Occurrence & controlling factors of inorganic (and organic) compounds in groundwater of urban and industrial areas

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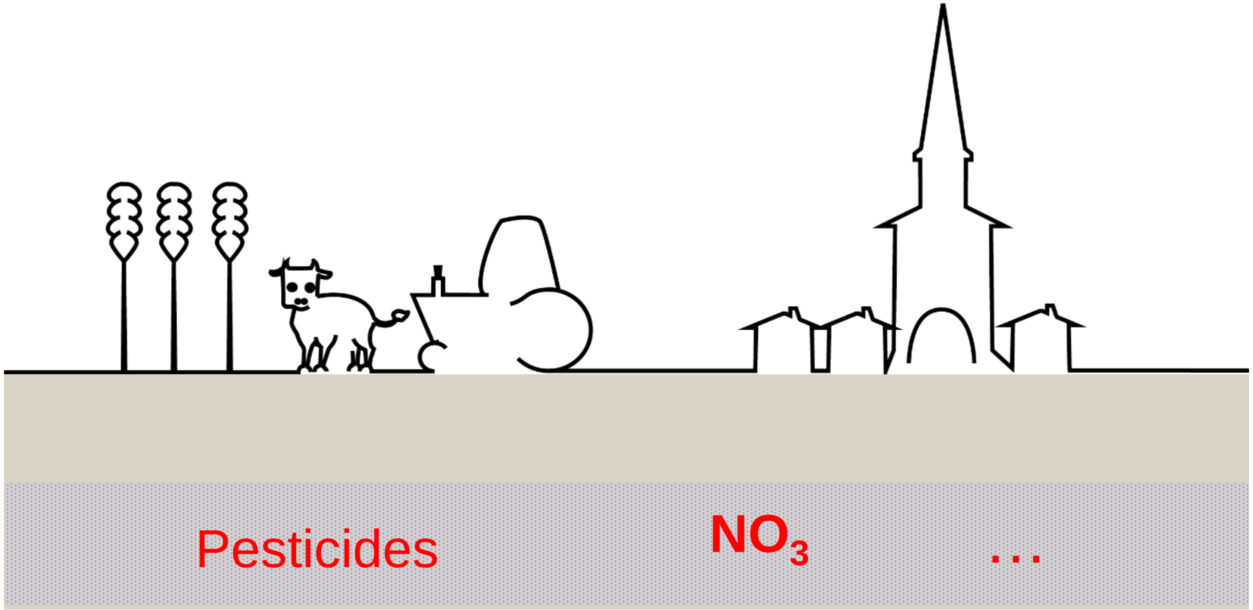
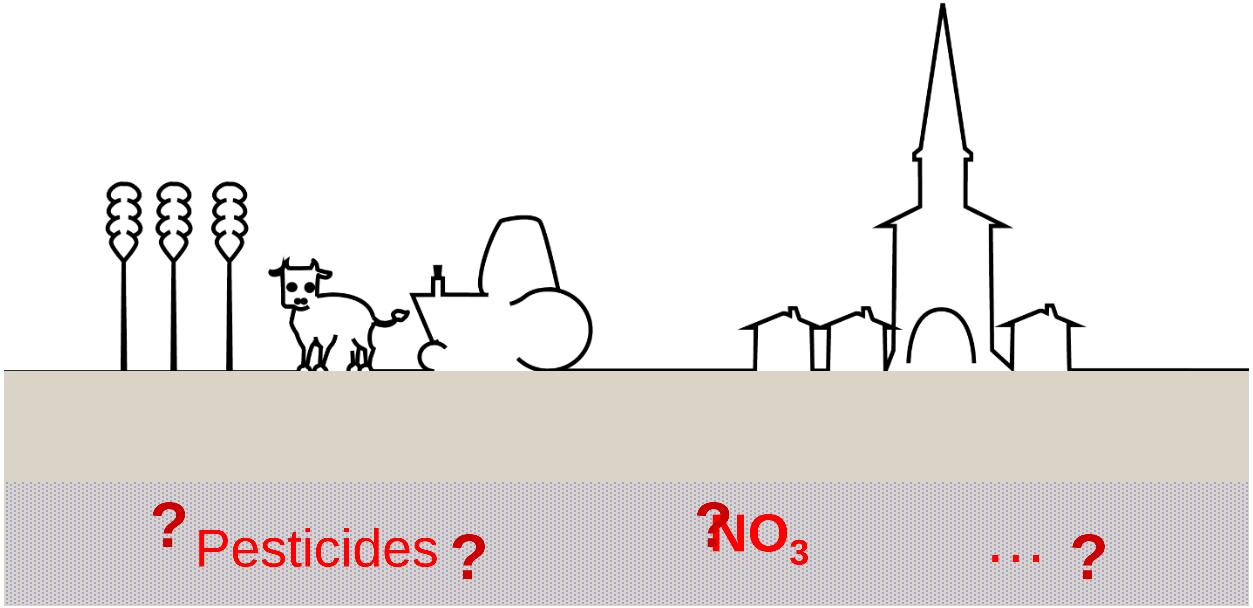
The WFD and the diffuse pollution of groundwater

In rural zones, diffuse pollution of groundwater is relatively well established and studied by hydrogeologists and decision makers…



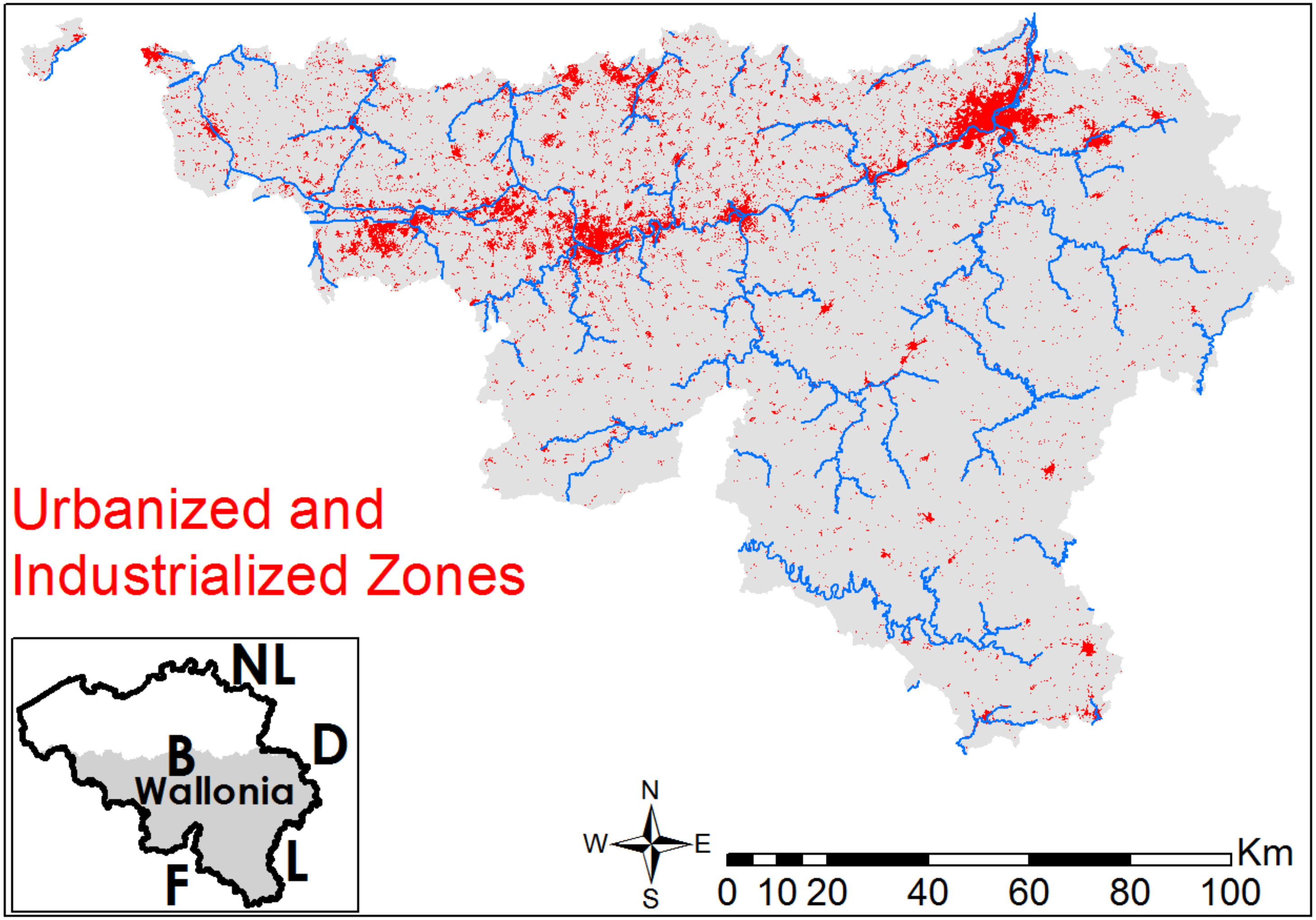
The WFD and the diffuse pollution of groundwater

In urbanised and industrialised zones (U&IZ), diffuse pollution of groundwater in usually less known…



- What are the most frequent pollutants?
- Difference between U&IZs and rural areas in terms of backgrounds?
- Mechanisms of occurrence? Man-induced or Natural factors?
- Consequences in terms of groundwater management?

To obtain pieces of answer to these questions: regional scale investigations in several U&IZ



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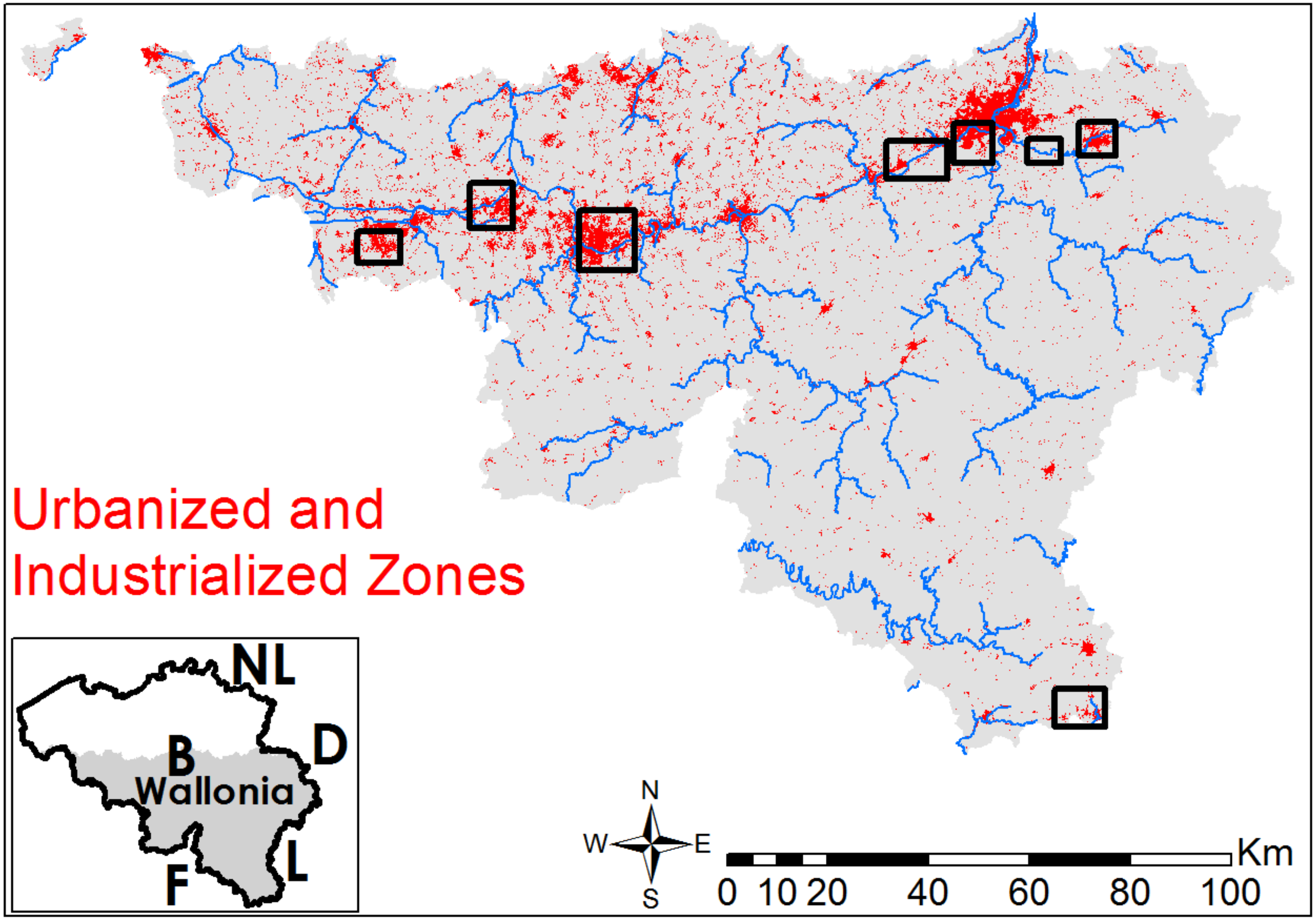
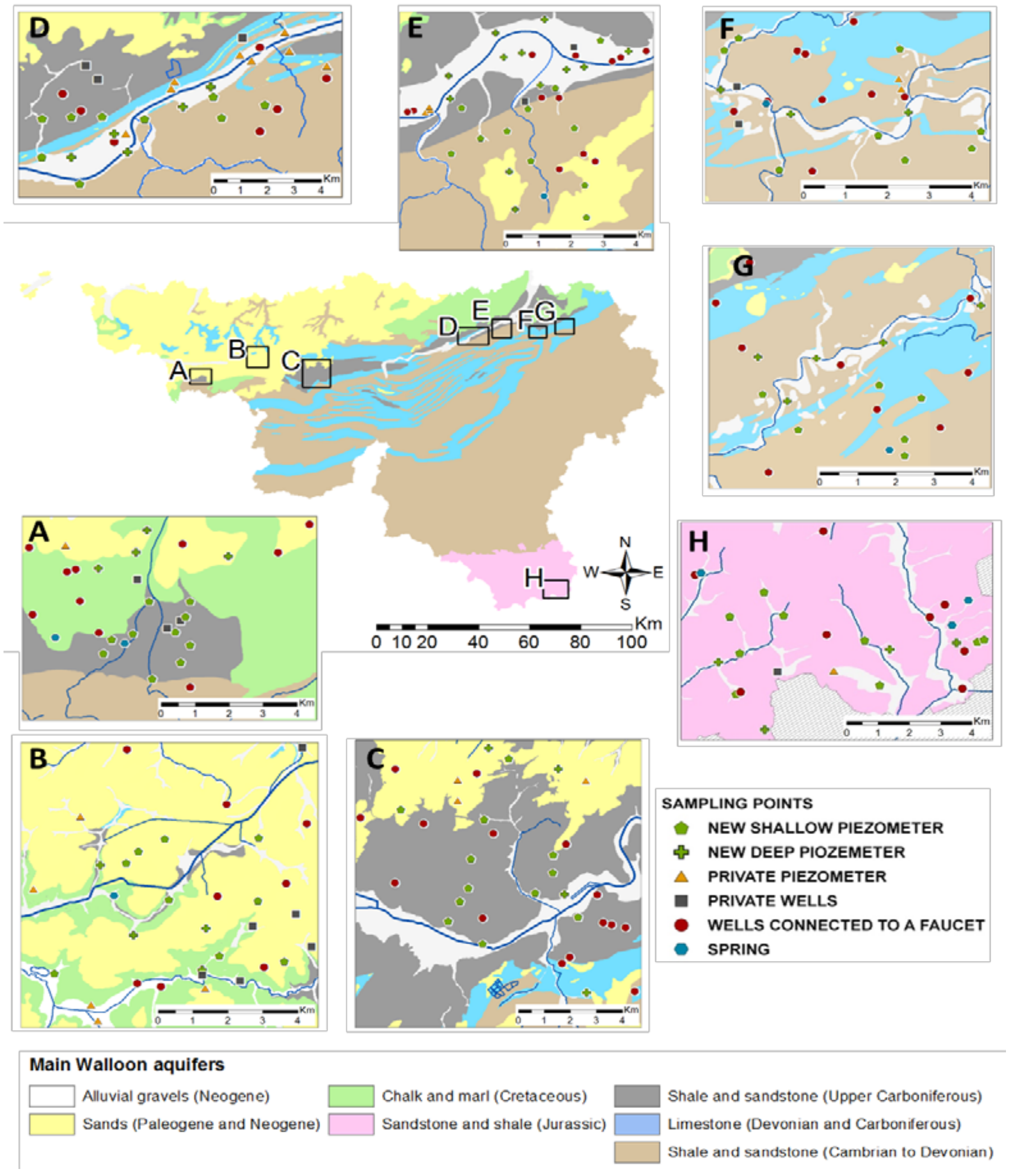


Investigations of different geological contexts



Selection of groundwater sampling locations in all sectors:

- **79 existing pumping wells**: Household, agricultural and industrial wells ;
- **40 existing piezometers**:
- **9 springs**
- **74 additional 2'' shallow piezometers**
- **58 additional 4'' deeper piezometers**

Two sampling campaigns over two years

101 parameters analysed on all collected groundwater samples

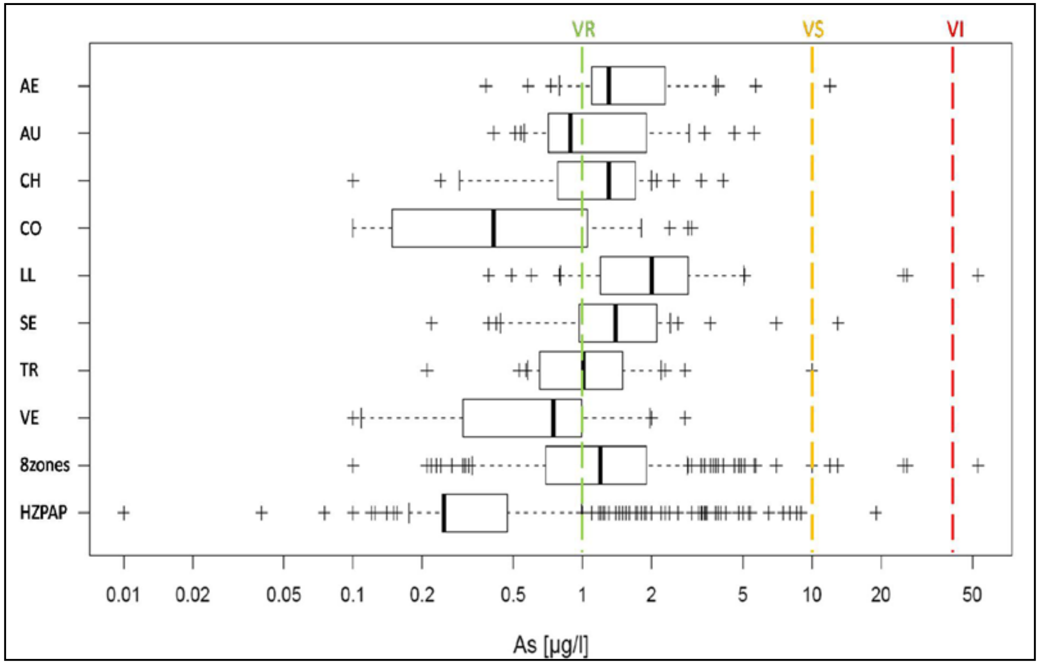
- **In–situ parameters**
  pH, temperature, CE, dissolved O^2, Eh
- **inorganic trace elements**
  Ag B Ba Be Sb Mo Se Cr As Cd Co Cu Hg Ni Pb V Al Zn
- **Organic micro-pollutants**
  16 PAH, BTEX, TPH C10-C35, 17 HVOC, chlorobenzenes, phenol index
- **Major /minor inorganic elements**
  Ca Mg K Na SiO_2 Fe Mn NH_4 HCO_3 Cl SO_4 NO_3 CO_3 NO_2

+ Compilation of existing data for the rest of the Walloon region (outside U&IZ's): **70870 records of inorganic compounds** on 7418 samples from 1965 sampling locations grouped into **1432 sampling sites**

Statistical and graphical description of the data

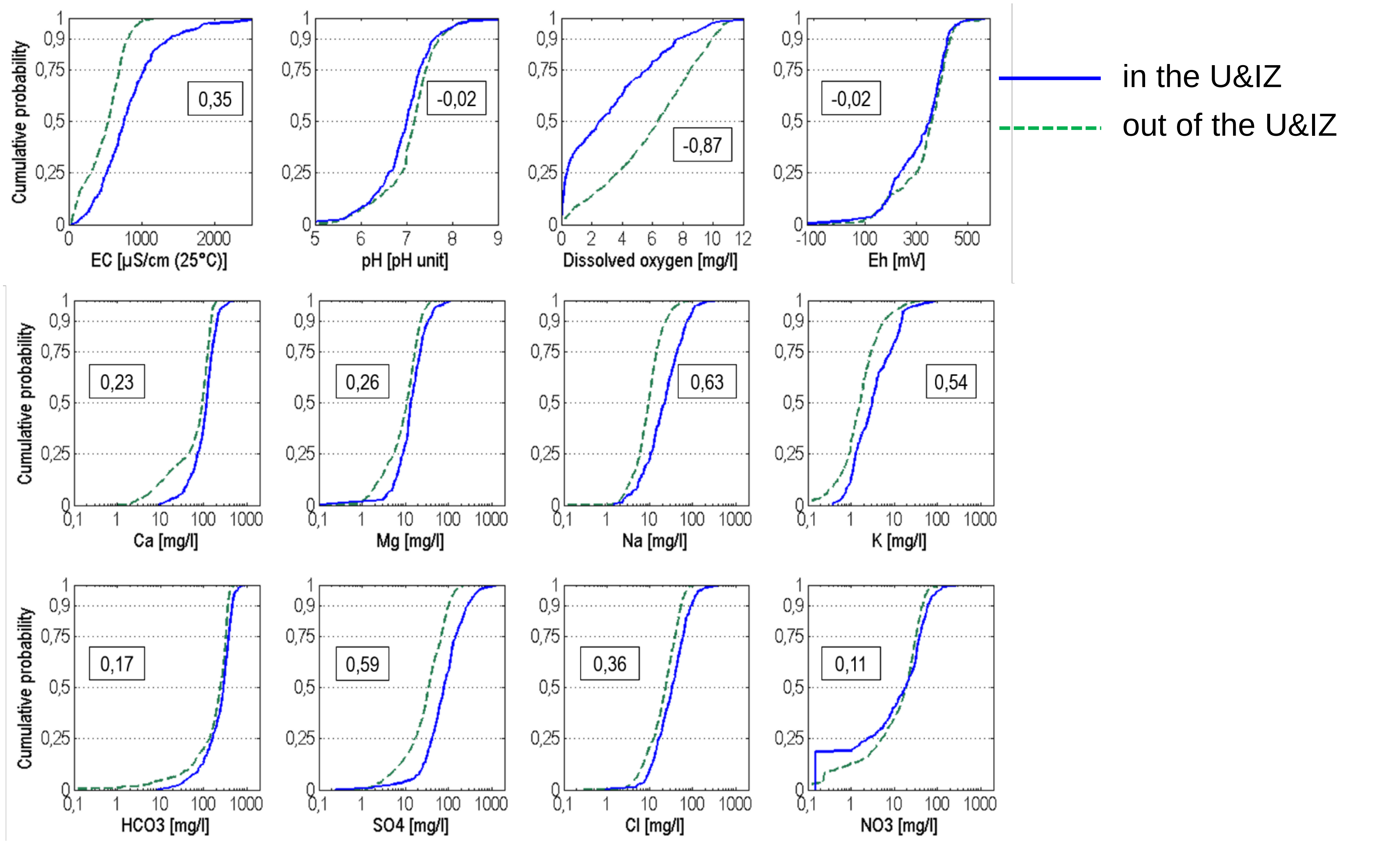
Dataset investigated using general statistical descriptors (FP6 BRIDGE procedure, Muller et al 2006)

- C<LOQ => C = LOQ/2
- Calculation of P25, P50, MEAN, P75, P90 percentiles
- Removal of atypical values C> P75 + ½ × (P75-P25)
- Representation as Box-Plots & Cumulative Distribution Function Plots (CDFPs)



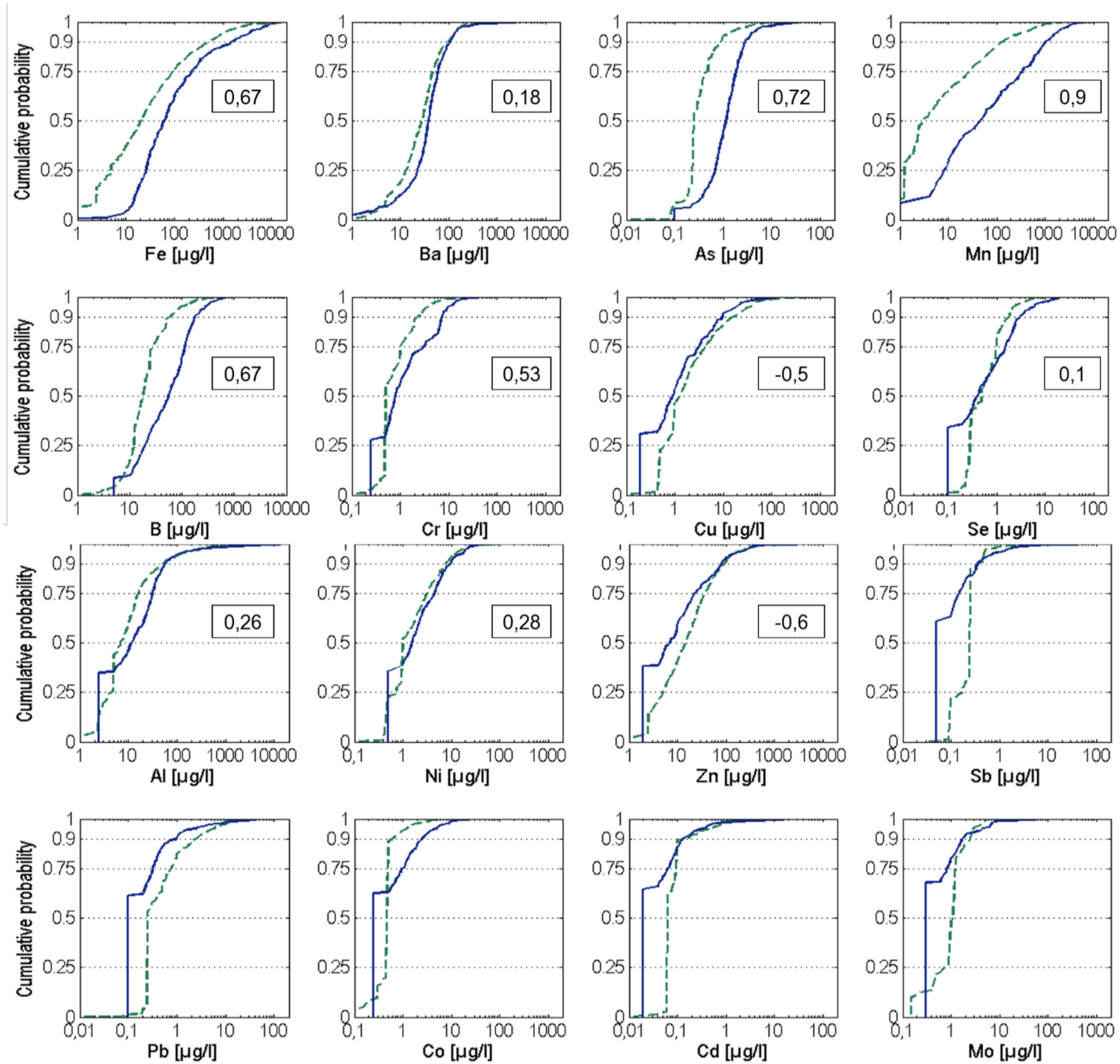
Major elements and physicochemical parameters

(cumulative distribution function plots)



Inorganic trace elements inside and outside de I&UZ

(cumulative distribution function plots)

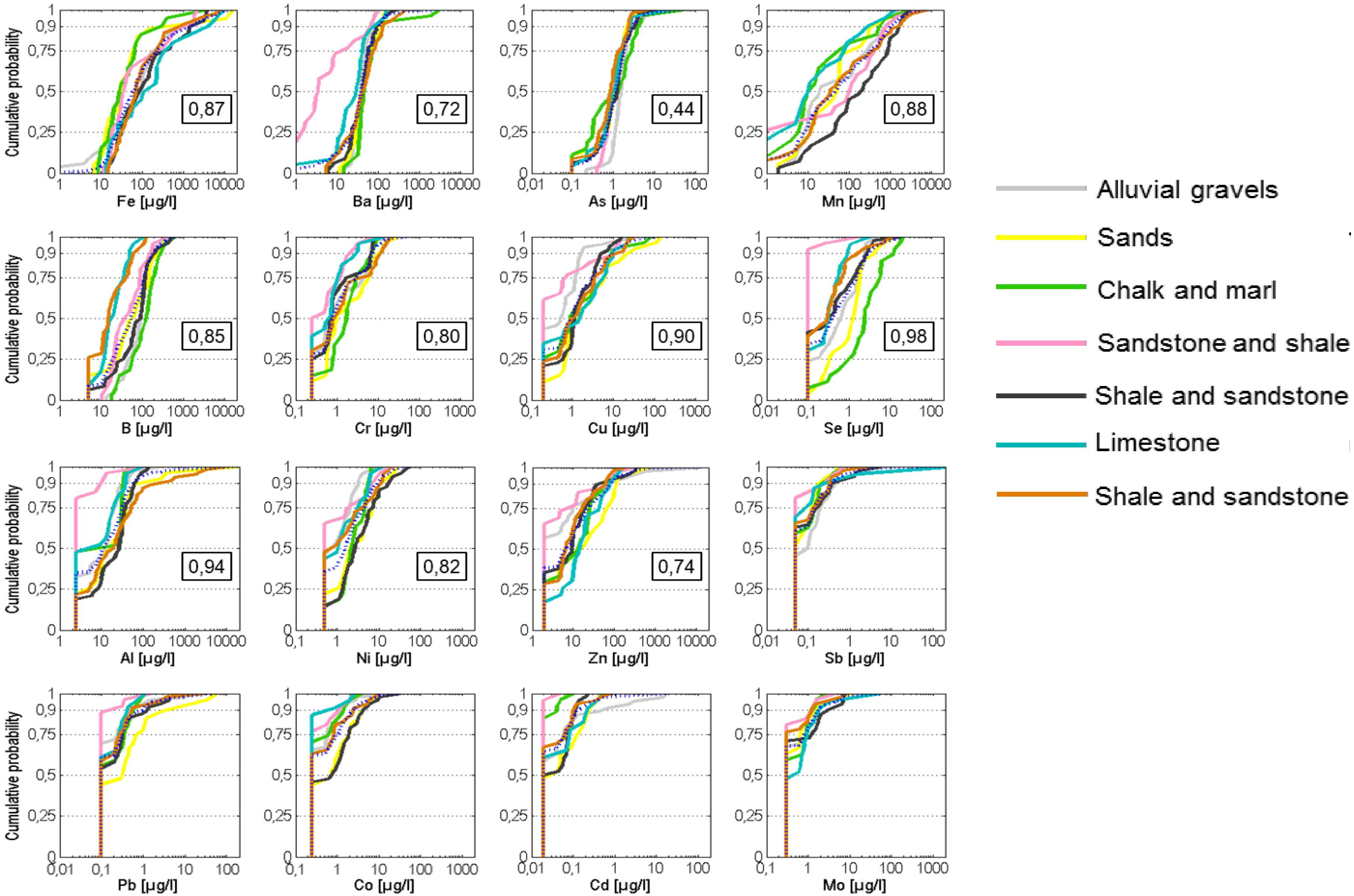


in the U&IZ

out of the U&IZ

Inorganic trace elements in the different geologies

(cumulative distribution function plots)



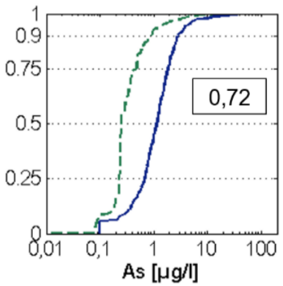
Cross-correlations between different parameters

	Fe	Ba	As	Mn	B	Cr	Cu	Se	Al	Ni	Zn	Sb	Pb	Co	Cd	Mo	O_2diss	CE	Eh	pH	Ca	Mg	Na	K	NH4	Cl	SO4	NO3	HCO3	SiO2
Fe			0,24	0,33				-0,17						0,27			-0,25		-0,26									-0,34		
Ba								0,16	0,17					0,17									0,21	0,16						
As				0,29	0,27							0,31	-0,17			0,29	-0,20	0,29	-0,19		0,31	0,19	0,15	0,24			0,30		0,17	0,19
Mn								-0,17		0,22							-0,40		-0,27	-0,19							0,16	-0,36		
B								0,21				0,16						0,37			0,31	0,24	0,39	0,45		0,23			0,32	
Cr							0,16	0,16					0,18																	
Cu										0,18	0,45		0,44		0,21				0,19			-0,16						0,23		
Se												0,24						0,21			0,21		0,30	0,24		0,16	0,26	0,45		
Al														0,27						-0,23			0,17							
Ni											0,19	0,17		0,44	0,34					-0,24			0,15	0,16			0,18			0,17
Zn															0,36									0,16				0,16		
Sb														0,18	0,21									0,27						
Pb																												0,18		
Co															0,21		-0,21			-0,20			0,16				0,18	-0,16		
Cd																				-0,17									-0,20	
Mo																								0,28						

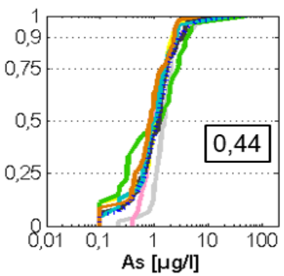
Kendall-tau, with significance level for $p<0.001$

Explaning factors: Example 1 : Arsenic

in U&IZ   out U&IZ



As higher in U&IZ compared to non U&IZ

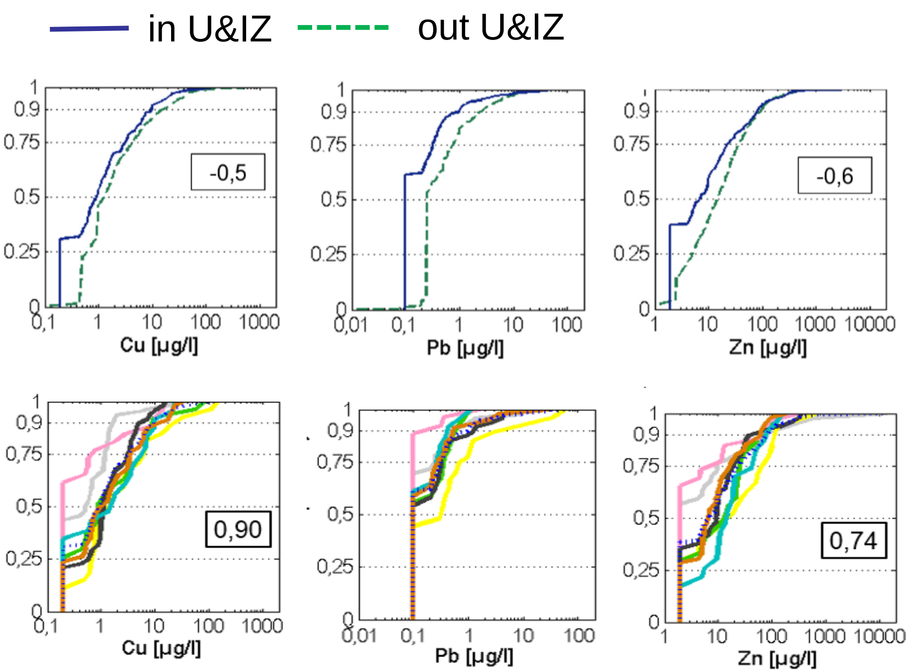


As not so geology dependent

As positively correlated with Fe, Mn, SO4…
negatively correlated with dissolved O2, Eh

→ As occurrence in groundwater related to changes in redox conditions in the U&I zones
→ Pyrite oxydation + co-precipitation with Fe – Mn oxy-hydroxides, followed by the dissolution of these minerals in reducing environments (e.g. Pauwels et al. 2010)

Explaining factors: Example 2 : Cu, Pb, Zn



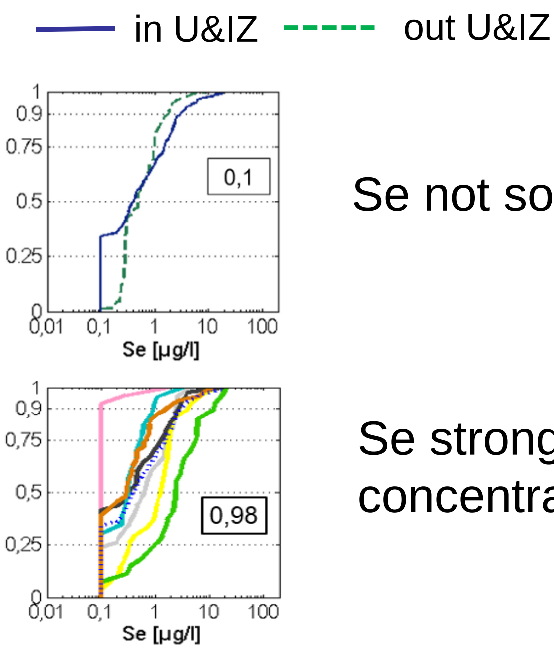
Cu, Pb, Zn slightly lower in U&IZ compared to non U&IZ

Cu, Pb, Zn relatively geology dependent

Cu, Pb, Zn positively correlated with each other
Cu positively correlated with NO_3,
Pb, Zn as well but to a lesser extent

→ Slightly reducing (anaerobic) redox conditions favour the occurrence of Cu, Pb and Zn in groundwater

Explaning factors: Example 3 : Selenium



Se not so different in and out of U&IZ

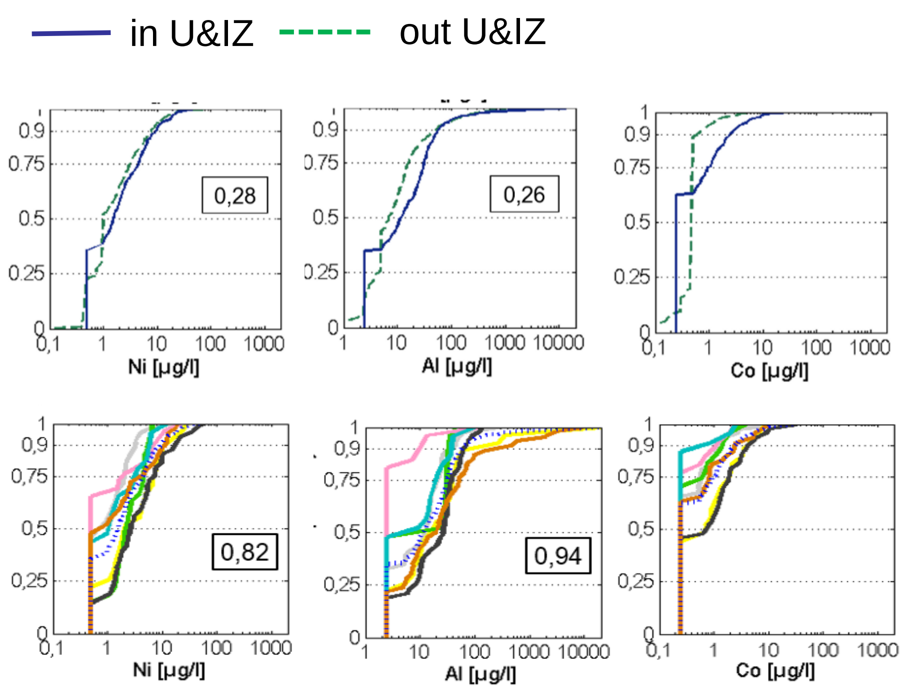
Se strongly geology dependent, with higher concentrations in chalk / sand aquifers

Se positively correlated with CE and major elements, particularly with nitrate

→ Geogenic origin, with selenium released by oxidation of sulfide minerals

→ Selenium also oxidized into selenate, remaing oxidized and dissolved because of high NO3 keeping oxidizing anaerobic conditions (e.g. Wright 1999, Bailey et al. 2011)

Explaning factors: Example 4 : Ni, Al, Co



Ni, Al, Co not very different in and out of U&Izs

Ni, Al, Co relatively geology dependent (higher in Carboniferous shale)

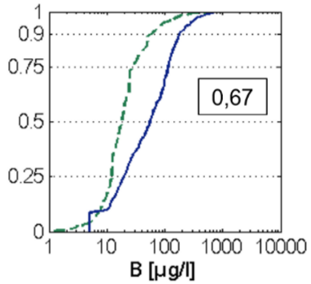
Ni, Al, Co negatively correlated with pH
Co correlated with Fe, Ni with Mn

→ Acidic conditions contribute to their solubility

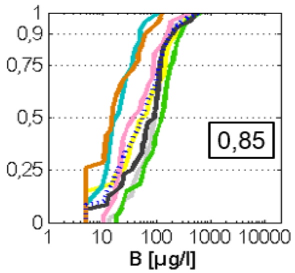
→ Source: sorption on Fe-Mn oxi-hydroxides and release when these mineral dissolve

Explaning factors: Example 5 : Boron

in U&IZ ----- out U&IZ



Boron higher in U&IZ compared to non U&IZ



Boron geologically dependent

Boron not correlated with redox indicators
correlated with CE and major elements,
particularly to K, Cl and Na

→ Boron occurrence in groundwater related to sewage waste waters
→ correlation with CE & EM + geology dependence → geogenic sources as well

Synthesis and conclusions

In urbanised and industrialised zones (U&IZ), the occurrence of inorganic pollutants in groundwater can be related to different factors…

External inputs from pollution sources:
no strong evidences, except for boron from waste waters

Geogenic sources:
evidences for several compounds such as Fe, Mn, As, Se …

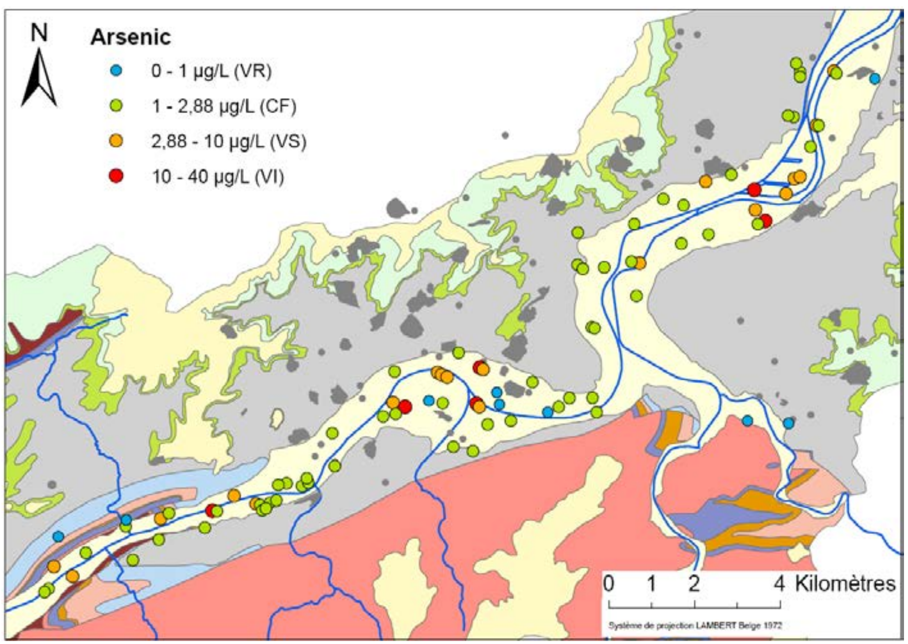
But among all, it seems that the most significant factor relates to changes in the environmental conditions in groundwater, especially **lower redox conditions, with anaerobic conditions** prevailing more often in the U&IZ than outside

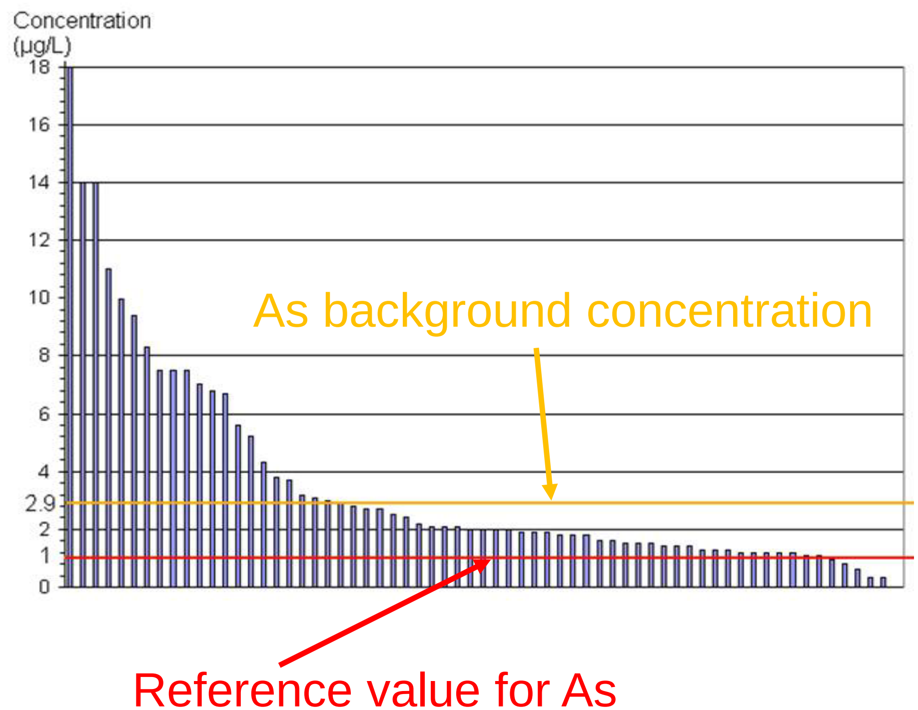
Synthesis and conclusions

In terms of decision-making related to groundwater management …

Trigger values for pollutant concentrations in groundwater to be adapted to account for the generalized pollution in the U&IZ (e.g. remedial objectives)

e.g. Arsenic in the Meuse alluvial aquifer around Liège





Synthesis and conclusions

In terms of decision-making related to groundwater management …

Trigger values for pollutant concentrations in groundwater adapted to account for the generalized pollution in the U&IZ (e.g. remedial objectives) → **BCK_CONC= P90**

	Fe	*Ba*	*As*	*Mn*	*B*	*Cr*	*Cu*	*Se*	*Al*	*Ni*	*Zn*	*Sb*	*Pb*	*Co*	*Cd*	*Mo*
Reference Value			*1,0*			*2,5*	*15,0*			*10*	*90*		*2,5*		*0,25*	
Alluvial gravels (Neogene)	1124	66,0	2,57	807	185	6,80	1,70	2,50	37,5	3,25	70,4	0,43	0,43	1,25	0,09	1,68
Sands (Paleogene and Neogene)	112	118	2,30	460	262	11,08	25,6	4,16	53,5	15,2	114	0,20	1,07	4,32	0,25	1,68
Chalk and marl (Cretaceous)	313	111	3,75	591	290	7,32	10,0	12,4	34,0	5,62	70,2	0,24	0,59	1,48	0,04	1,32
Sandstone and shale (Jurassic)	1306	67,5	2,95	875	180	2,20	9,70	*0,20*	10,0	8,70	72,5	0,26	0,21	1,15	*0,04*	1,25
Shale and sandstone (Upper Carboniferous)	1774	91,4	2,88	1710	206	7,20	5,75	2,86	64,3	19,0	47,6	0,35	0,46	3,90	0,12	3,25
Limestone (Devonian and Carboniferous)	4325	85,6	2,40	744	50,8	3,20	9,68	1,07	34,8	6,00	80,0	0,28	0,41	0,79	0,29	1,60
Shale and sandstone (Cambrian to Devonian)	886	118	2,40	1670	66,5	12,0	13,9	1,75	87,8	11,5	61,5	0,35	0,47	2,50	0,11	1,30

Resulting background concentrations for the main aquifer contexts of the Walloon region (conc. In µg/L)

Synthesis and conclusions

In terms of decision-making related to groundwater management …

In the scope of the Water Framework Directive, **elevated background concentrations should also lead to revision of groundwater quality objectives and management plans** to account for these specific contexts (excessive costs, technical infeasibility of remedial options…)

Any questions?

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