



Université
de Liège



Multivariate statistics
to understand
the geochemical processes
induced by groundwater pollution
Multi-scale applying

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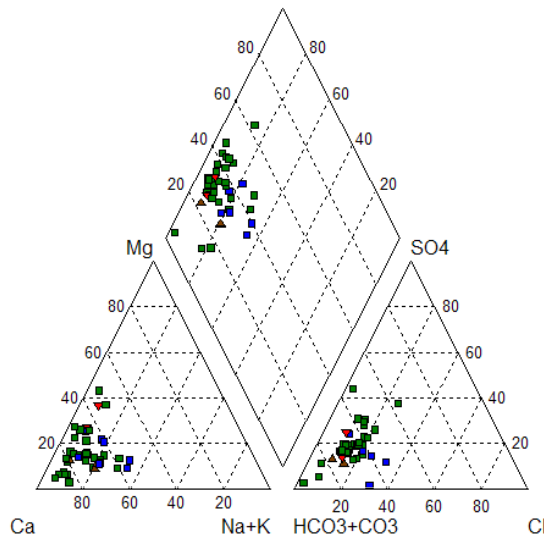
Hydrogeochemical data set :

Many sampling points & many parameters

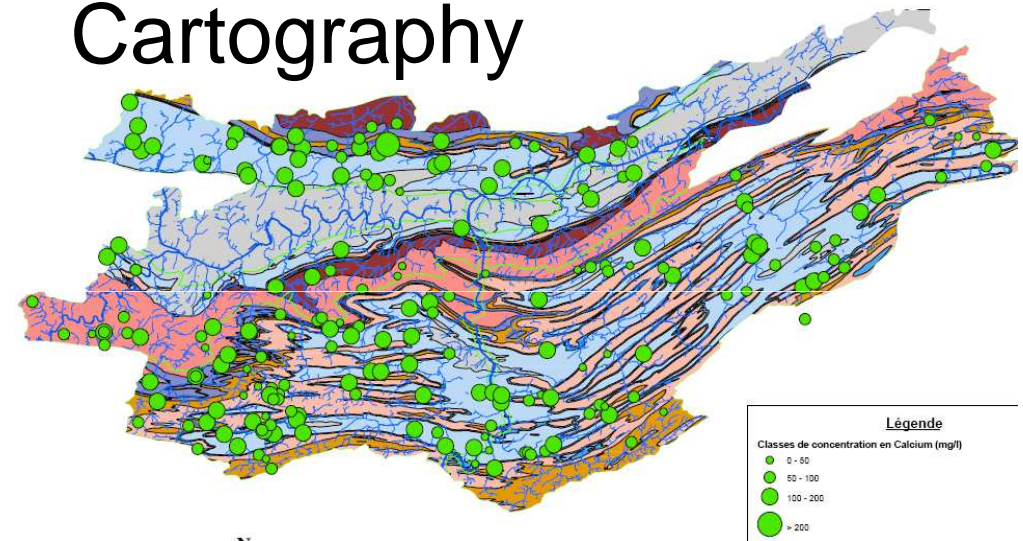
num	Ca	Mg	Na	K	Fe	Mn	NH4	Cl	SO4	NO2	NO3	CO3	HCO3	SiO2	F	H2PO4	B	Al	Sb	As	Ba	Be	Cd	Cr	Co	Cu	Hg	Mo	Ni	Pb	Se	V	Zn	
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
625	328,269	44,706	81,967	2,79	0,115	0,012	2,834	110,806	653,304	<= 0,20	22,063	5,711	319,828	3,577	< 0,20	< 0,20	64	< 5,0	0,18	3,4	40	< 0,10	2,3	1,1	< 0,50	1,2	< 0,020	< 0,60	1,1	1,3	2,5	< 2,5	340	
912	148,064	15,425	23,759	3,82	0,016	0,246	0,978	47,169	122,584	<= 0,40	33,282	2,816	307,513	13,42	<= 0,40	<= 0,40	100	14	0,18	2,5	32	< 0,10	< 0,040	6	< 0,50	1,4	< 0,020	1,3	1,4	< 0,20	0,9	< 2,5	< 4,0	
914	216,374	58,084	23,163	3,11	6,53	1,31	1,808	16,731	535,568	<= 0,40	<= 0,60	2,722	258,923	15,69	<= 0,40	<= 0,40	62	13	0,13	2,6	11	< 0,10	< 0,040	< 0,50	2	< 0,40	< 0,020	0,7	5,2	< 0,20	< 0,20	< 2,5	< 4,0	
944	221,826	46,781	23,329	2,26	1,24	0,123	2,329	82,75	413,684	<= 0,40	4,076	2,892	245,144	7,129	<= 0,40	<= 0,40	53	< 5,0	0,23	5,7	31	< 0,10	0,13	0,53	< 0,40	< 0,020	< 0,60	< 1,0	< 0,20	0,75	< 2,5	55		
907	126,167	5,45	19,167	4,32	0,039	0,601	<= 0,20	37,938	90,792	<= 0,40	3,722	3,303	273,615	12,11	0,55	<= 0,40	180	< 5,0	0,28	1,3	25	< 0,10	0,41	6,7	0,51	38	< 0,020	1	2,1	9,3	0,34	< 2,5	40	
656	140,597	26,433	55,288	15,421	0,063	1,96	0,842	66,681	289,28	<= 0,20	5,091	0,266	231,122	8,12	< 0,20	< 0,20	120	12	< 0,10	1,3	22	< 0,10	0,15	8,2	1,1	< 0,40	< 0,020	0,67	1,8	< 0,20	0,8	< 2,5	5,1	
657	207,229	69,48	53,405	7,432	0,03	1,87	<= 0,10	101,364	427,239	<= 0,20	31,429	0,802	356,834	11,47	< 0,20	< 0,20	72	12	< 0,10	1,8	21	< 0,10	1,9	0,69	1,1	< 0,40	< 0,020	< 0,60	3	0,37	0,94	< 2,5	110	
658	239,635	53,437	48,148	7,053	0,067	0,178	<= 0,10	100,832	412,153	<= 0,20	40,866	0,839	348,238	9,985	< 0,20	< 0,20	60	22	0,13	1,9	20	< 0,10	0,27	< 0,50	0,67	< 0,40	< 0,020	< 0,60	1,2	< 0,20	3,4	< 2,5	370	
659	139,754	54,216	439,51	10,172	3,25	0,778	2,277	154,719	353,571	<= 0,20	<= 0,30	4,492	1204,079	7,535	< 0,20	< 0,20	150	47	< 0,10	3,1	41	< 0,10	< 0,040	7,4	< 0,50	< 0,40	< 0,020	< 0,60	< 1,0	< 0,20	< 0,20	< 2,5	< 4,0	
660	235,479	55,248	235,747	13,731	0,027	0,798	<= 0,10	79,565	695,962	<= 0,20	38,469	0,843	529,916	2,435	< 0,20	< 0,20	150	36	< 0,10	1,9	19	< 0,10	0,083	0,54	< 0,50	< 0,40	< 0,020	< 0,60	1,2	< 0,20	0,68	< 2,5	< 4,0	
661	204,381	24,652	43,689	1,94	0,023	0,007	<= 0,10	92,712	199,068	<= 0,20	46,182	0,945	366,284	8,38	< 0,20	< 0,20	190	10	< 0,10	1,4	47	< 0,10	< 0,040	2,1	< 0,50	1,2	< 0,020	< 0,60	1,7	< 0,20	0,95	< 2,5	4,4	
662	172,65	17,253	58,314	1,97	0,027	2,15	<= 0,10	142,1	58,108	<= 0,20	12,125	0,634	398,575	7,836	< 0,20	< 0,20	270	14	< 0,10	2,7	44	< 0,10	0,1	7,2	0,56	2	< 0,020	< 0,60	4,8	0,24	< 0,20	2,5	11	
663	180,389	39,843	34,419	14,618	0,189	0,476	1,201	57,649	212,786	<= 0,20	<= 0,30	2,218	430,725	1,631	< 0,20	< 0,20	150	11	< 0,10	2,1	34	< 0,10	0,047	7,1	< 0,50	0,65	< 0,020	< 0,60	< 1,0	< 0,20	0,56	< 2,5	< 4,0	
956	156,104	16,969	45,797	11,665	0,198	1,17	0,835	50,103	177,514	<= 0,20	<= 0,30	2,674	367,625	5,054	< 0,20	< 0,20	86	< 5,0	< 0,10	1,2	45	< 0,10	< 0,040	6,5	0,52	< 0,40	< 0,020	< 0,60	1,0	< 0,20	< 0,20	< 2,5	< 4,0	
957	62,18	6,002	24,855	2,59	0,3	0,632	1,055	28,273	28,958	<= 0,20	<= 0,30	1,042	197,774	4,786	0,67	1,39	25	< 5,0	< 0,10	6,7	93	< 0,10	< 0,040	< 0,50	< 0,50	< 0,40	< 0,020	2,3	2,5	< 0,20	< 0,20	< 2,5	< 4,0	
958	284,046	62,176	53,145	18,765	1,22	4,43	7,68	63,778	604,07	<= 0,20	<= 0,30	2,077	432,249	6,688	< 0,20	< 0,20	200	< 5,0	0,15	4,3	57	< 0,10	< 0,040	1,4	7,6	< 0,40	< 0,020	1,1	8,2	< 0,20	< 0,20	< 2,5	< 4,0	
959	268,32	9,2	7,954	23,505	0,1	0,035	<= 0,20	12,523	486,431	<= 0,20	17,19	1,721	206,126	33,1	< 0,20	< 0,20	100	< 5,0	0,72	11	12	< 0,10	0,049	9,5	< 0,50	1,1	< 0,020	8	< 1,0	< 0,20	4,8	43	< 4,0	
960	110,963	14,67	40,296	4,17	0,841	1,2	1,774	45,323	71,306	<= 0,20	1,063	2,542	333,728	3,3	< 0,20	< 0,20	96	< 5,0	0,13	7,5	60	< 0,10	< 0,040	0,82	0,66	< 0,40	< 0,020	1,2	< 1,0	< 0,20	0,47	< 2,5	5	
961	85,922	7,616	32,477	3,48	0,494	0,817	1,884	55,918	28,798	<= 0,20	<= 0,30	3,13	259,288	0,79	< 0,20	< 0,20	49	< 5,0	< 0,10	8,3	200	< 0,10	< 0,040	< 0,50	< 0,50	< 0,40	< 0,020	2	< 1,0	< 0,20	< 0,20	< 2,5	4,7	
962	209,72	25,876	46,069	17,603	0,299	1,9	3,212	63,346	355,717	<= 0,20	8,169	2,849	325,741	0,63	< 0,20	< 0,20	120	7,7	0,27	2,9	170	< 0,10	0,091	0,6	1,6	0,6	< 0,020	4,7	2,5	< 0,20	1,5	2,7	9,1	
963	198,608	115,553	101,316	29,392	0,266	1,2	4,213	157,202	383,548	<= 0,20	<= 0,30	2,933	645,47	1,17	< 0,20	< 0,20	280	< 5,0	0,21	3,7	50	< 0,10	0,14	1	1,7	< 0,40	< 0,020	4,8	5,3	< 0,20	0,86	< 2,5	32	
963	177,189	53,091	167,647	17,766	11,3	4,2	7,387	215,743	238,814	<= 0,20	<= 0,30	2,538	634,961	12,15	< 0,20	< 0,20	170	5,6	0,47	14	290	< 0,10	< 0,040	0,81	0,78	0,61	< 0,020	3,2	2,4	< 0,20	< 0,20	3,7	6	
964	189,475	51,082	89,526	20,903	0,307	0,646	1,777	121,459	195,984	<= 0,20	4,671	3,362	575,28	13,37	0,32	< 0,20	170	< 5,0	0,20	3	55	< 0,10	0,1	8,9	2,3	0,74	< 0,020	3,8	4,6	< 0,20	1,9	< 2,5	23	
612	79,698	6,612	33,766	2,88	8,81	1,44	2,777	114,705	38,12	<= 0,20	<= 0,30	4,12	225,513	2,853	0,65	< 0,20	31	< 5,0	< 0,10	10	160	< 0,10	< 0,040	< 0,50	< 0,50	0,48	< 0,020	2,8	< 1,0	< 0,20	< 0,20	< 2,5	< 4,0	
613	185,263	13,262	68,755	5,857	0,035	2,43	0,3	114,705	125,373	<= 0,20	17,7	4,319	401,28	6,22	< 0,20	< 0,20	420	< 5,0	< 0,10	2,5	49	< 0,10	0,48	0,61	< 0,50	0,81	< 0,020	1,4	2,3	< 0,20	4,3	< 2,5	31	
614	193,3	17,496	44,422	2,54	0,144	0,3	0,3	114,705	133,638	<= 0,20	30,164	3,54	482,46	4,906	< 0,20	< 0,20	160	< 5,0	< 0,10	1,5	21	< 0,10	< 0,040	< 0,50	< 0,50	0,4	< 0,020	< 0,60	1,4	< 0,20	< 0,20	< 2,5	< 4,0	
615	185,187	15,974	62,582	18,737	0,033	0,1	0,1	114,705	127,22	<= 0,20	34,976	4,338	412,63	6,957	< 0,20	< 0,20	170	< 5,0	0,12	2	74	< 0,10	0,26	1,5	< 0,50	2,1	< 0,020	1,6	3,2	< 0,20	0,98	< 2,5	20	
616	167,318	18,61	27,152	7,295	0,148	1,375	28,3	51,132	36,316	<= 0,20	36,316	3,877	377,319	3,37	< 0,20	< 0,20	560	< 5,0	1,6	2,2	100	< 0,10	0,16	0,94	0,50	1,7	< 0,020	1,3	2,7	< 0,20	9,4	< 2,5	23	
617	182,482	23,808	33,779	3,61	0,043	0,287	1,02	46,5	29,392	<= 0,20	36,708	4,551	495,45	3,354	< 0,20	< 0,20	130	< 5,0	0,14	1,8	59	< 0,10	< 0,040	< 0,50	< 0,50	0,61	< 0,020	< 0,60	1,6	< 0,20	1,9	< 2,5	< 4,0	
618	183,517	16,569	90,153	7,184	3,15	3,04	2,292	107,74	146,746	<= 0,20	<= 0,30	3,451	470,26	4,766	< 0,20	< 0,20	96	< 5,0	< 0,10	14	170	< 0,10	< 0,040	0,64	0,97	0,57	< 0,020	0,76	4,8	< 0,20	< 0,20	< 2,5	< 4,0	
619	117,142	11,124	22,736	0,229	0,026	0,026	1,838	34,4	44,725	<= 0,20	50,075	2,723	332,25	2,683	< 0,20	< 0,20	37	< 5,0	< 0,10	1,2	40	< 0,10	< 0,040	2,6	< 0,50	< 0,40	< 0,020	< 0,60	< 1,0	< 0,20	0,55	< 2,5	< 4,0	
620	158,115	21,295	143,741	10,312	0,076	0,949	2,928	114,705	173,161	<= 0,20	<= 0,30	2,936	359,76	6,344	< 0,20	< 0,20	80	< 5,0	0,13	1,8	83	< 0,10	0,09	0,52	1,3	1,1	< 0,020	< 0,60	6,7	< 0,20	< 0,20	< 2,5	< 4,0	
837	93,885	8,837	212,794	107,22	0,731	2,68	21,6	114,705	43,316	<= 1,00	<= 1,50	0,736	393,536	8,827	<= 0,40	4,06	790	12	0,14	3,2	46	< 0,10	0,049	0,59	0,03	42	23	< 0,20	3,2	< 2,5	< 4,0			
838	208,645	16,173	514,09	37,887	1,1	1,98	34,4	20,996	1097,752	<= 1,00	127,99	1,315	703,																					

Usual data treatment not suitable to many parameters

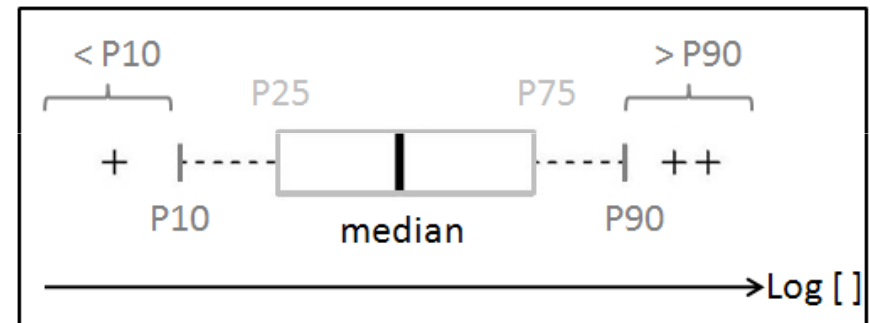
Classical diagrams



Cartography

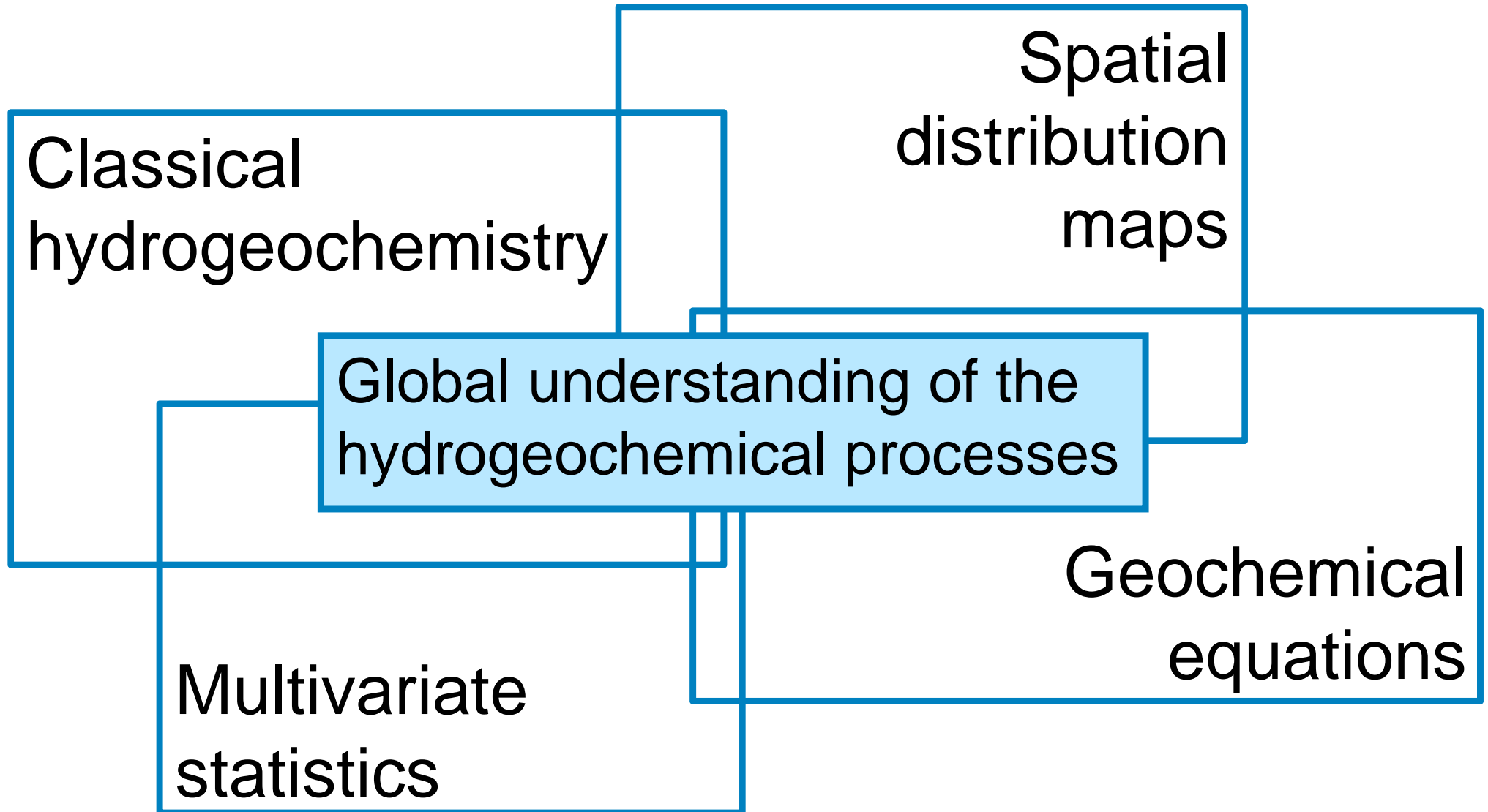


Univariate statistics



→ Need a global understanding of the processes

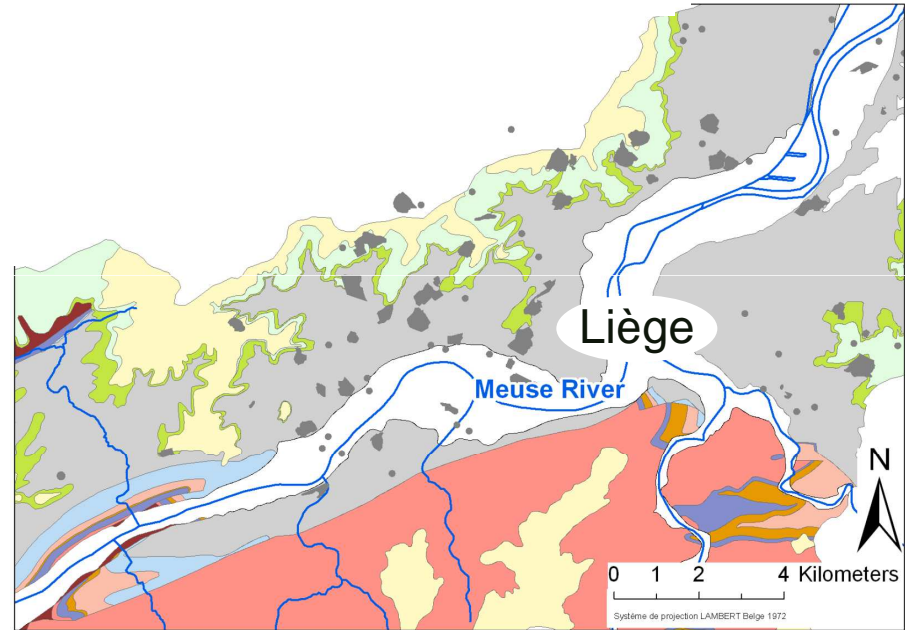
Combined approaches to investigate a step further the dataset



Combined approaches: 2 examples in the Meuse Valley near Liège

Regional scale :

the alluvial aquifer
of the Meuse river



Local scale :

a contaminated site

COMBINED APPROACHES

EXAMPLE 1

Regional scale :
the alluvial aquifer
of the Meuse river

Alluvial aquifer of the Meuse river near Liège

in a strongly urbanized and industrialized area

heavily contaminated

at the regional scale

with various types of contaminants

Hydrogeologic context

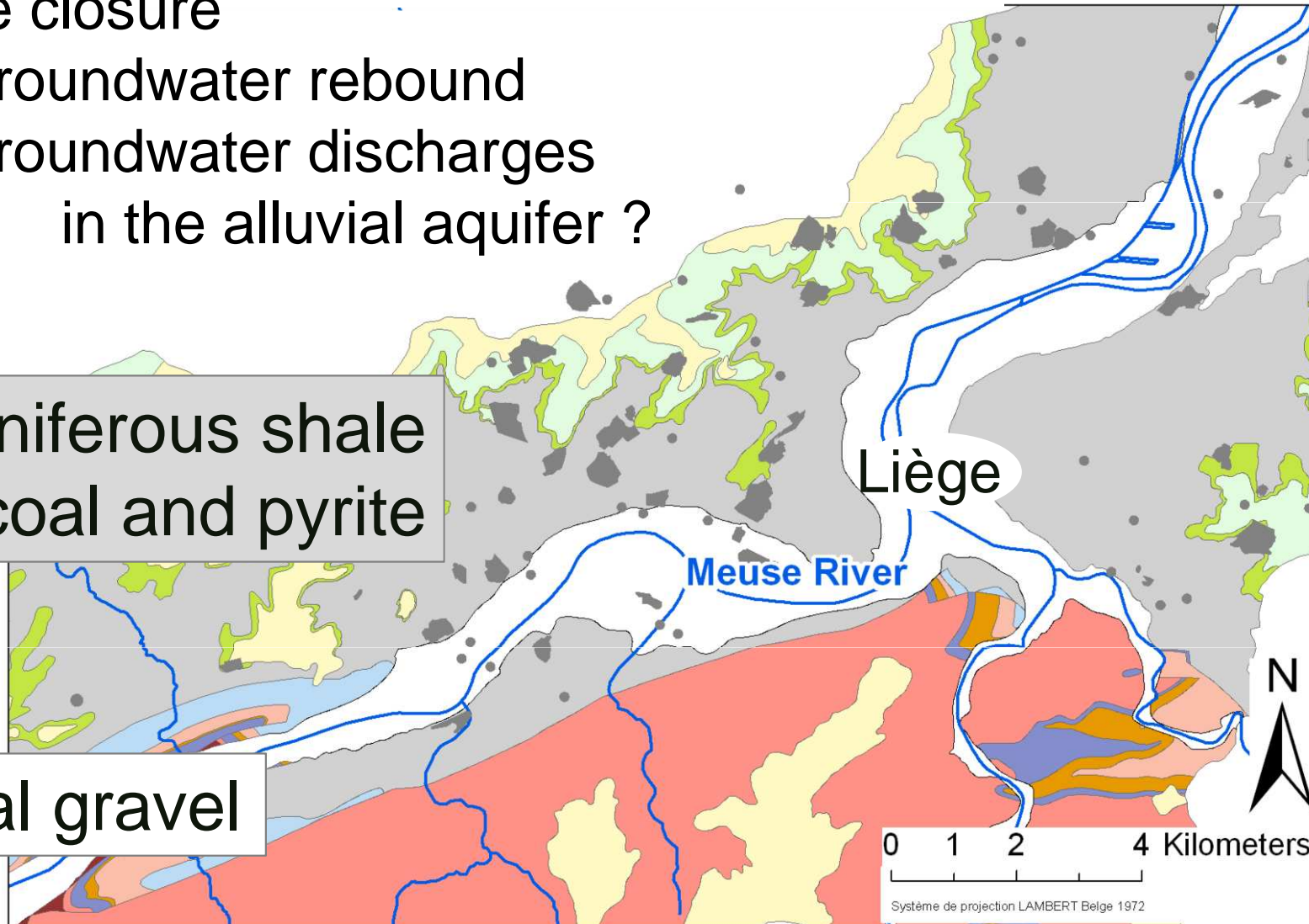
Mine closure

→ groundwater rebound

→ groundwater discharges
in the alluvial aquifer ?

Carboniferous shale
with coal and pyrite

Alluvial gravel



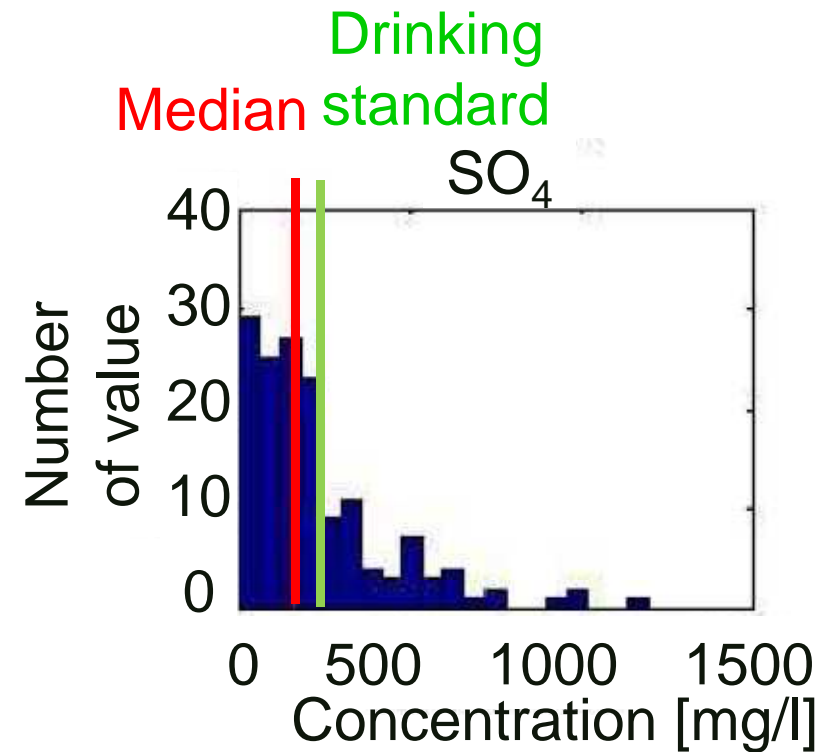
Many sources of contamination contribute to poor quality

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

Anthropogenic

'Natural'

Sulfate is the main degrading factor



Sulfate is both

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

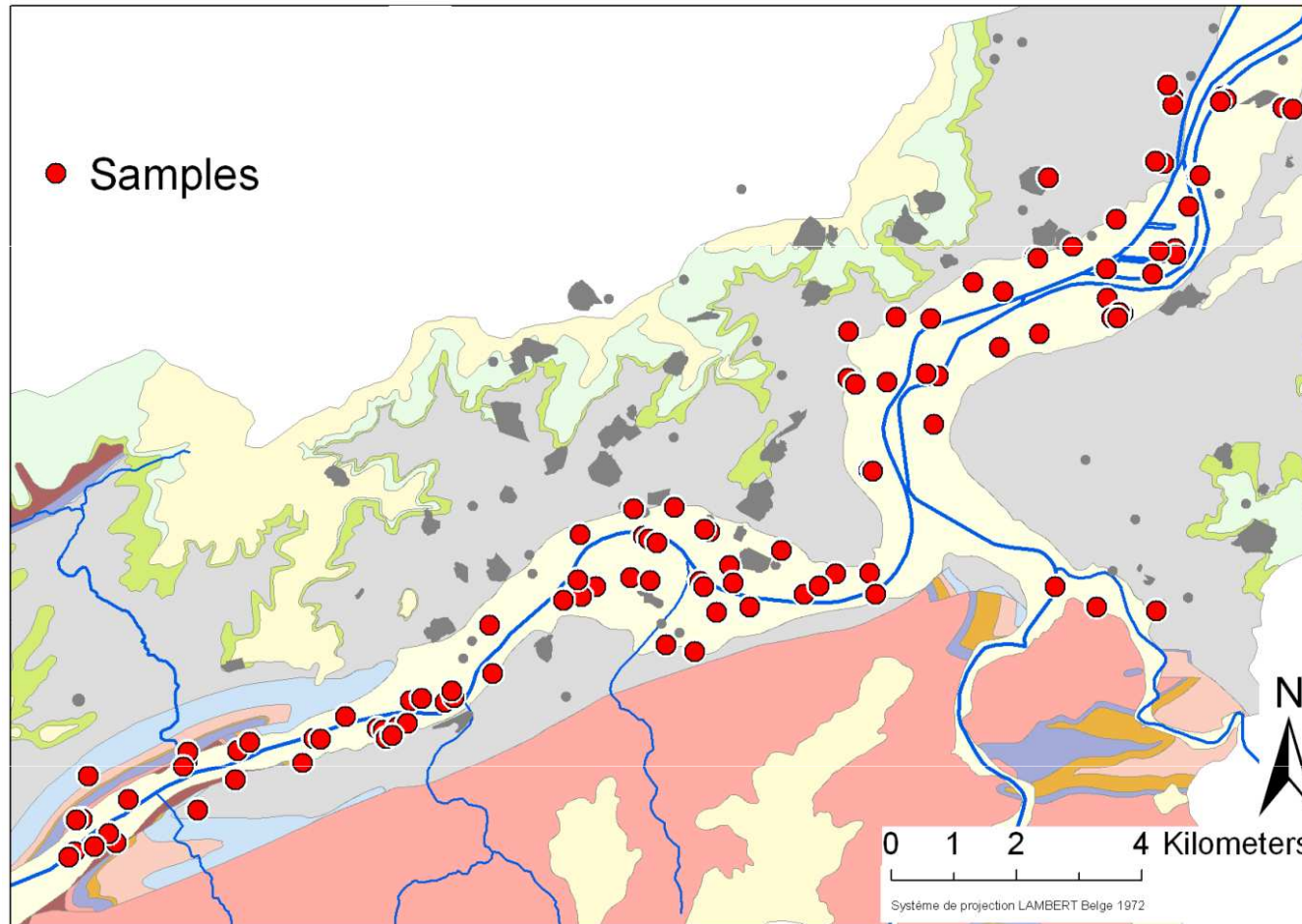
Need a global understanding of the hydrogeochemical processus

To determine

- the most contaminated sectors of the alluvial aquifer
- the origin of the inorganic contaminations (natural or anthropogenic?)

→ Hydrogeochemical investigation
using different combined approaches

90 groundwater samples

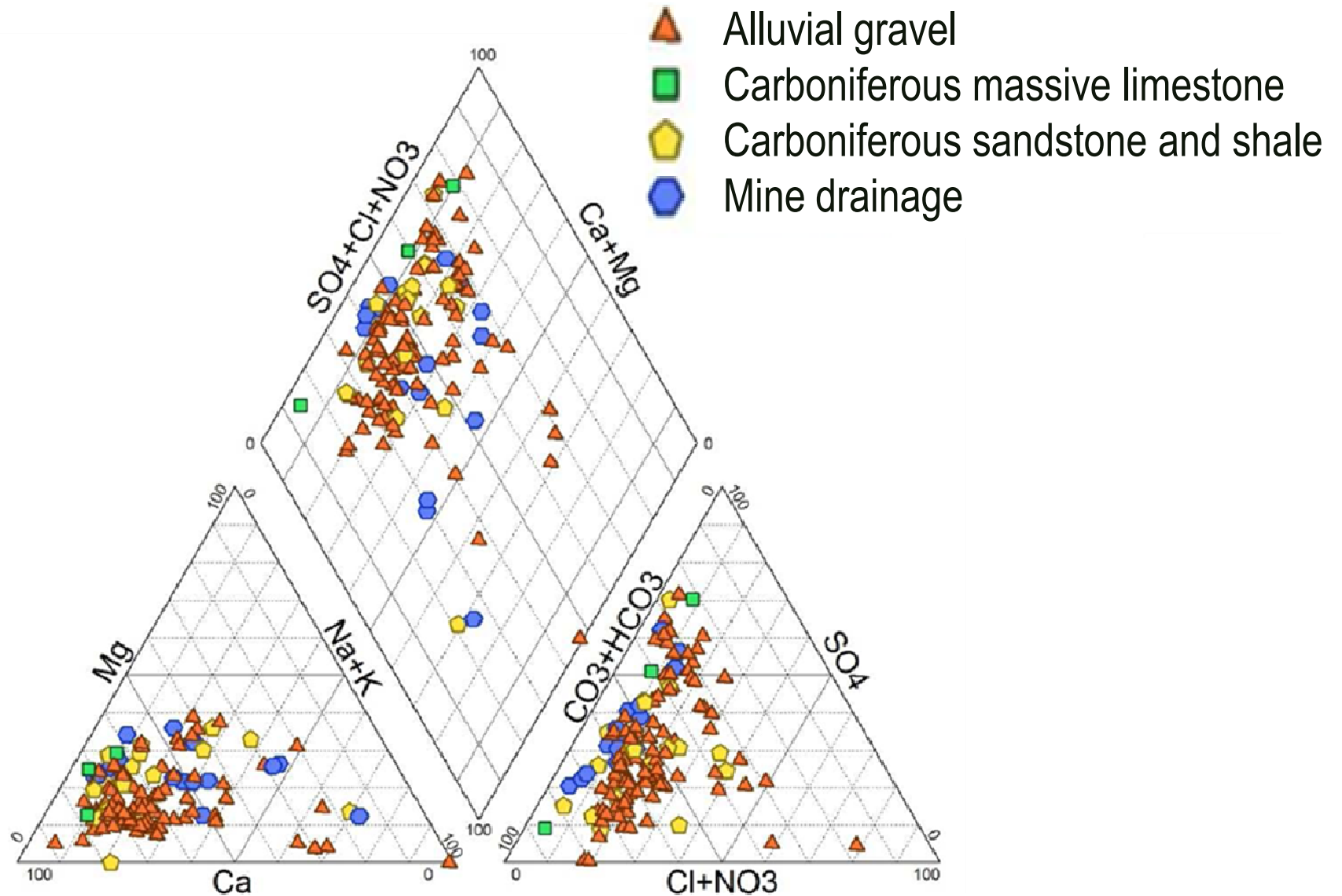


Major and minor compounds

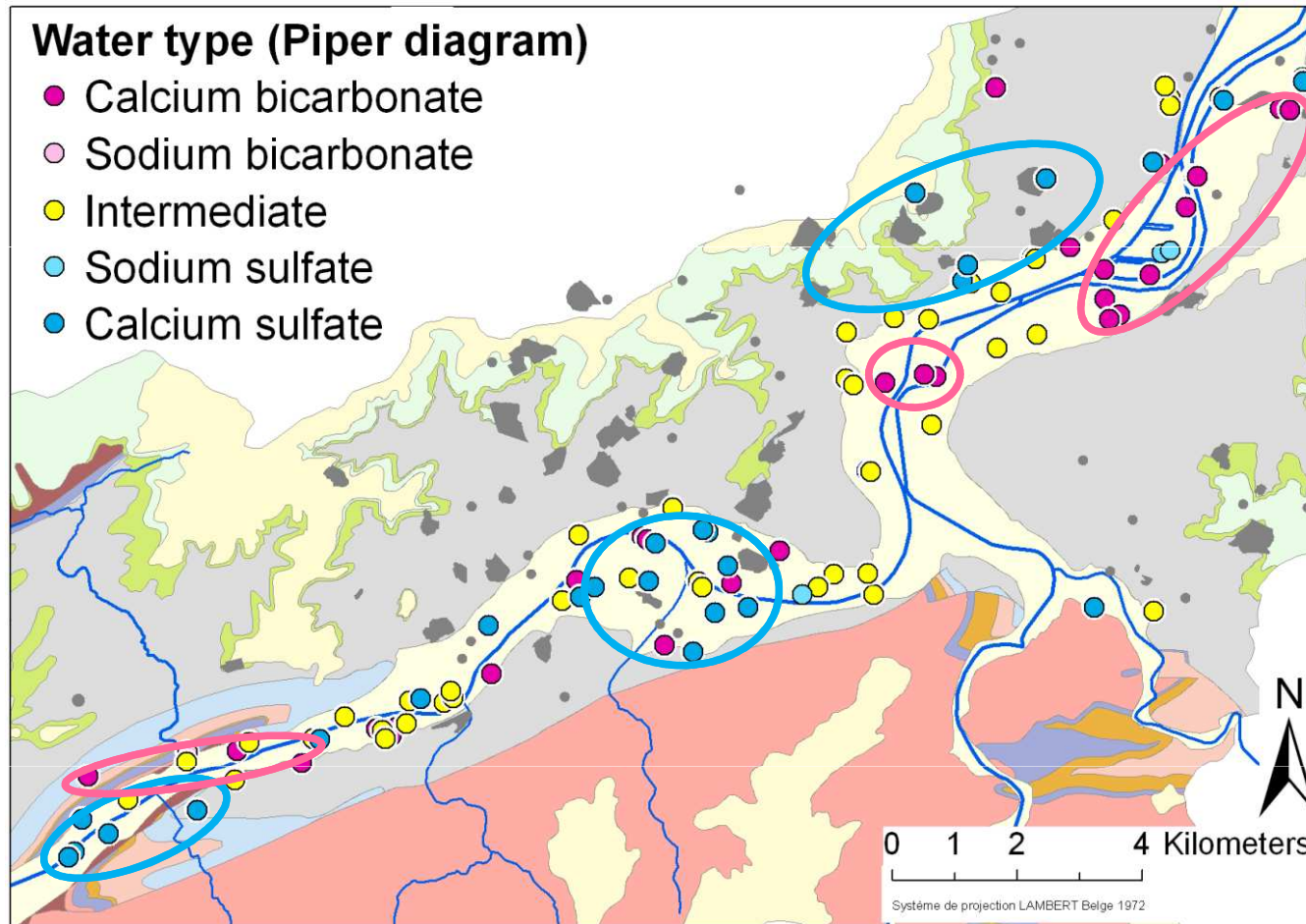
+ inorganic contaminants

usually observed in such urban environments

Calcium sulfate or calcium bicarbonate types



Cartography of the water types (Piper diagram)

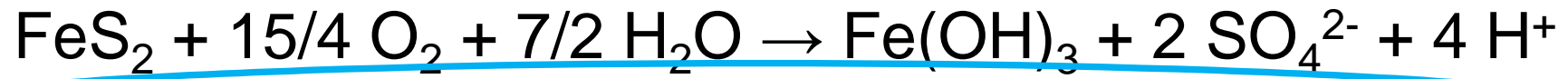
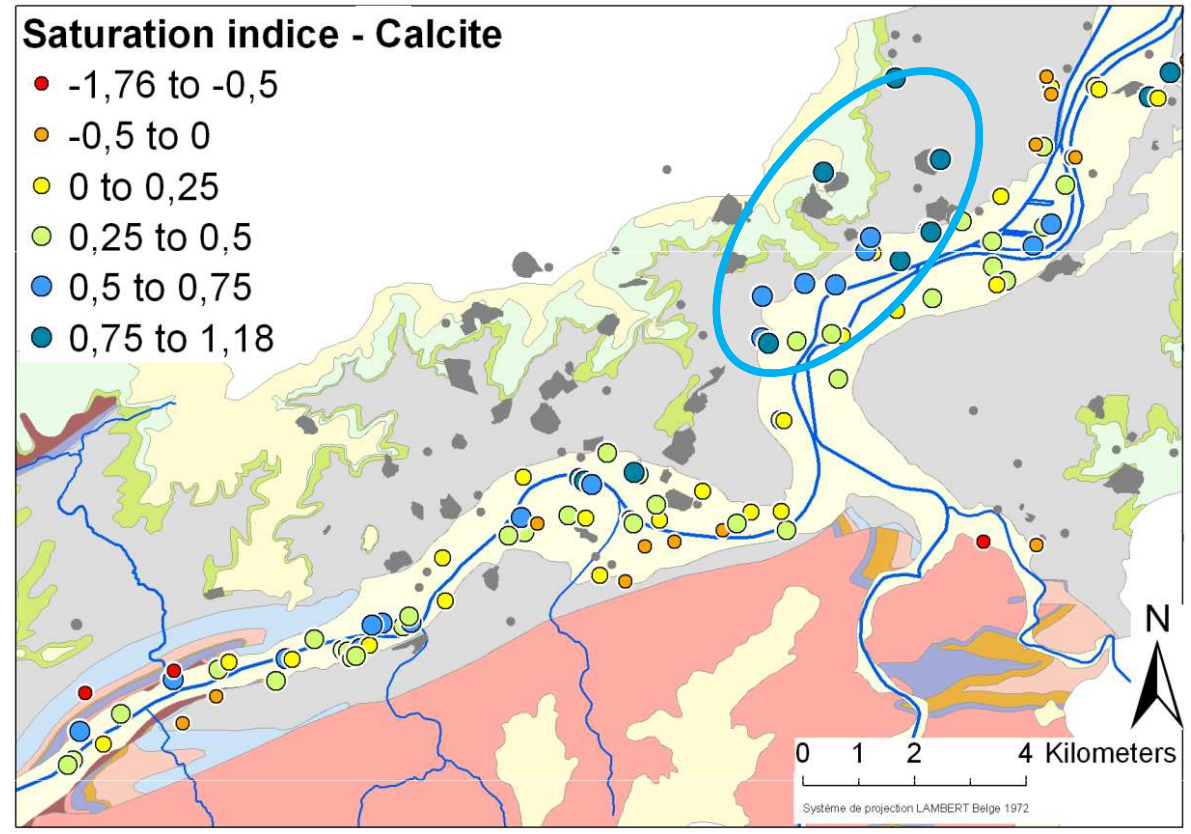


3 major areas of calcium sulfate type

3 major areas of calcium bicarbonate type

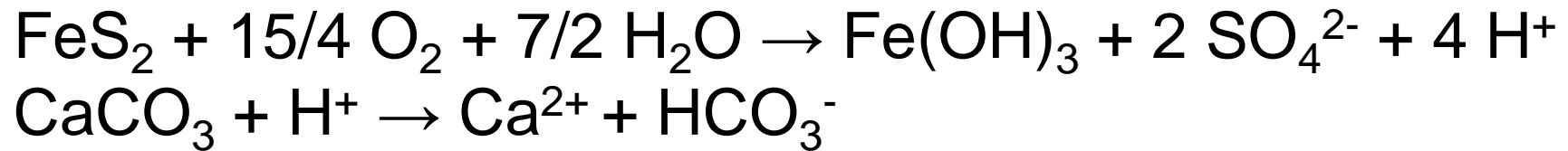
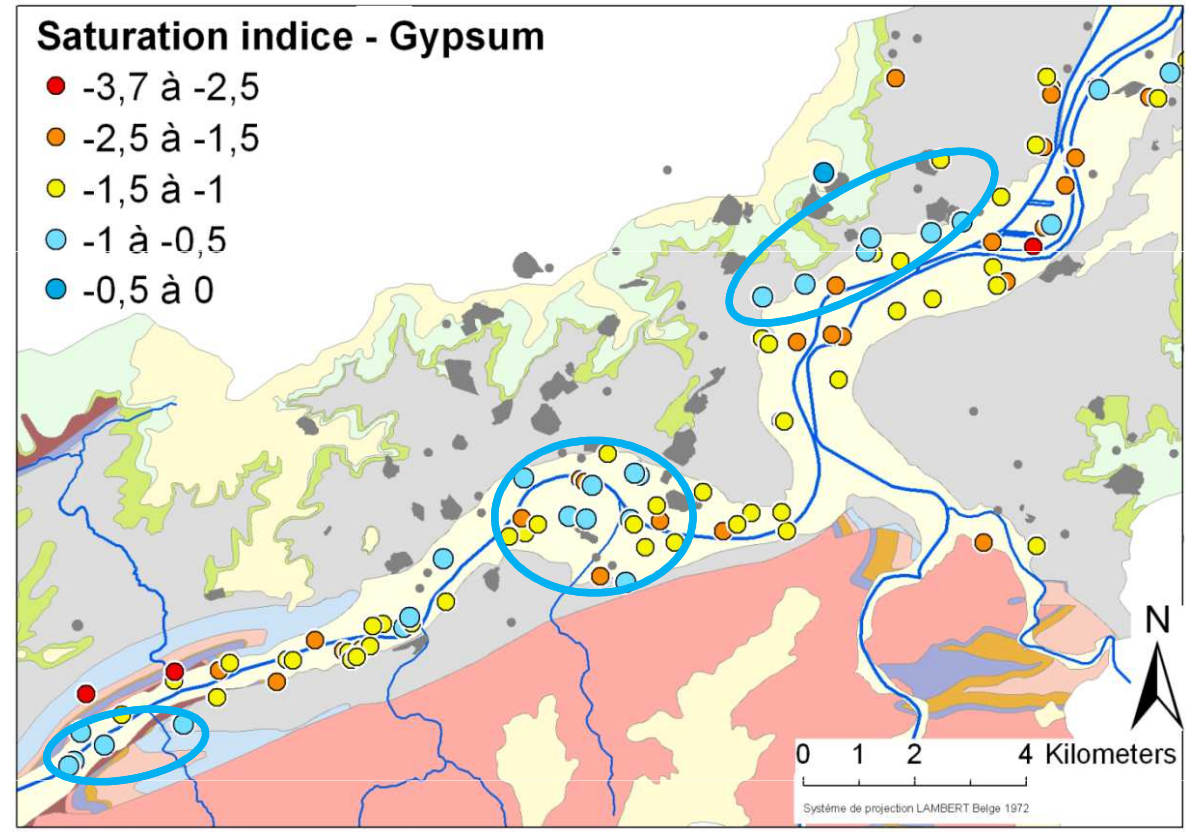
Changes in groundwater composition in relation with acid mine drainage

SI >> 0

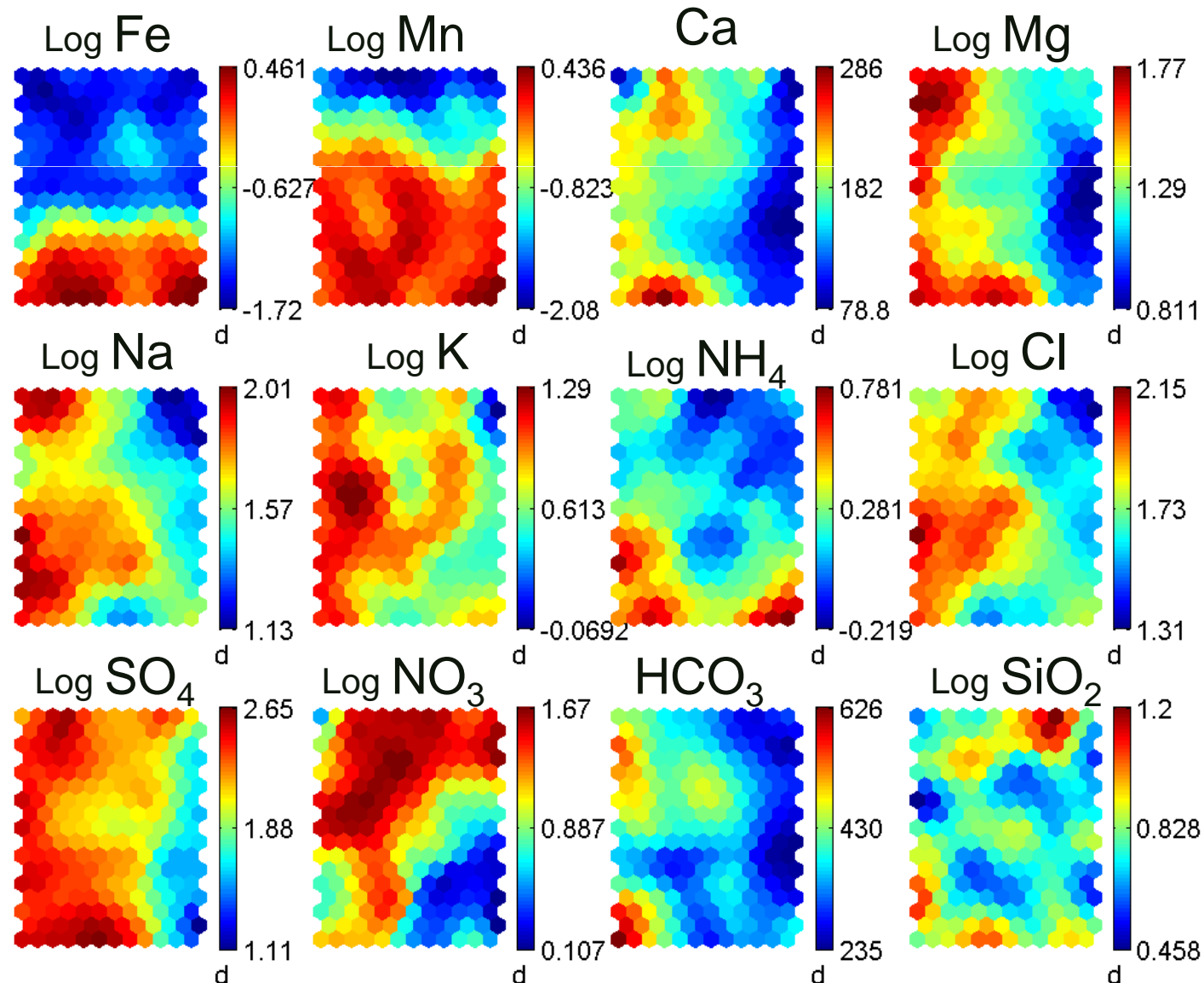


Changes in groundwater composition in relation with acid mine drainage

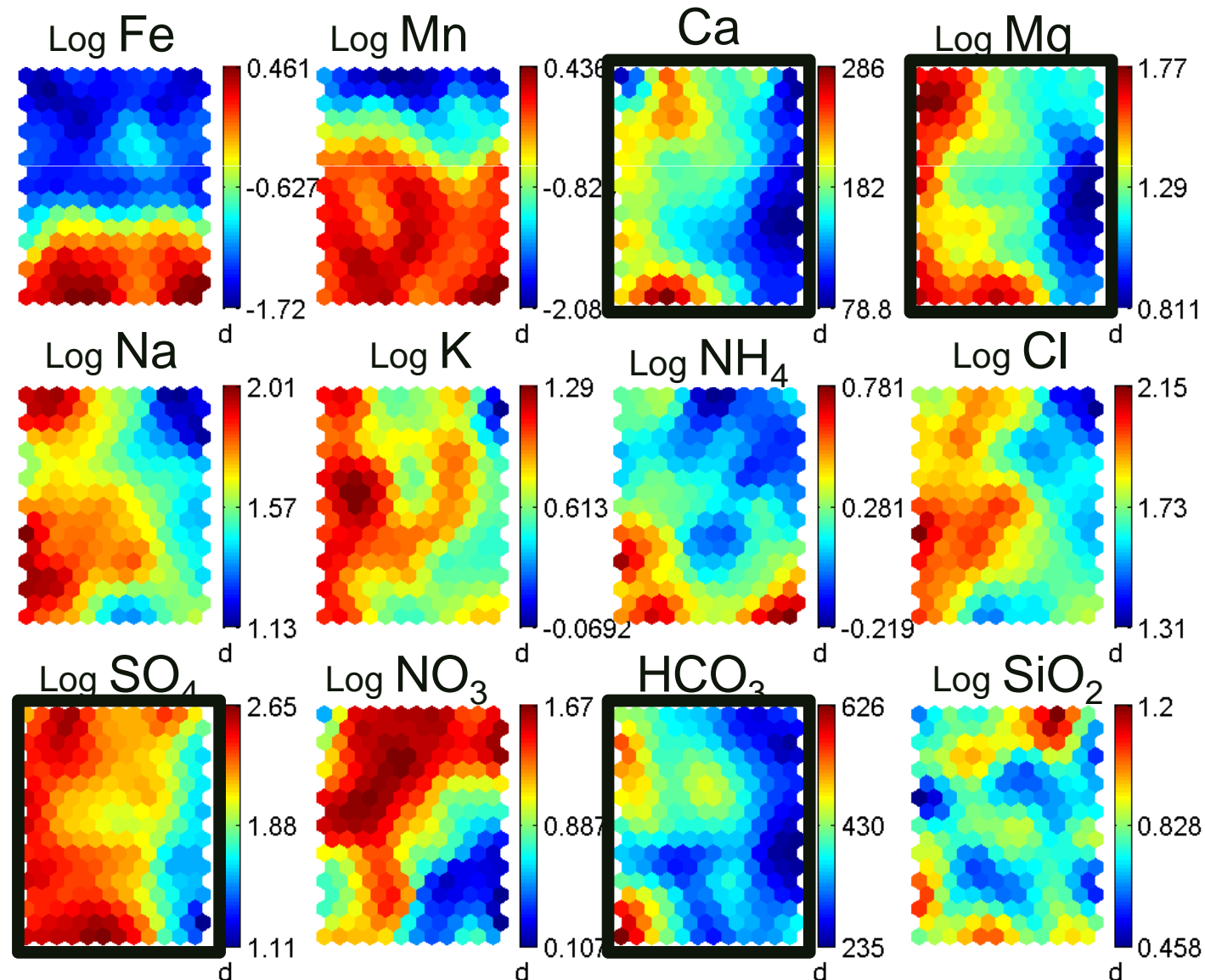
SI \approx 0



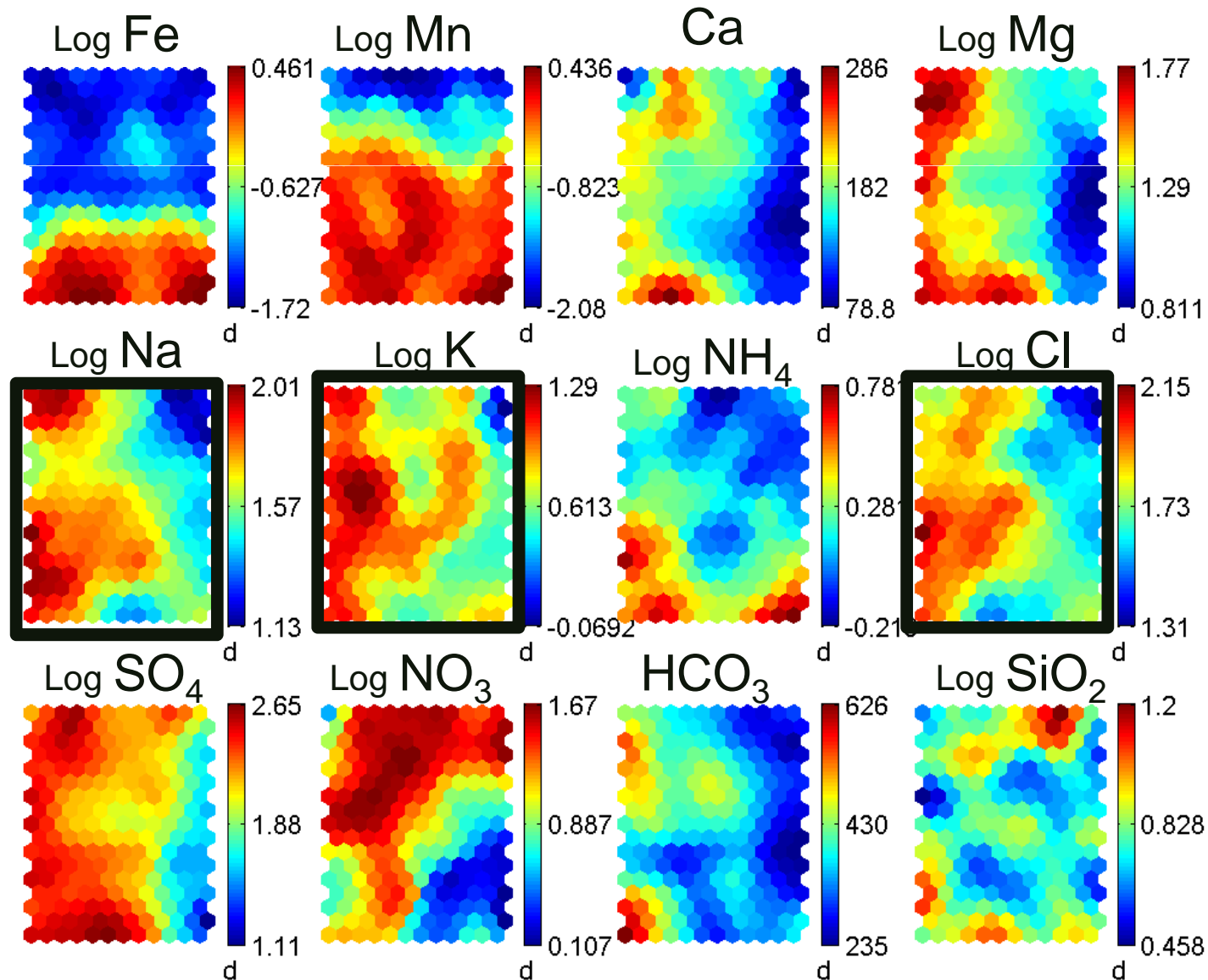
A non-linear multivariate statistical method is applied (Self Organizing Maps)



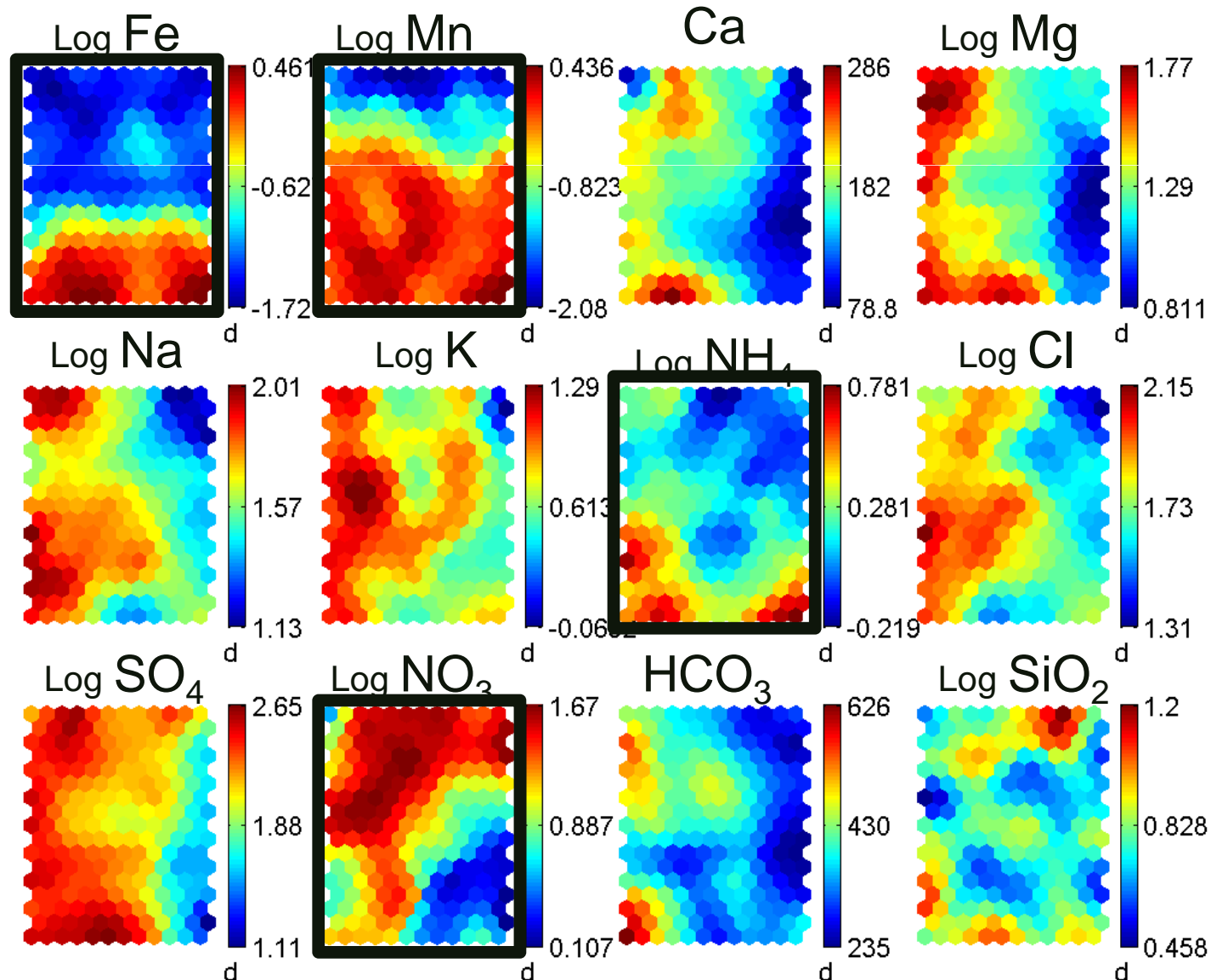
A non-linear multivariate statistical method is applied (Self Organizing Maps)



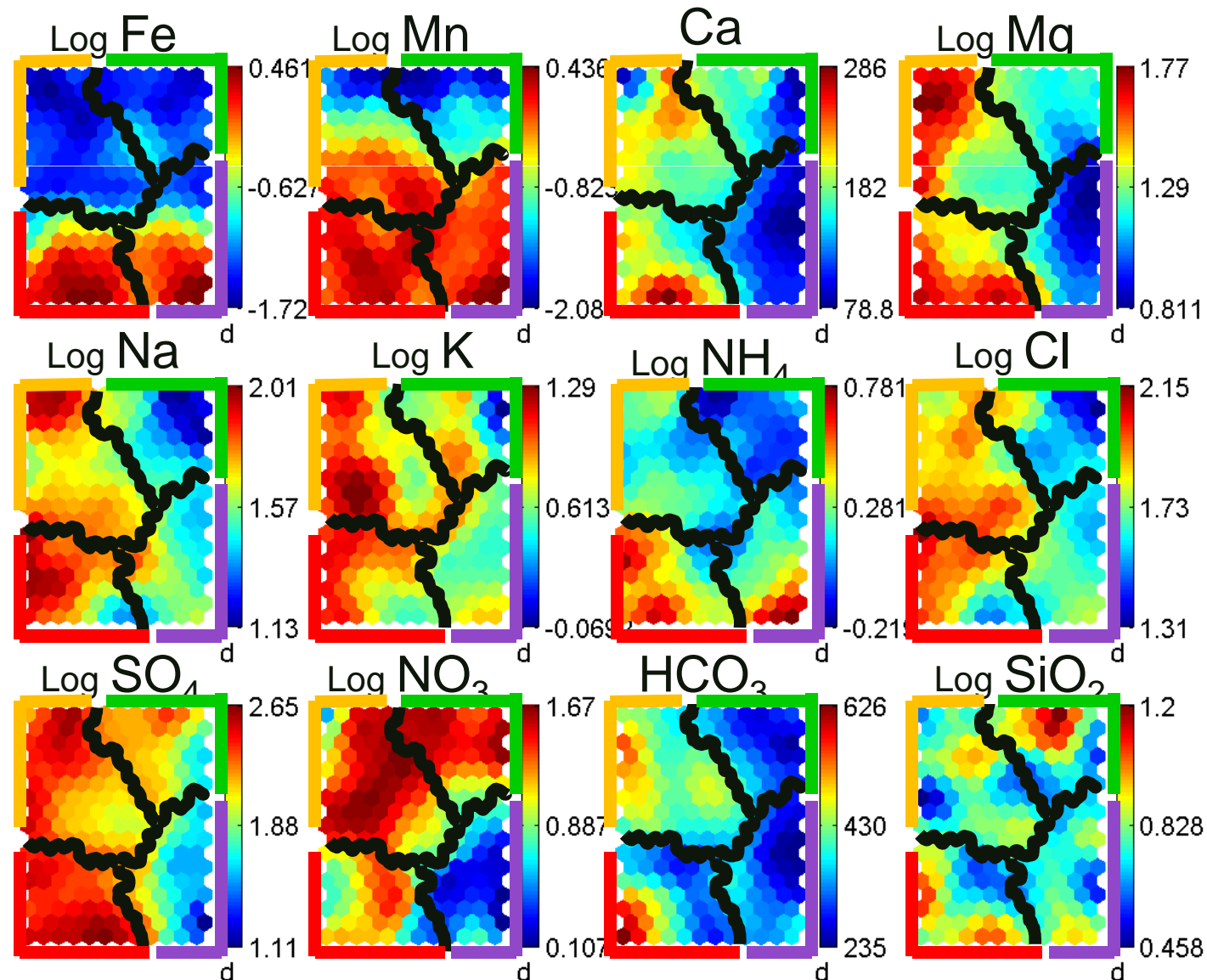
A non-linear multivariate statistical method is applied (Self Organizing Maps)



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

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	+-
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K	--
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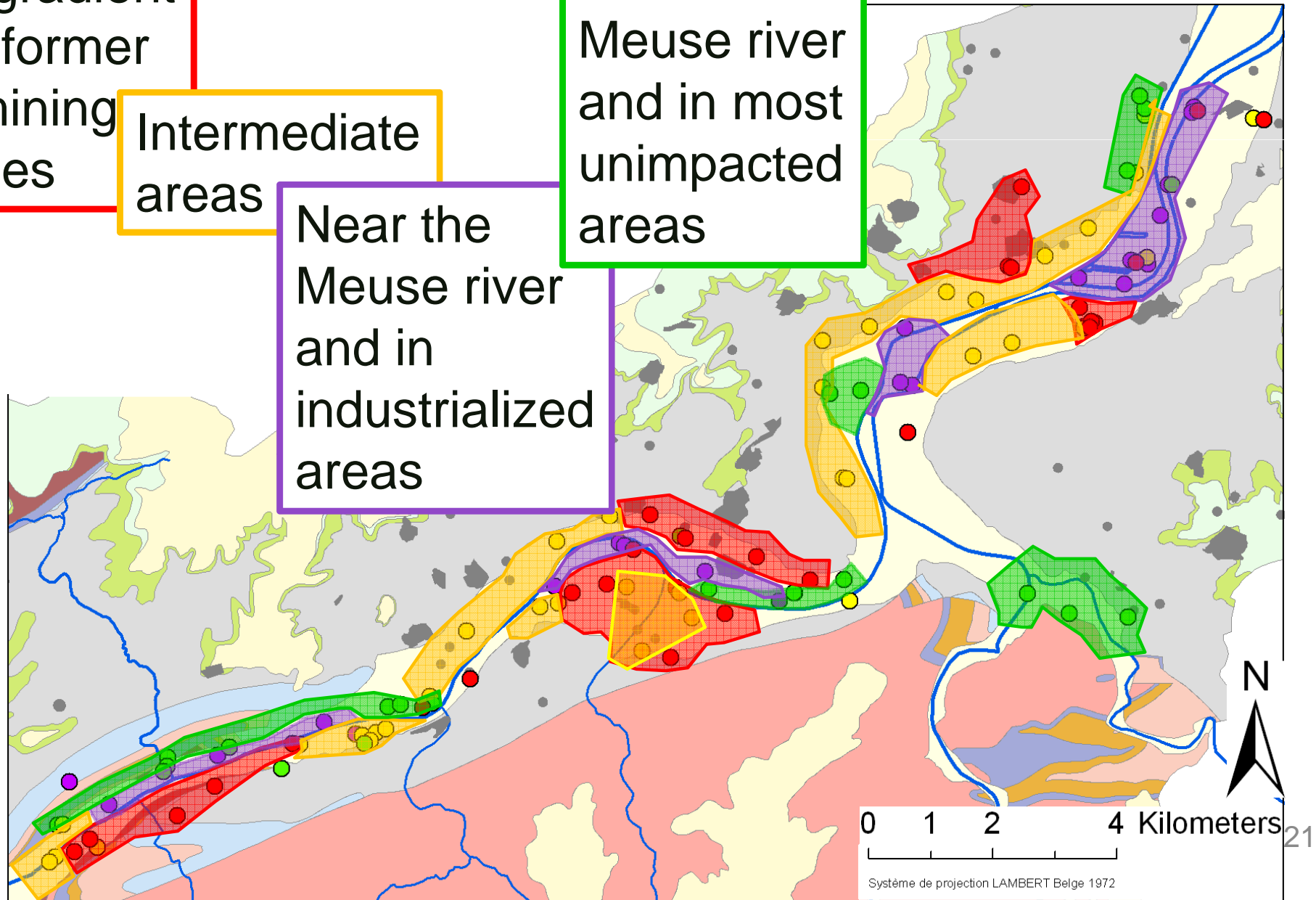
Combined approaches to determine the different hydrogeochemical sectors

Downgradient of the former coal mining activities

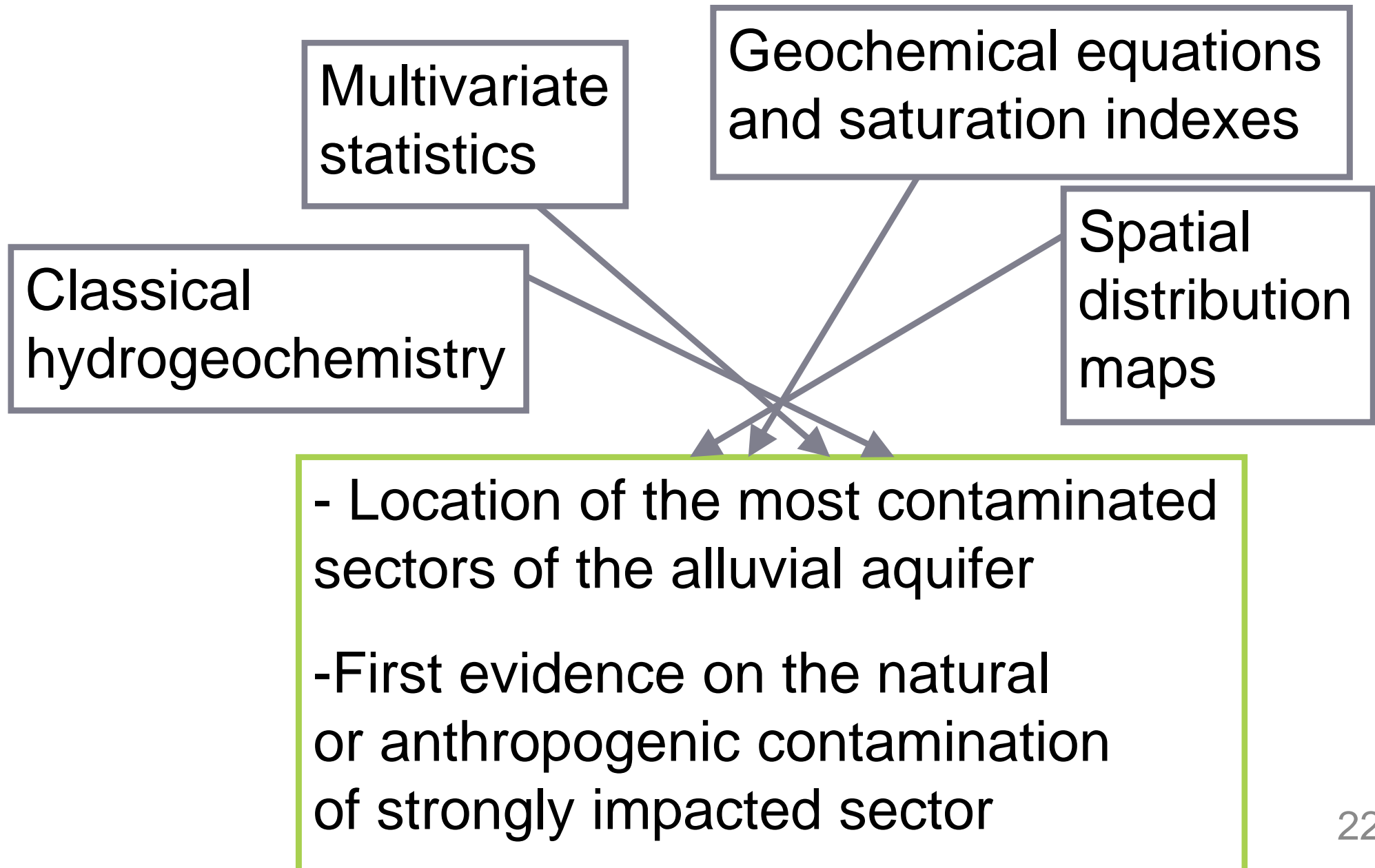
Intermediate areas

Near the Meuse river and in industrialized areas

Near the Meuse river and in most unimpacted areas



Contribution / advantage of using different combined approaches

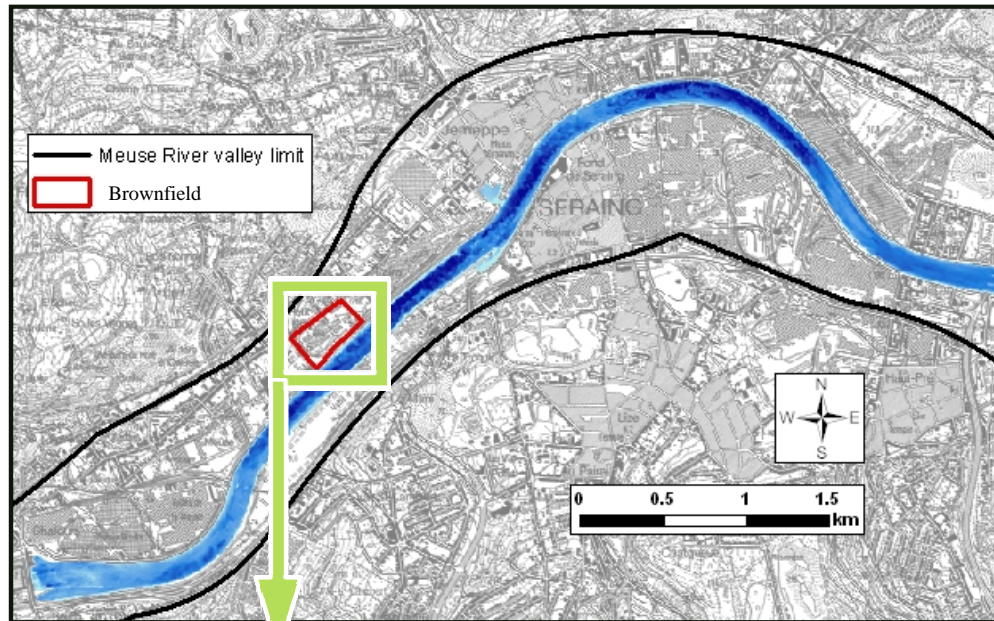


COMBINED APPROACHES

EXAMPLE 2

Local scale :
a contaminated site

Investigations and modelling performed in a brownfield in the area of Liège



Alluvial aquifer

25 m from the Meuse River

Polluting activities
from 1922 to 1984

Soil and groundwater
highly polluted by
organic (BTEX and PAHs)
and inorganic
(metals, Fe and sulphate)
compounds

Many hydrogeochemical data available

Benzene concentration

Eh, O₂, pH, Electrical Conductivity

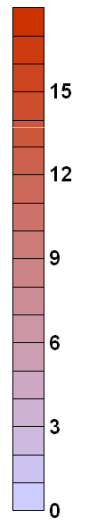
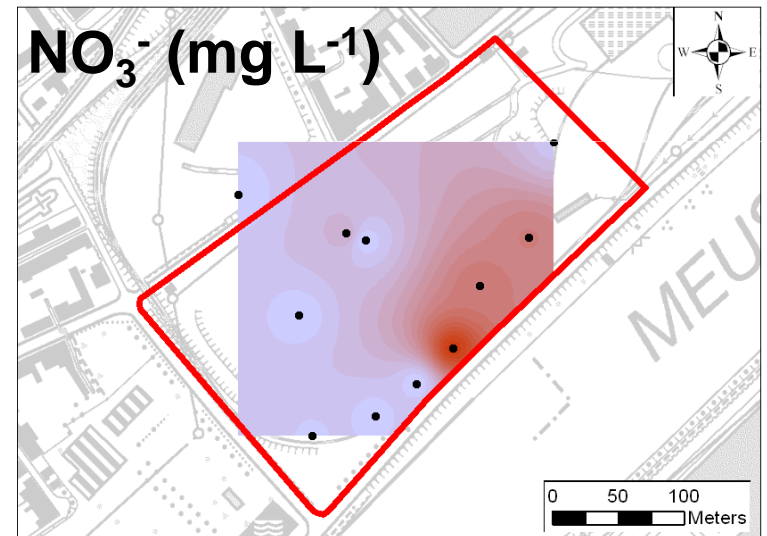
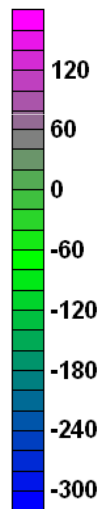
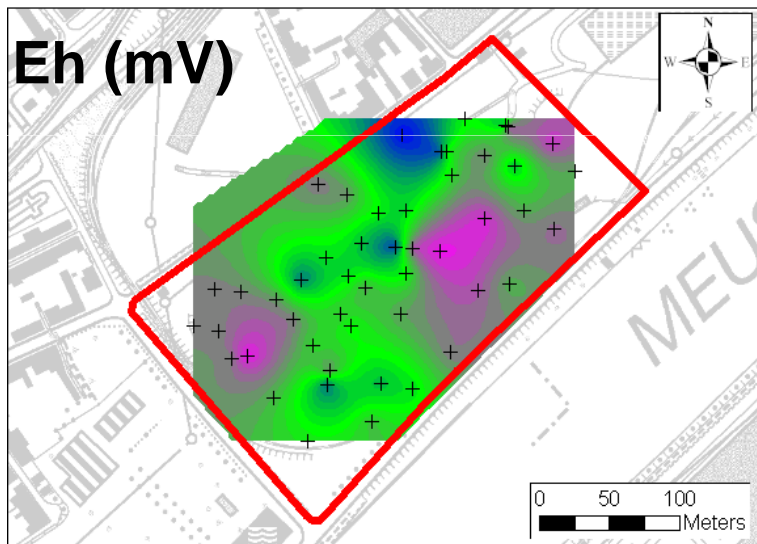
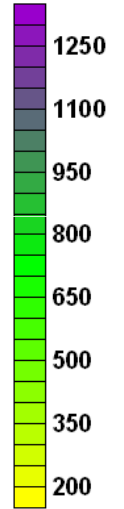
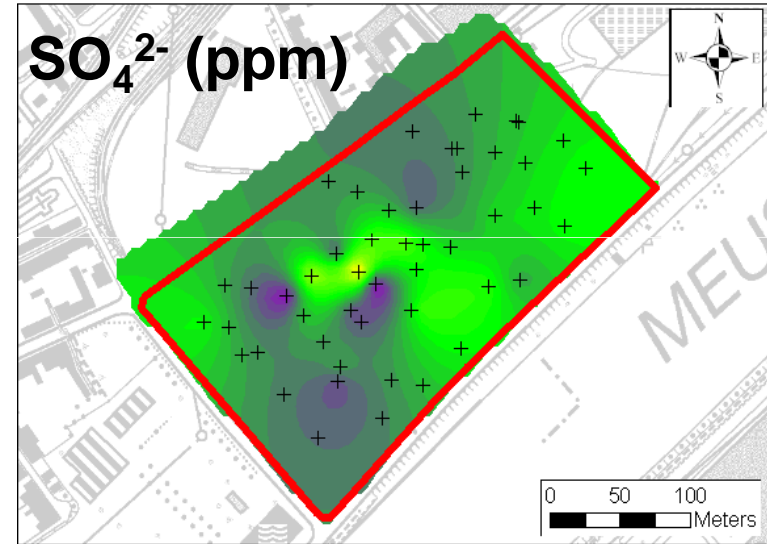
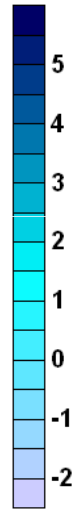
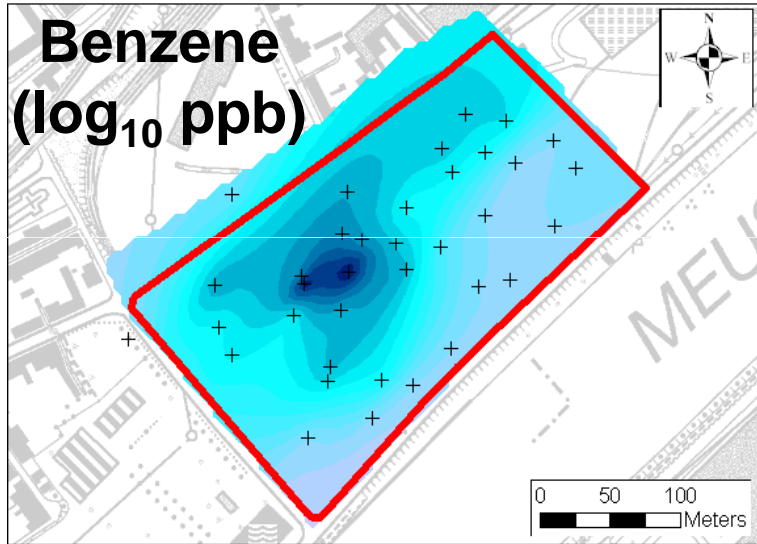
HCO₃⁻, Ca²⁺, Mg²⁺, Cl⁻, Na⁺, K⁺,
SO₄²⁻, HS⁻, NO₃²⁻, NH₄⁻, CH₄

Fe, Mn, As, Zn, Cd

¹³C isotope of benzene

Complex spatial distributions on groundwater

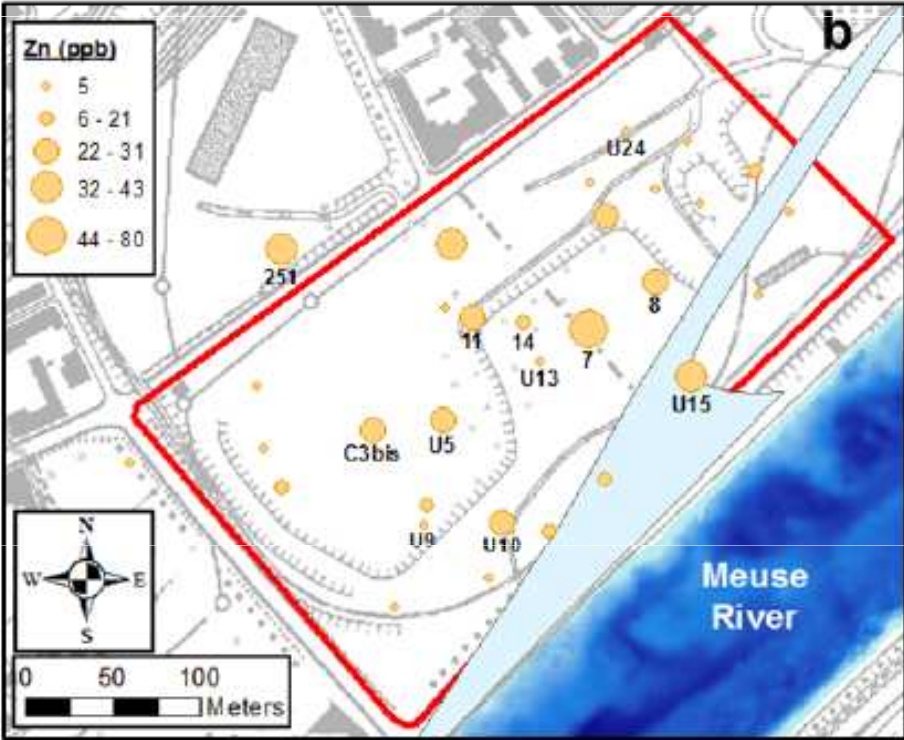
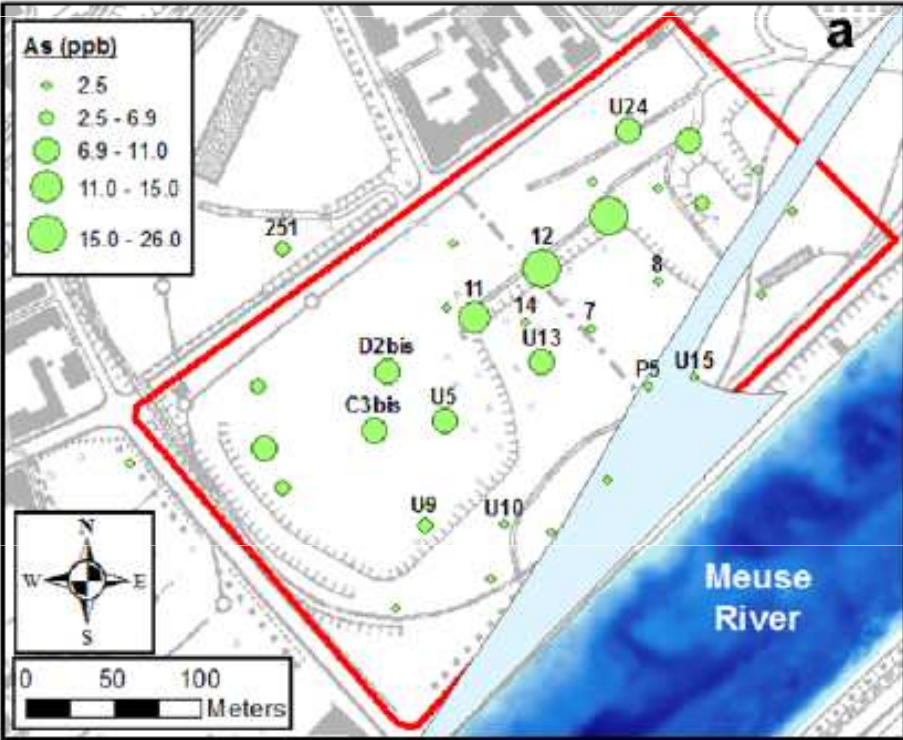
Benzene and redox indicators:



Complex spatial distributions on groundwater Metallic trace elements:

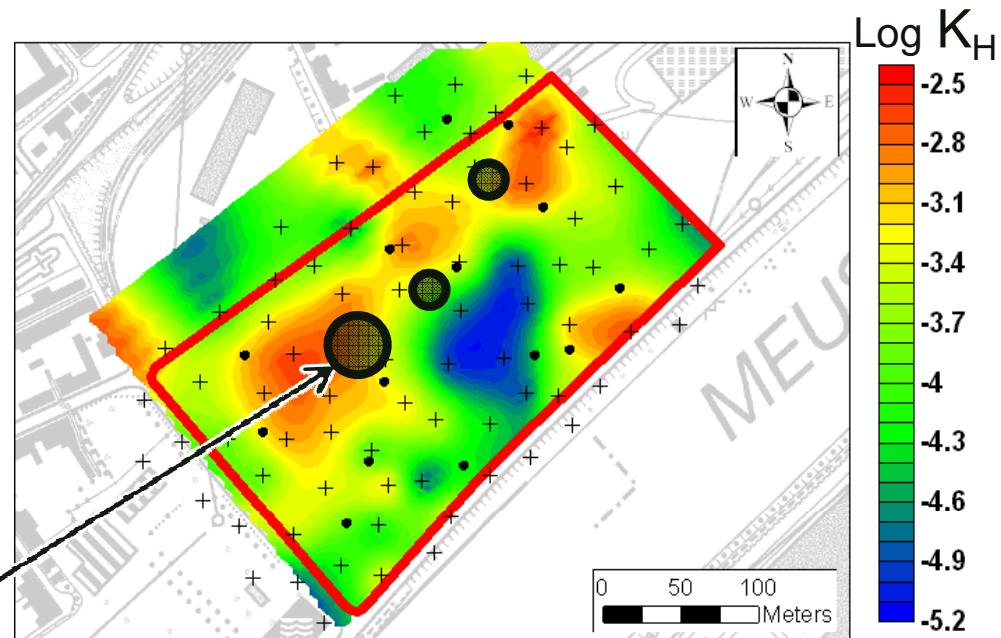
As

Zn



Detailed characterization of the hydraulic conductivity (K_H)

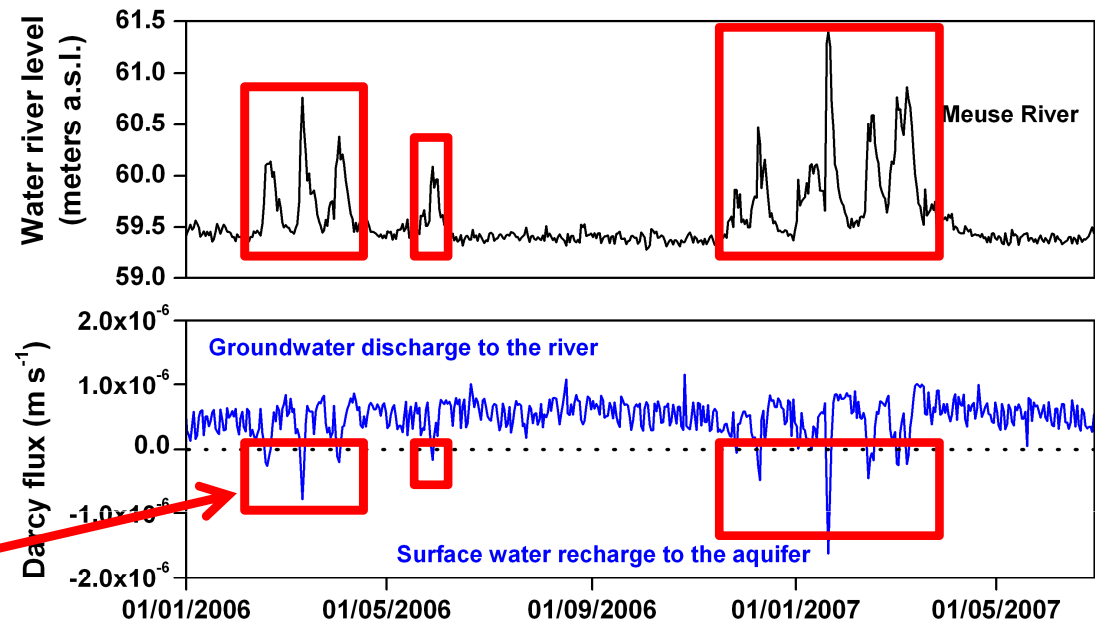
Almost 3 orders of magnitude
between low-K and high-K
zones



main benzene contamination area

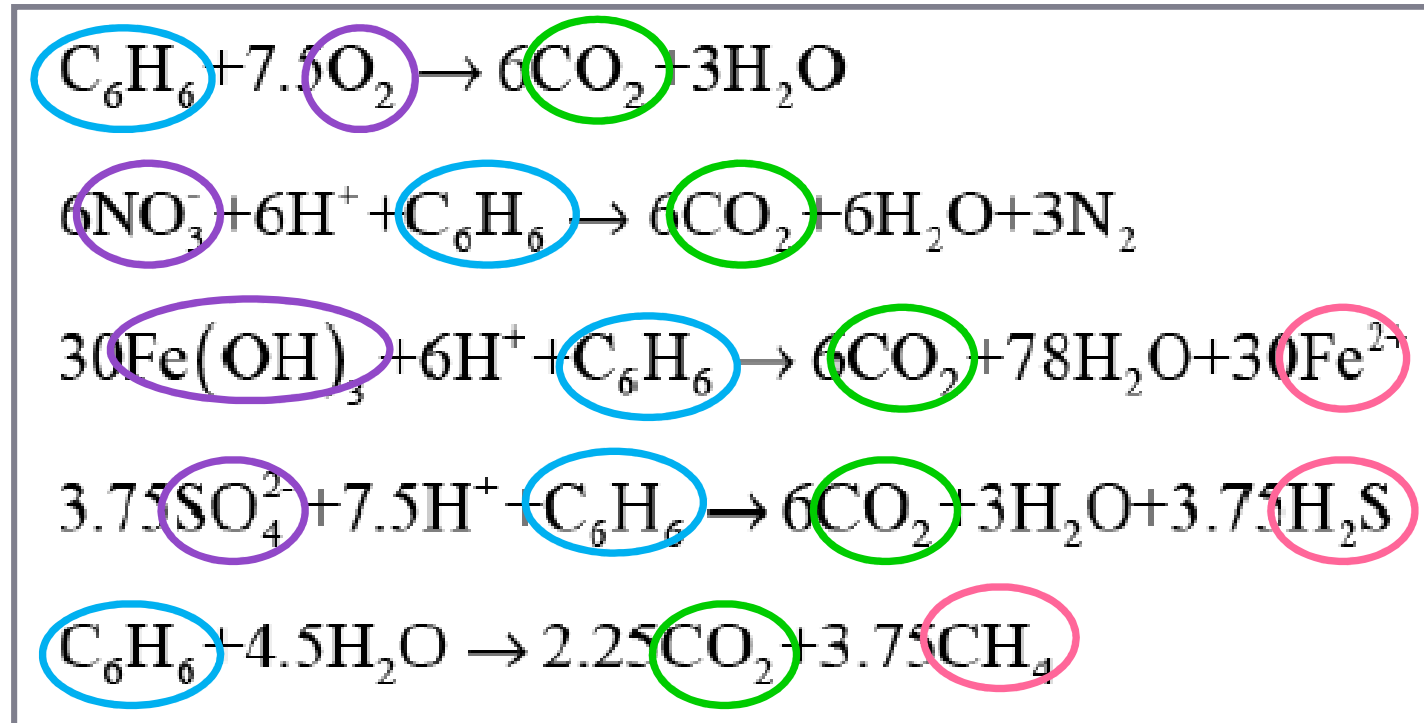
Numerical modeling results allow to characterize groundwater – river interactions

Variable fluxes at the groundwater – river interface



Sometimes: infiltration of oxygenated surface water into the aquifer

Aquifer geochemical footprints of natural attenuation of benzene (theory)



Lu et al., 1999

Decrease of electron acceptors

Generation of the products of acceptors reductions

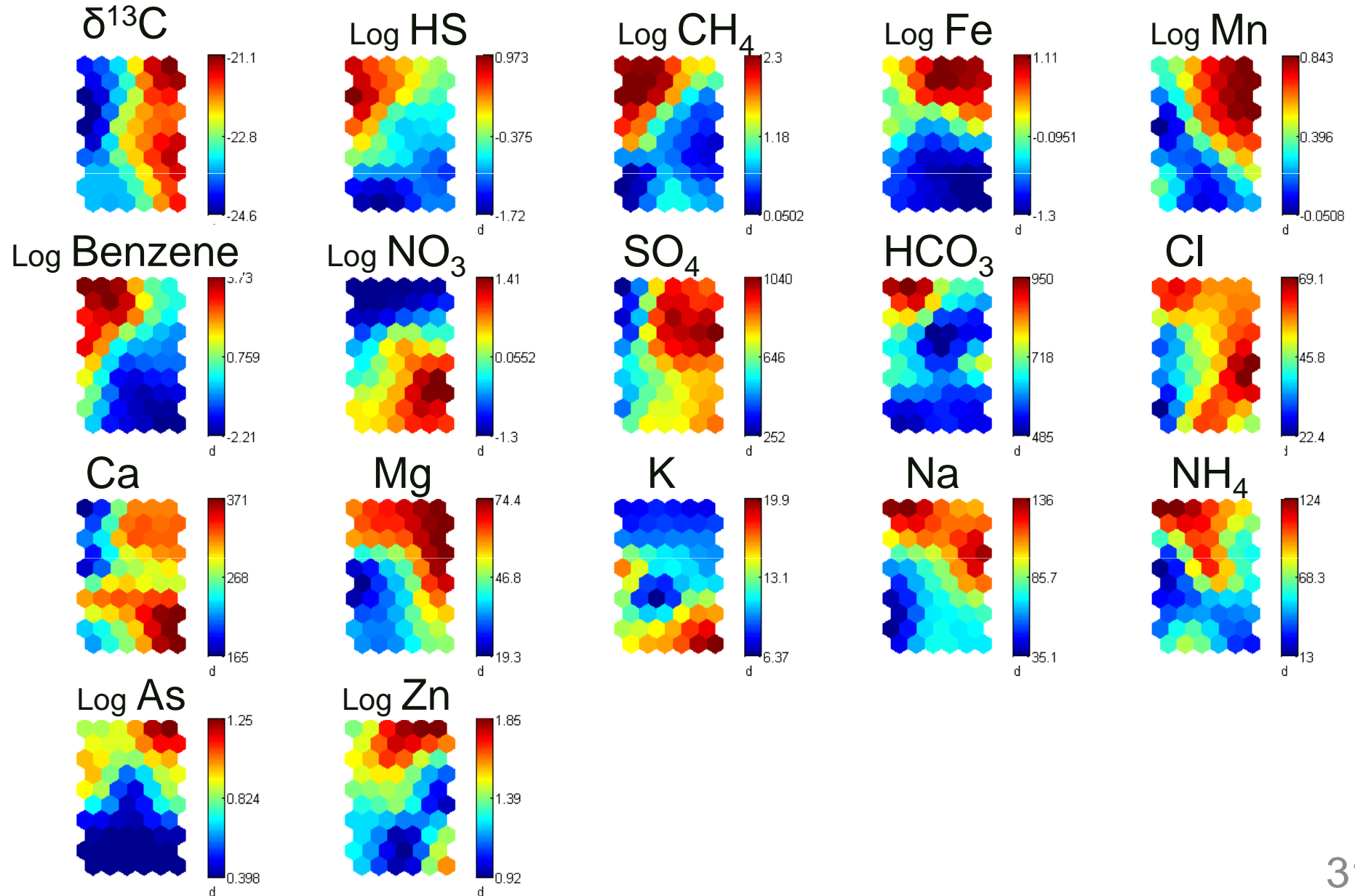
Increased concentration of dissolved CO₂

Change in the alkalinity

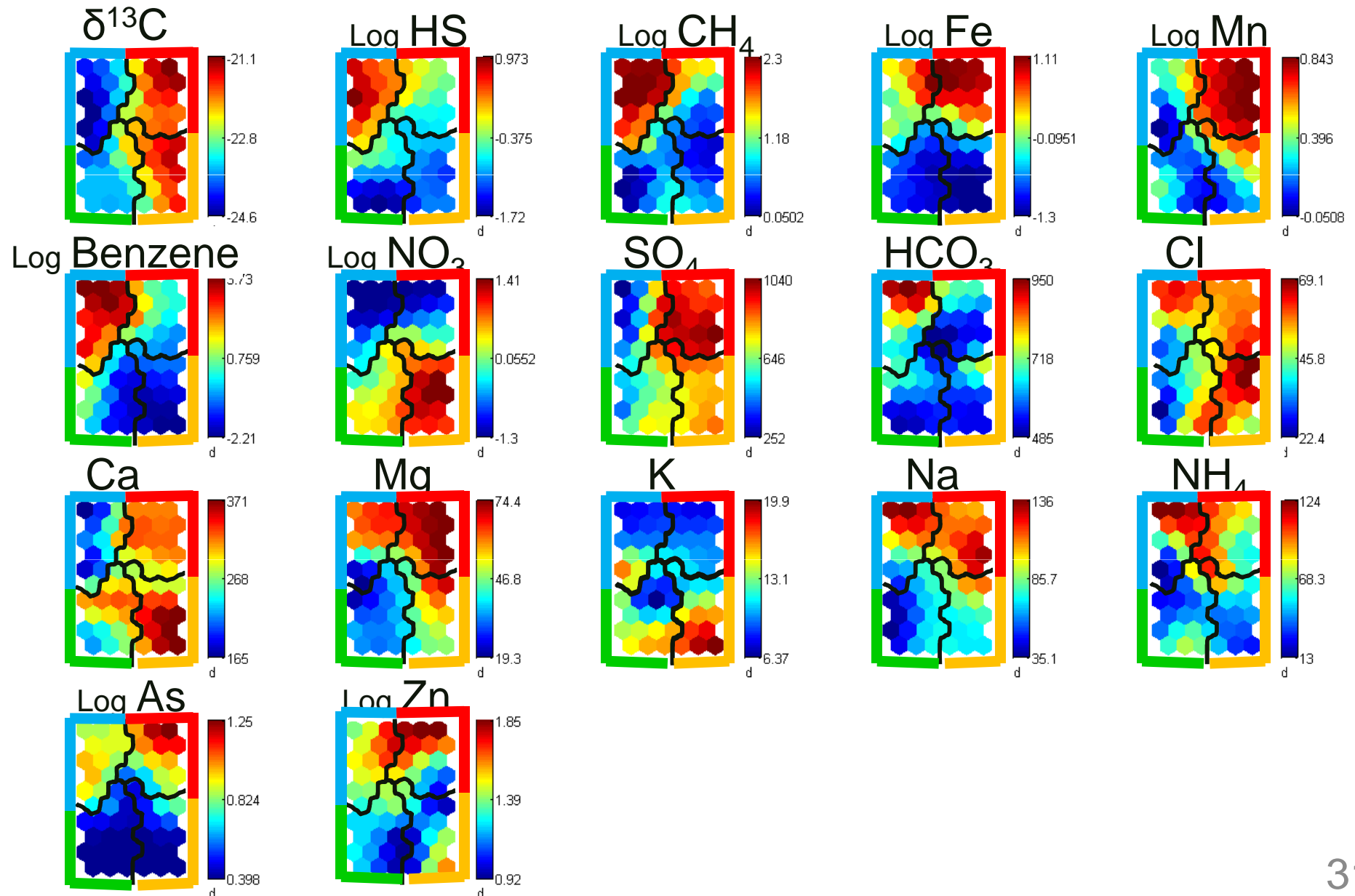
Decrease of benzene concentrations

Increase of $\delta^{13}\text{C}$ ratios in benzene (^{13}C enrichment)

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

High benzene
concentrations

$\delta^{13}\text{C}$ low

Eh negative

Redox sequence:
HS⁻ high
CH₄ high

HCO₃⁻ high
Ca²⁺ low

As medium
Zn medium

Medium benzene
concentrations

$\delta^{13}\text{C}$ high

Eh negative

Redox sequence:
HS⁻ medium
CH₄ medium

HCO₃⁻ medium
Ca²⁺ medium

As high
Zn high

Low benzene
concentrations

$\delta^{13}\text{C}$ medium

Eh positive

Redox sequence:
NO₃²⁻ high
Fe, Mn low

HCO₃⁻ low
Ca²⁺ high

As low
Zn medium

Low benzene
concentrations

$\delta^{13}\text{C}$ low

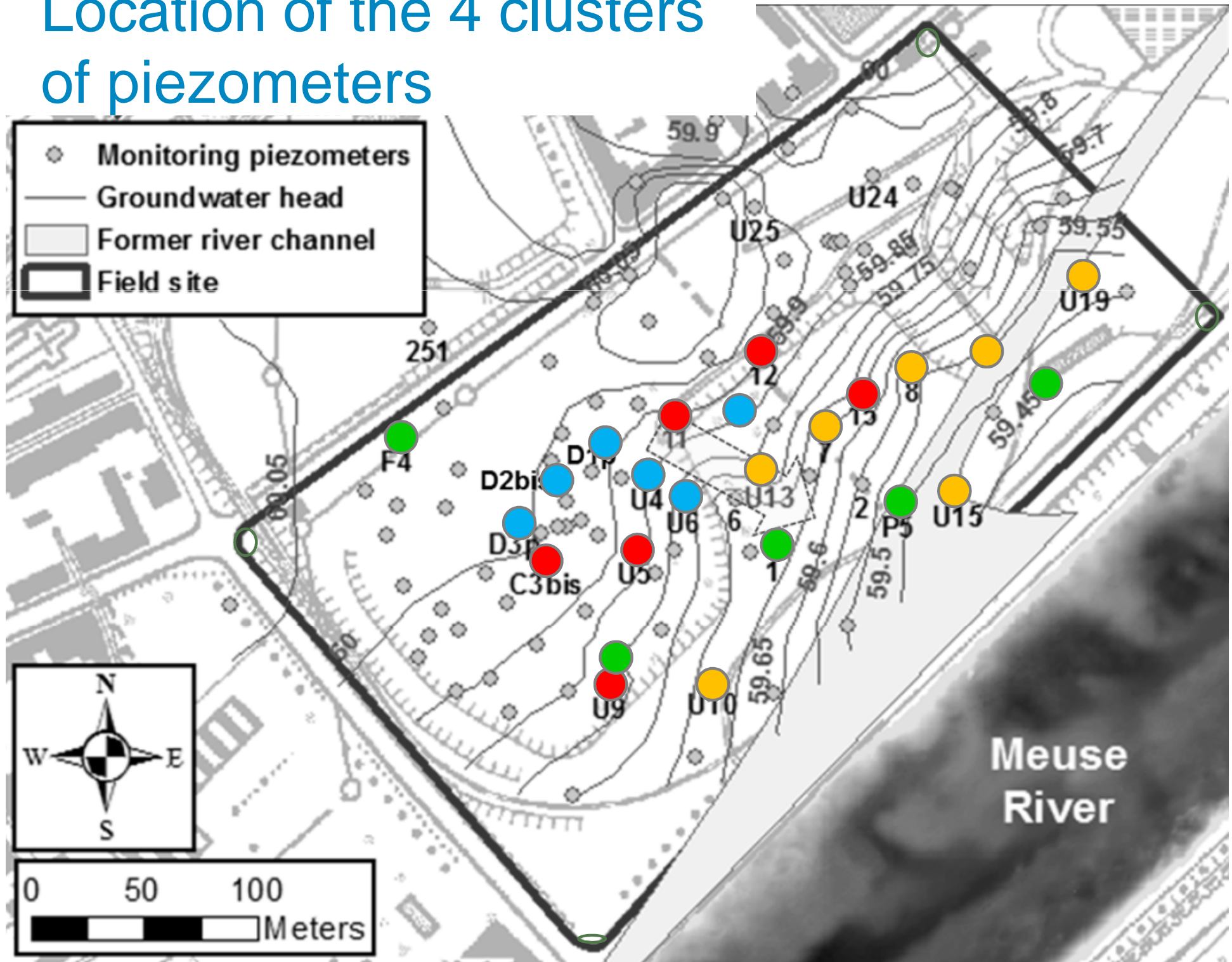
Eh positive

Redox sequence:
NO₃²⁻ medium
Fe, Mn low

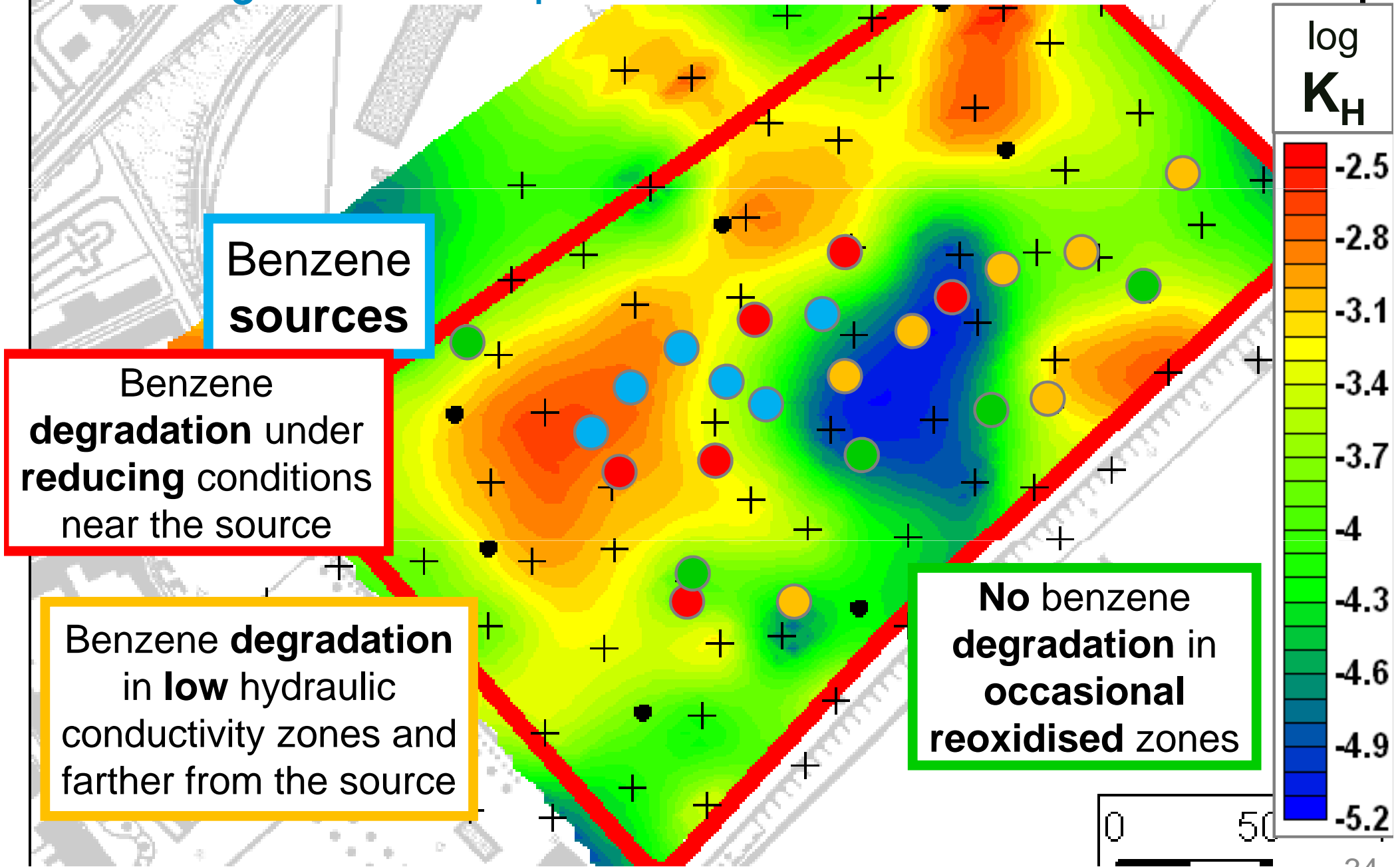
HCO₃⁻ low
Ca²⁺ medium

As low
Zn low

Location of the 4 clusters of piezometers

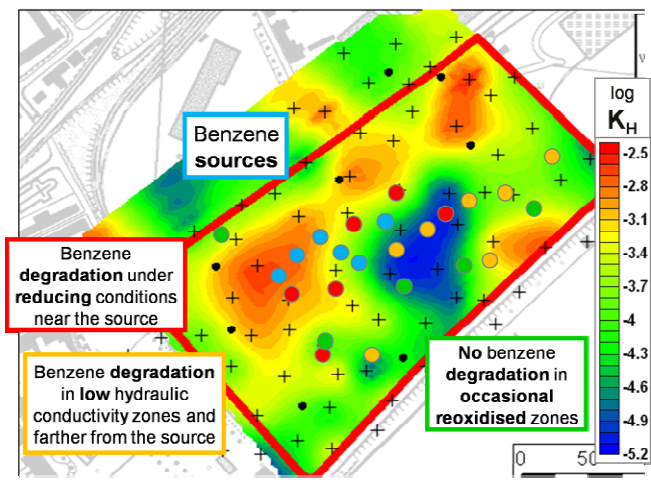
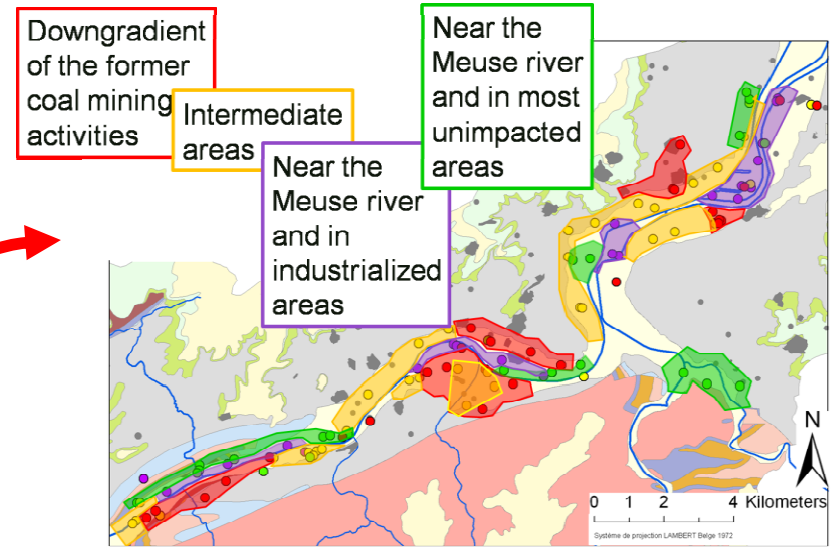
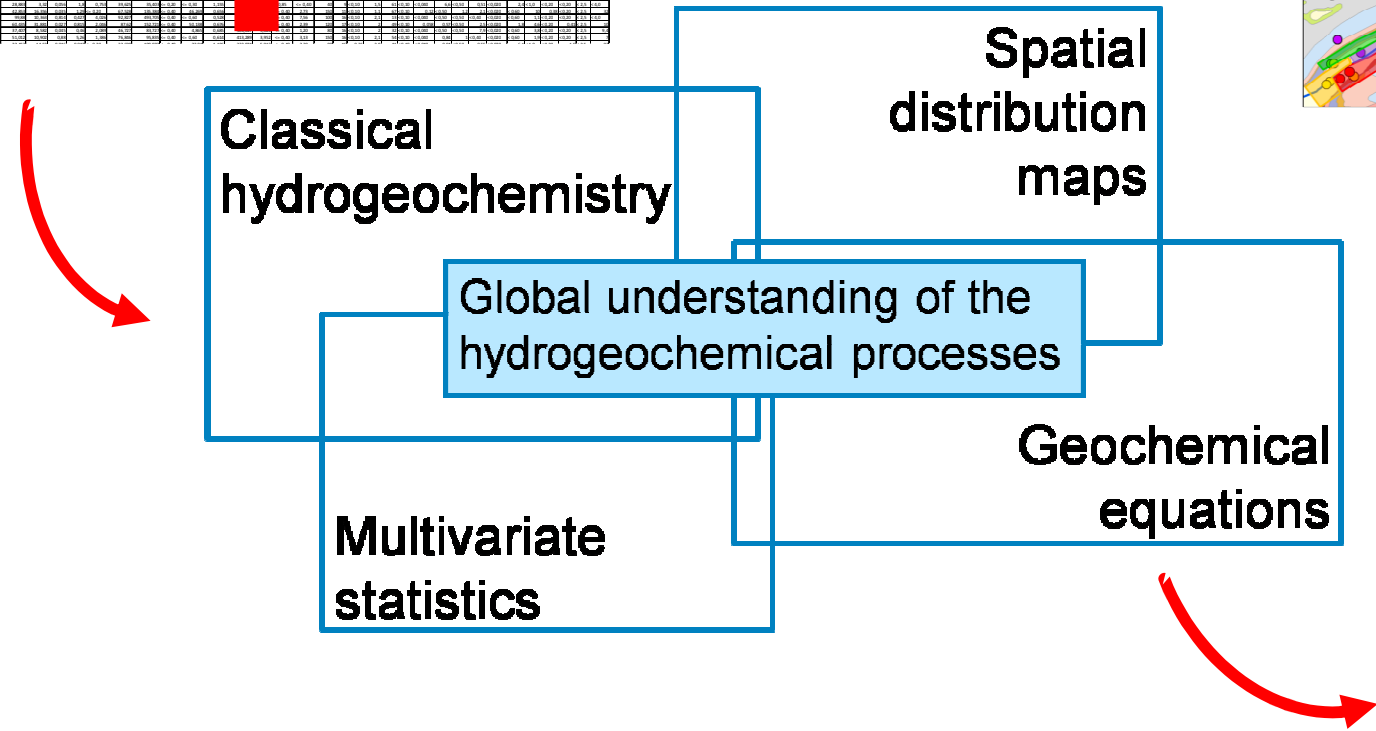
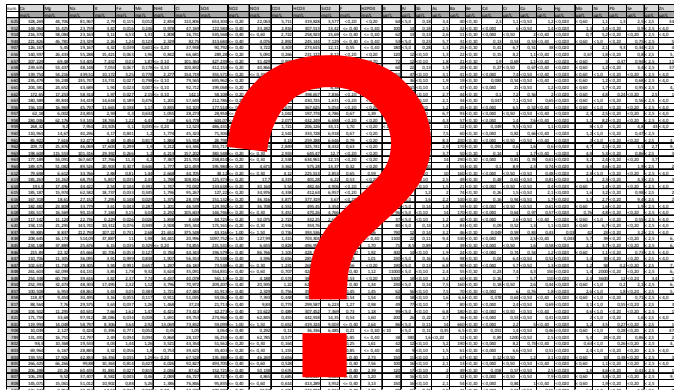


Multivariate statistics for a better understanding of the geochemical processes and their location



Multivariate statistics to understand the geochemical processes induced by groundwater pollution

Multi-scale applying



Hydrogeology 
Environmental Geology

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ALAIN DASSARGUES
SERGE BROUYÈRE