A multi-tracer approach for the identification of different pollution sources in sub-urban groundwater catchments

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In the context of the *project CASPER* (SPGE agreement with University of Liège, SWDE and SPAQuE) for the *Development of an integrated methodology for the protection of catchments in sub-urban areas*

1. CONTEXT

Management and protection of water catchments (water quality)
Drinking water distribution in **Wallonia** ≃ 76 % linked to groundwater catchments

Sub-urban area (≃ 25% SWDE catchments)

Relevant diversity of pollution sources linked to land use occupation: pollutants of **agricultural origin, economic & industrial activities**, **accidental sources** (spills), **continuous, hidden sources** linked to sewage systems, dumps (known/unknown), treated or untreated domestic wastewaters, sinkholes, private or industrial product storage systems (oil tanks), **interactions with watercourses** characterized by poor chemical quality

Urban water cycle: **Increase of the impermeable surfaces** due to the construction of houses and traffic lanes, car parks, ...; **Increase in domestic water consumption** because of the increase in individual households per house) and comfort use such as swimming pools, gardens **(despite the water-efficient machines)**

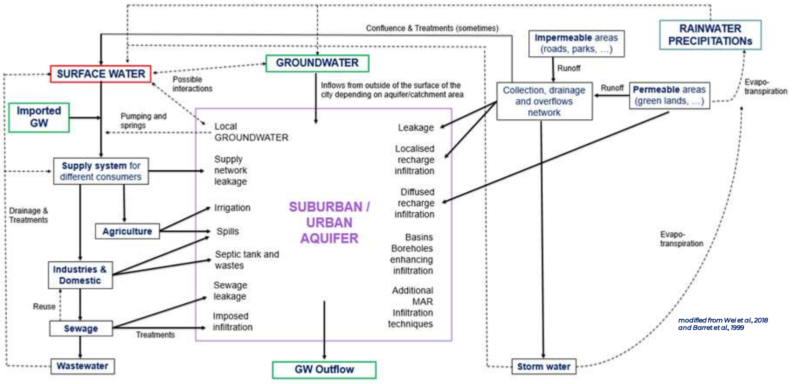
Problems
- **nitrate** (agricultural vs urban)
- **specific substances** (pesticides, sulfates, chlorides, chlorinated solvents, etc.)
- **mixed and varied pollutions**

OBJECTIVES

1) **Discriminate between different types of waters and pollution sources (mixtures)**
Identification of a range of tracer substances and approaches: specific molecules, isotopes, drugs, microbial biomarkers, etc.

2) **Variety of supporting tools**
Field measurements/acquisition
Integration of different types of lab analyses (isotopes, pharmaceutical compounds, bacteria, etc.)
Integration of a tool for the estimation of the quality of watercourses in contact with the aquifers
Adaptation of a tool to estimate and assess the pollution risk of areas

3) **Definition of a decision-making reference system establishing the importance of pollution** (prioritizing remediation measures)
Digital modelling of flows and transport (MODFLOW/MT3DMS)
Quantification and modelling of pollutants mass fluxes and discharge,
Scenario analysis and associated risks



2. INTEGRATED METHODOLOGY CONCEPTs and APPLICATIONs

PILOT SITE: Boussu (western Belgium, Mons basin), **exploited chalk aquifer in a sub-urban area** impacted by various sources of pollutants: old dumps and slag heaps surrounding the site, railway wastes, discharges from small and medium-sized enterprises, hospitals, housing, sewage system and agriculture.

1st) Determination of the **CAA – catchment area of the abstraction**; and **PAFA – part of aquifer feeding the abstraction**, the land surface perimeter in which abstracted groundwater is recharged, either by direct or indirect infiltration of surface water (procedure by Vandenberghe et al. 2015).

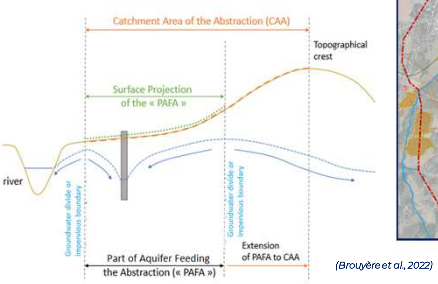
2nd) **Collection** on **historical data** available for the site (landuse, presence of known sources of pressures and contamination, flow rates and hydrogeochemical data

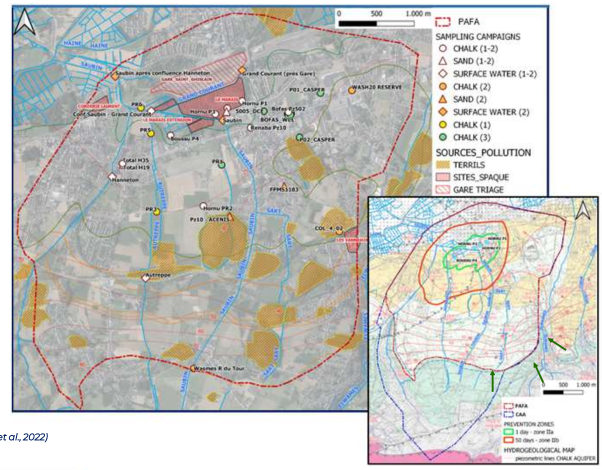
3rd) Surface and groundwater monitoring network for different **sampling campaigns,** focus on a combination of physicochemical parameters, traditional hydro-chemicals and a **set of more advanced indicators and analysis**:

- **Stable isotopes of NO_3^- and Boron** → urban effluents vs agricultural fertilisers (Nikolenko et al., 2018; Widori et al., 2005).
- **Stable isotopes of SO_4^{2-}** → anthropic activity, dissolution of evaporates, or alteration of carbon mines waste (Knöeller et al., 2011).
- **Isotopes of Chlorinated Solvents (H, Cl, C)** → degree of reductive transformation by comparing isotope signatures of the intermediates (Åkesson et al., 2021).
- **Occurrence of Gd (Rare Earth Element)** → indicate wastewaters and sewage leaks (Boester & Rüde, 2020).
- **Occurrence of pharmaceutical and lifestyle products** → anthropogenic contamination (Neufcourt, 2017).
- **Abundance of bacterial populations (16S rRNA Amplicon Sequencing)** and their affinity/resistance to some specific substances/elements (database: MiDAS and BacMed) → specific sources and biochemical reactions.

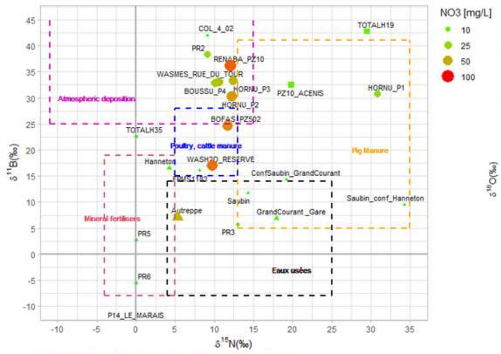
4th) Evaluation of the contribution of the different pollution sources identified in the catchment area based on **in situ measurement and numerical modelling of pollutant mass fluxes** and discharge (MODFLOW, MT3DS).

In theory ...

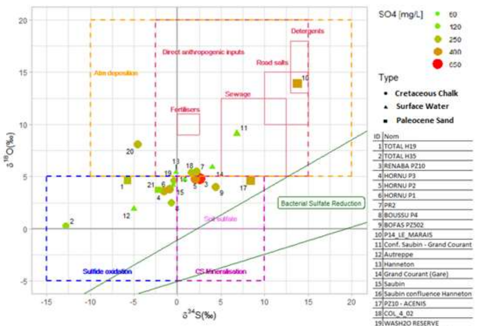




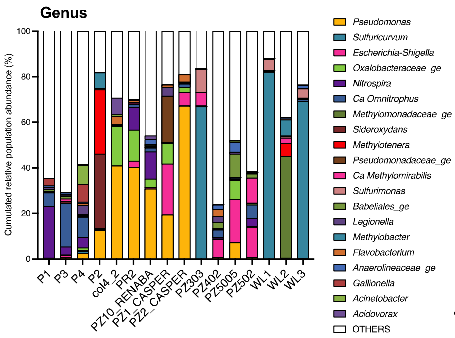
(Brouyère et al, 2022)

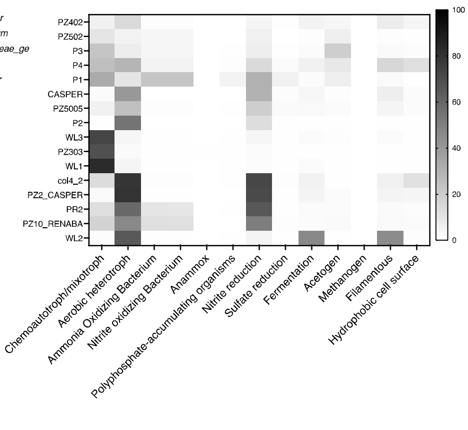


Precision d15N ±0,4‰ and d11B ±2,6‰



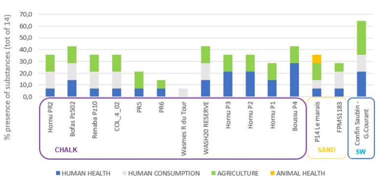
Precision d34S ±0,4‰ and d18O ±0,6‰





HUMAN HEALTH	HUMAN CONSUMPTION	AGRICULTURE	ANIMAL HEALTH
Carbamazépine	Caféine	Bentazone	Sulfaméthazine
Hydrochlorothiazide	Cotinine	MCPA	Clorsulon
Paracétamol		Isoproturon	Dicyclanil
Sulfaméthoxazole		Diclorobenzamide	Florfénicol

Selection of few substances for each of the 4 categories analysed used mainly as a proof of hypothesis contamination's origin



4. HYPOTHESIS ON POLLUTANTS' ORIGINS

Selenium → natural diffuse origin - presence of clay layer - stable values along years (corresponding studies in Mons chalk aquifer)

Sulphates → slag-heaps and carbon mine waste (S/E located – "point" source) + domestic wastewaters (diffuse source) - check presence of sulphur oxidizing bacteria

Nitrate → mixed diffuse origin: wastewaters + agriculture (thinner layer of sands S/E); points with denitrification confirmed by bacteria abundance (and presence of NO_2, Mg, etc.)

Pharmaceutical (human health related) and lifestyle substances → their presence confirms wastewater contamination (probably also from hospital wastewaters and medical wastes from known/unknown landfills)

Chlorinated solvents → point source pollution but no links with surrounding known landfills; possible links with garage-carwash and laundry activities all around the area; possibly also hospital cleaning (?)

5. TO GO FURTHER...

Drilling of additional monitoring wells in the chalk aquifer to perform **in situ measurements** of the contribution of the different pollution sources (of chlorinated solvents and sulfates) identified in the catchment area (applying the "**single well FVPDM dilution method**")

Optimise the numerical hydrogeological model to reproduce/simulate the pollutant discharge and mass fluxes

Development of a flow-based risk assessment framework at the regional scale following the approach proposed in the Pollusol2 project (SPAQuE-Ulg), considering the cumulative effect of multiple pollution sources located in the catchment area and the potential overall deterioration of groundwater in the whole catchment or at specific locations (exploited groundwater catchment points).

Correlation analysis and clustering (SOMs, t-SNE) on the results of hydrogeochemicals – isotopes - bacteria