27th September 2016

Occurrence of greenhouse gases (CO_2, N_2O and CH_4) in groundwater of the Walloon Region (Belgium)

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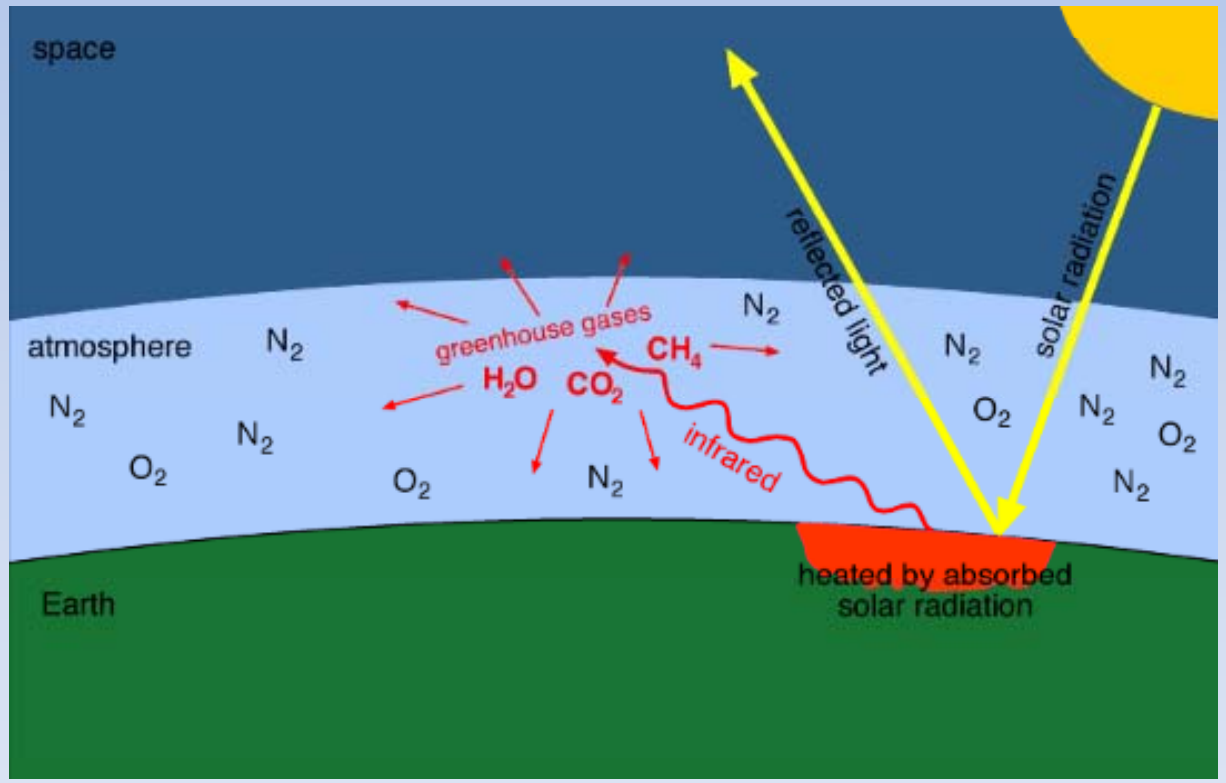
OUTLINE

1. Introduction

Importance of GHGs

✓GHGs are essential for life

✓ Without GHGs temperatures on Earth surface would fall from 15°C to -18 °C



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

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WHAT IS THE PROBLEM?

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

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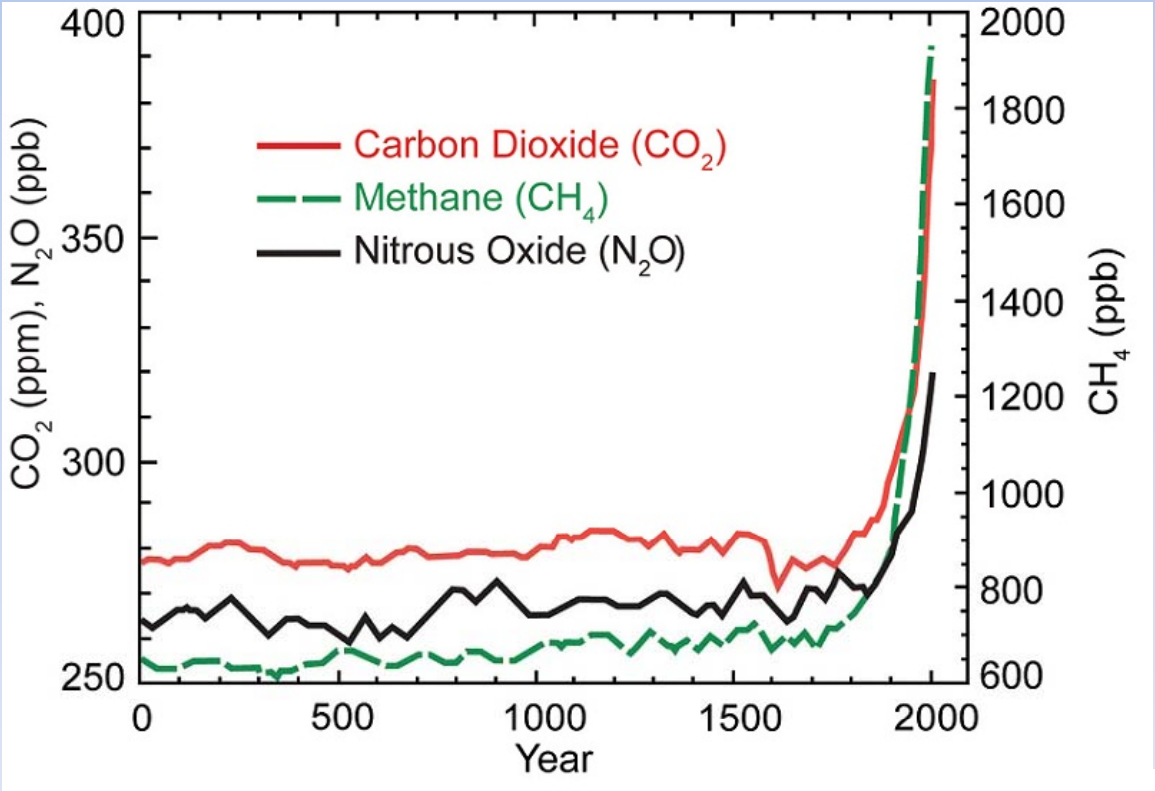
WHAT IS THE PROBLEM?



Source: U.S. National Assessment (2014)

1. Introduction

Source of GHGs

CARBON DIOXIDE (CO_2)

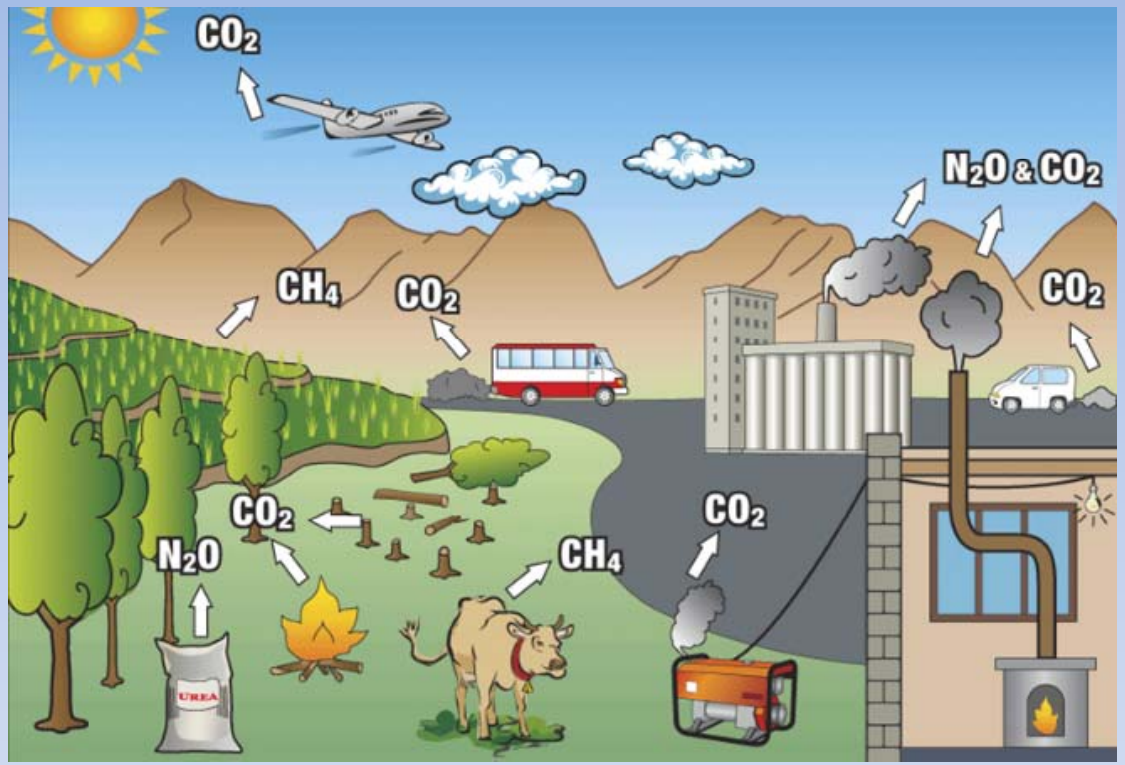
- ✓ Fossil fuel burning
- ✓ Changes in land use
- ✓ Industrial activities

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

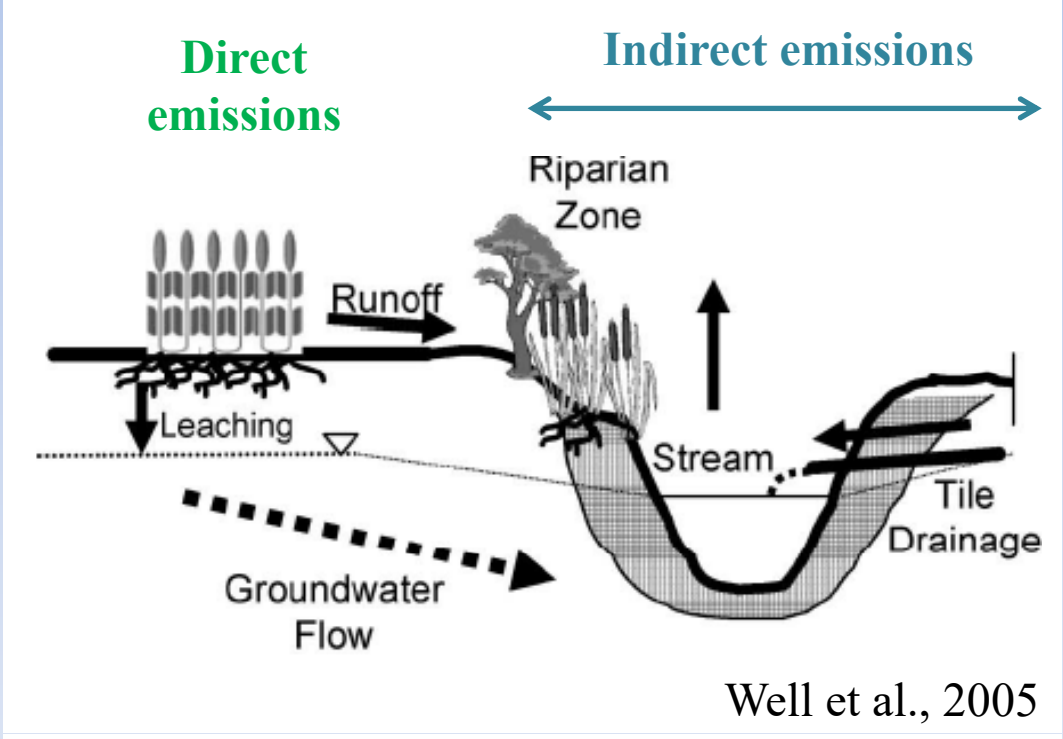


1. Introduction

Groundwater as a source GHGs

Groundwater has been proposed as a potential indirect source of GHGs to the atmosphere.

Agricultural areas (Anderson et al., 2014: Jahangir et al., 2012, Minamikawa et al., 2011)



Well et al., 2005

Some examples…

Jahangir et al. (2012)→ **Groundwater** indirect **N_2O emissions** via denitrification **represented** the **3–11%** of total N_2O emissions.

Anderson et al. (2014)→ **20 %** of total **N loss from** a riparian area may be attributed to **N_2O emissions** from **shallow groundwater** via denitrification.

1. Introduction

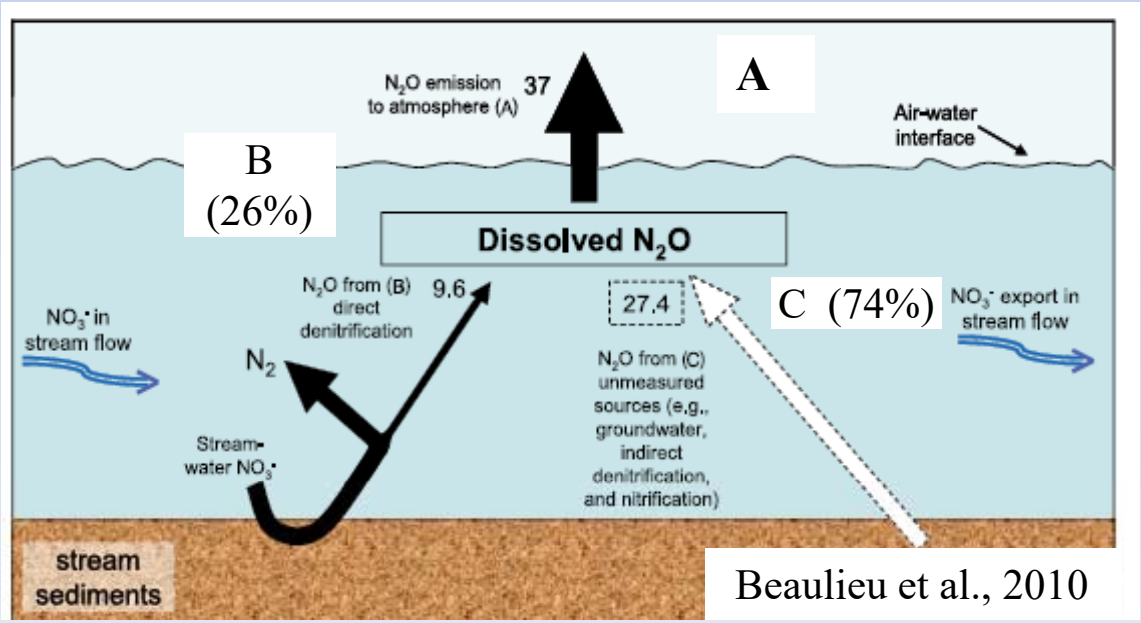
Groundwater as a source GHGs

Groundwater has been proposed as a potential indirect source of GHGs to the atmosphere.

Riverine areas (Beaulieu et al., 2010, Hotchkiss et al., 2015)

10% of the **global anthropogenic N_2O** emission **rate** was due to microbial transformations **in river networks**

Average N_2O fluxes estimated **A=B+C**



Beaulieu et al., 2010

(A) N_2O produced in the stream temporarily resides in a pool of dissolved N_2O before being emitted to the atmosphere.

(B) In-situ N_2O produced by denitrification in stream

(C) Other **unmeasured sources** N_2O sources:

- ✓ **Inputs supersaturated GW**
- ✓ indirect Nitrif/Denitrif from soils

1. Introduction

Aims of the research

Investigate the occurrence GHGs in groundwater of the Walloon Region (Belgium)

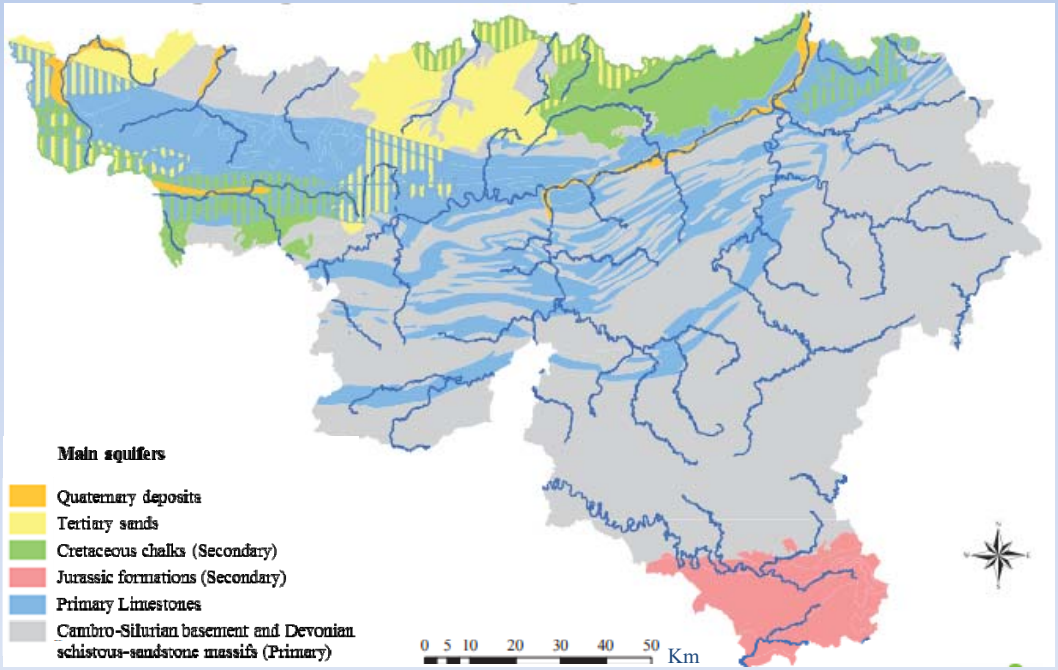
- ✓ Identification of the hydrogeological contexts and in situ conditions
- ✓ Identification of the geochemical processes

2. Methodology

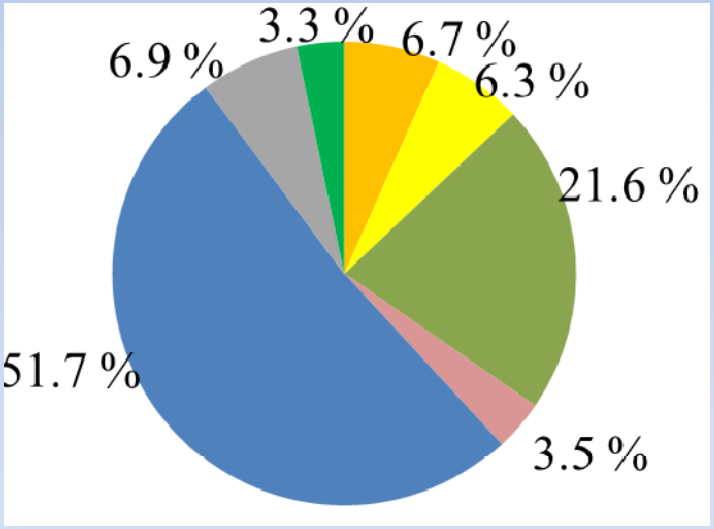
Walloon Region (Belgium)

- Extension: 16844 Km^2
- Land use: agricultural (51,8%) >forests (29,4%)>urban (14,3%)
- Groundwater represents the 78 % of water supply (297,5 million m^3)

Main aquifers



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

2. Methodology

Sampling campaigns

GHGs (C1-C3)

✓ CO_2, N_2O, CH_4

General analysis

✓ Minor and major elements (C1-C3)

✓ Metals (Fe/Mn) (C3)

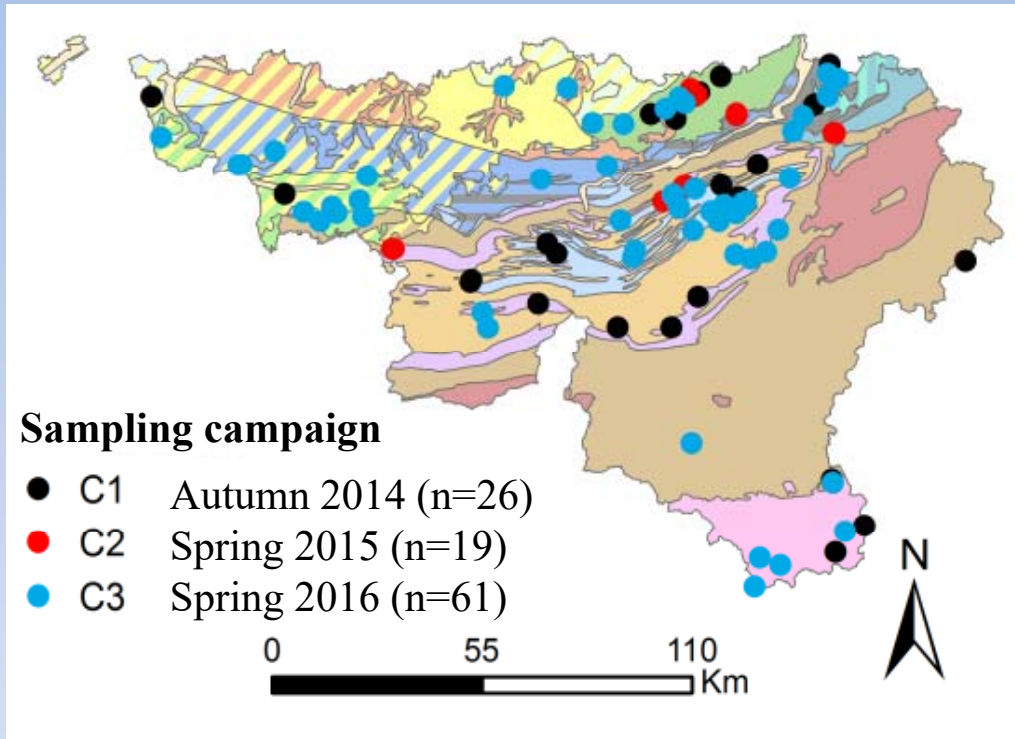
Environmental isotopes (C3)

✓34S and 18O from sulphate
✓15N and 18O from nitrate
✓18O and D from water

Insitu paremeters (C1-C3)

✓O_2/EC/PH/Temp

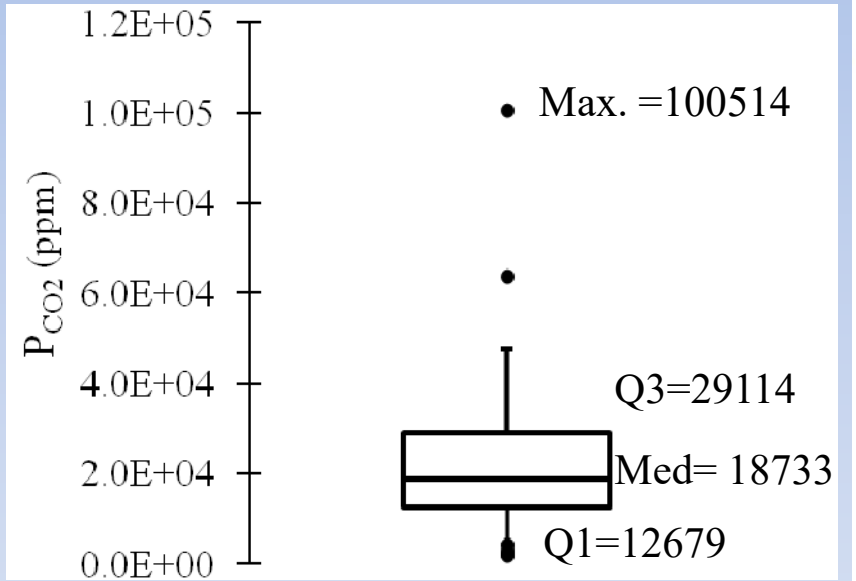
Spatial distribution of the sampling points



3. Results

Concentrations of Carbon dioxide ($_pCO_2$)

Range→ 1769-100514 ppm
Average→ 22003 ppm



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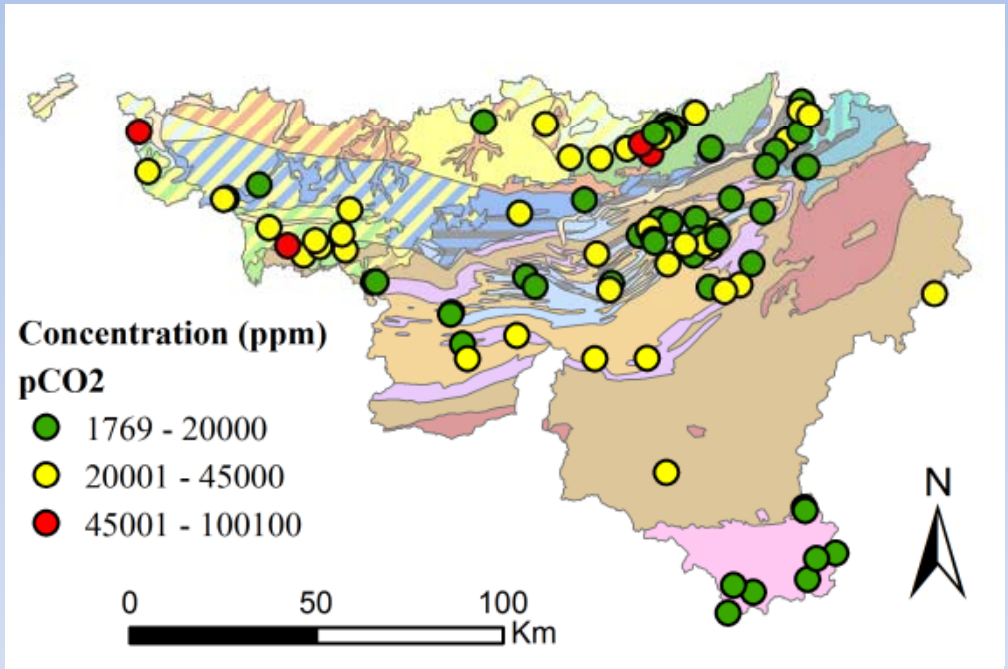
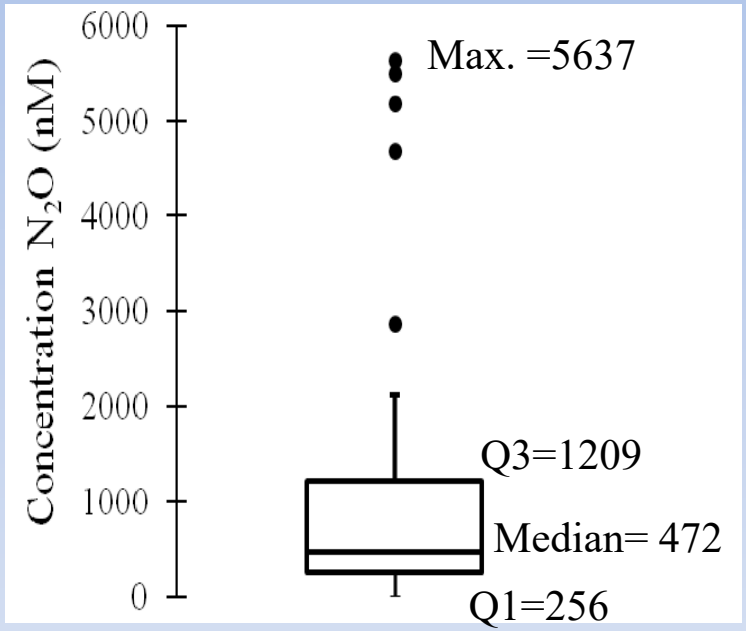


3. Results

Concentrations of Nitrous oxide (N_2O)

Range→ 1-5637 nM
Average→ 996 nM



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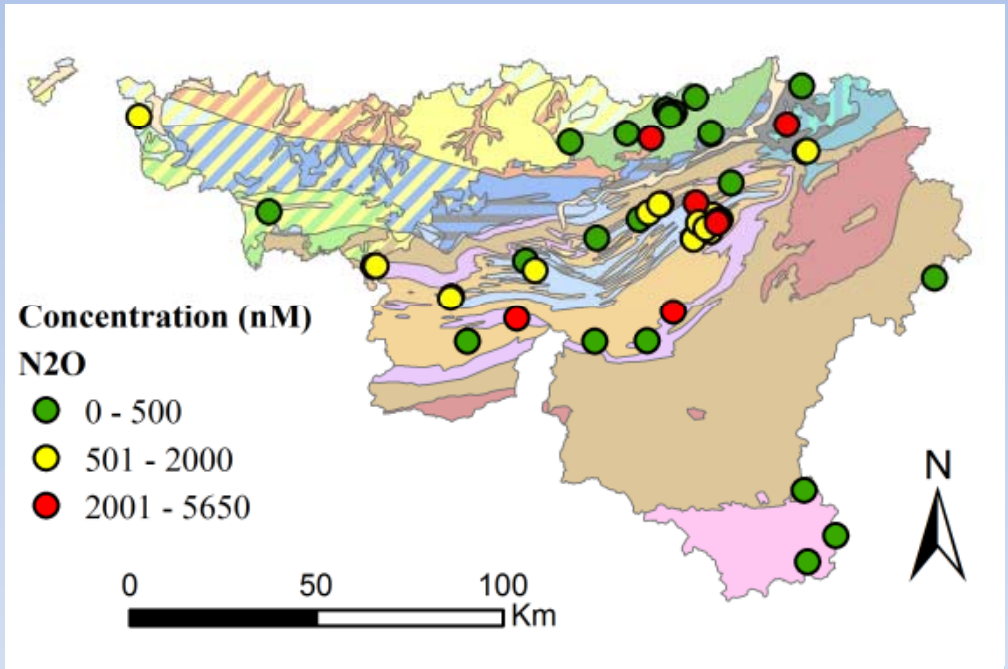
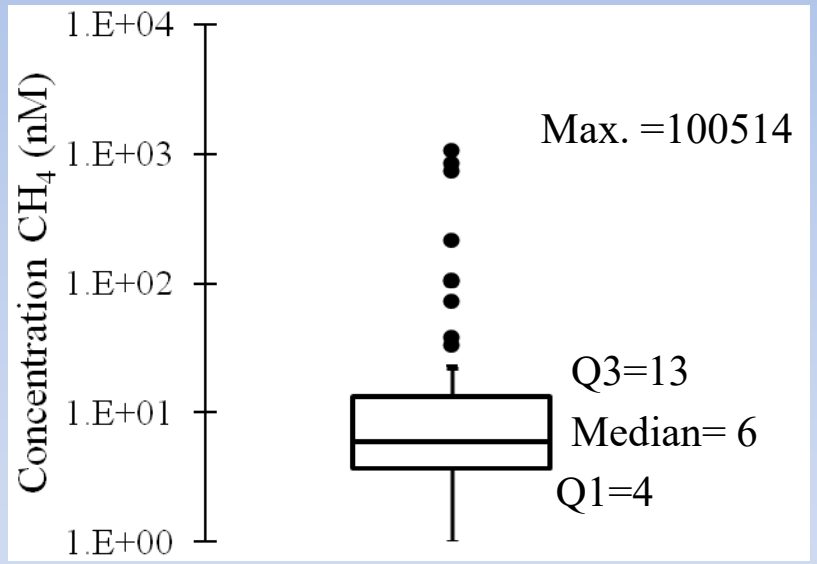


3. Results

Concentrations of Methane (CH_4)

Range→ 0-1064 nM
Average→ 64 nM



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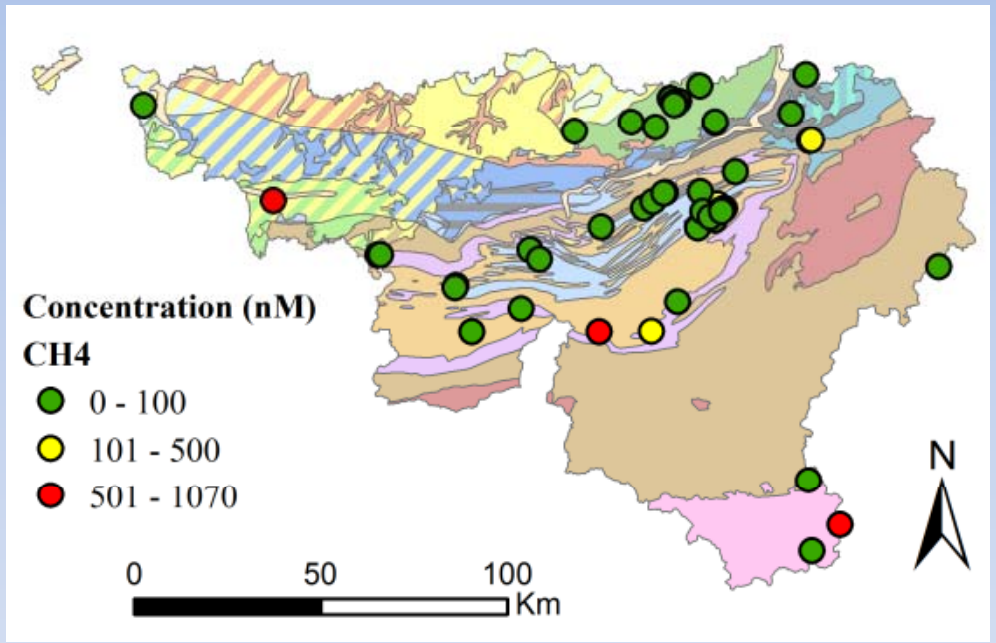

4. Discussion

Occurrence of N_2O in groundwater

Denitrification: $NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow \mathbf{N_2O} \rightarrow N_2$

$\mathbf{N_2O}$

↑

Nitrification: $NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$

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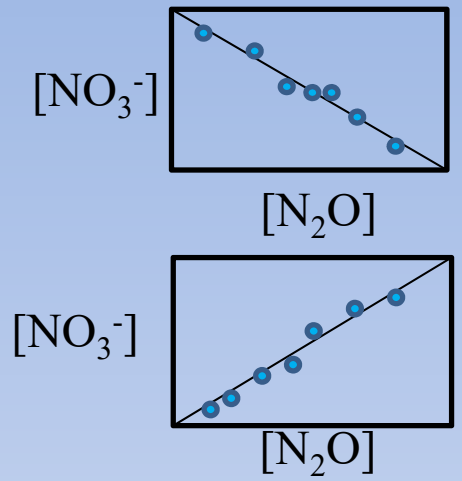

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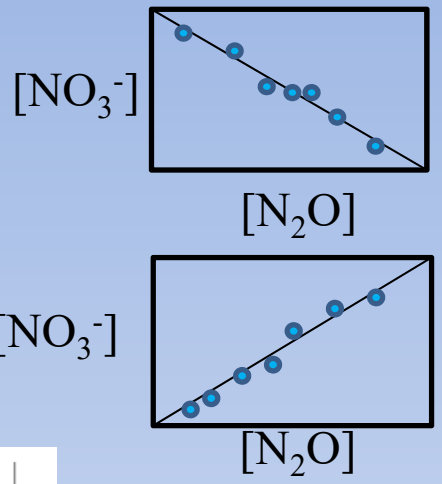

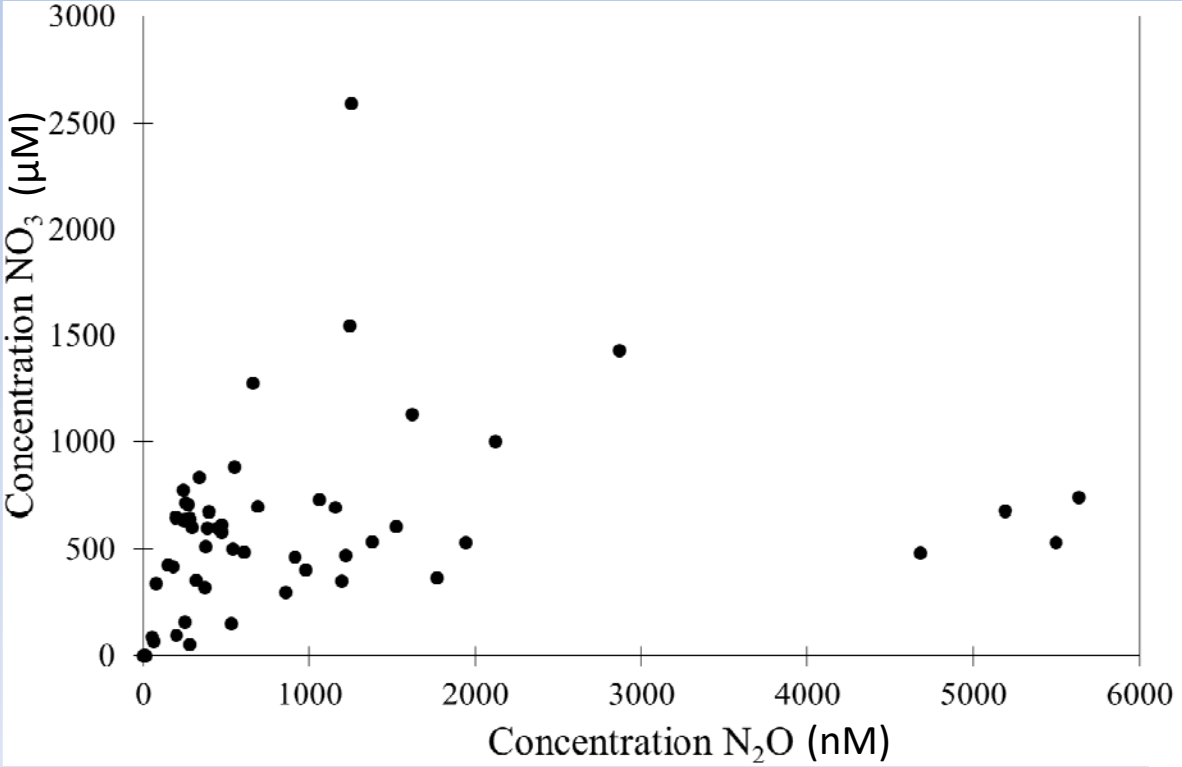

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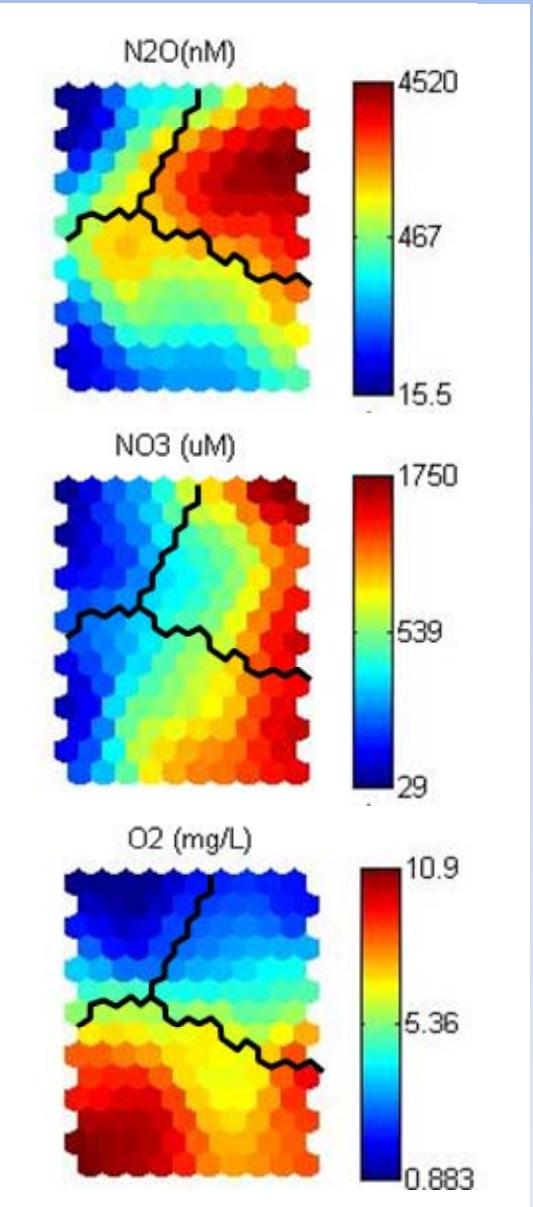
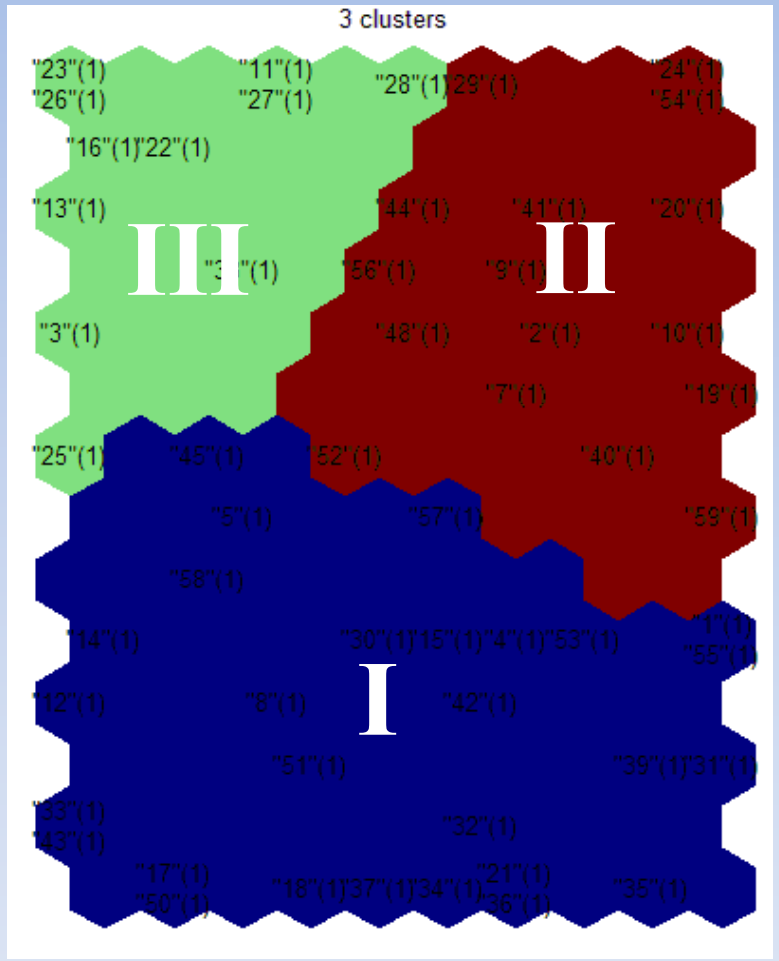


Self-Organizing Maps (SOMs)



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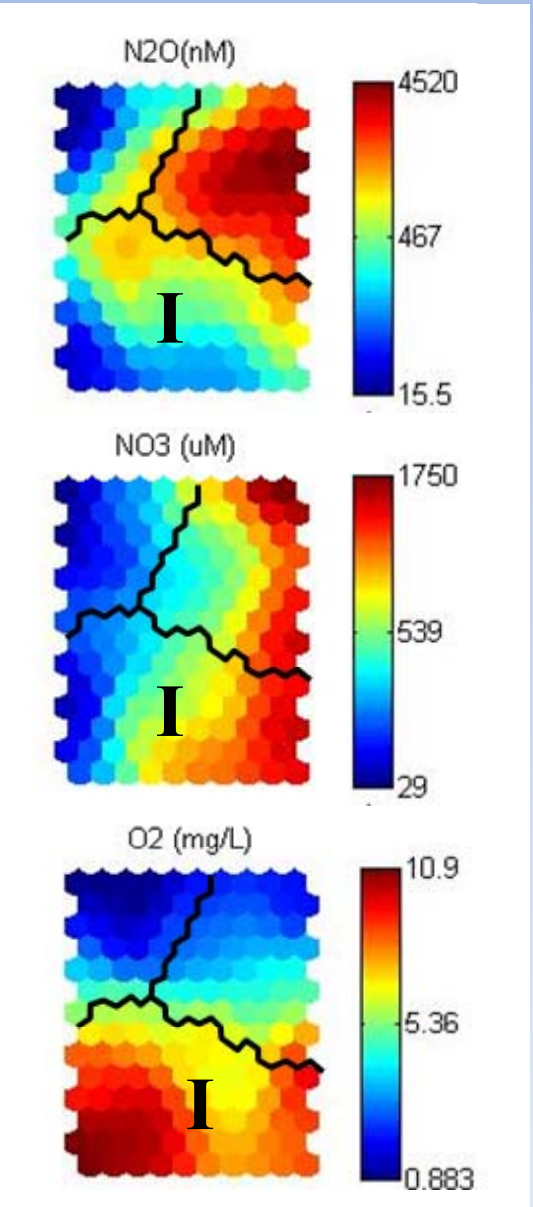
Occurrence of N_2O in groundwater



Average concentrations

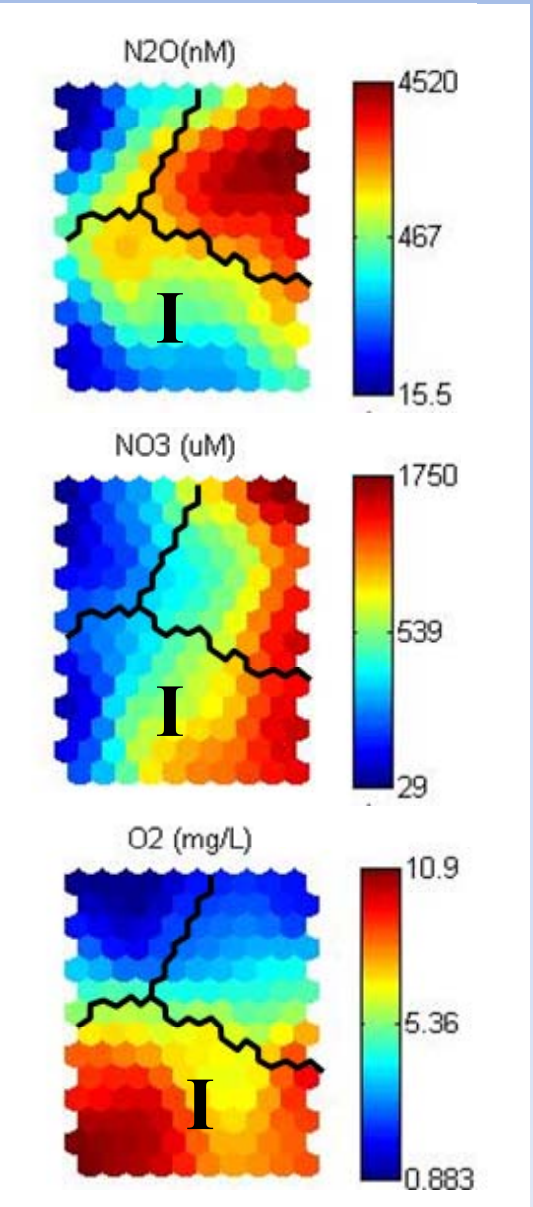
Group	N_2O (nM)	O_2 (mg/L)	NO_3 (μM)
I	516.55	7.51	564.37
II	2377.31	3.64	831.28
III	188.15	1.51	215.04

Group I

High concentrations of O_2
Medium concentrations of N_2O and NO_3^-

4. Discussion

Occurrence of N_2O in groundwater



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NITRIFICATION

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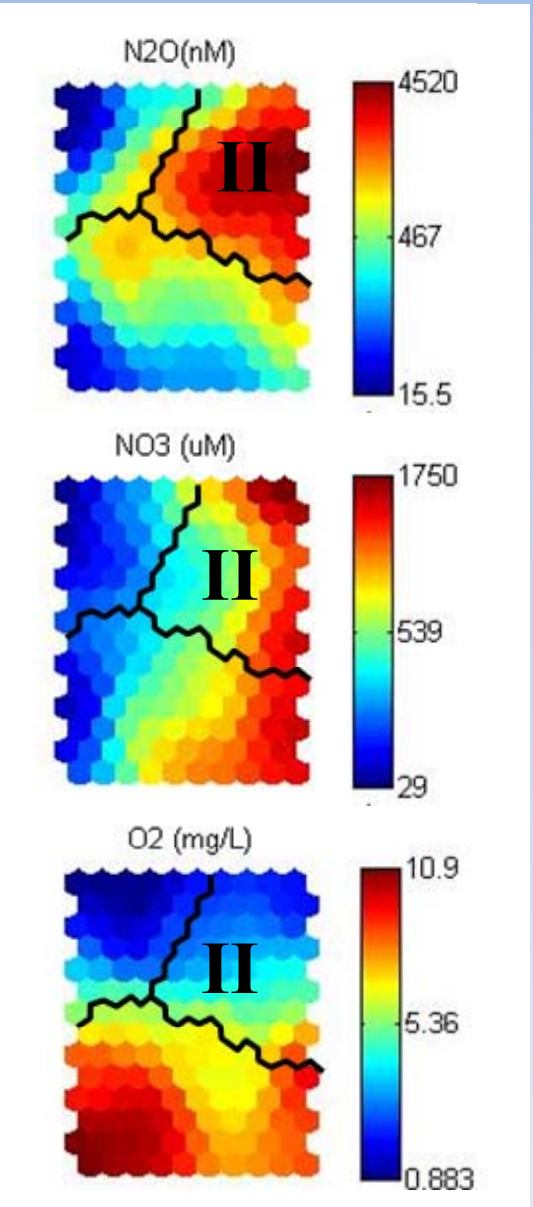

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Moderate O_2

High concentrations of N_2O and NO_3^-

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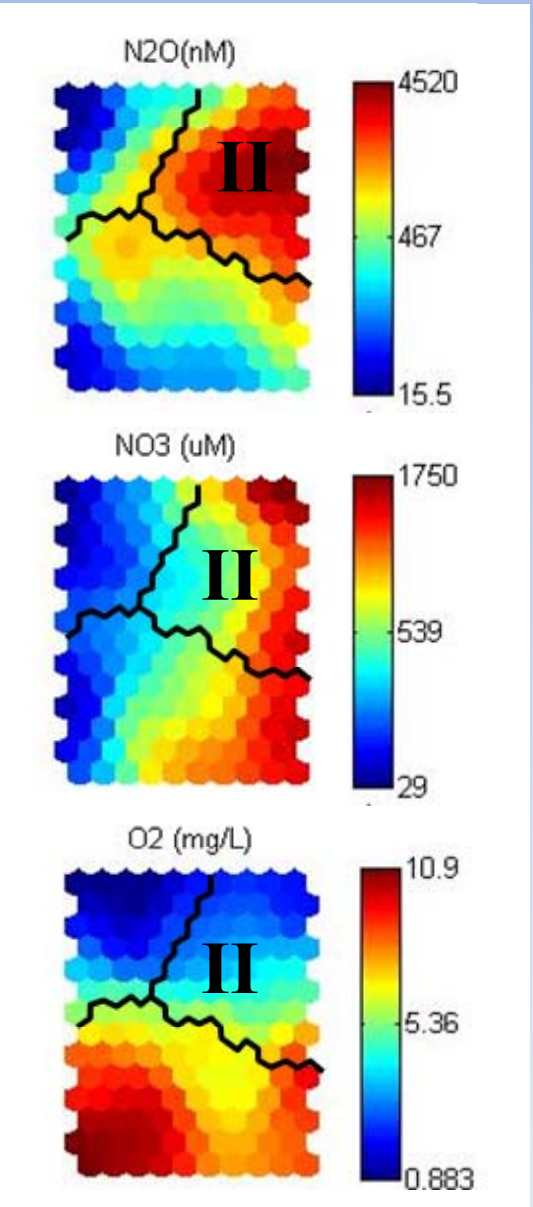

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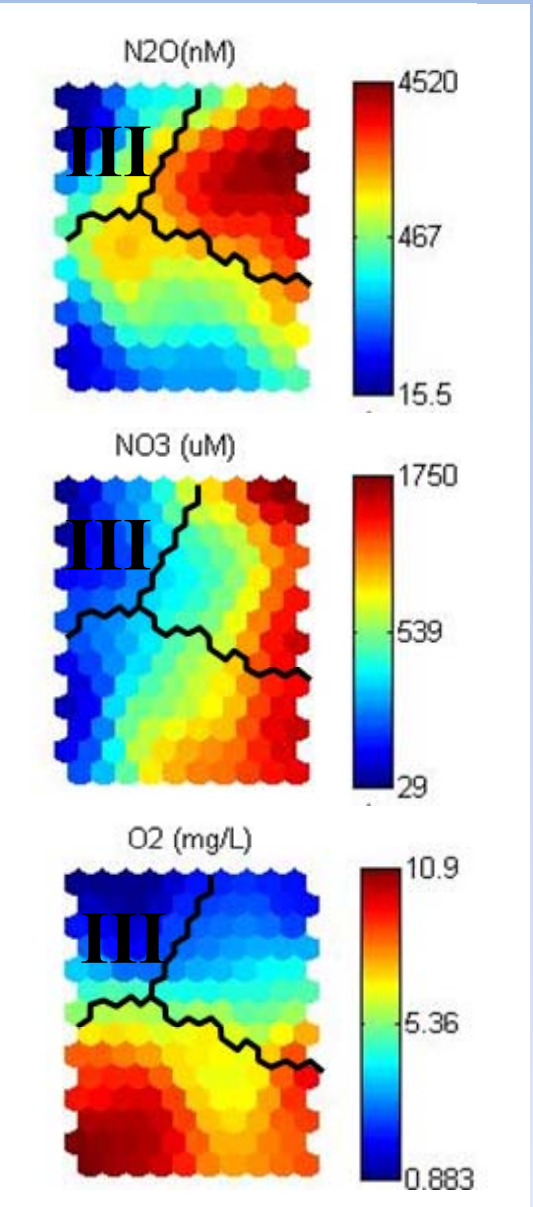
Occurrence of N_2O in groundwater



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Group III

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Low concentrations of N_2O and NO_3^-

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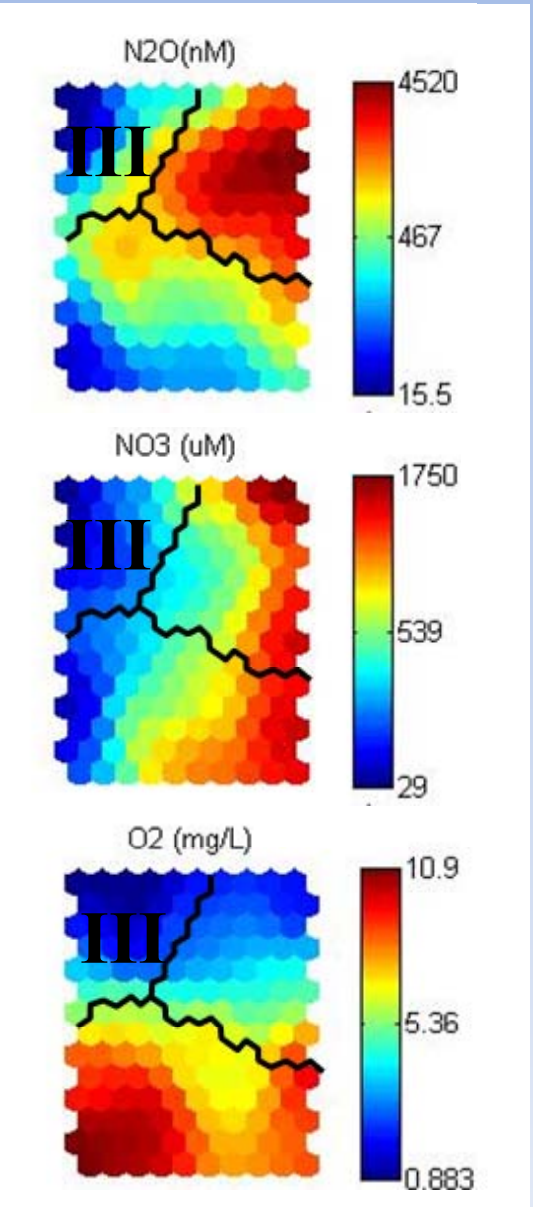
Occurrence of N_2O in groundwater



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DENITRIFICATION

$NO_3^- \rightarrow N_2O \rightarrow N_2$

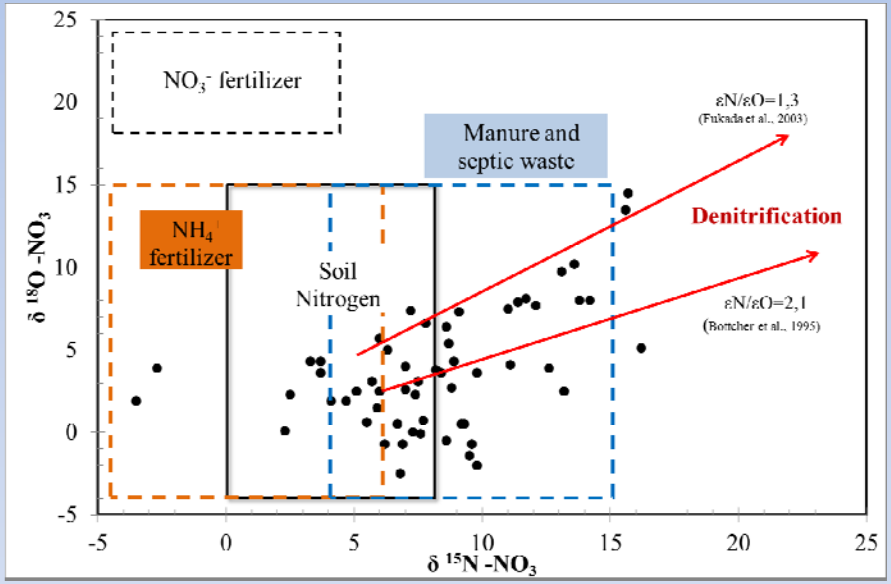
4. Discussion

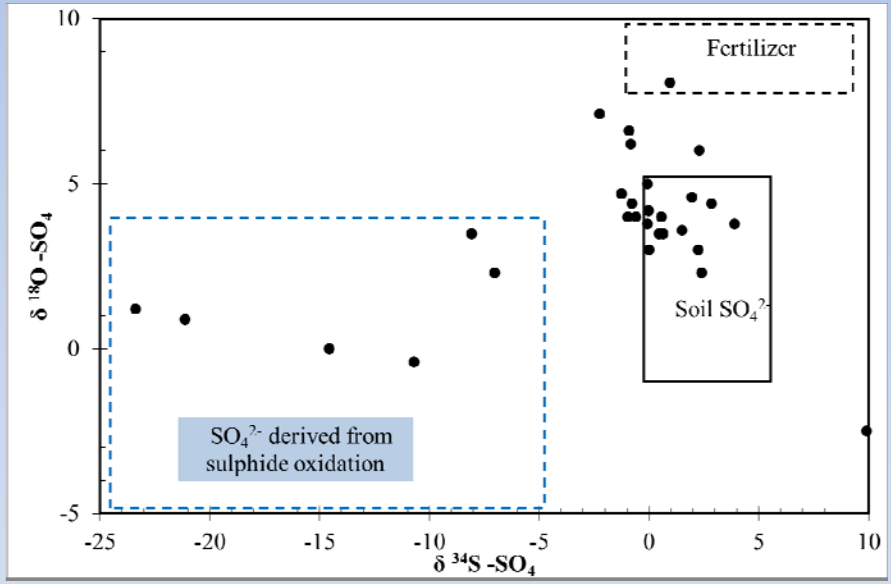
Occurrence of N_2O in groundwater

Environmental isotopes coupled with hydrochemistry data

Identify origin of nitrogen

Processes that produce/consume N_2O





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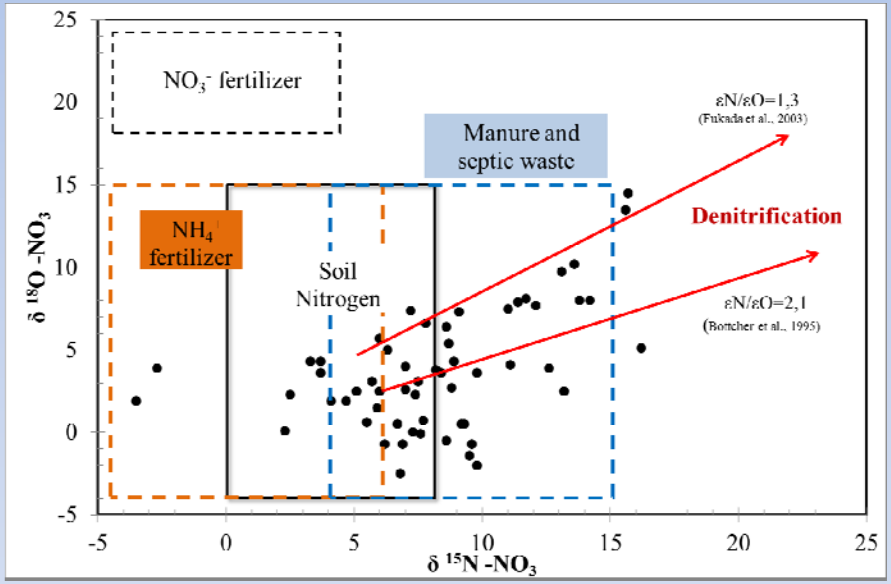
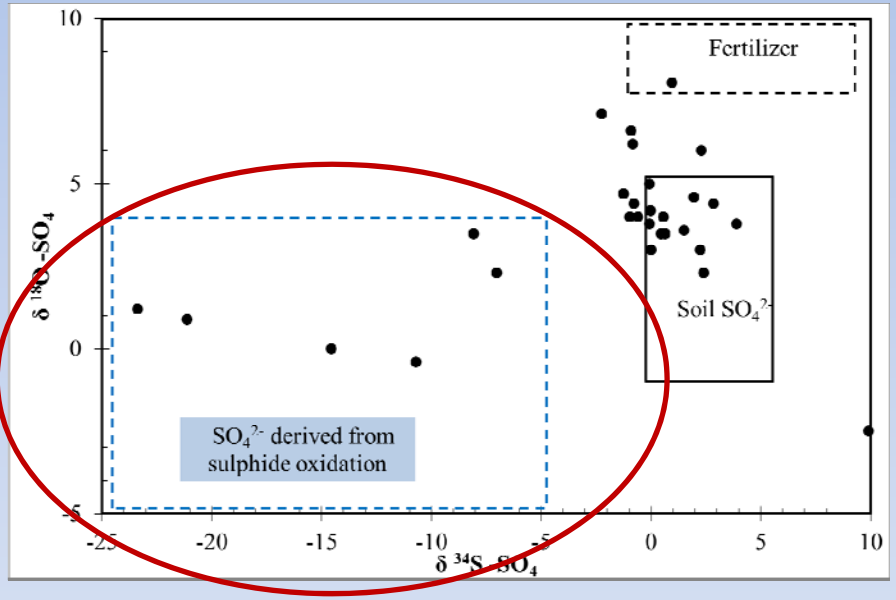




Autotrophic denitrification (Pyrite as electron donor):

$$5\,FeS_2 + 14NO_3^- + 4H^+ \rightarrow 7N_2 + 10SO_4^{2} + 5Fe^{2+} + 2H_2O$$

5. Conclusions

1. Groundwater of Walloon Region is oversaturated in CO_2 and N_2O relative to the atmospheric concentrations.

2. Preliminary results show that N_2O is produced by nitrification and denitrification and also consumed by denitrification.

3. Most favourable conditions for the accumulation of N_2O in groundwater seems to occur when NO_3^- is available and at medium oxygen concentrations.

Future work :

Integrate all the data available (environmental isotopes)
Investigate the occurrence of CO_2 and CH_4

Thank you for your attention

Acknowledgements. A. Jurado gratefully acknowledge the financial support from the University of Liège and the EU through the Marie Curie BeIPD-COFUND postdoctoral fellowship programme (2015-2017 from FP7-MSCA-COFUND, 600405).

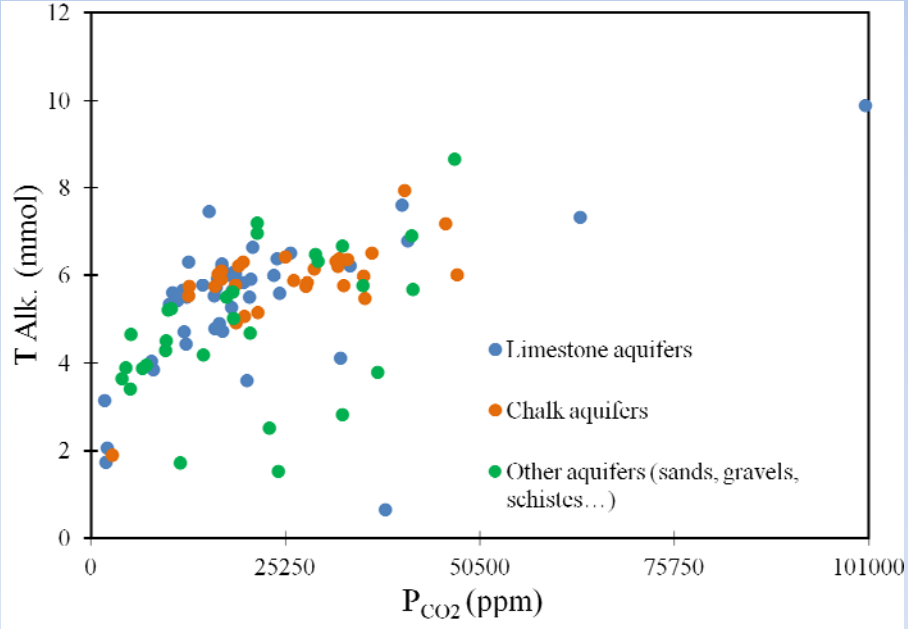
4. Discussion

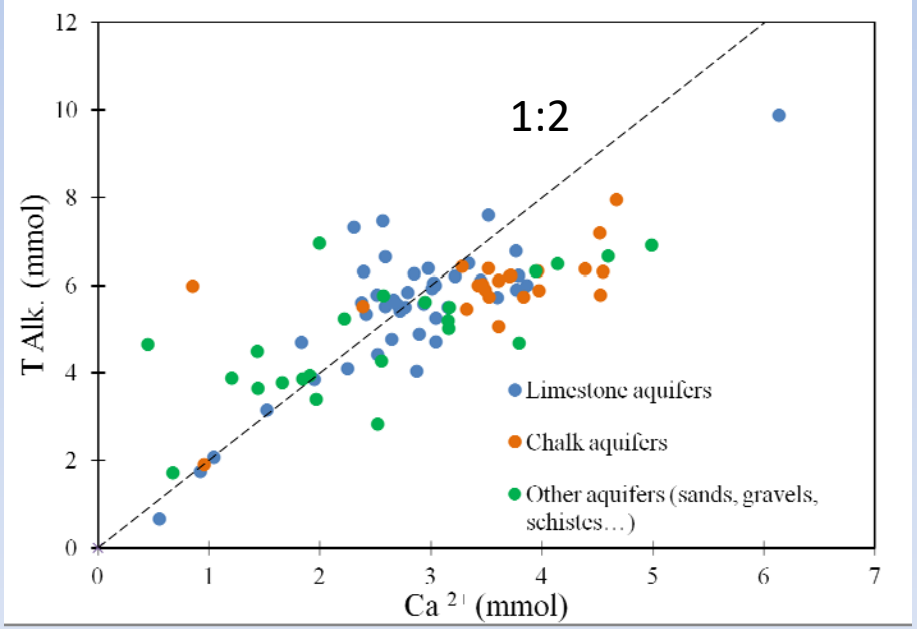
Occurrence of CO_2 in groundwater

High PCO_2 in groundwater

Water percolating through the soil becomes enriched in CO_2
High PCO_2 can contribute to the dissolution of carbonate formations

Carbonates dissolution: $CO_2 + CaCO_3\ (s) + H_2O \rightarrow 2HCO_3^- + Ca^{2+}$





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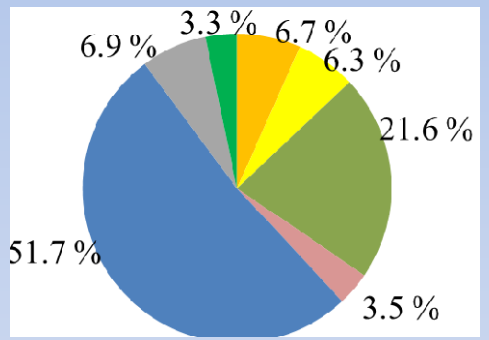
Groundwater abstraction (%, 2012)



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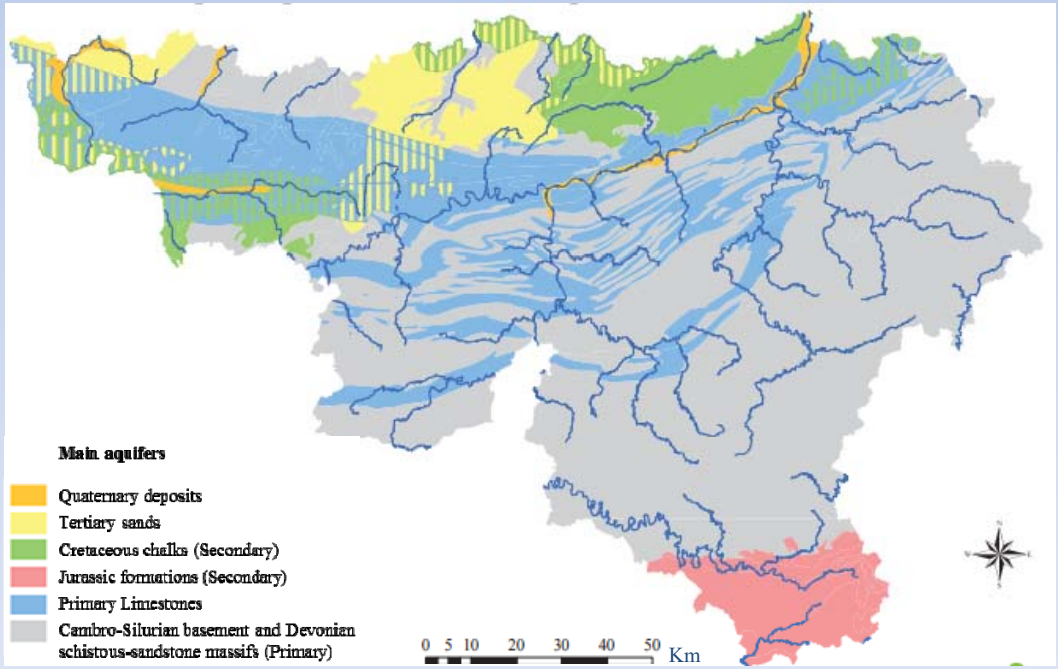
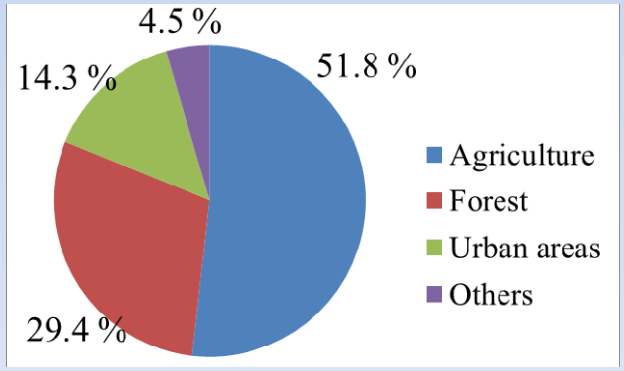


Land use



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