Contribution of groundwater to greenhouse gases emissions

Lessons learned from case studies in the Walloon region of Belgium

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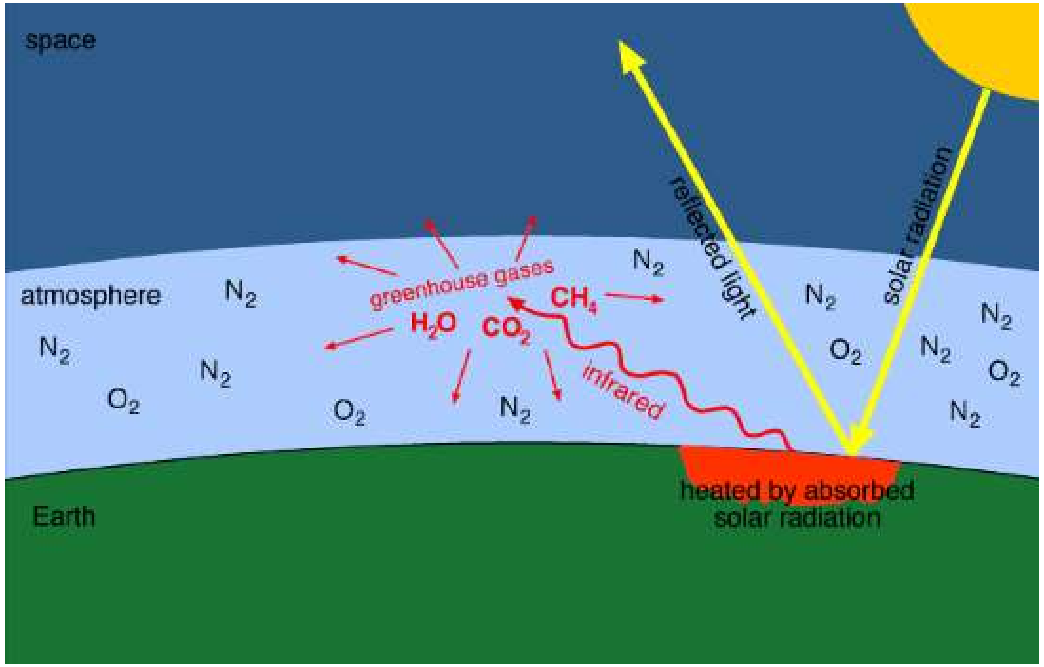
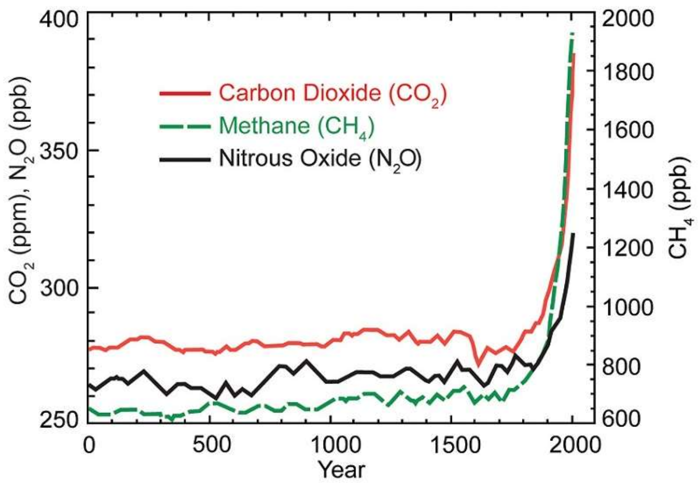
Context of the study : Greenhouse gases emissions and climate change



Source: http://www.ehso.com/climatechange/climatechangecauses-greenhouseeffect.php



CO_2

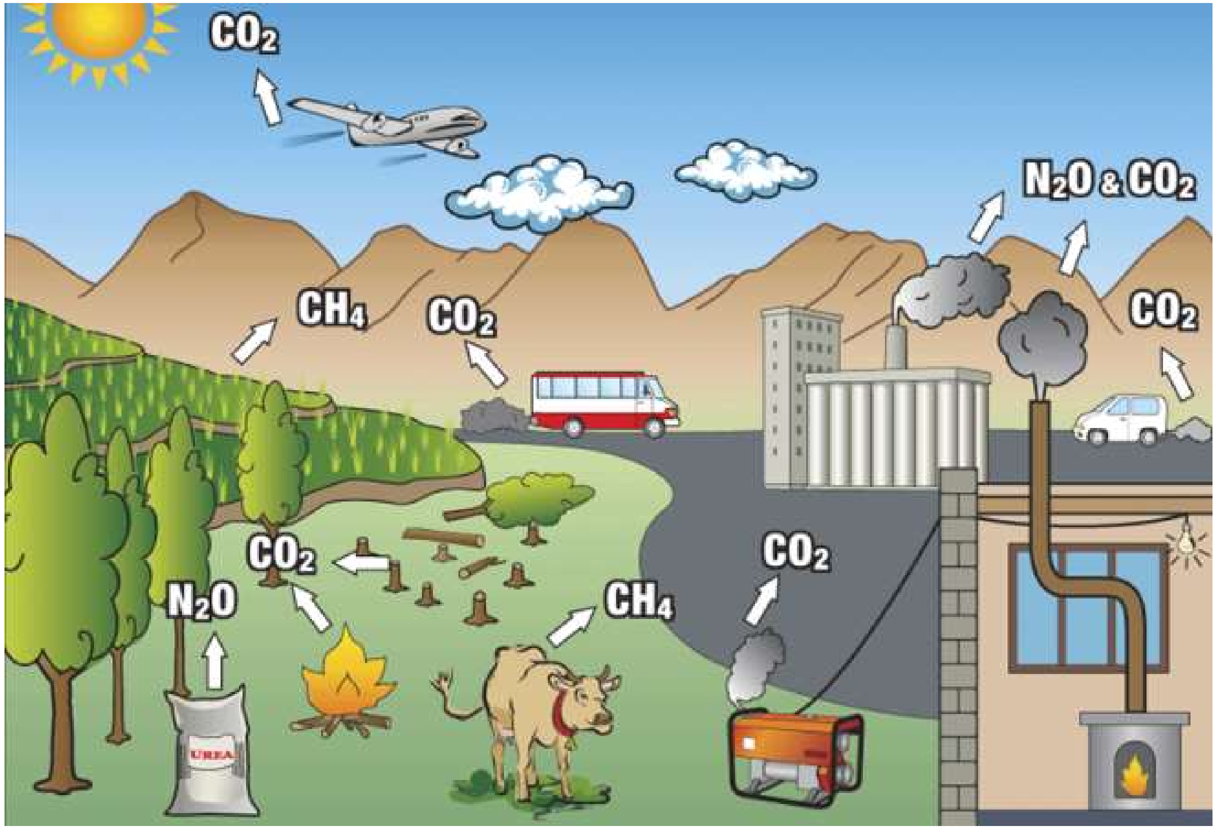
CH_4 → Most significant greenhouse gases

N_2O → Strong ozone depleting substance

Agricultural landscapes : 1/3 of total anthropogenic emissions (Gilbert 2012)

Source: U.S. National Assessment (2014)

Context of the study : Greenhouse gases emissions and climate change



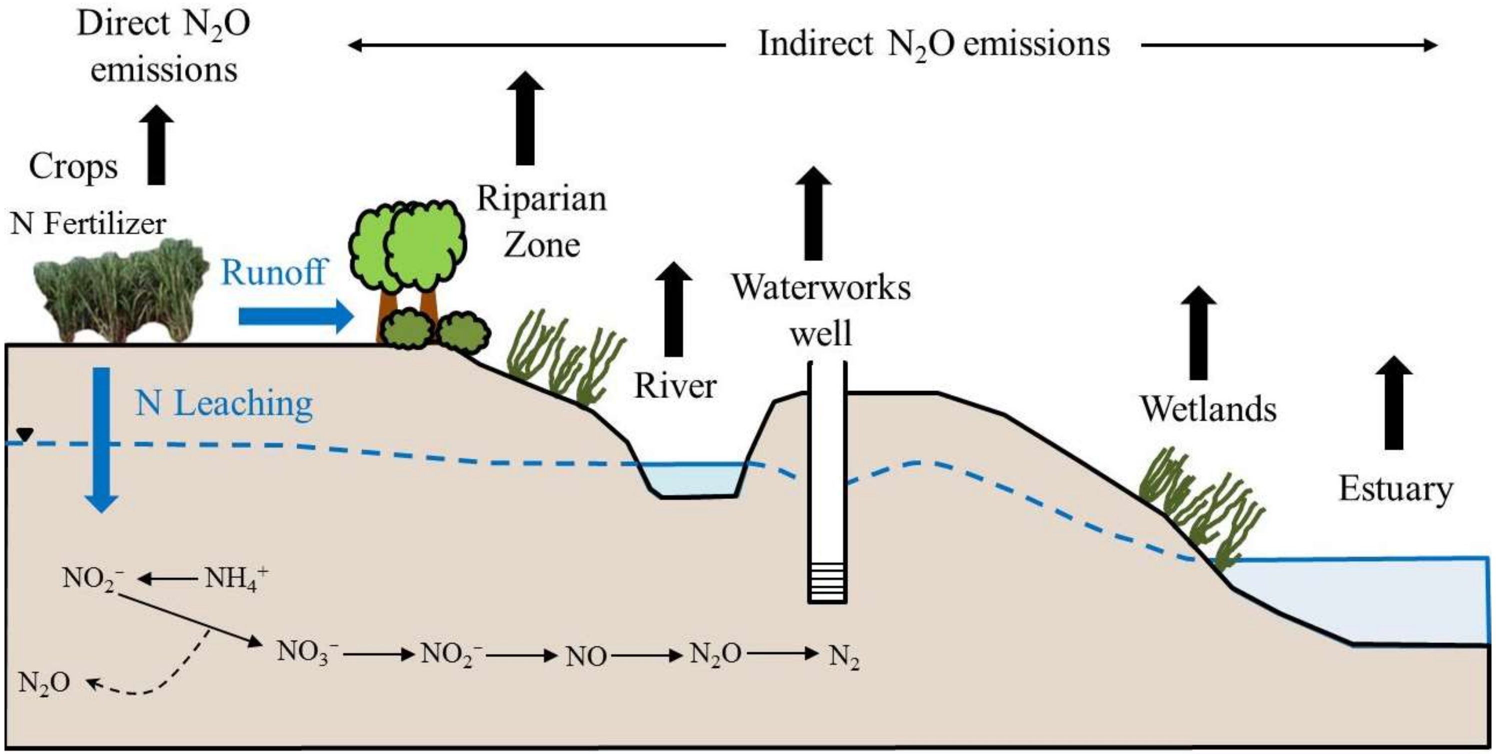
CARBON DIOXIDE (CO_2)
- ✓ Fossil fuel burning
- ✓ Changes in land use
- ✓ Industrial activities

NITROUS OXIDE (N_2O)
- ✓ Agricultural activities
- ✓ Fossil fuel combustion and industrial processes
- ✓ Natural processes (i.e soils)

METHANE (CH_4)
- ✓ Fossil fuel production, distribution and use
- ✓ Livestock farming
- ✓ Landfills and waste
- ✓ Wetlands

Direct vs Indirect emissions : Groundwater as a source of GHGs

Groundwater has been proposed as a potential indirect source of GHGs to the atmosphere, particularly in agricultural areas (Anderson et al., 2014: Jahangir et al., 2012, Minamikawa et al., 2011)



Source:
Jurado et al.
STOTEN (2017)

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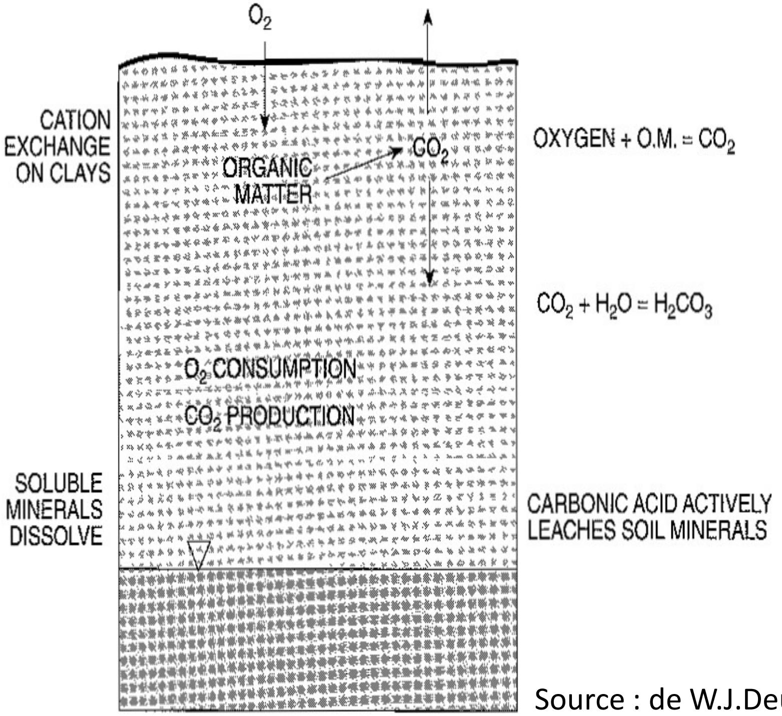
Carbon dioxide CO_2



Source : de W.J.Deutsch

CO_2 production in soils

Carbonate speciation

$CO_2(g) + H_2O <-> H_2CO_3^*$ $K_{H,CO2} = [H_2CO_3^*]/P(CO_2) = 10^{-1,5}$

$H_2CO_3^* <-> HCO_3^- + H^+$ $K_{a1} = [H+][HCO_3^-]/[H_2CO_3^*] = 10^{-6,3}$

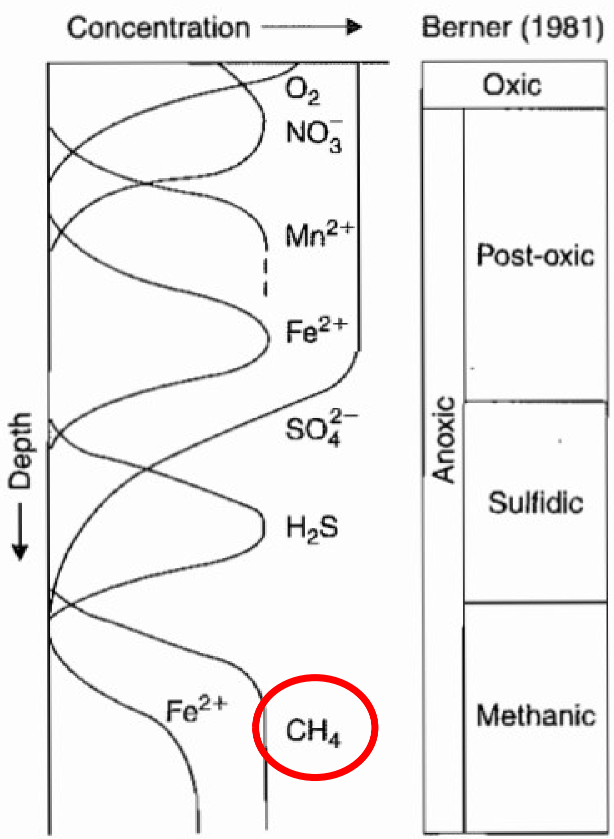
$CO_3^{2-} + H^+ <-> HCO_3^-$ $K_{a2} = [H+][CO_3^{2-}] /[HCO_3^-] = 10^{10,3}$

Dissolution of carbonate minerals

$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-}$ $K_{calcite} = [Ca^{2+}] [CO_3^{2-}] = 10^{-8.48}$

Groundwater as a source of GHGs : Production – Consumption mechanisms

Methane CH_4



Environment	Characteristic phases
I. Oxic ($m_{O_2} \geq 10^{-6}$)	Hematite, goethite, MnO_2-type minerals: no organic matter
II. Anoxic ($m_{O_2} < 10^{-6}$)	
A. Sulfidic ($m_{H_2S} \geq 10^{-6}$)	Pyrite, marcasite, rhodochrosite, alabandite: organic matter
B. Nonsulfidic ($m_{H_2S} < 10^{-6}$)	
1. Post-oxic	Glauconite and other Fe^{2+}–Fe^{3+} silicates (also siderite, vivianite, rhodochrosite): no sulfide minerals: minor organic matter
2. Methanic	Siderite, vivianite, rhodochrosite: earlier formed sulfide minerals; organic matter

Source : Appelo & Postma, Chap. 9, p.440

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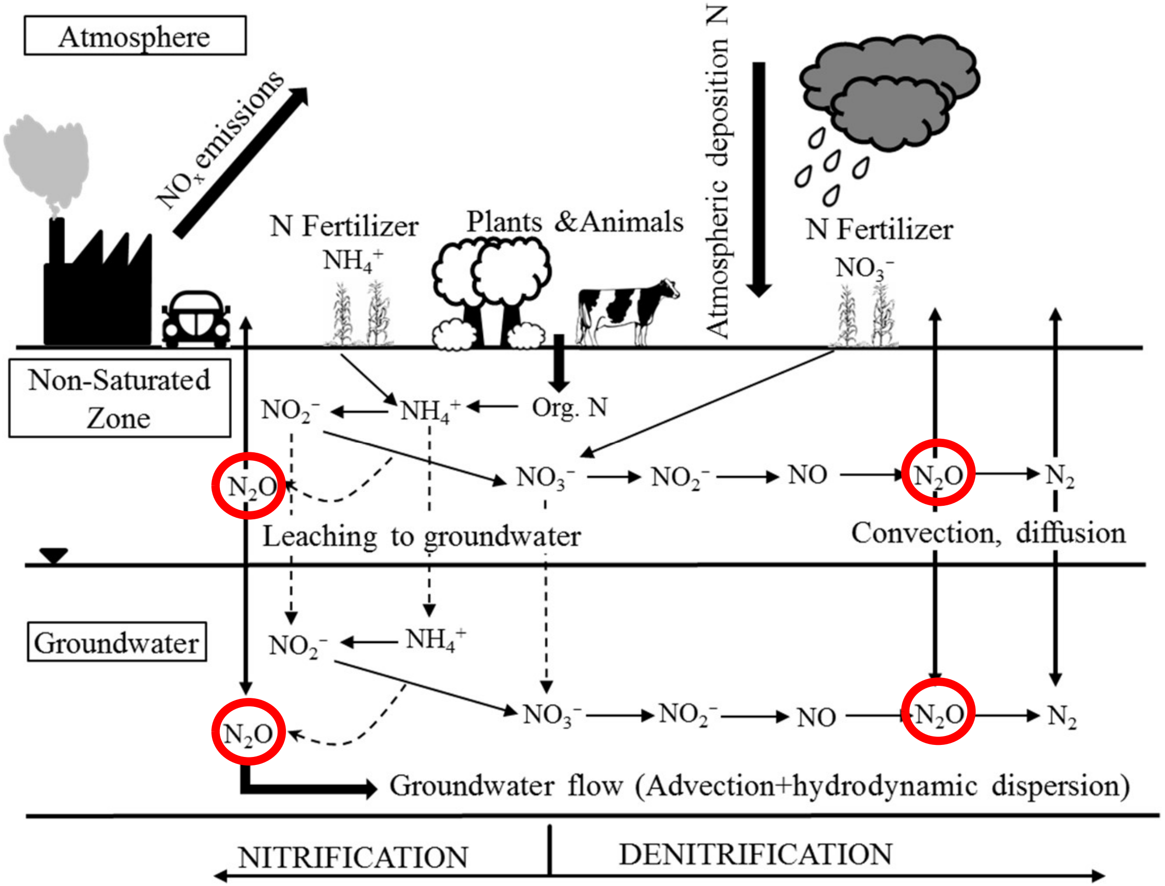
Groundwater as a source of GHGs : Production – Consumption mechanisms

Nitrous oxide N_2O

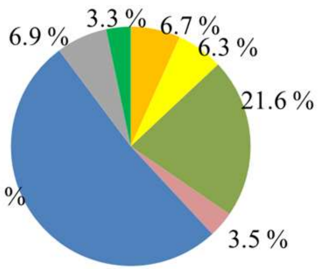


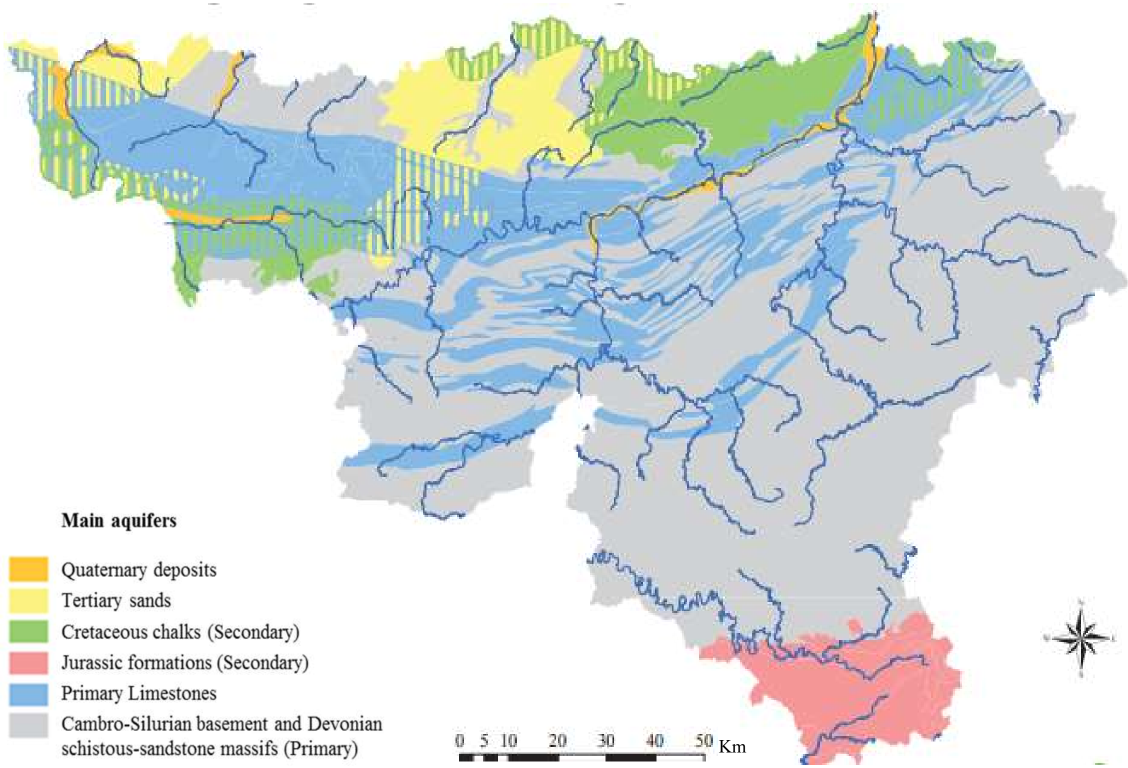
In this context, several questions arise:

1. What are the mechanisms effectively driving the production and consumption of GHGs in groundwater?
2. To which extent does groundwater contributes to GHGs emissions in the atmosphere?

Case studies in the Walloon Region of Belgium

Groundwater abstraction (%, 2012)



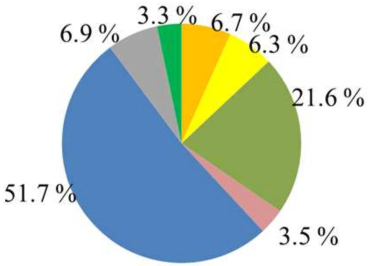


SPW-DGO3 (2015). Etat des nappes d'eau souterraine de Wallonie. Edition : Service public de Wallonie, DGO 3 (DGARNE), Belgique. Dépôt légal D/2015/11802/64 - ISBN 978-2-8056-0190-3

- Land use: agricultural (51,8%) >forests (29,4%)>urban (14,3%)

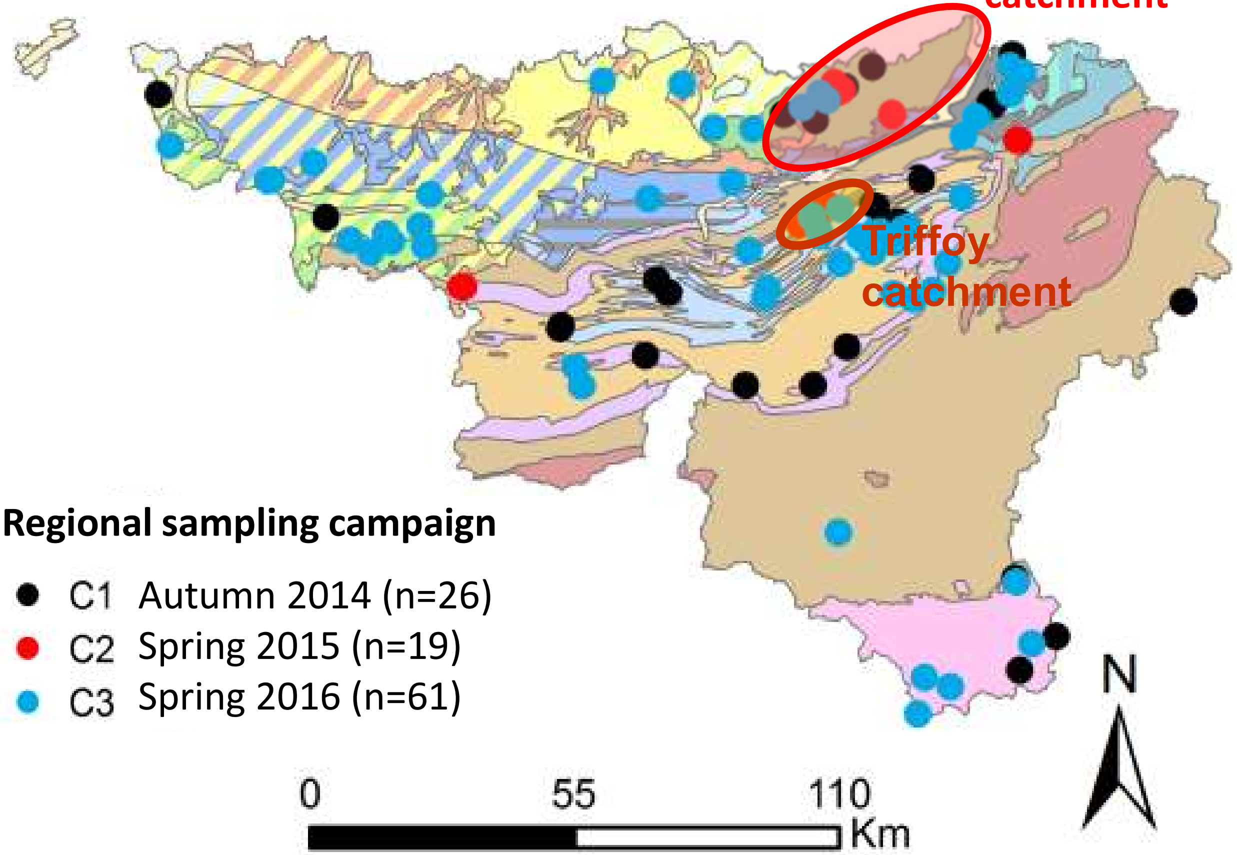
Case studies in the Walloon Region of Belgium

Groundwater abstraction (%, 2012)



SPW-DGO3 (2015). Etat des nappes d'eau souterraine de Wallonie. Edition : Service public de Wallonie, DGO 3 (DGARNE), Belgique. Dépôt légal D/2015/11802/64 - ISBN 978-2-8056-0190-3

At regional scale + …



Case studies in the Walloon Region of Belgium

GHGs

- ✓ CO_2, N_2O, CH_4

General chemical analyses

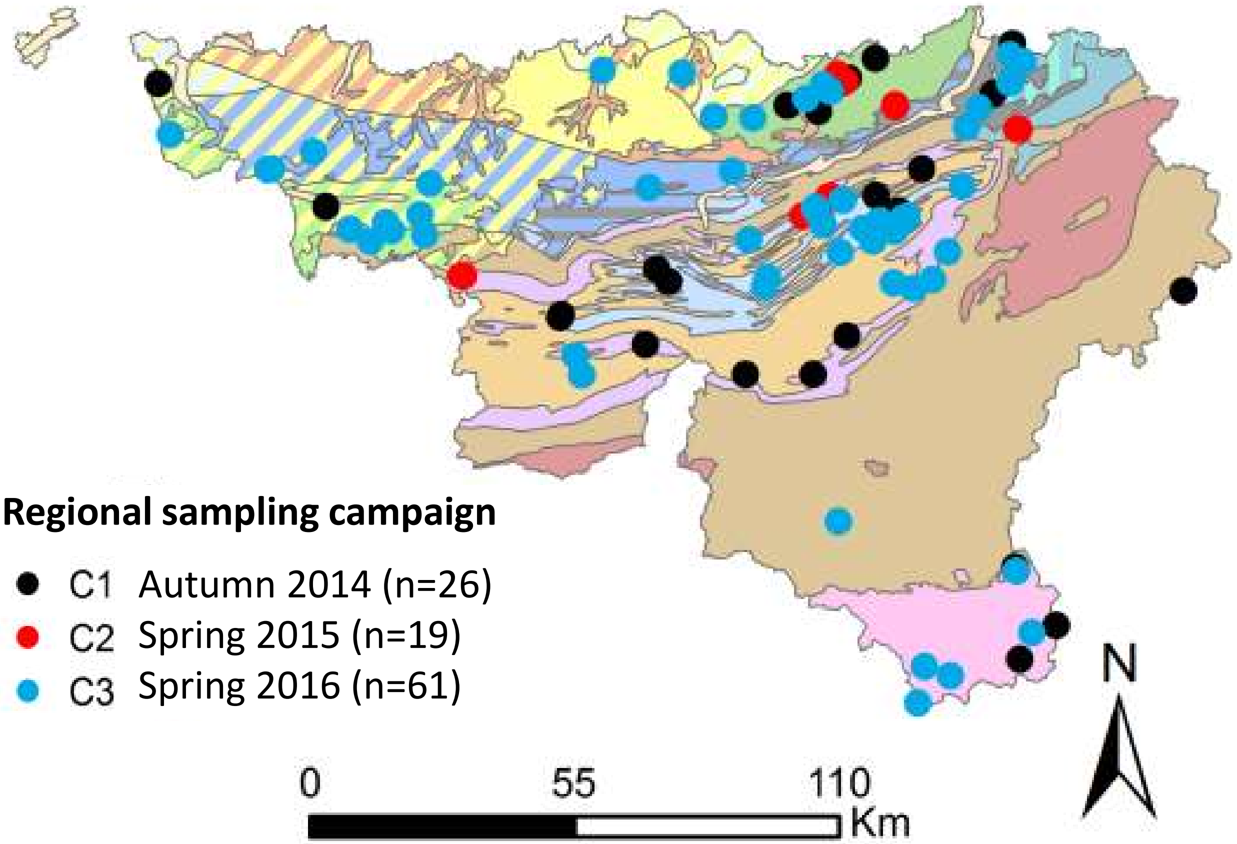
- ✓ Minor and major elements
- ✓ Metals (Fe/Mn)

Environmental isotopes

- ✓ $\delta^{34}S$ and $\delta^{18}O$ from sulphate
- ✓ $\delta^{15}N$ and $\delta^{18}O$ from nitrate
- ✓ $\delta^{18}O$ and D from water

In situ parameters

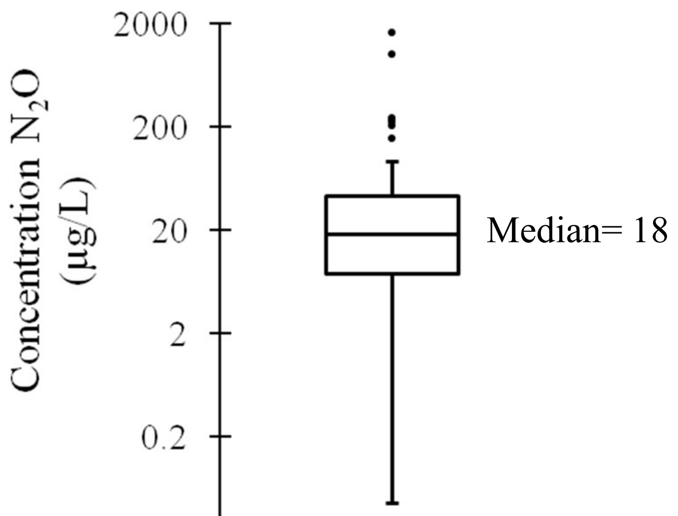
- ✓ O_2/EC/pH/T°



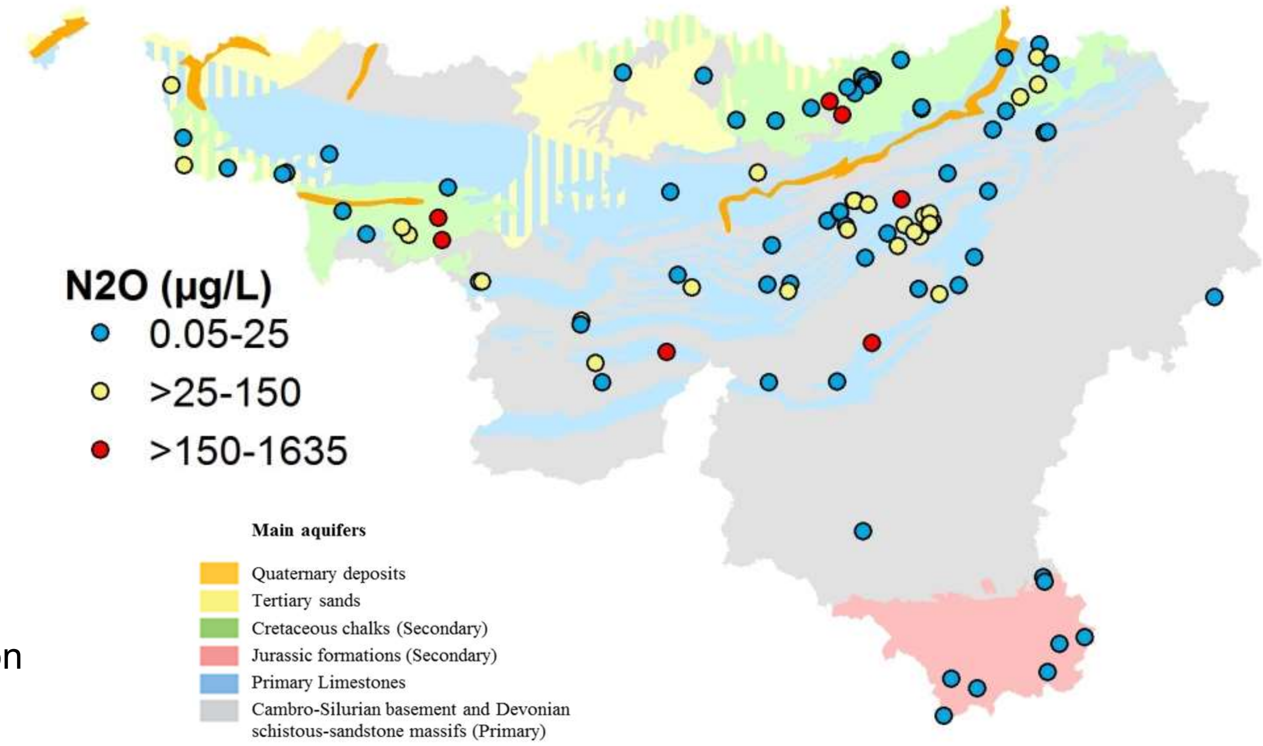
Occurrence of GHGs in groundwater : Observed concentrations

Concentrations of Nitrous Oxide (N_2O)

Range→ 0.05 – 1631µg/L
Average→ 55.8 µg/L



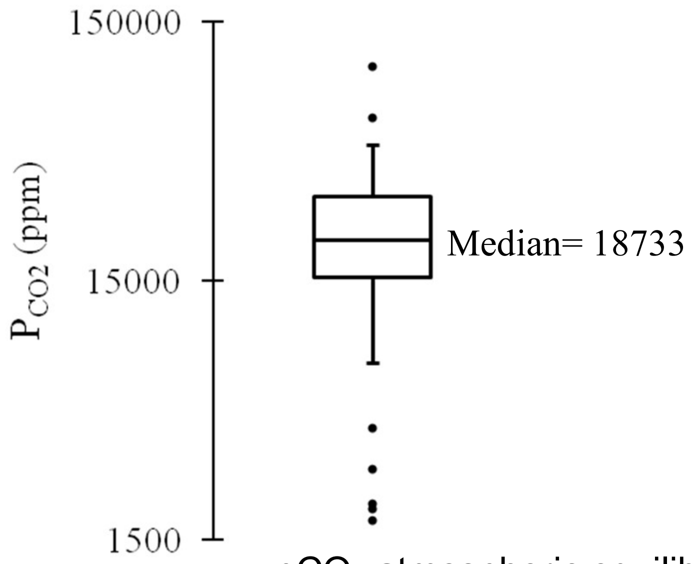
N_2O atmospheric equilibration concentration = **0,55 µg/L**

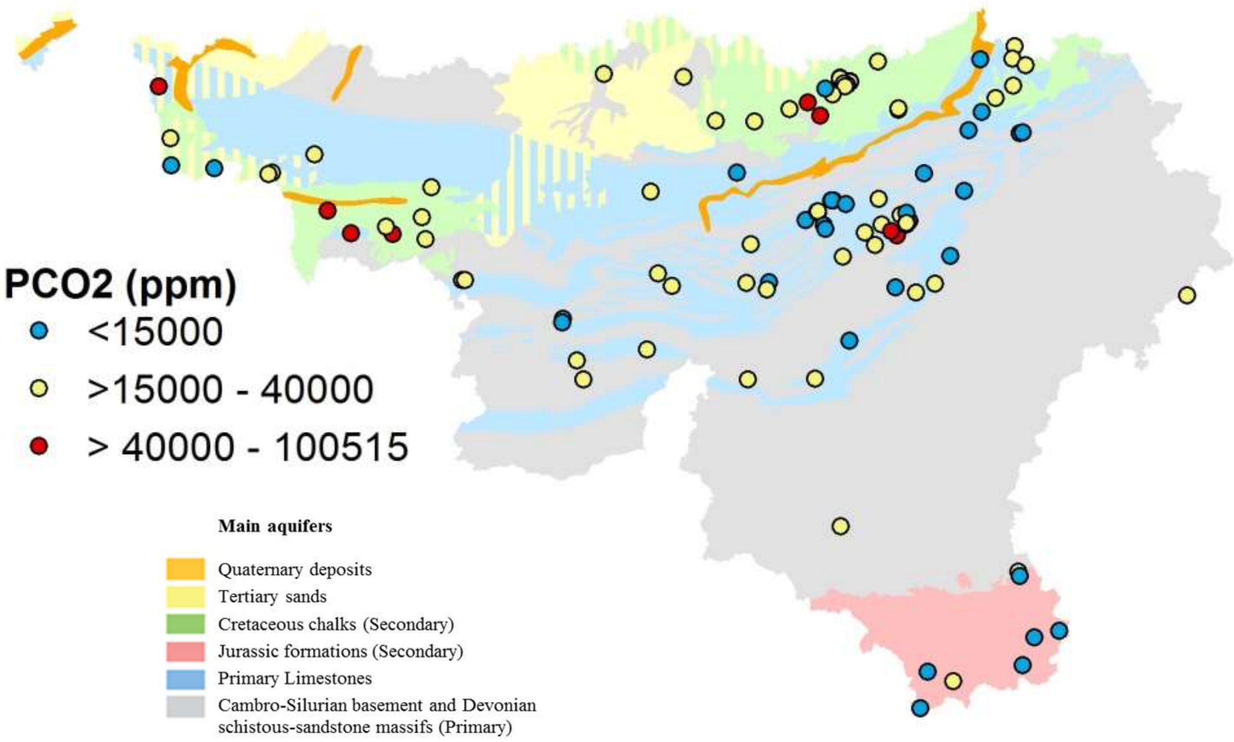


Occurrence of GHGs in groundwater : Observed concentrations

Concentrations of Carbon Dioxide (pCO_2)

Range→ 1769-100514 ppm
Average→ 22003 ppm



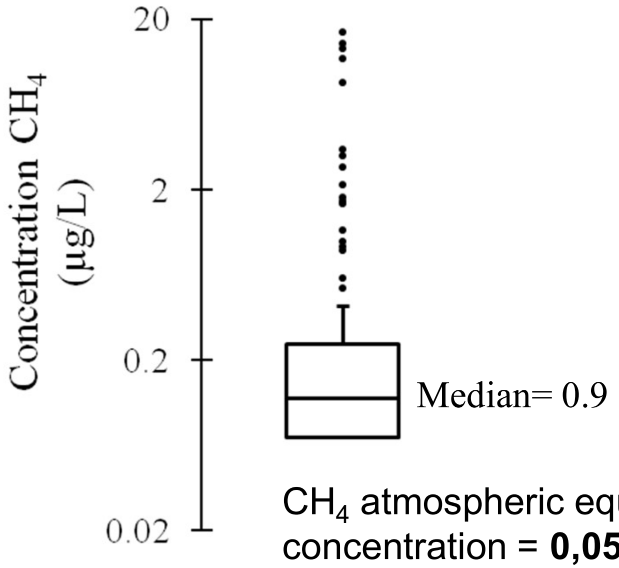


pCO_2 atmospheric equilibration concentration = **400 ppm**

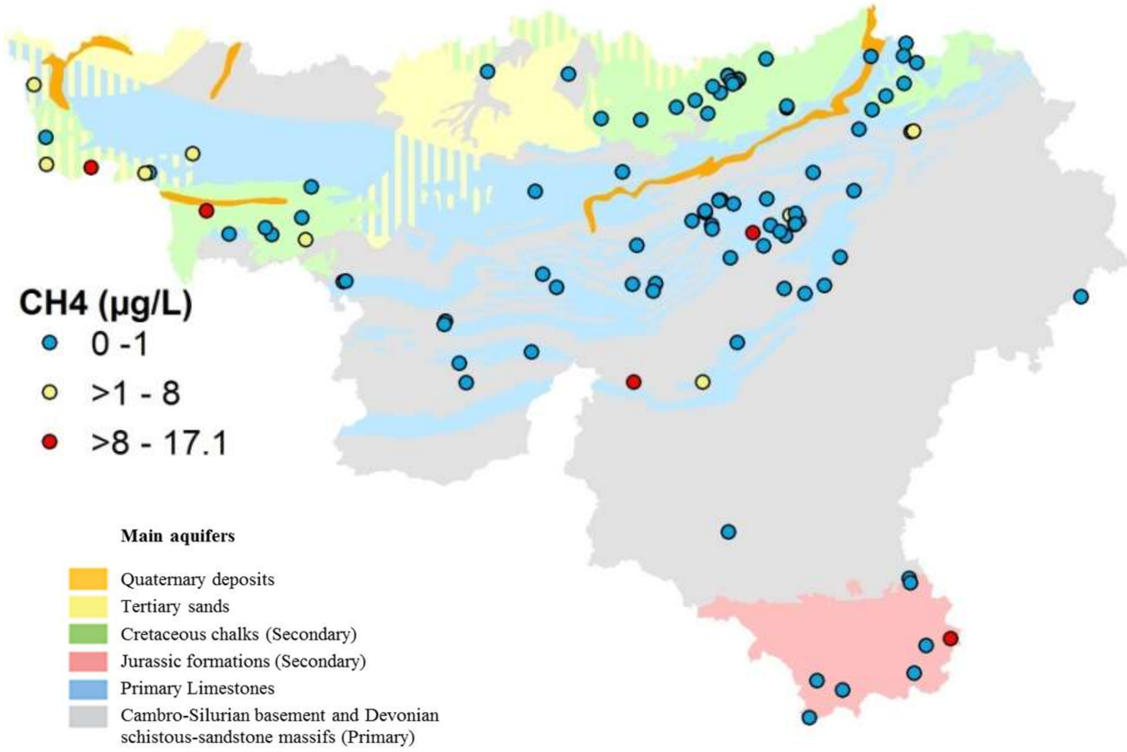
Occurrence of GHGs in groundwater : Observed concentrations

Concentrations of Methane (CH_4)

Range→ 0 – 17.1 µg/L
Average→ 0.12 µg/L

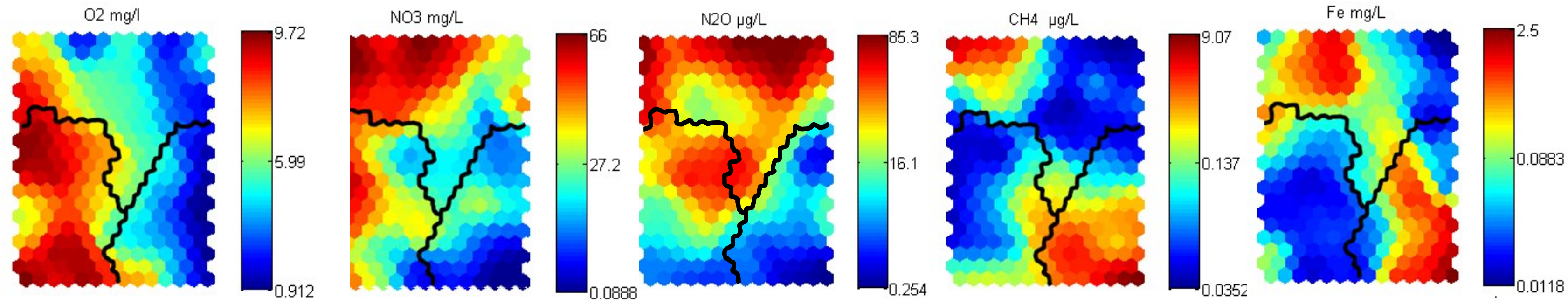


CH_4 atmospheric equilibration concentration = **0,056 µg/L**



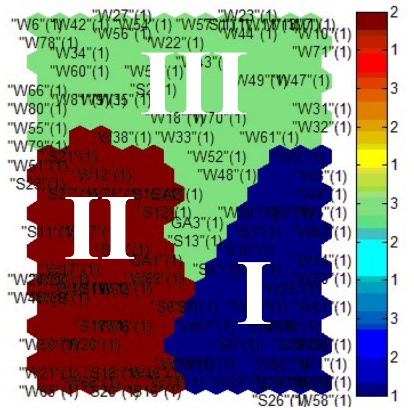
Occurrence of GHGs in groundwater : Controlling factors

Self-Organizing Maps – SOMs (non parametric multivariate statistics)



Average concentrations

	O2 mg/l	N2O µg/L	NO3 mg/L	Fe mg/L	CH4 µg/L
G1	2.82	6.10	12.37	0.57	2.07
G2	8.48	21.30	32.11	0.05	0.12
G3	5.33	126.98	47.18	0.11	0.30

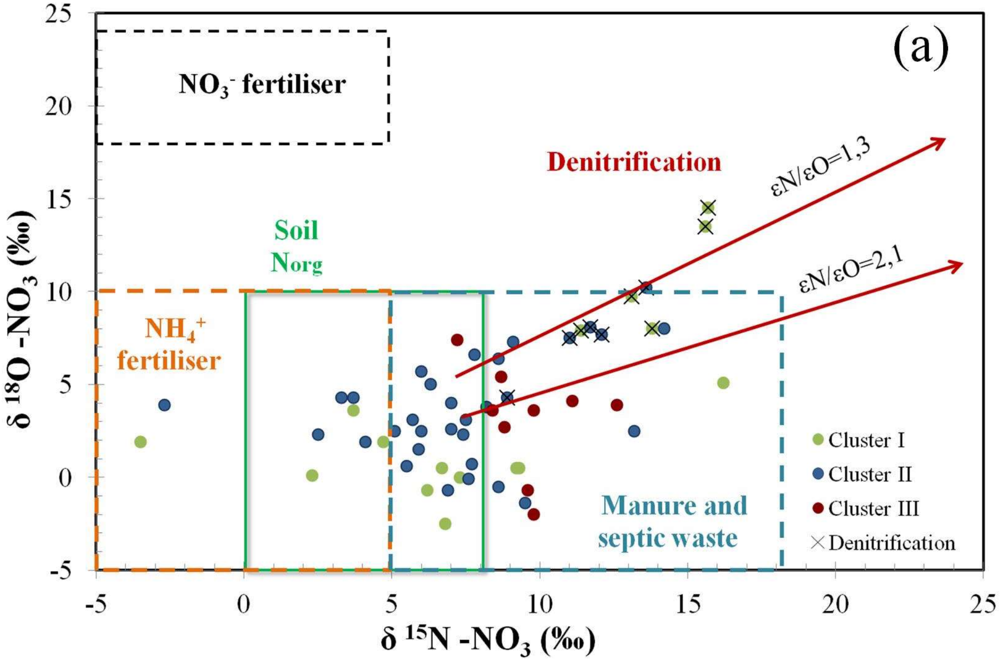


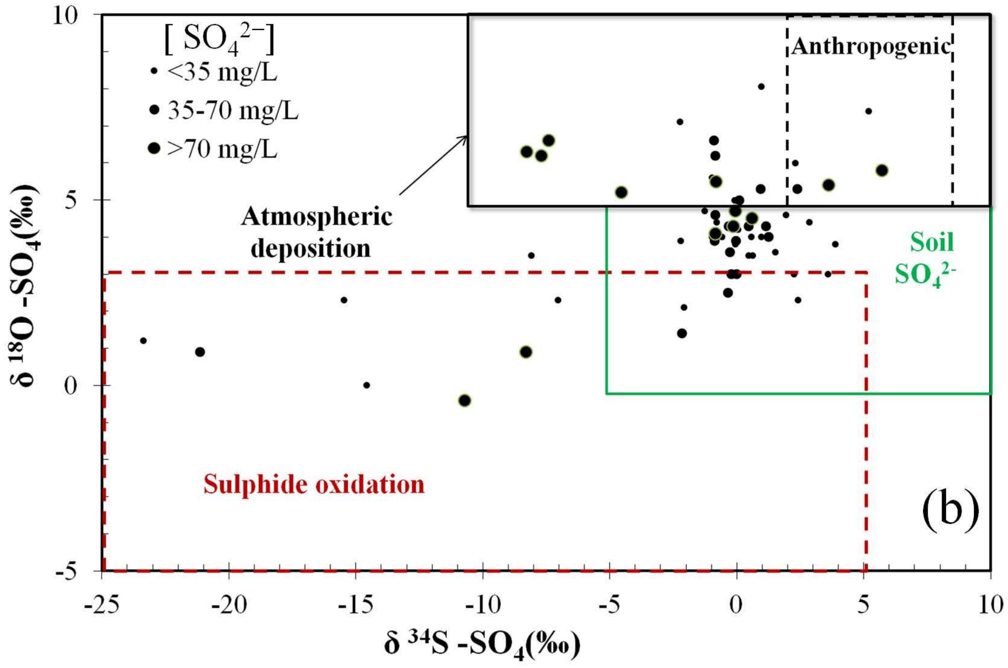
Occurrence of GHGs in groundwater : Controlling factors

G1	↓ $[O_2]$, $[N_2O]$ and $[NO_3]$ ↑ $[CH_4]$ and [Fe]	DENITRIFICATION NO_3 → **N_2O** → N_2	Initial METHANOGENESIS
G2	↑ $[O_2]$ ↑ $[NO_3]$ Average $[N_2O]$ ↓ $[CH_4]$ and [Fe]	NITRIFICATION	
G3	↑ $[N_2O]$, $[NO_3]$ ↑ $[O_2]$ ↓ $[CH_4]$ and [Fe]	DENITRIFICATION NO_3 → **N_2O** → ~~N_2~~ NITRIFICATION	

Most favourable conditions for the accumulation in aquifers

Occurrence of GHGs in groundwater : stable isotopes of NO_3 & SO_4





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Occurrence of GHGs in groundwater : Calculated N_2O emissions

Direct emissions …

0.3 x 200 kg N Ha^{-1} y^{-1} x 0.0053

Direct N_2O emissions from agricultural soils of Belgium

↓

9.76 kg N_2O-N Ha^{-1} y^{-1}

(Roelandt et al., 2007)

…vs indirect emissions

$$E_{N2O-catc} = 0,3 \times NLeach \times EF5g$$
$$= 0,3 \times NLeach \times \frac{N-N_2O}{N-NO_3}$$
$$= 0,3 \times 200\ kg\ \mathrm{N\ Ha}^{-1}\mathrm{y}^{-1} \times 0,0053$$

(IPCC, 2006)

Agricultural areas

↓

0.32 kg N_2O-N Ha^{-1} y^{-1}

~3,5%

Q abstraction x [N_2O-N] $_{average}$

GW abstraction

↓

0.011 kg N_2O-N Ha^{-1} y^{-1}

~0,1%

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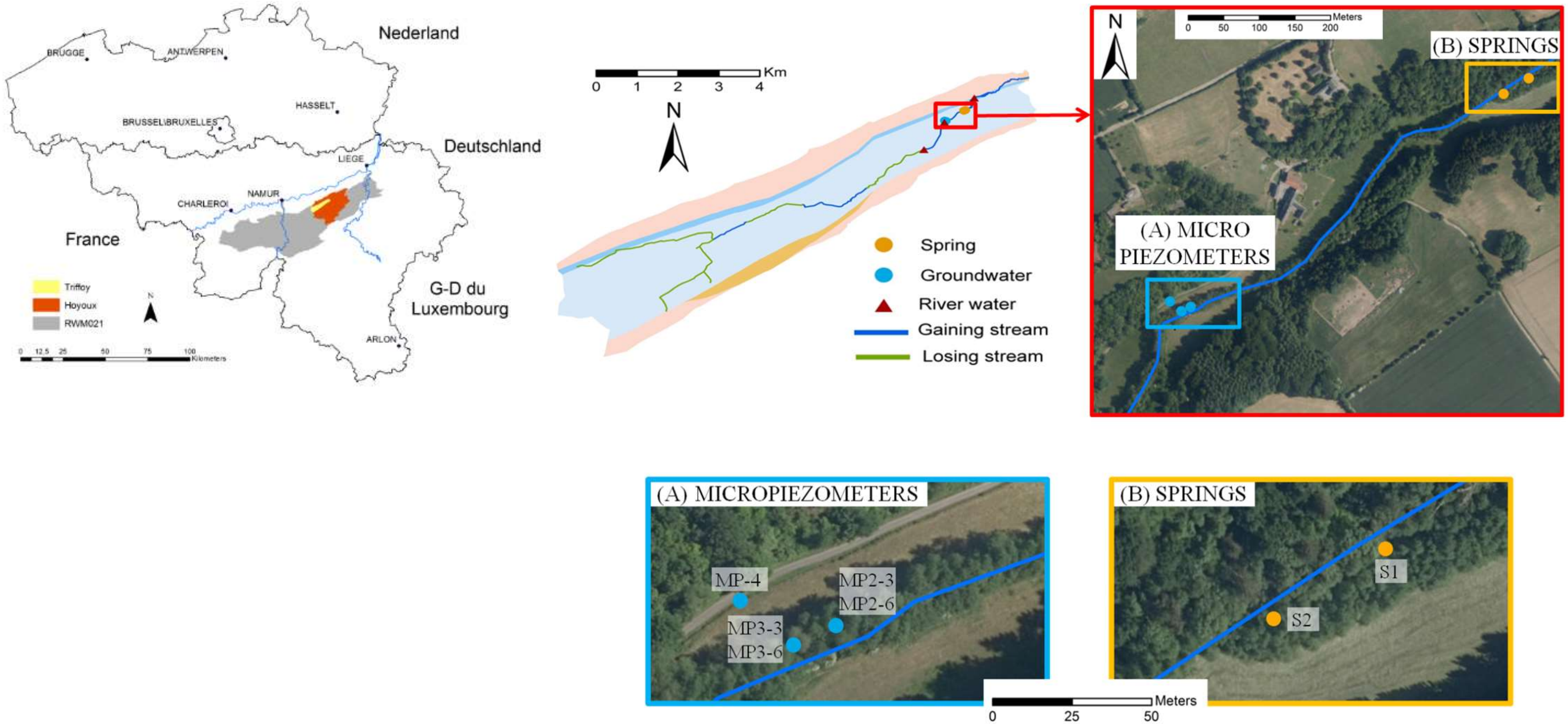
Occurrence of GHGs in groundwater : Triffoy river catchment



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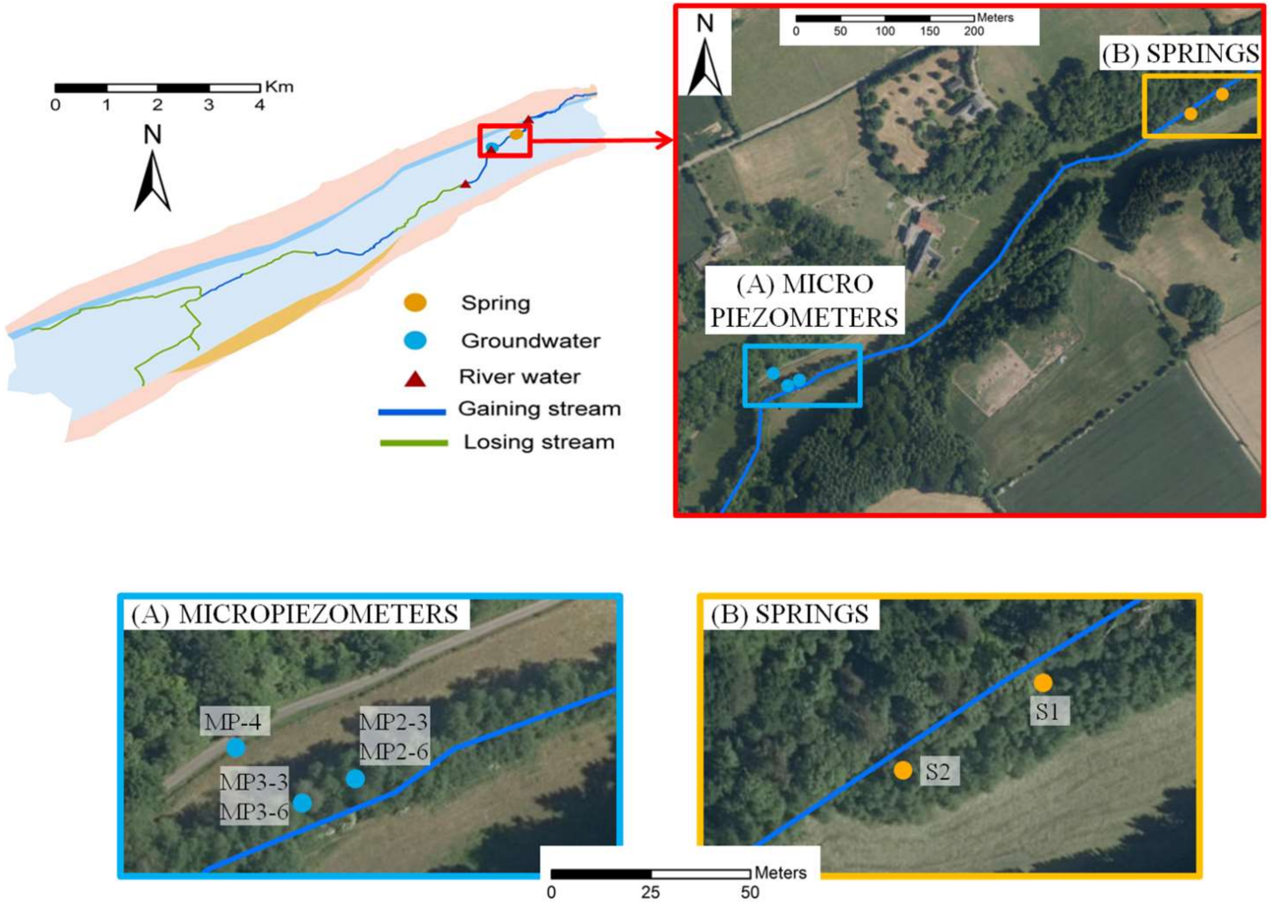
Occurrence of GHGs in groundwater : Triffoy river catchment

- Agricultural catchment
- River flows through Carboniferous limestone syncline between two Frasnian-Famennian sandstone crests
- Monitored river stretch = 2 km gaining stream with average discharge of 5870±1310 m^3 d^{-1}.
- River and groundwater samples collected from October 2016 to May 2017 for the analysis of GHGs, major and minor ions and stable isotopes of nitrate



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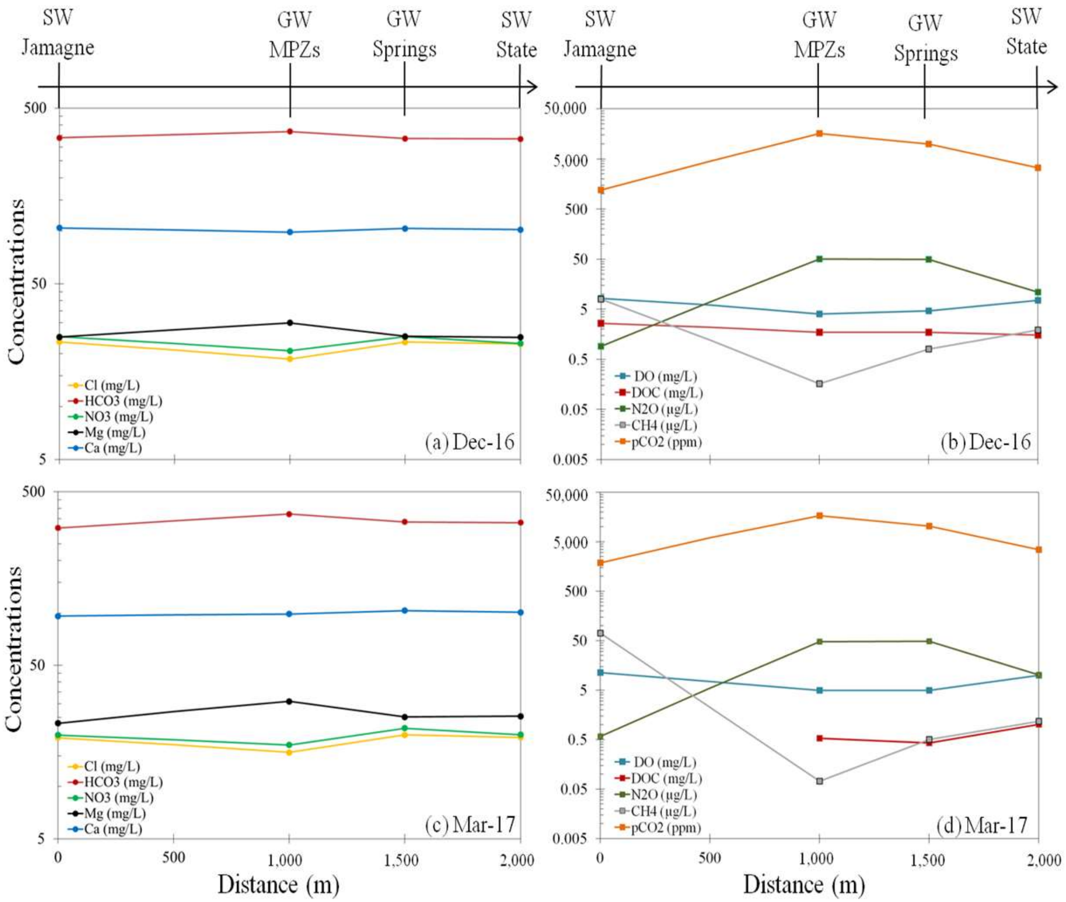
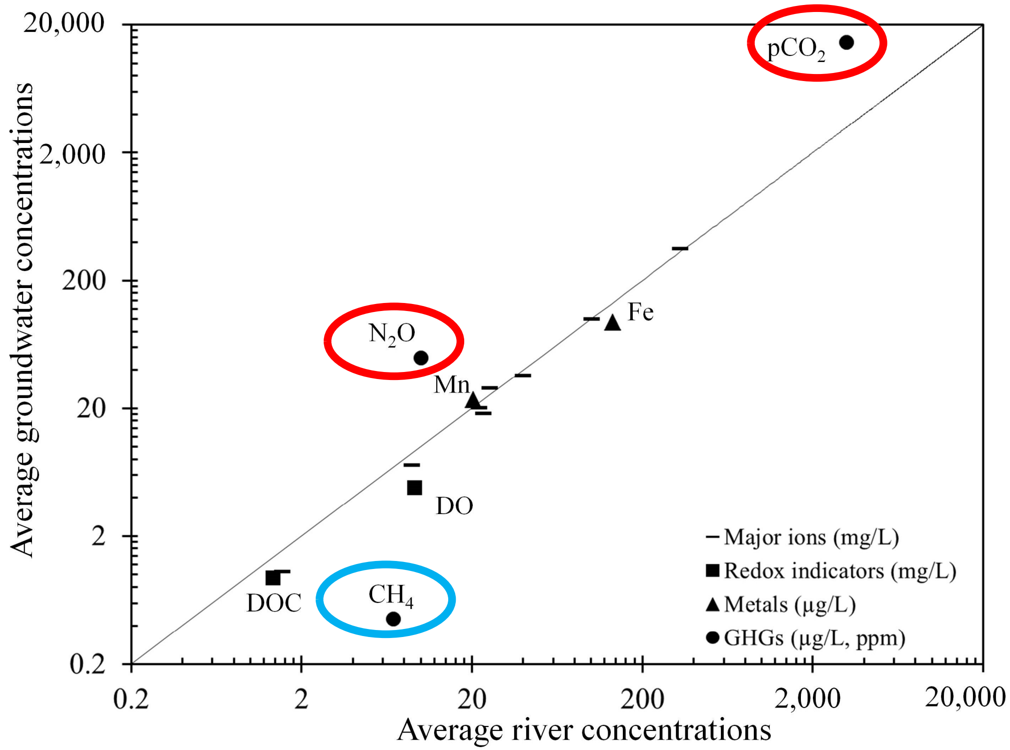
Occurrence of GHGs in groundwater : GW & SW hydrogeochemistry





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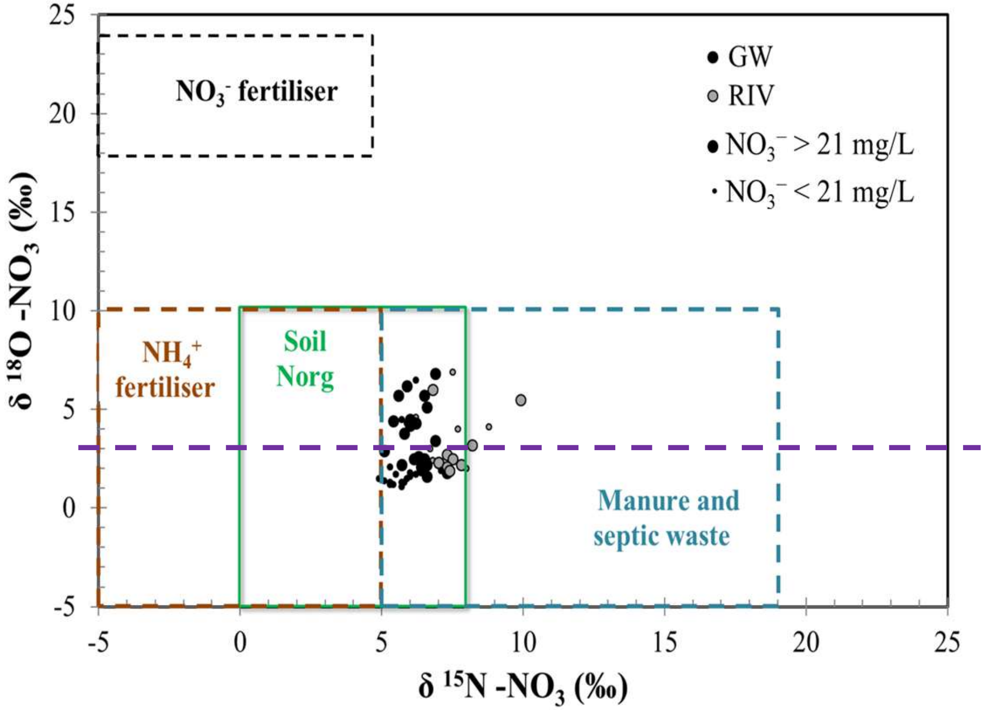
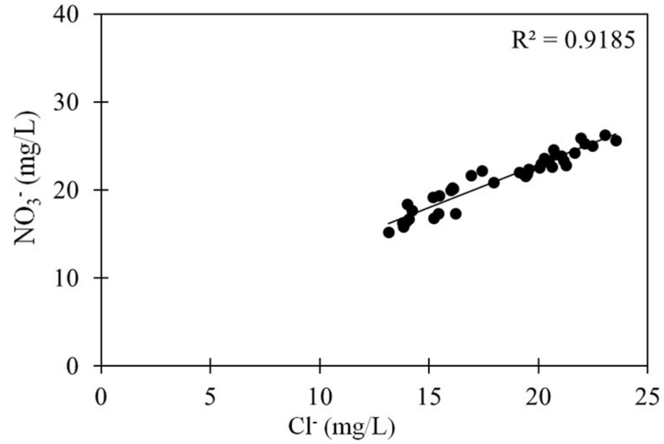
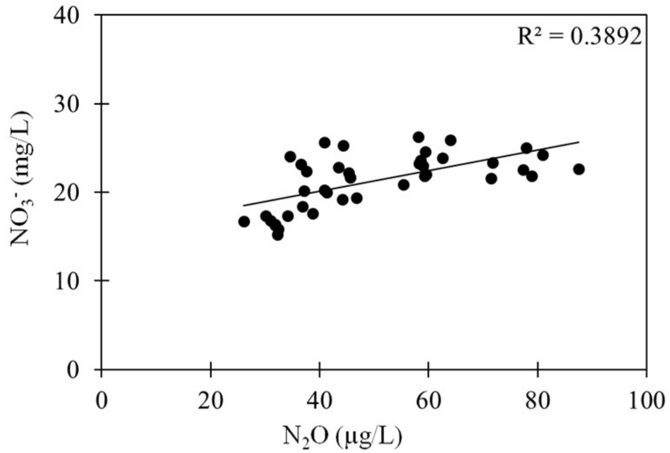
Occurrence of GHGs in groundwater : N_2O production – consumption mechanisms : Nitrification



When nitrification occurs:

$\delta^{18}O_{NO3} = 2/3\ \delta^{18}O_{water} + 1/3\ \delta^{18}O_{atmos} \sim +3$ ‰





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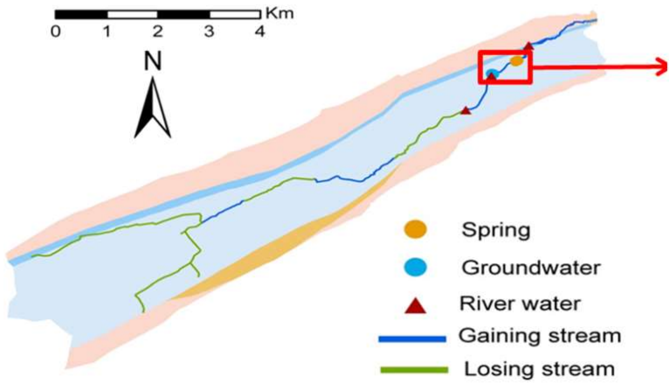
Groundwater emissions of GHGs : mass balance over river stretch / catchement

Regional scale …



$$E_{GHG-catch} = \frac{Q_{dis}\left[C_{GHG-Gw} - C_{GHG-Eq}\right]}{A_{catch}}$$

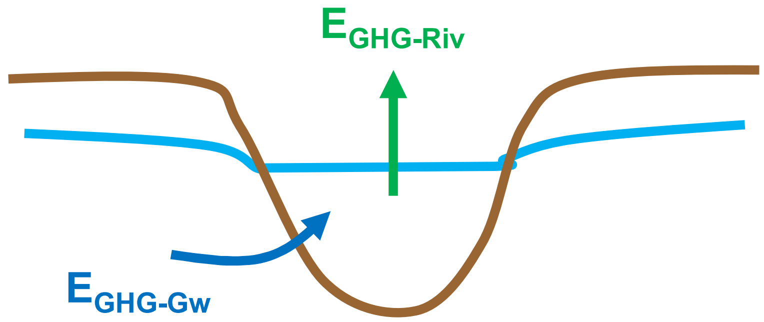
IPCC 2006 : *(for N_2O only)*

$$E_{N2O-catch} = 0{,}3 \times NLeach \times EF5g$$
$$= 0{,}3 \times NLeach \times \frac{N-N_2O}{N-NO_3}$$

…vs local scale

$$E_{GHG-Riv} = k \times \left[C_{GHG-Riv} - C_{GHG-Eq}\right]$$

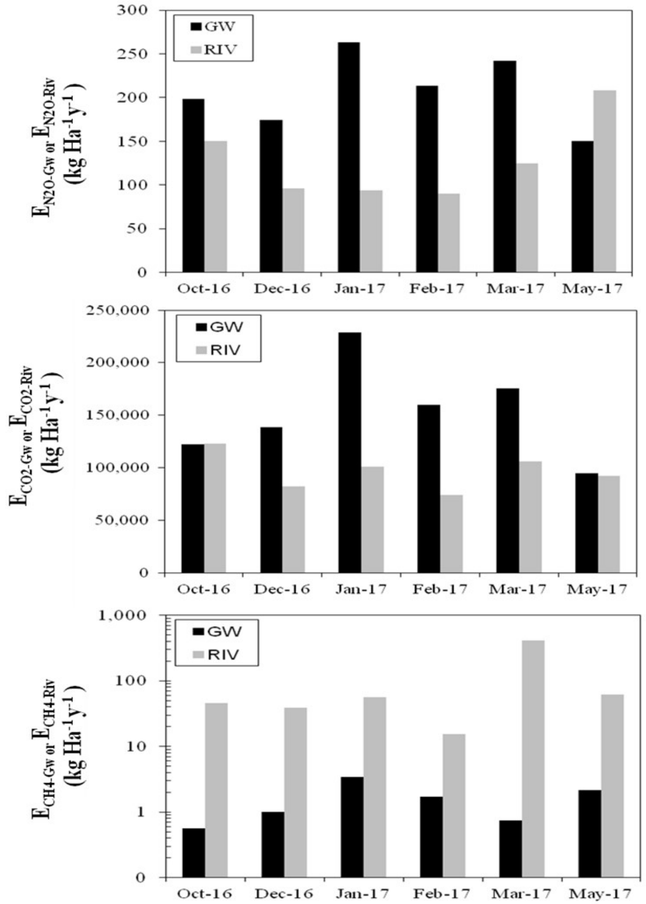
k: gas transfer velocity



$$E_{GHG-Gw} = \frac{Q_{dis}\left[C_{GHG-Gw} - \left[C_{GHG-Eq}\right]\right]}{A_{river}}$$

Occurrence of GHGs in groundwater : calculated emissions

	N_2O (kg x ha^{-1} x year^{-1})	CO_2 (kg x ha^{-1} x year^{-1})	CH_4 (kg x ha^{-1} x year^{-1})
Mean local $E_{GHG\text{-}Gw}$	207	1,5 x 10^5	1,6
Mean local $E_{GHG\text{-}Riv}$	126,9	9,7 x 10^4	105
Mean catchement $E_{GHG\text{-}catch}$	0,040	29,8	3 x 10^{-4}
IPCC Mean catchement $E_{GHG\text{-}catch}$ (*for N_2O only*)	0,037	--	--



Rem : Local estimate of EFG5 coefficient 3 times higher than the default value proposed by IPCC (0,0069 ± 0,0018 vs. 0,0025)

Occurrence of GHGs in groundwater : Conclusions

- Groundwaters of Walloon Region are oversaturated in CO_2 and N_2O relative to the atmospheric concentrations.

- Results show that N_2O is essentially produced by nitrification, but also, to a less extent during denitrification which in turn can contribute to N_2O consumption

- Most favourable conditions for the accumulation of N_2O in groundwater seems to occur when NO_3^- is available, with medium oxygen concentrations

- Methane is promoted in reducing groundwater conditions (null and low oxygen, NO_3 and N_2O and presence of Fe) but most often, CH4 is essentially produced in surface waters

- Indirect emissions from aquifers of the Walloon Region is a minor pathway of N_2O atmospheric emissions but their quantification help to better constrain the N_2O budget

Acknowledgements – Further reading

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This project has also received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 675120 (PhD grant O.Nikolenko)

Related papers:

Jurado Elices, A., Borges, A., Pujades, E., Hakoun, V., Otten, J., Knoeller, K., & Brouyère, S. (2018, January). Occurrence of greenhouse gases in the aquifers of the Walloon Region (Belgium). Science of the Total Environment. http://hdl.handle.net/2268/215313

Jurado, A., Borges, A., Pujades, A., Briers, P., Nikolenko, O., Dassargues, A., & Brouyère, S. (2018). Dynamics of greenhouse gases in the river-groundwater interface in gaining river stretch (Triffoy catchment, Belgium). Hydrogeology Journal. http://hdl.handle.net/2268/226422

Nikolenko, O., Jurado Elices, A., Borges, A., Knöller, K., & Brouyère, S. (2017, October). Isotopic composition of nitrogen species in groundwater under agricultural areas: A review. Science of the Total Environment. http://hdl.handle.net/2268/215300

Jurado Elices, A., Borges, A., & Brouyère, S. (2017). Dynamics and emissions of N2O in groundwater: A review. Science of the Total Environment, 584-585C, 207-218. http://hdl.handle.net/2268/207095

Acknowledgements – Further reading

<u>Other papers +/- related to climate change issues:</u>

Brouyère, S., Carabin, G., & Dassargues, A. (2004). Climate change impacts on groundwater resources: modelled deficits in a chalky aquifer, Geer basin, Belgium. Hydrogeology Journal, 12(2), 123-134. http://hdl.handle.net/2268/2332

Goderniaux, P., Brouyère, S., Wildemeersch, S., Therrien, R., & Dassargues, A. (2015). Uncertainty of climate change impact on groundwater reserves - Application to a chalk aquifer. Journal of Hydrology, 528, 108-121. http://hdl.handle.net/2268/183447

Blenkinsop, S., Harpham, C., Burton, A., Goderniaux, P., Brouyère, S., & Fowler, H. J. (2013). Downscaling transient climate change with a stochastic weather generator for the Geer catchment, Belgium. Climate Research. http://hdl.handle.net/2268/147930

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Goderniaux, P., Brouyère, S., Fowler, H. J., Blenkinsop, S., Therrien, R., Orban, P., & Dassargues, A. (2009). Large scale surface – subsurface hydrological model to assess climate change impacts on groundwater reserves. Journal of Hydrology, 373, 122-138. http://hdl.handle.net/2268/12082