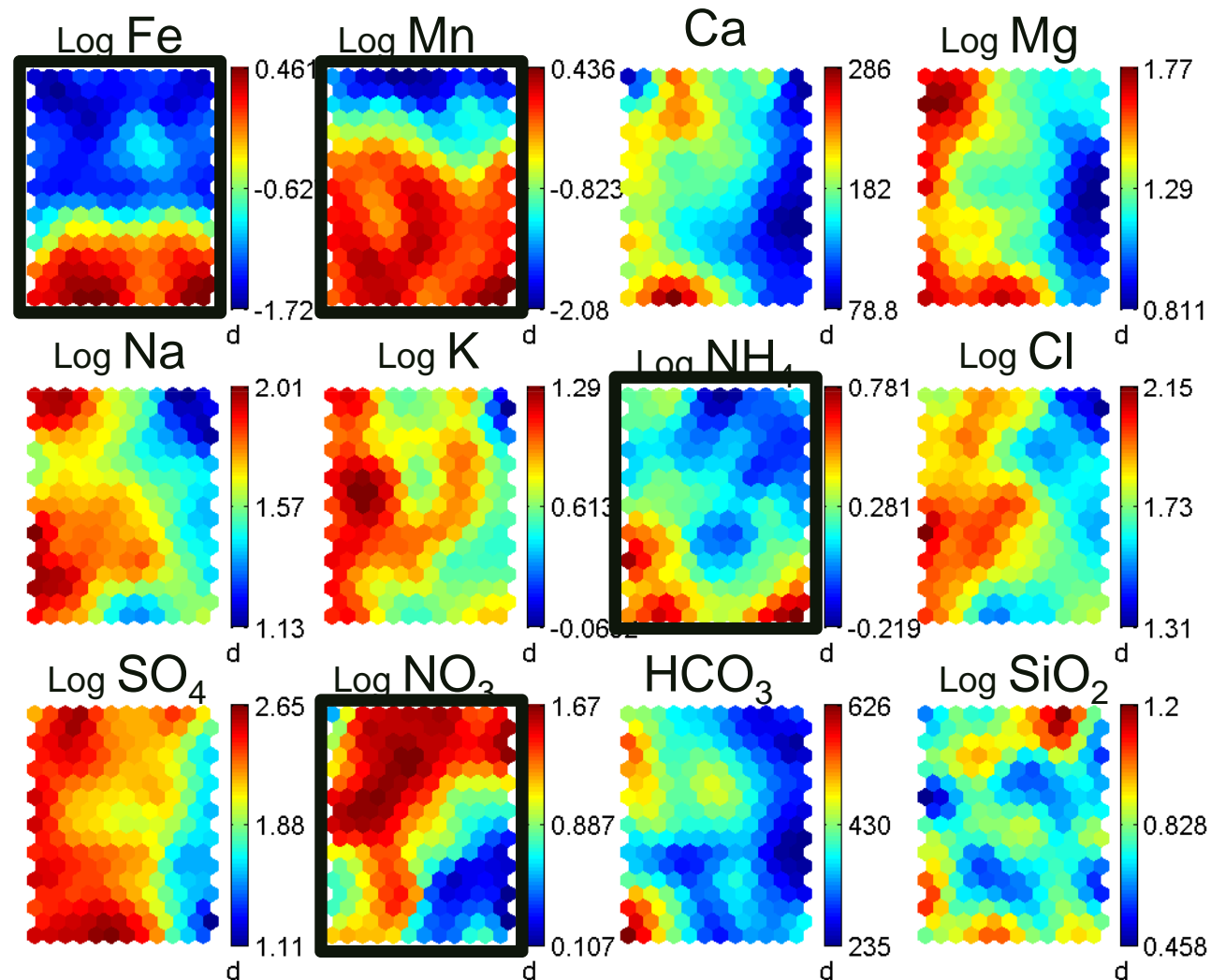
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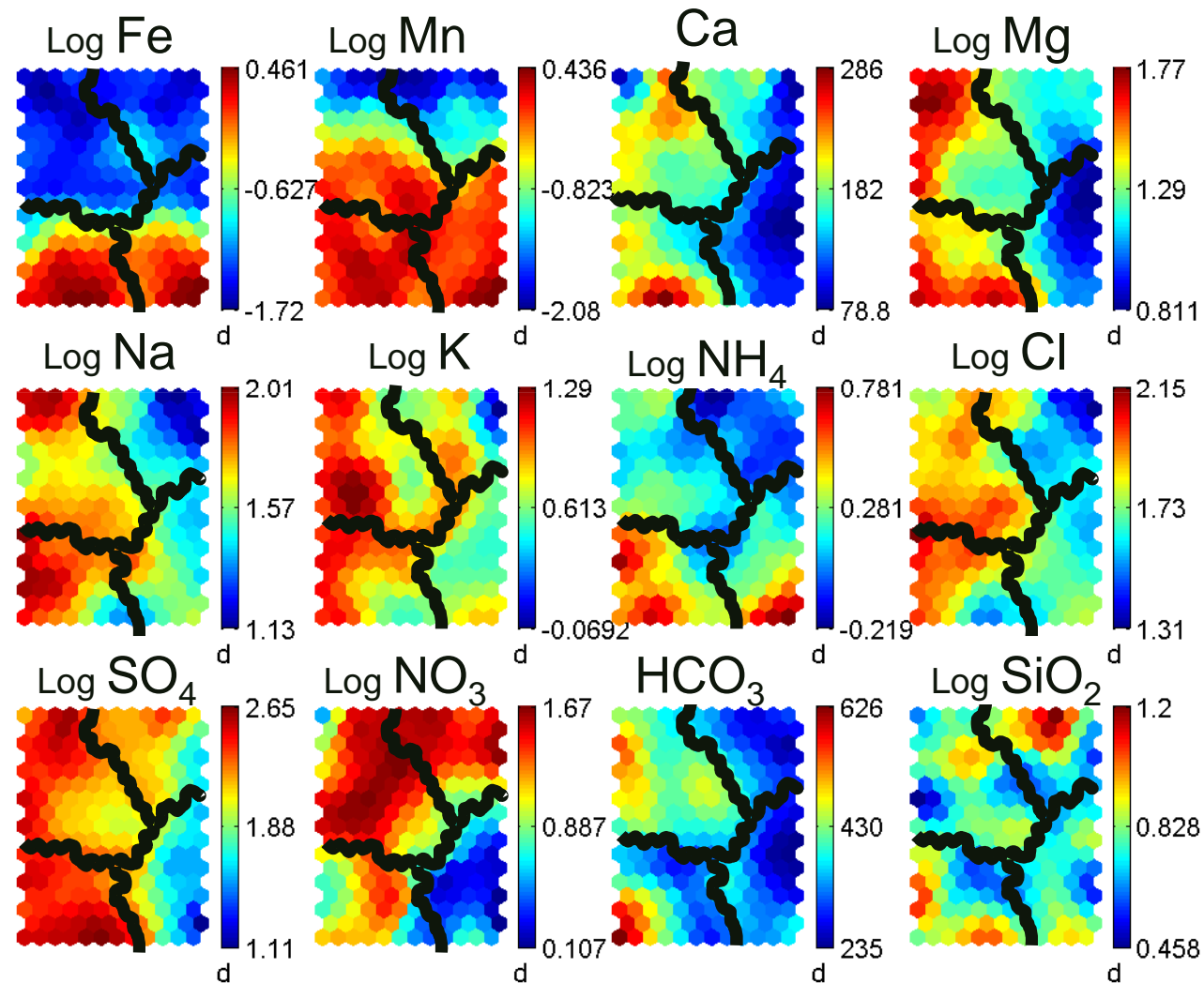
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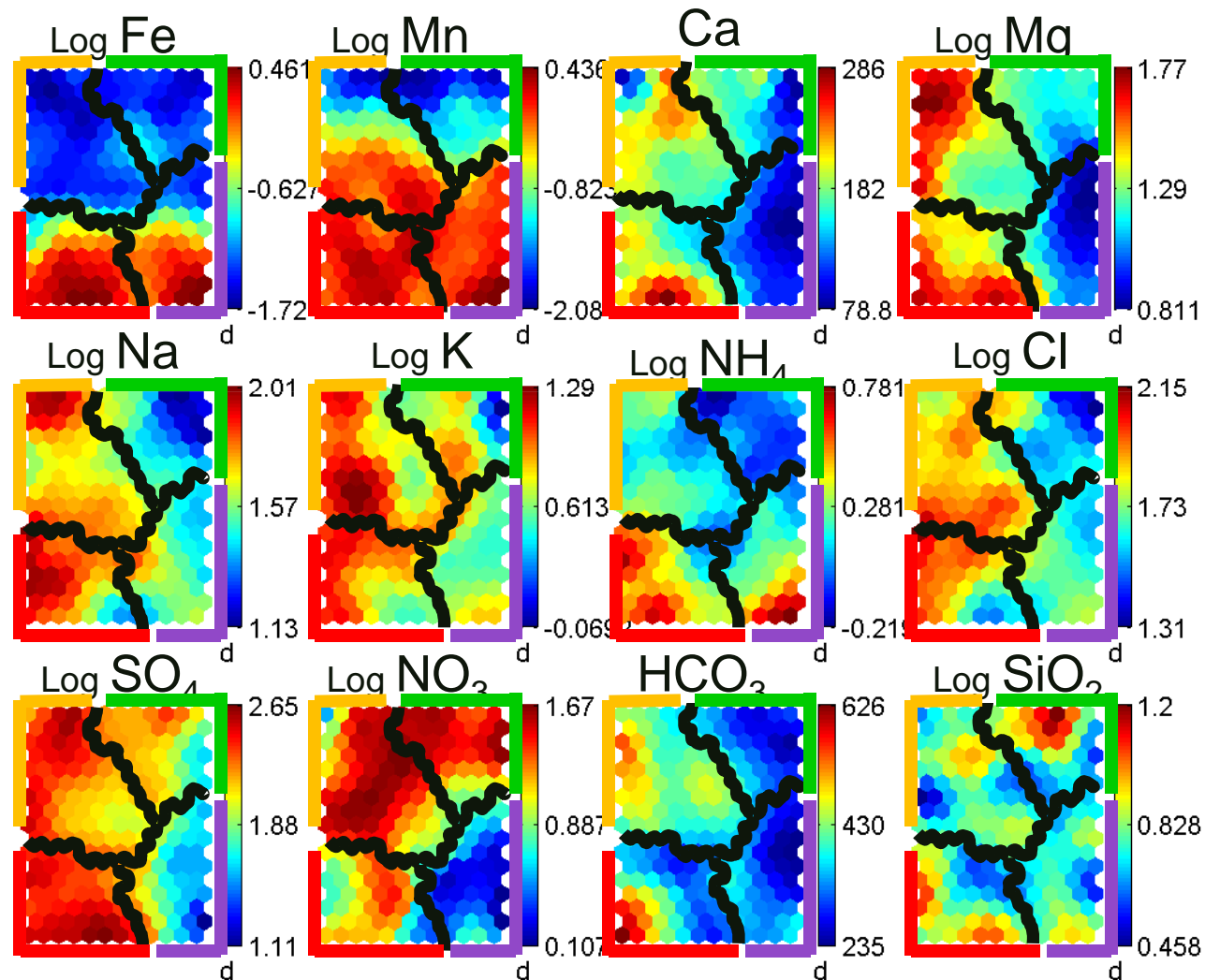
A non-linear multivariate statistical method is applied (Self Organizing Maps)



Non-linear multivariate statistics (Self Organizing Maps) divides the data set into 4 clusters



Non-linear multivariate statistics (Self Organizing Maps) divides the data set into 4 clusters



Non-linear multivariate statistics (Self Organizing Maps)

divides the data set into 4 clusters

Concentration + high +- medium - low - - very low

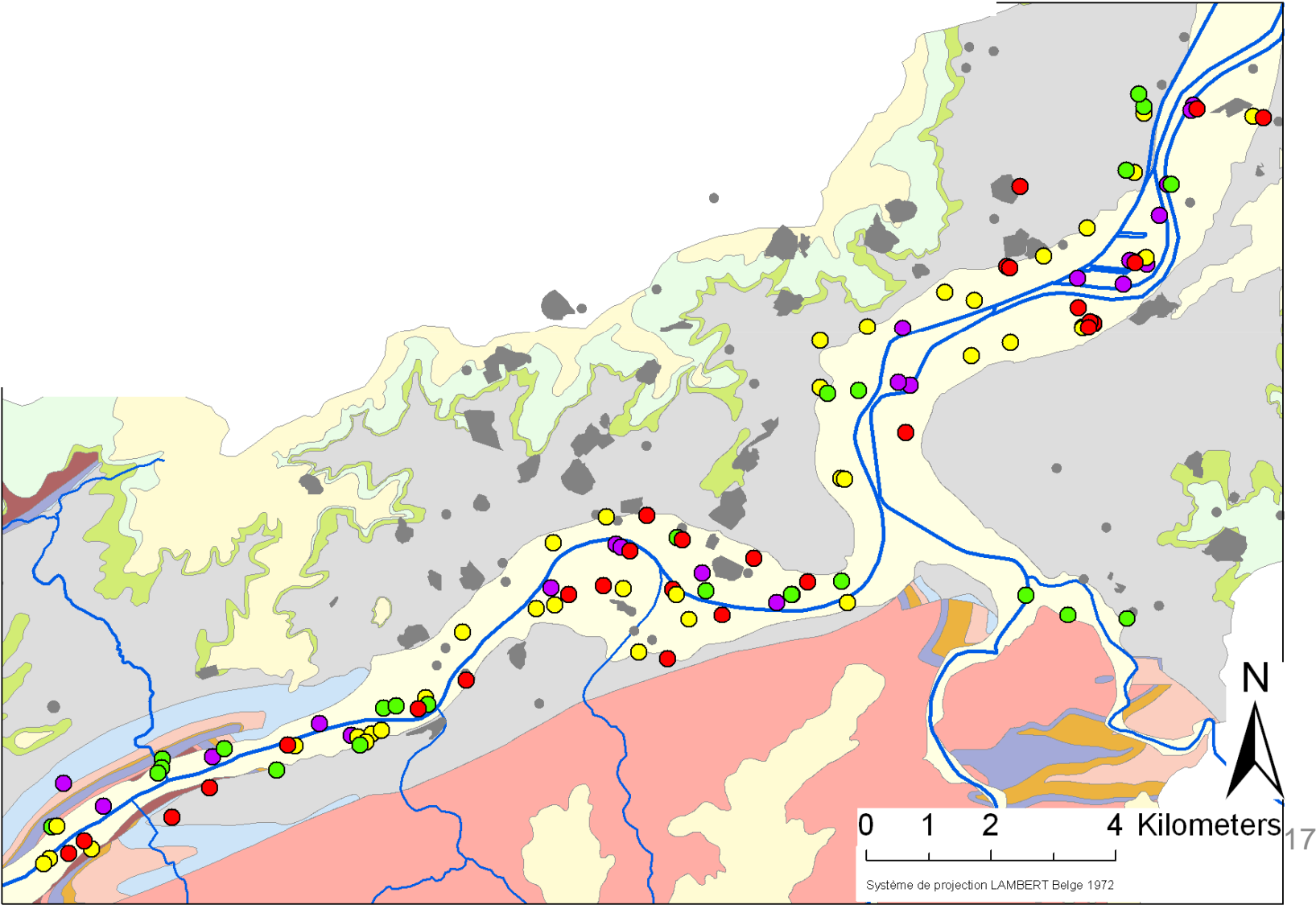
Fe	+
Mn	+
NH ₄	+
NO ₃	-
Ca	+
Mg	+
HCO ₃	+
SO ₄	+
Na	+
K	+
Cl	+

Fe	-
Mn	+-
NH ₄	+-
NO ₃	+
Ca	+
Mg	+
HCO ₃	+
SO ₄	+
Na	+
K	+
Cl	+

Fe	+
Mn	+
NH ₄	+
NO ₃	- -
Ca	- -
Mg	- -
HCO ₃	-
SO ₄	- -
Na	-
K	-
Cl	-

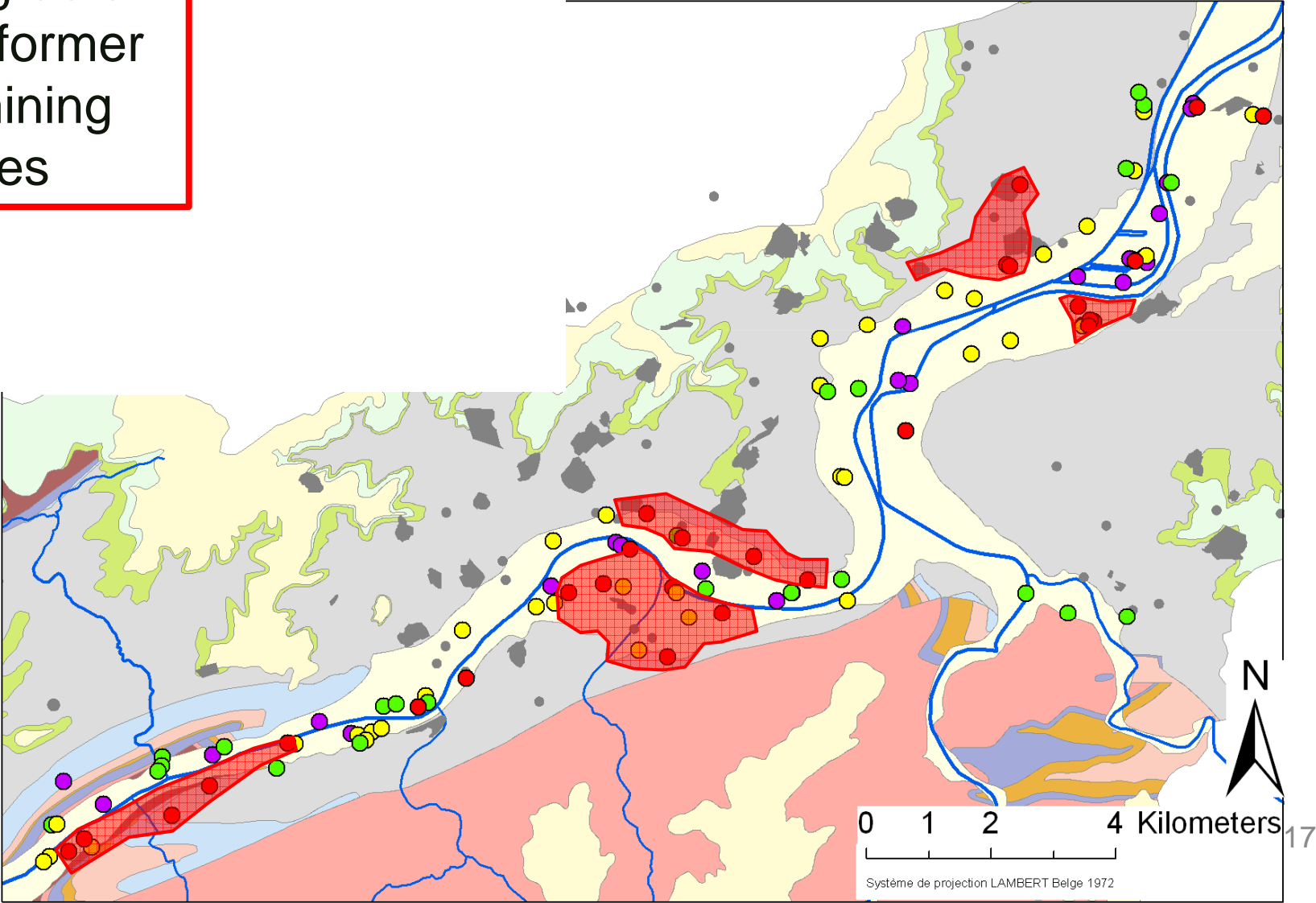
Fe	-
Mn	- -
NH ₄	-
NO ₃	+
Ca	-
Mg	+-
HCO ₃	-
SO ₄	+-
Na	- -
K	- -
Cl	- -

The groundwater body divided from the 4 clusters



The groundwater body divided from the 4 clusters

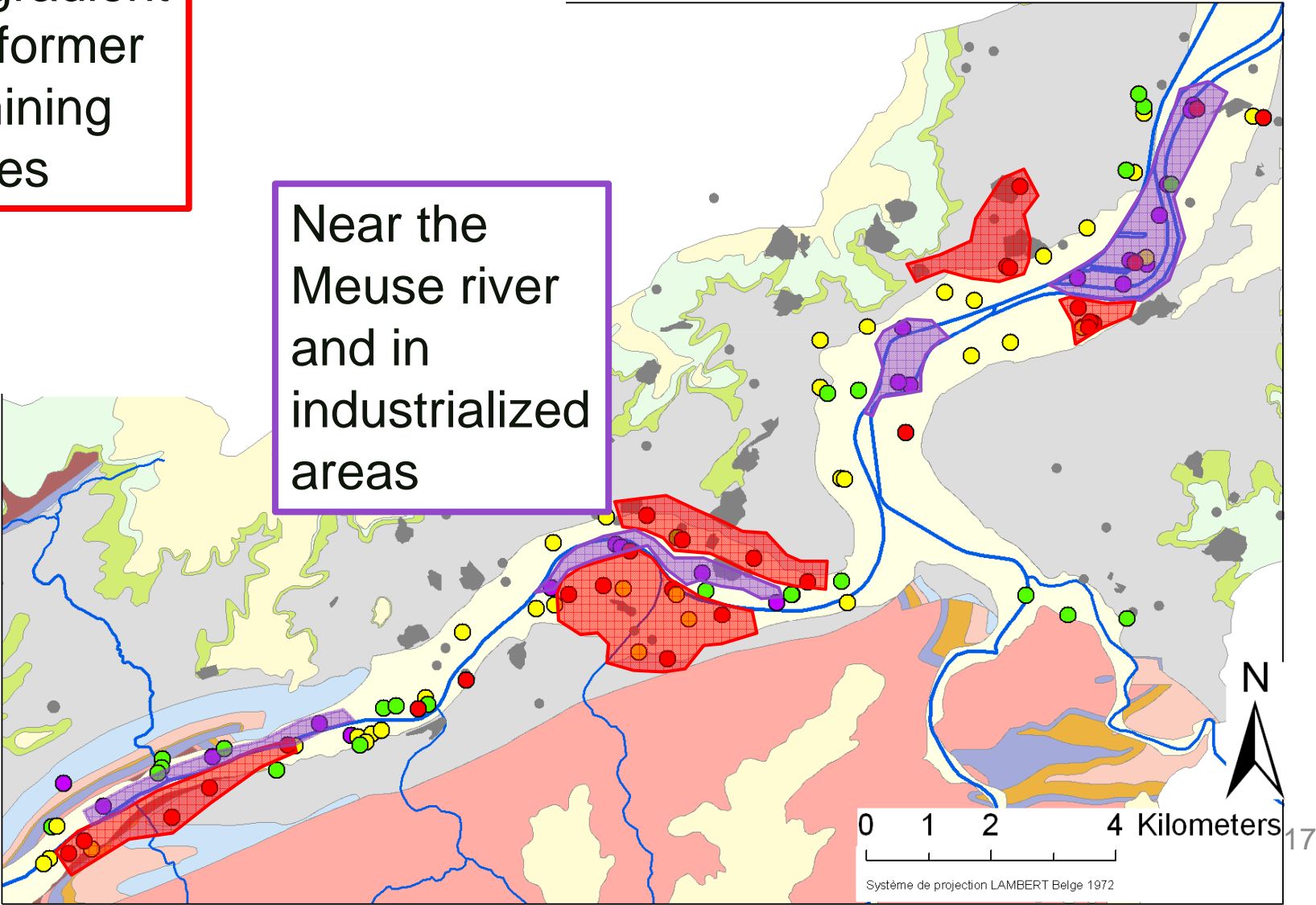
Downgradient
of the former
coal mining
activities



The groundwater body divided from the 4 clusters

Downgradient of the former coal mining activities

Near the Meuse river and in industrialized areas

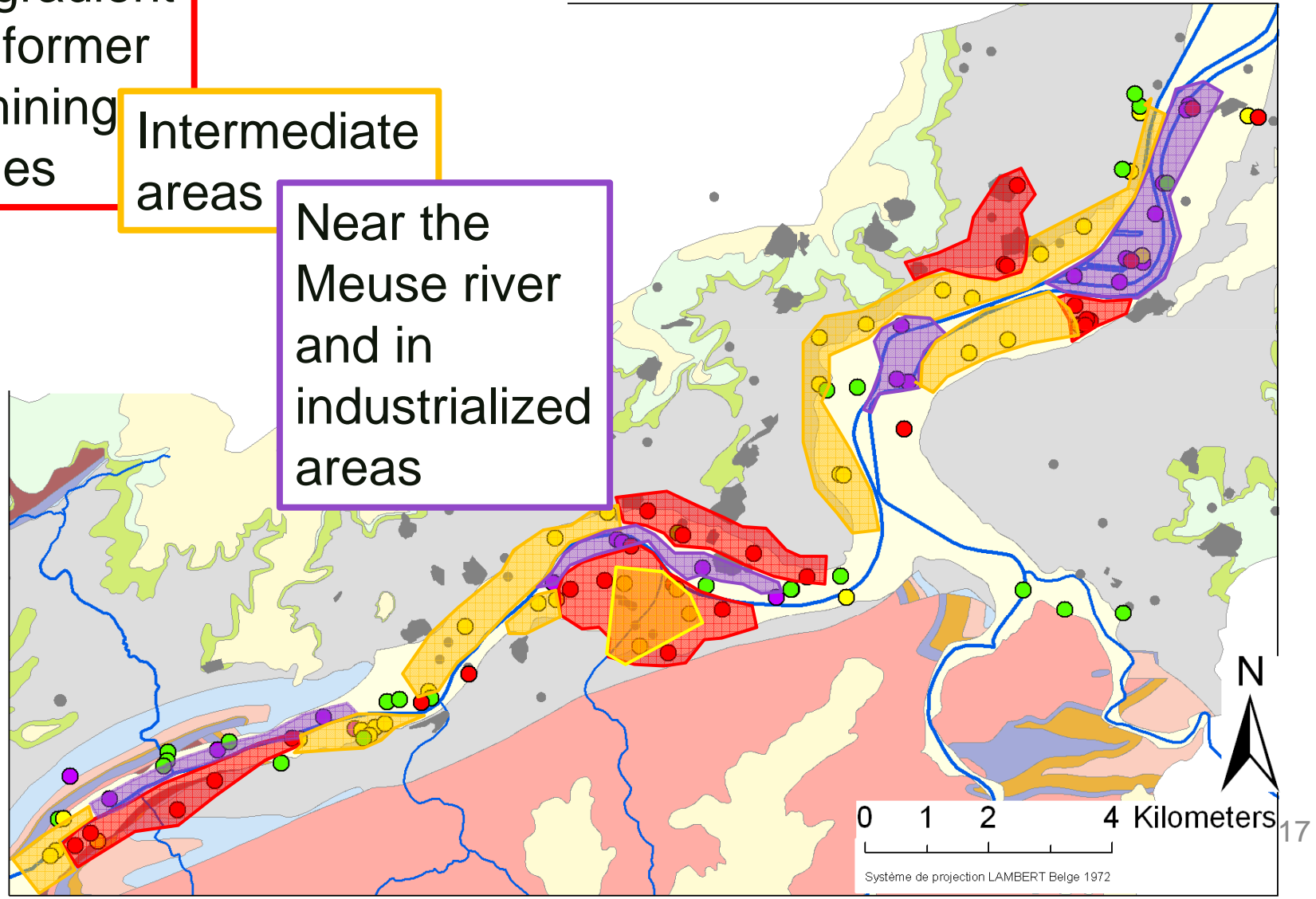


The groundwater body divided from the 4 clusters

Downgradient of the former coal mining activities

Intermediate areas

Near the Meuse river and in industrialized areas



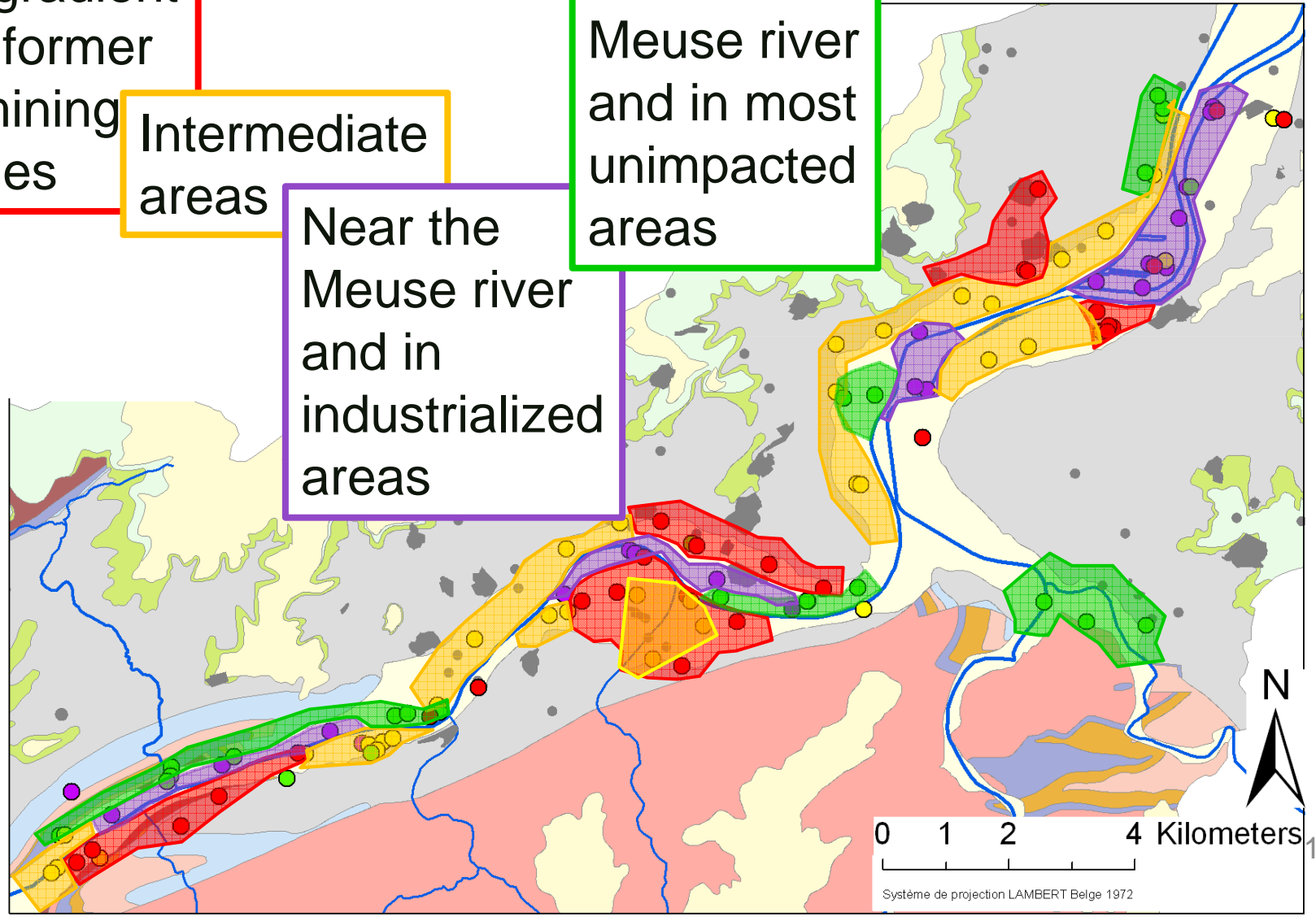
The groundwater body divided from the 4 clusters

Downgradient of the former coal mining activities

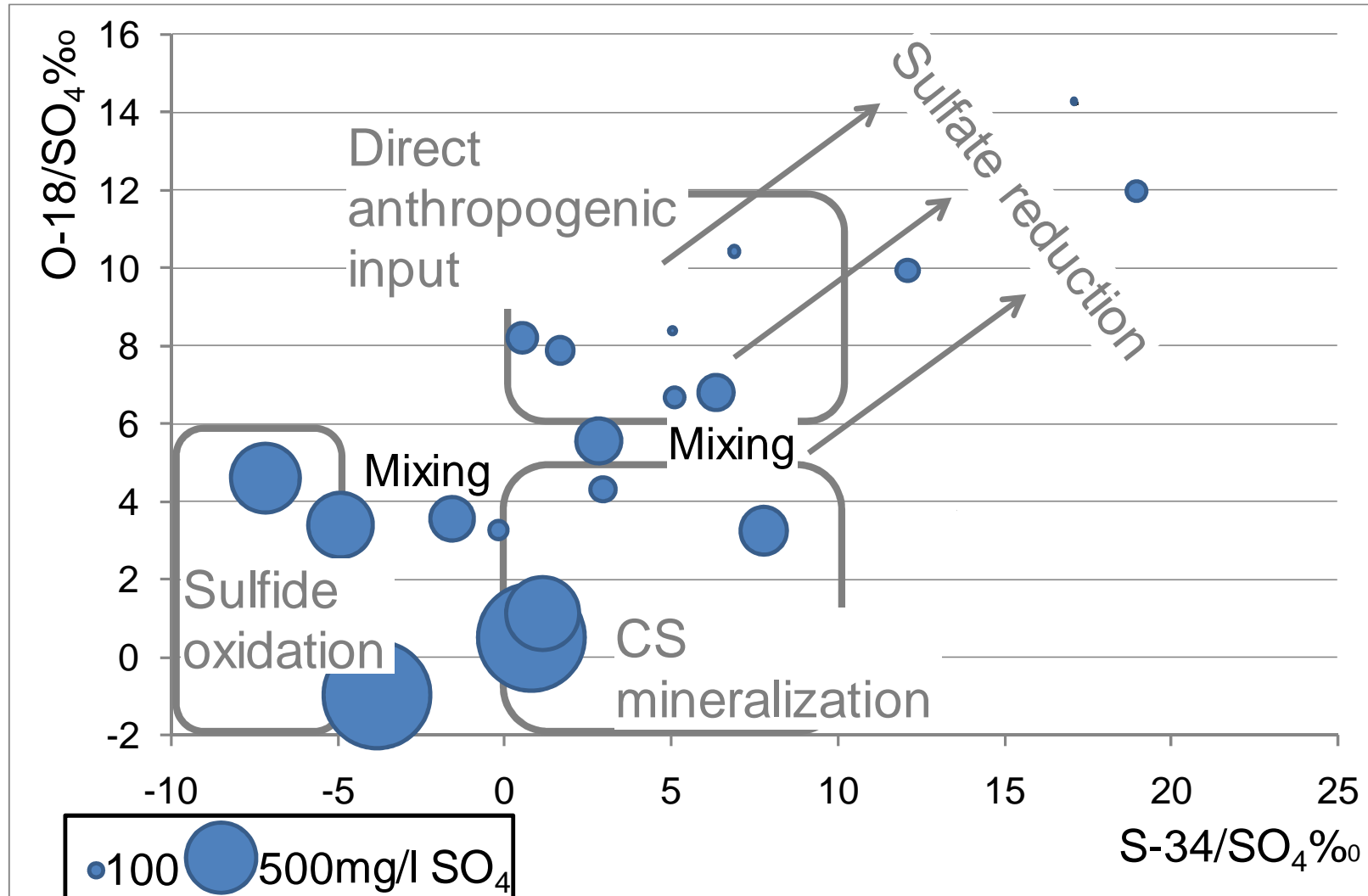
Intermediate areas

Near the Meuse river and in industrialized areas

Near the Meuse river and in most unimpacted areas



SO₄ origin based on the isotopic analyses (2nd sampling campaign - 19 groundwater samples)



(from Knöller, 2005)

Conclusion of the isotopic analysis

SO ₄ concentrations	Sulfur isotopic ratio	SO ₄ origin
High	Low	SO ₄ naturally present : mineralisation or oxydation
Low	High	Anthropogenic pollution or SO ₄ reduction

⇒ The highest SO₄ concentrations associated with natural or regional sources of contamination

Natural or anthropogenic origin ?

Many sources of contamination contribute to poor quality

- brownfields
- urban waste
- atmospheric deposits
related to industrial emissions
- subsurface acid drainage
from former coal mining activities

Further investigations

Complementary sampling campaign
for isotopic analyses

to better characterize the various sources
of these contaminants (end-members)

and their respective contribution
to the global qualitative state
of the alluvial aquifer

Hydrogeology 
Environmental Geology

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