

Using pharmaceuticals as tracers of urban sources of nitrate in groundwater

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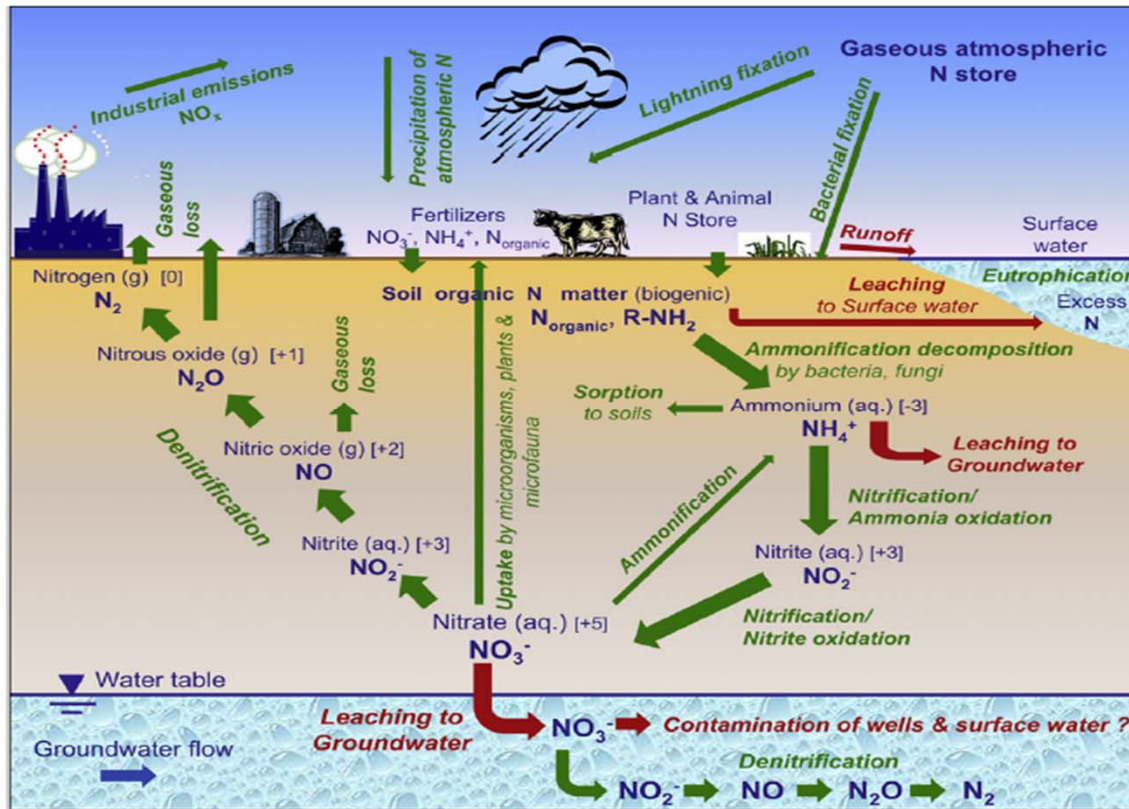
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Nitrate in groundwater : still a threat and a challenge...



Source: Rivet et al., 2008

→ Strong need to identify the sources in order to take appropriate measures for N reduction in surface and subsurface waters

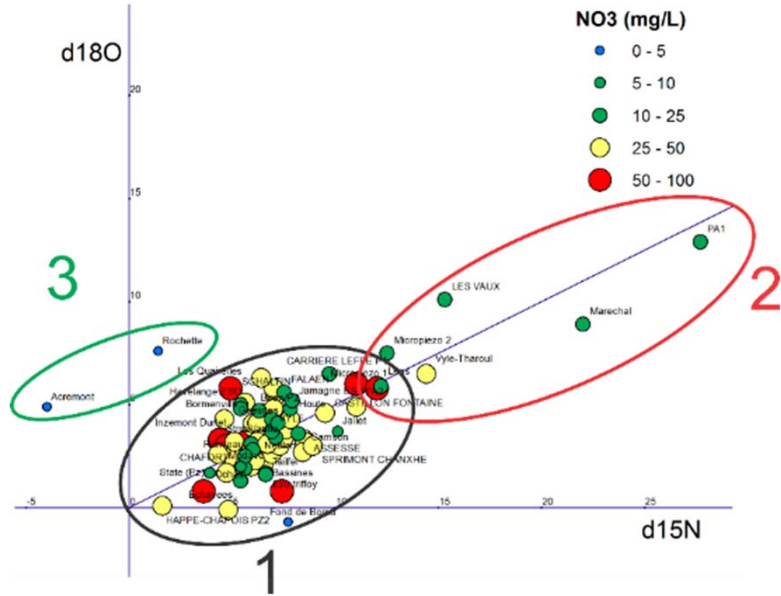
- Risk for human health (max 50 mg/L) and aquatic ecosystems (max 25 mg/L)
- Various sources of pollution
- Urban : **waste water**
- Agriculture:
 - Synthetic fertilisers
 - **Organic fertilisers**
 - **Manure**
- Various N forms with complex reaction pathways, under changing redox conditions

Various methods are available to identify N sources

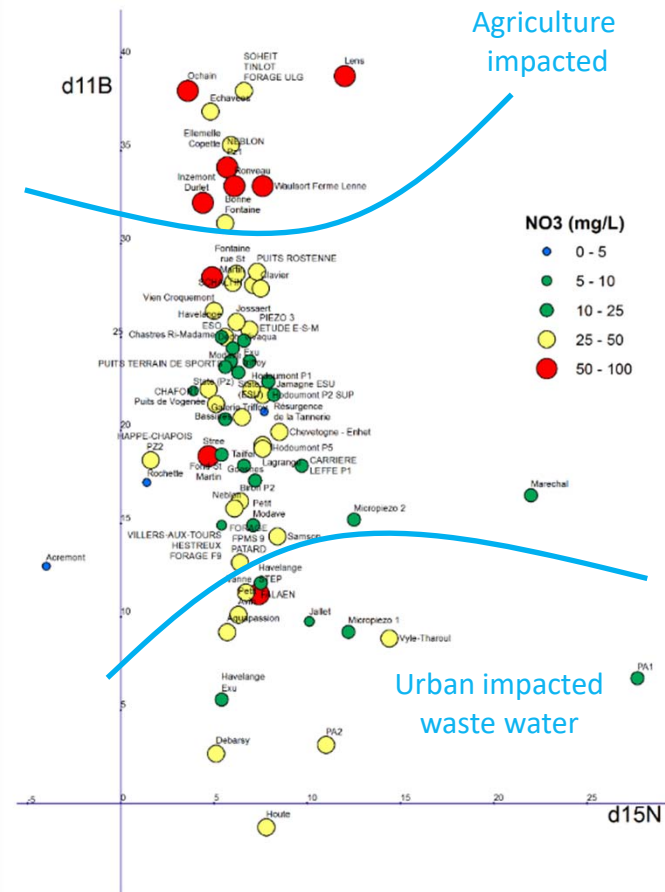
Land use

Anthropogenic pollution indicators
such as Cl, SO₄, OM, Boron ...

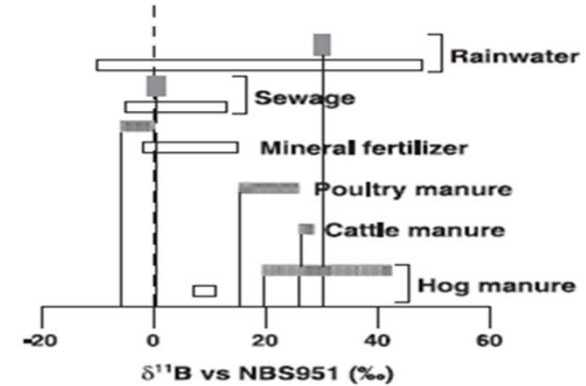
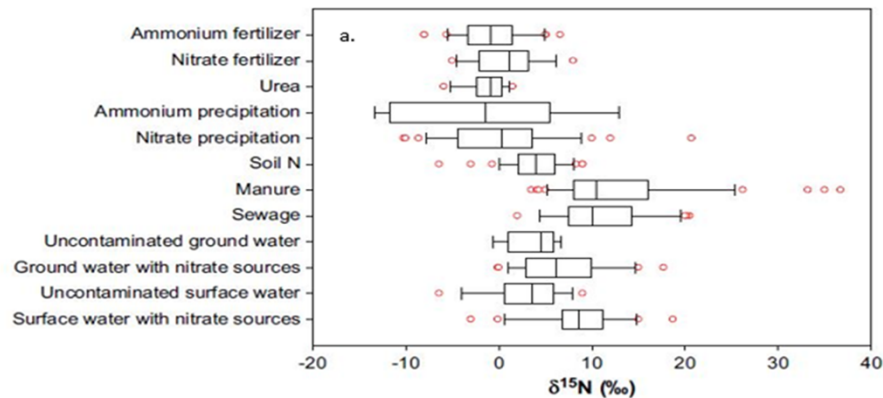
Nitrate stable isotopes,
in particular $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$



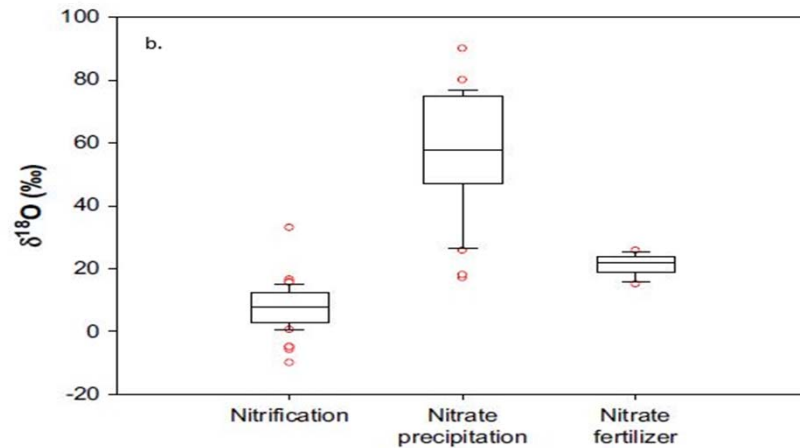
Boron stable isotopes, in particular $\delta^{11}\text{B}$



Various methods are available to identify N sources



Widory et al., 2009



Xue et al., 2009

→ There is still a need to identify other N sources markers!

Candidates : **Pharmaceutical compounds!**

Use of pharmaceutical compounds as N-markers

Potential chemical markers of urban sources in groundwater :

- high solubility;
- low to non-volatile;
- persistent;
- naturally absent in groundwater

Substances for human use → domestic waste water

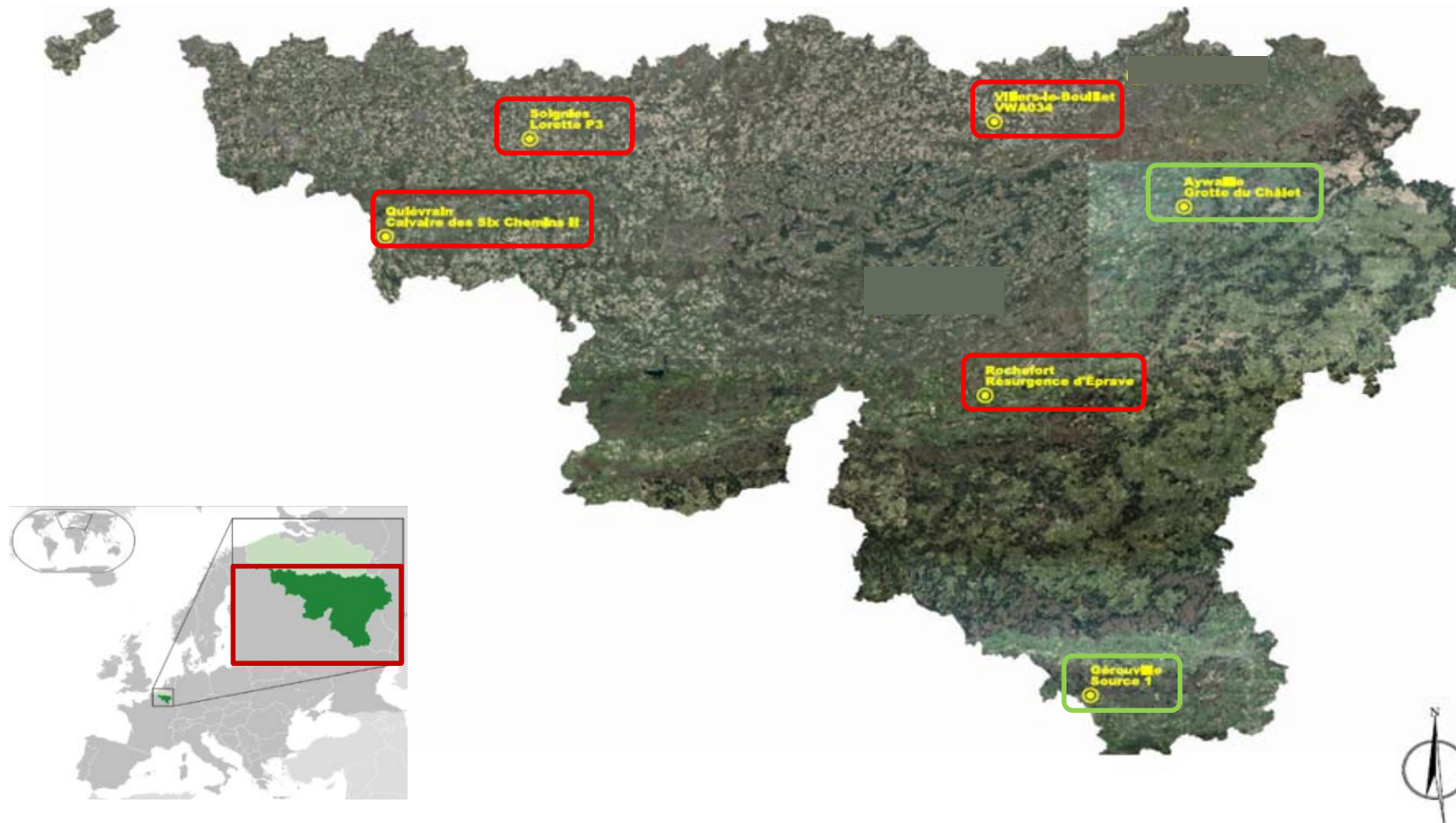
Veterinary substances → agricultural waste water (manure...)

Inventory on 54 compounds in waters, at the scale of the Walloon Region in Belgium: IMHOTEP project

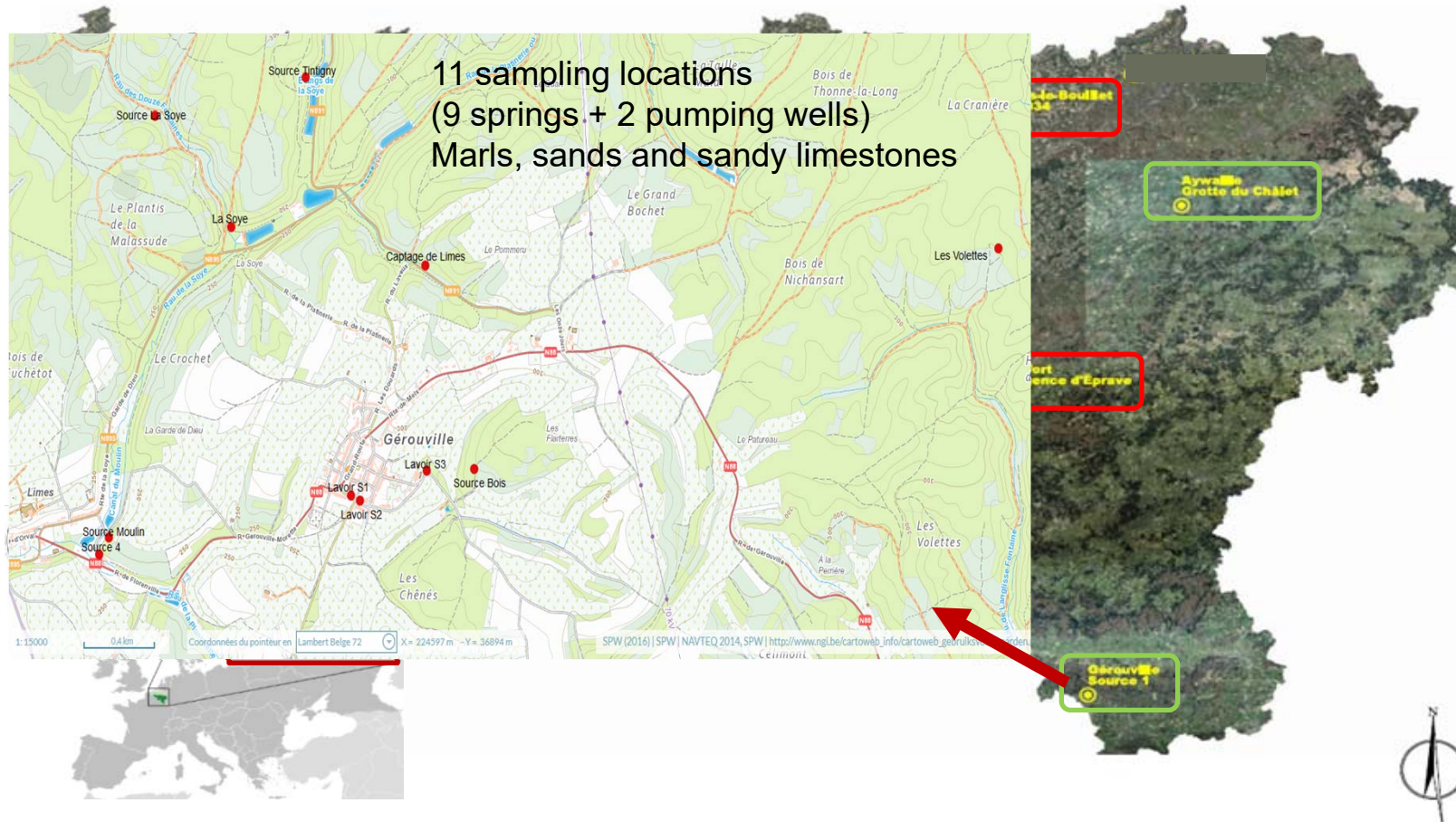
Anti-pain & Anti-inflammatory	Antibiotics	Cardiovascular	Pest control
Diclofénac	Clarithromycine	Aténolol	Clorsulon
Ibuprofène	Florfénicol	Acide fénofibrique	Dicyclanil
Hydroxyibuprofène	Lincomycine	Irbésartan	Lévamisole
Kétoprofène	Sulfaméthazine	Losartan	Métrifonate
Naproxène	Sulfadiazine	Métoprolol	Parconazole
Paracétamol	Sulfaméthoxazole	Nafronyl	Diuretics
Tramadol	Triméthoprim	Pravastatine	Furosémide
Hormones	Antiacids	Ramipril	Hydrochlorothiazide
17a-EthinylEstradiol (EE2)	Ranitidine	Ramiprilate	Life-style products
17β-estradiol (E2)	Antidepressants	Rosuvastatine	Caféine
Estriol (E3)	Carbamazépine	Sotalol	Cotinine
Estrone (E1)	10,11-Epoxy-carbamazépine	Trimétazidine	Pesticides
Mestranol	Citalopram	Contrasting agents	BAM
Progestérone	Oxazépam	Ioméprol	Bentazone
	Venlafaxine	Iopromide	Isoproturon
			MCPA
			Triclosan

Human – **Veterinary** – Mixed
 In **bold** : most detected

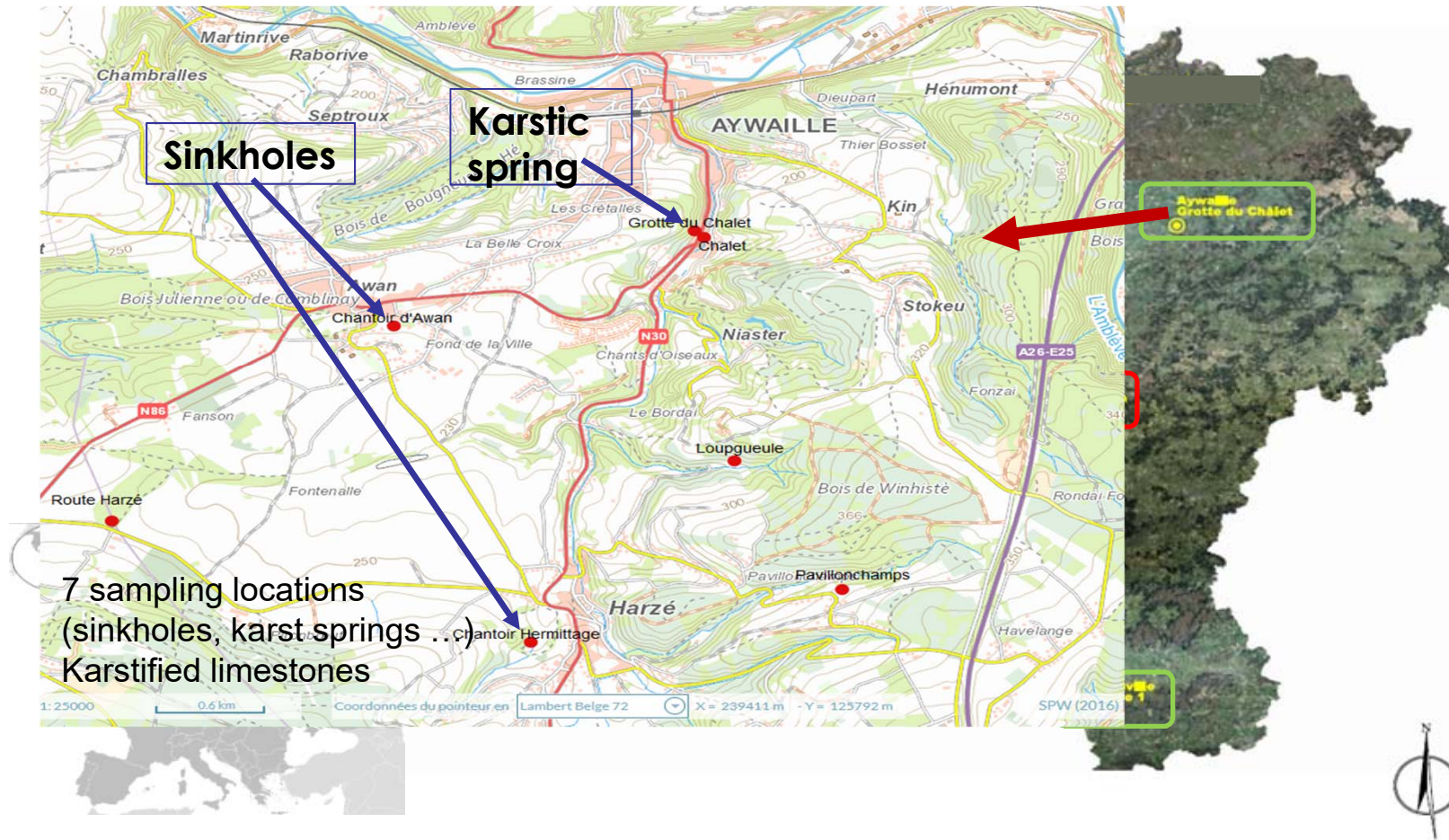
Selection of sampling locations for specific investigations on NO₃ sources: 4 IMHOTEP sites + 2 sub-catchments of interest



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Selection of sampling locations for specific investigations on NO₃ sources: 4 IMHOTEP sites + 2 sub-catchments of interest



Sampling campaign : field measurements and lab analyses

- Field parameters (CE, pH, T°, DO)
- Major anions and cations (Ca, Mg, Na, K, HCO₃, SO₄, Cl)
- Some minor anions and cations (Sr, Li, ...) + dissolved and total Fe and Mn
- Nitrogen species : NO₃, NO₂, NH₄, Kjeldahl-N (NKJ)
- COD, TOC
- Nitrate isotopes ($\delta^{15}\text{N-NO}_3$, $\delta^{18}\text{O-NO}_3$)
- Boron isotopes ($\delta^{11}\text{B}$ in B)
- Pharmaceuticals

ULiège (BE)

SWDE lab (BE)

UFZ Leipzig (DE)

VITO (BE)

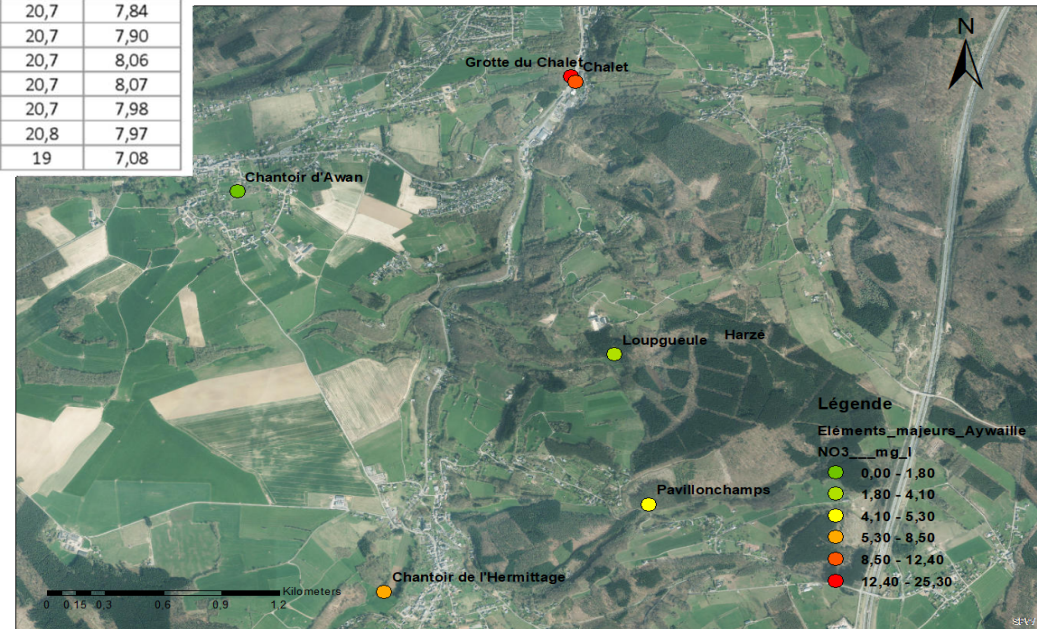
SWDE lab (BE)

Exploration of chemical data : various maps and graphs

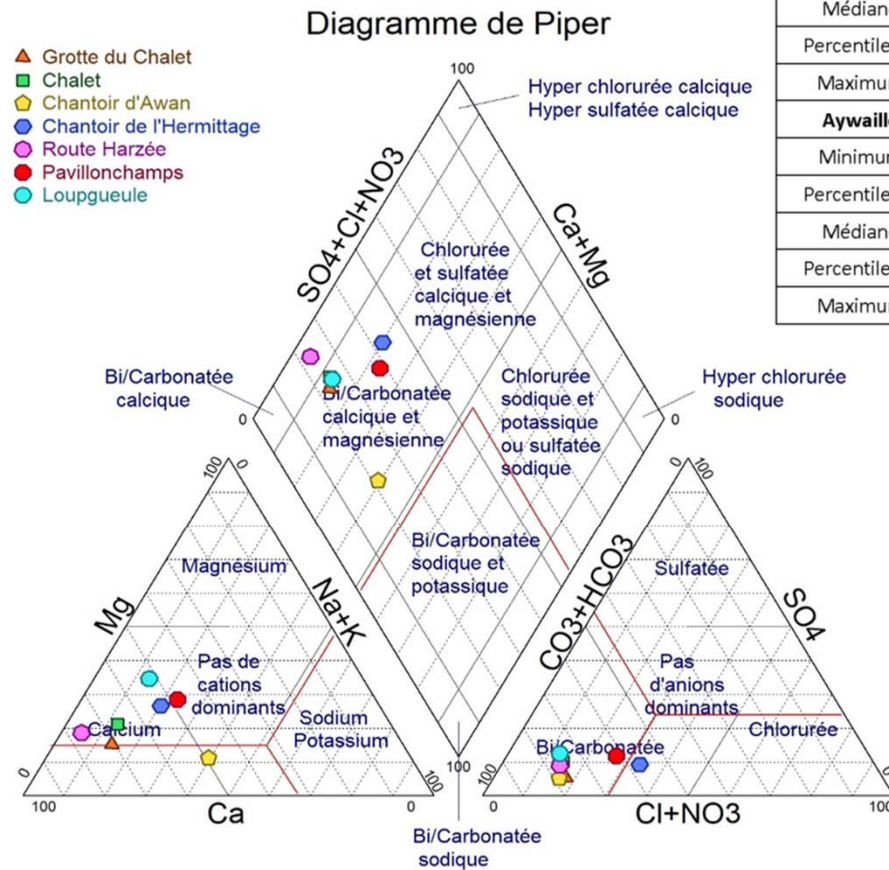
Echantillons	Localité	T(°C)	Cond. (µS/cm)	TDS (%)	DO (mg/l)	pH	Cond.25°C (µS/cm)	T_labo (°C)	pH_labo
Les volettes	Gérouville	19,48	364	0,26	7,4	6,9	366,2	20,2	8,07
Captage de Limes	Gérouville	20,13	371	0,27	7,36	6,85	392,2	20,4	8,14
Source 4	Gérouville	17,06	411	0,31	8,48	6,91	462,4	20,5	8,08
Source Moulin	Gérouville	19,87	345	0,25	7,43	7,1	364,5	20,7	8,16
Lavoir S1	Gérouville	18,79	844	0,62	6,78	8,24	900,8	20,7	8,24
Lavoir S2	Gérouville	18,56	573	0,43	7,14	8,27	699,6	20,7	8,30
Lavoir S3	Gérouville	14,6	559	0,45	9,94	8,15	613,0	20,6	7,93
Source bois	Gérouville	15,51	510	0,41	7,72	8,39	579,6	20,4	7,99
Source La Soye	Gérouville	11,18	425	0,38	11,12	7,93	419,1	20,3	8,01
La soye	Gérouville	15,4	314	0,25	9,18	8,8	365,0	20,3	8,21
Source Tintigny	Gérouville	15,58	323	0,26	9,8	8,23	363,5	20,3	8,08
Grotte du Chalet	Aywaille	15,53	463	0,37	10,43	6,79	516,7	20,7	8,13
Chalet	Aywaille	19,57	498	0,36	7,94	7,13	384,9	20,8	8,17
Chantoir d'Awan	Aywaille	19,95	1042	0,75	6,74	6,78	1189,8	20,8	8,18
C.de l'Hermitage	Aywaille	21,46	130	0,09	7,73	13,49	123,2	20,9	7,61
Route Harzé	Aywaille	19,91	585	0,42	6,92	8,33	635,8	20,9	8,38
Pavillonchamps	Aywaille	21,01	213	0,15	8,01	6,46	193,2	20,7	7,84
Loupgueule	Aywaille	20,52	120	0,09	7,84	6,44	179,9	20,7	7,90
Eprave 1	Eprave	16,85	380	0,29	12,44	6,47	410,6	20,7	8,06
Eprave 2	Eprave	/	/	/	/	/	409,9	20,7	8,07
Soignies P3	Soignies	11,49	638	0,56	0,29	6,26	866,6	20,7	7,98
Quiévrain	Quiévrain	14,69	730	0,59	6,52	6,44	903,4	20,8	7,97
VWA034	V. Waleffe	13,3	954	/	3,6	6,77	1073,7	19	7,08

Data exploration (here: field and lab parameters)

Cartographic representation of land use and chemical compounds



Exploration of chemical data : various maps and graphs

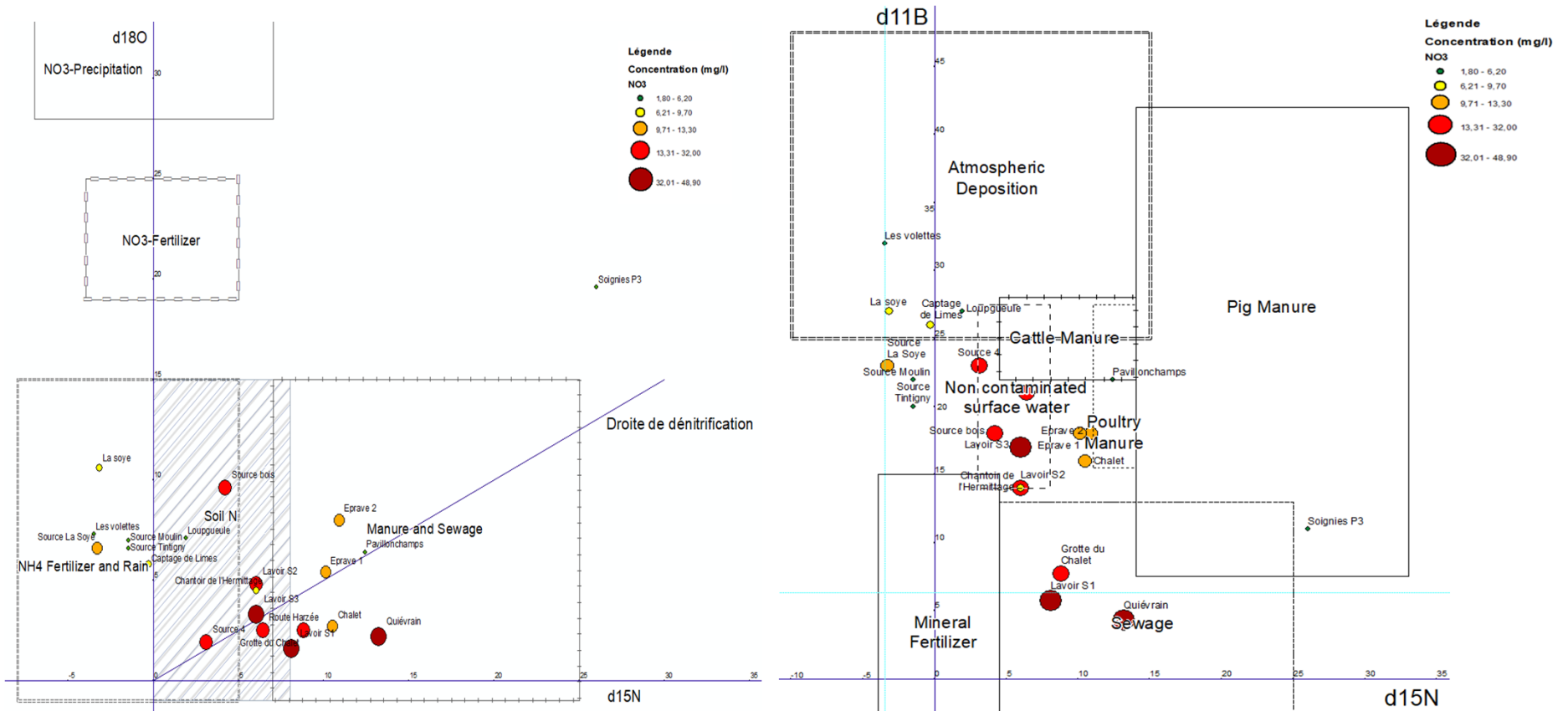


Hydrochemical facies

	NH ₄	NKJ	DCO	NO ₃	NO ₂	TOC
	(mg/l)	(mg/l N)	(mg/l O ₂)	(mg/l)	(mg/l)	(mg/l C)
Gérouville						
Minimum	0,00	0,00	0,00	4,40	0,00	0,34
Percentile 25	0,00	0,00	0,81	11,90	0,00	0,96
Médiane	0,00	0,00	0,81	11,90	0,00	0,96
Percentile 75	0,00	0,00	1,39	26,45	0,01	1,13
Maximum	0,02	0,40	2,26	45,80	0,02	1,59
Aywaille						
Minimum	0,00	0,00	0,98	1,80	0,00	0,89
Percentile 25	0,00	0,00	0,81	11,90	0,00	0,96
Médiane	0,00	0,10	4,27	8,50	0,04	2,02
Percentile 75	0,00	0,00	1,39	26,45	0,01	1,13
Maximum	57,00	38,00	146,21	25,30	0,61	25,27

Statistics on waste water indicators

Exploration of chemical data : various maps and graphs



Data on stable isotopes

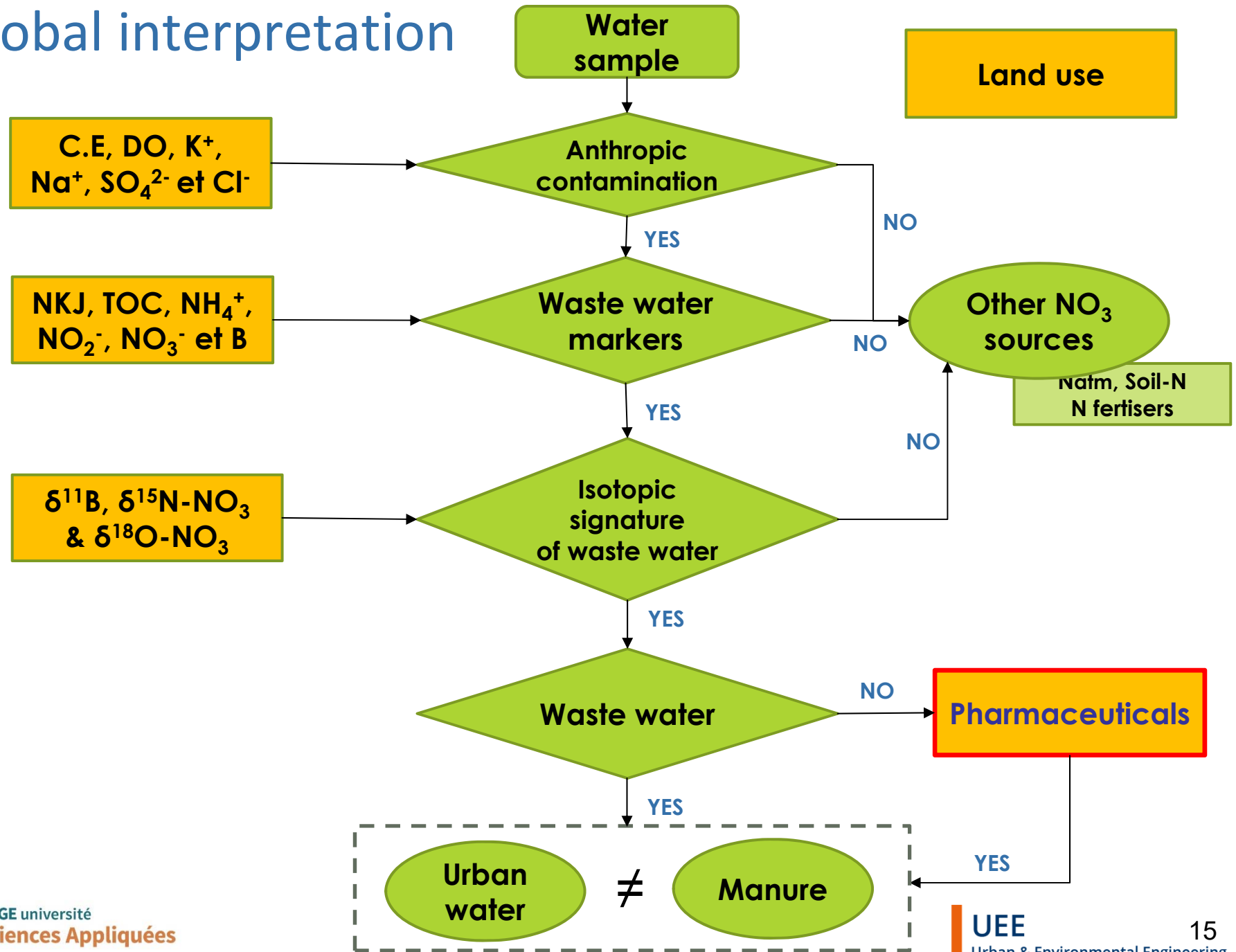
Exploration of chemical data : various maps and graphs

Substances/Nom de l'échantillon	Les voiettes	Captage de Limes	Source 4	Source Moulin	Lavoir S1	Lavoir S2	Lavoir S3	Source bois	Source La Soye	La soye	Source Tintigny	% de substances (> LQ)	% de substances (entre LD et LQ)
Cafeine	0,00	0,00	6	55,21	13,34	6,00	0,00	6,00	33,16	0,00	0,00	18,18	27,27
Carbamazepine	0,00	0,00	0,2	0,00	1,09	2,63	0,00	0,82	0,00	0,00	0,00	27,27	9,09
Cotinine	0,3	0,00	0,00	0,00	1,14	7,75	0,30	0,80	1,67	0,30	0,30	36,36	36,36
Diclofenac	0,00	0,00	0,00	6,89	19,14	0,00	0,00	18,01	0,00	0,00	0,00	27,27	0,00
Hydrochlorothiazide	0,00	0,00	0,22	0,00	0,65	30,68	0,00	0,55	0,10	0,00	0,10	36,36	18,18
Irbesartan	0,00	0,00	0,00	0,00	0,00	26,34	0,00	0,00	0,00	0,00	0,00	9,09	0,00
Paracetamol	0,00	0,00	0,00	0,00	106,23	0,64	0,00	98,80	1,41	0,00	0,00	36,36	0,00
Sotalol	0,15	0,15	0,15	0,00	43,66	0,42	0,00	36,92	0,00	0,00	0,00	27,27	27,27
Sulfamethoxazole	0,00	0,00	0,00	0,00	5,47	2,08	0,00	3,91	0,00	0,00	0,00	27,27	0,00
Venlafaxine	0,52	0,52	0,25	0,00	0,00	1,27	0,00	0,00	0,25	0,00	0,00	27,27	18,18
% de substances (> LQ)	10,00	10,00	10,00	20,00	80,00	90,00	0,00	80,00	30,00	0,00	10,00		
% de substances (entre LD et LQ)	20,00	10,00	40,00	0,00	0,00	10,00	10,00	10,00	20,00	10,00	20,00		

Substances/Nom de l'échantillon	Grotte du Chalet	Chalet	Chantoir d'Avan	Chantoir de l'Hermitage	Route Harzé	Pavillon-champs	Loupgueule	% de substances (> LQ)	% de substances (entre LD et LQ)
Cafeine	27,31	168,68	33401,8	57,48	190,3	21,47	6	85,71	14,29
Carbamazepine	5,91	1,9	7,89	0,2	0,00	0,00	0,00	42,86	14,29
Cotinine	3,34	8,83	7348,34	3,64	0,89	0,00	0,3	85,71	0,00
Diclofenac	10,29	8,44	3944,03	0,00	0,00	0,00	0,00	42,86	0,00
Hydrochlorothiazide	30,47	56,2	2022,11	102,5	0,28	10,38	0,00	85,71	0,00
Irbesartan	35,94	1,27	9936,56	34,59	0,00	0,00	0,00	57,14	0,00
Paracetamol	2,98	67,94	208803,21	1,44	0,77	0,00	1,54	85,71	0,00
Sotalol	10,15	0,86	163,00	0,00	0,00	0,00	0,00	42,86	0,00
Sulfamethoxazole	6,14	0,00	0,00	0,00	0,00	0,00	0,00	14,29	0,00
Venlafaxine	28,95	62,08	163,61	0,00	0,25	1,12	0,00	57,14	14,29
% de substances (> LQ)	100,00	90,00	90,00	50,00	40,00	30,00	20,00		
% de substances (entre LD et LQ)	0,00	0,00	0,00	10,00	10,00	0,00	10,00		

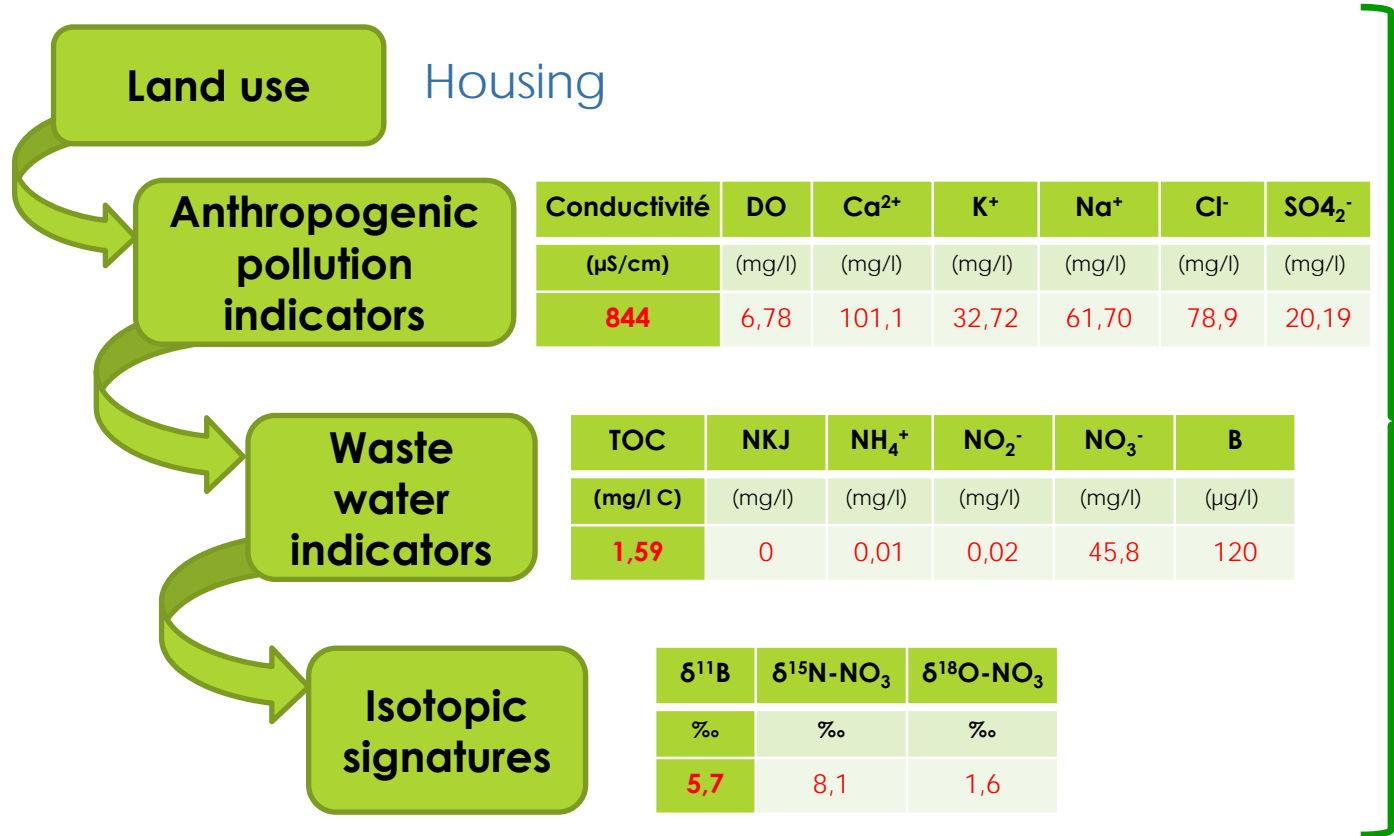
Results
on pharmaceuticals

Global interpretation



Two examples to conclude...

▶ Example : Lavoir S1



Expected NO₃ origin: urban water

Two examples to conclude...

► Example : Soignies P3

NO₃ potential origin

Urban waste water or manure?

Pharmaceutical compounds

CAF	CBZ	COT	DIC	HYD	IRB	PAR	SOL	SUF	VEN
(ng/l)	(ng/l)	(ng/l)	(ng/l)	(ng/l)	(ng/l)	(ng/l)	(ng/l)	(ng/l)	(ng/l)
31	164	1,9	28	322	101	0	51	48,3	5,1

Presence of medical substances for human beings;
Absence of veterinary substances

NO₃ of urban waste water origin

Any questions?

Acknowledgement



Groundwater Quality 2019

Groundwater Quality 2019

The next IAHS conference on Groundwater Quality (**GQ 2019**) will be held in Liège (Belgium) on 9-12 September 2019 !

With the support of IAHS, UK CL:AIRE, NICOLE and EU H2020 ITN INSPIRATION

More information : aimontefiore.org/GQ2019

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