

Evidencing biodegradation of organic pollutants using push-pull tracer experiments

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Faculté : Faculté des Sciences appliquées

Diplôme : Cours supplémentaires destinés aux étudiants d'échange (Erasmus, ...)

Année académique : 2020-2021

URI/URL : <http://hdl.handle.net/2268.2/11326>

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UNIVERSITY OF LIÈGE
Faculty of Applied Science

Evidencing biodegradation of organic pollutants using push-pull tracer experiments

Master's thesis carried out to obtain the degree of Master of Science in Geological and Mining Engineering by Hallberg Kajsa-Stina

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Academic Year 2020-2021

ACKNOWLEDGEMENT

This MSc report has been challenging, a great learning experience and not to say very interesting. I had the opportunity to dive into a real site investigation with extremely talented people, through a collaboration with SPAQuE. I am grateful to my supervisor Dr. Serge Brouyère for his great knowledge, expertise and constructive criticism, thank you. I would also like to thank Samuel Wildemeersch, from SPAQuE for his advice and help during a number of sunny field days. Pierre Jamin has also been a tremendous help in this the practical process and during the field days, thank you.

With that said, it could not have been done without the support of my loving family and my dear Fredrik for their encouragement and support. I would like to express a specific gratitude to my dear sister for all her expertise, knowledge and help with advice and proofreading. Additionally I would like to extend a thank you to all the lovely people that I had the pleasure to encounter during my exchange period in Liège. Thanking you for making this time memorable and keeping the light and spirit up even during the tuff times that followed the pandemic, I am most grateful.

ABSTRACT

The main objective for this MSc has been to test the use of reactive push-pull tracer experiments to evidence biodegradation of organic pollutants. To do so, the old slag heap Bois Saint-Jean site in Liège (Belgium) has been investigated to evidence microbial degradation of elevated residual benzene concentration ($4.5 - 320 \mu\text{g/L}$) even after ISCO treatment. Hence, to see if monitored natural attenuation is an option for the elimination of the residual pollution.

Groundwater samples were collected and slug tests were performed, to better understand the chemical and biological processes together with the hydrodynamics of the site. This was additionally used to dimension the push-pull experiments. Isotopic investigations, further helped to demonstrate and distinguish biodegradation from physical processes occurring in the aquifer. The push-pull tracer tests were undertaken into two piezometers (P301 and P302) with different resting times of the tracers in the aquifer ($\sim 21\text{h}$ and $\sim 64\text{h}$ respectively). The results of the chemical composition of the groundwater in the potential source zone indicate high concentrations of sulphate and sodium, which most likely are results from the previous ISCO treatment with sodium persulfate. Biodegradation parameters such as redox potential and dissolved oxygen indicated reducing anoxic conditions in the aquifer. Therefore, biodegradation could potentially occur under sulphate reducing conditions. At the same time, nitrate was barely detected in groundwater, which may have also potentially resulted from biodegradation. As a result, sulphate and nitrate were both selected as reactive tracers for the push-pull experiment.

In the end, results from the push-pull tracer experiments have demonstrated biodegradation of benzene most probably under denitrifying conditions in the vicinity of each piezometer. A rough estimation indicated a high degradation rate of 0.524 day^{-1} . This most likely corresponds to best-case degradation scenario since nitrate electron acceptors are delivered through the tracer injections. Nonetheless, even if most results clearly indicate a very active and responsive microbiological activity contributing to benzene degradation, further investigation will be necessary. Indeed, to give a more quantitative response to the question about whether the observed natural attenuation mechanisms occur at aquifer scale and if they are sufficient to guaranty that residual benzene can be eliminated naturally. Or if biodegradation should be further stimulated through the injection of electron-acceptors as done during the push-pull experiment.

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I. SECTION 1: PROJECT OBJECTIVES

1.1 GENERAL CONTEXT

Polluted site from industrial activities are a problem all over the world. Within the EEA-39 countries (countries involved in the European Environment Agency), the number of potentially contaminated sites was estimated in 2011 to 2.5 million (EEA, 2019). Approximately 14% were reported as “highly likely to be contaminated”. Of these sites, little less than half have been identified (45%), and around 51300 sites have been remediated (EEA, 2019). In Belgium alone 79.1% of the contaminated sites are caused by industrial activities (EEA, 2019). It was also reported by the EEA in 2019, that the sector contributing to most local soil contamination is the production sector (~ 60%).

It has been reported that many groundwater contaminations originate from point sources (Meckenstock *et al.*, 2015), where industries fall under. Due to the specific source of the contamination, contamination plumes often result from this kind of pollution source with higher concentrations of the pollutants (Meckenstock *et al.*, 2015).

Benzene (C₆H₆), an aromatic hydrocarbon stated to be the most prominent of the BTEX (benzene, toluene, ethylbenzene and xylene), has been reported widely spread in the environment polluting sediments, soils and groundwater (Langenhoff *et al.*, 2009; Vogt *et al.*, 2007). This organic compound can be found in crude oil and other petroleum products (Leusch and Bartkow, 2010), and such kind of pollutions have been linked to industrial activities (Langenhoff *et al.*, 2009). Exposure to benzene (through air or through food and drinks) has been reported to cause numerous hazards to human beings such as rapid heart rate, headaches, confusion, unconsciousness, coma, leukemic and death alongside many more symptoms and health effects (Leusch and Bartkow, 2010). For aquatic organisms, it has also been stated to be toxic (Leusch and Bartkow, 2010). Due to benzene’s toxicity, the EU limit has been set to 1µg/L in groundwater (EU Directiv 2006/118/EC – Annex 3, 2006). As a result, it has been considered to be the most persistent and toxic petroleum compound (Johnson *et al.*, 2003).

This indicates a strong need of remediation and rehabilitation of soils and groundwater contaminated with benzene. Both in order to use the contaminated sites again but also in order to avoid further spreading of the pollution which can have toxic effects on both human and aquatic organisms.

For the remediation of groundwater, the most commonly used method has been the *pump-and-treat* treatment. Other remediation techniques involve chemical treatment, thermal treatment, air sparging and bioremediation (Brusseau *et al.*, 2019). All which include active remediation processes. Natural attenuation involves physical, chemical and biological processes. The physical processes involve dispersion, sorption, dilution and volatilization (Johnson *et al.*, 2003). This indicate that pollutant concentrations can be reduced without any quantity change, so potential without being less hazardous for the environment. For this reason, it is of important to distinguish the biological processes from the abiotic ones. The monitoring of biodegradation of benzene through natural attenuation has been stated to be one of the most common remediation techniques when feasible (Johnson *et al.*, 2003). It is also often considered when the contaminated site need a “finishing touch”, since no active measures are taken to enhance and stimulate the degradation. Natural attenuation as a remediation method, rather investigates on the basis weather or not natural biodegradation of a specific pollutant occurs in the intrinsic environment, whiteout external help and interference. To be used as a remediation technique

monitoring is necessary to be included in order to follow up that the evolution degradation continuously (Rügner *et al.*, 2006). This is followed by monitoring the evolution, so that the degradation continuous to occur.

There are different ways and indicators that can be used to demonstrate that natural attenuation of organic contaminants by biodegradation might occur in the groundwater. These involve studying the evolution of redox potentials, isotopic fractionation of organic molecules, consumption of electron acceptors and donors, or/ and the investigation of the microbiological community (Meckenstock *et al.*, 2015; Søndergaard, 2009; Scroth *et al.*, 2001; Bombach *et al.*, 2010; Istok *et al.*, 1997; Langenhoff *et al.*, 2009; Cho *et al.*, 2013).

Whether or not natural attenuation or active remediation measures are being applied to degrade organic pollutants for groundwater remediation, the biological process of biodegradation remains the main focus of both measures. Within the scope of this thesis, the aim will be to try to demonstrate biodegradation of benzene through in-situ measurements using reactive push-pull tracer experiments.

1.2 SUPPORTING CASE STUDY

1.2.1 LOCATION

The site *Bois Saint-Jean* is located within the municipality of Seraing, belonging to the province of Liège in Wallonia, Belgium. More precisely, the site is situated between the University of Liège at Sart-Tilman in the South, LIEGE Science Park to the East/ South-East and in the North to the clustered activities of Ougrée and Kinkempois marshalling yard, North-West and North-East respectively. The more precise boundaries of the site constitute of LIEGE Science Park and the University in the (South) together with the Renory creek in the to the East and the Biez-du-Moulin stream in the West, Figure 1. The site stretches over an area of 146.3 ha (read line in Figure 1).



Figure 1. Localisation of the Bois Saint-Jean site from orthophotoplans (2015), from SPAQuE (2017).

The area of investigation is located in the middle-South of the Bois Saint-Jean, within zone 6, Appendix B Figure 2, also seen as the little orange quadrangle in Figure 1. The area of investigation, surrounded by the four piezometers Pz01, Pz12, Pz18 and Pz19 is estimated to cover a surface of 1.34 ha, Figure 2. Additionally, 12 piezometers were drilled within the site, 10 of which were used as injection wells for the ISCO remediation process and 2 as monitoring wells, Figure 2. However, PI01 was removed due to dysfunction.

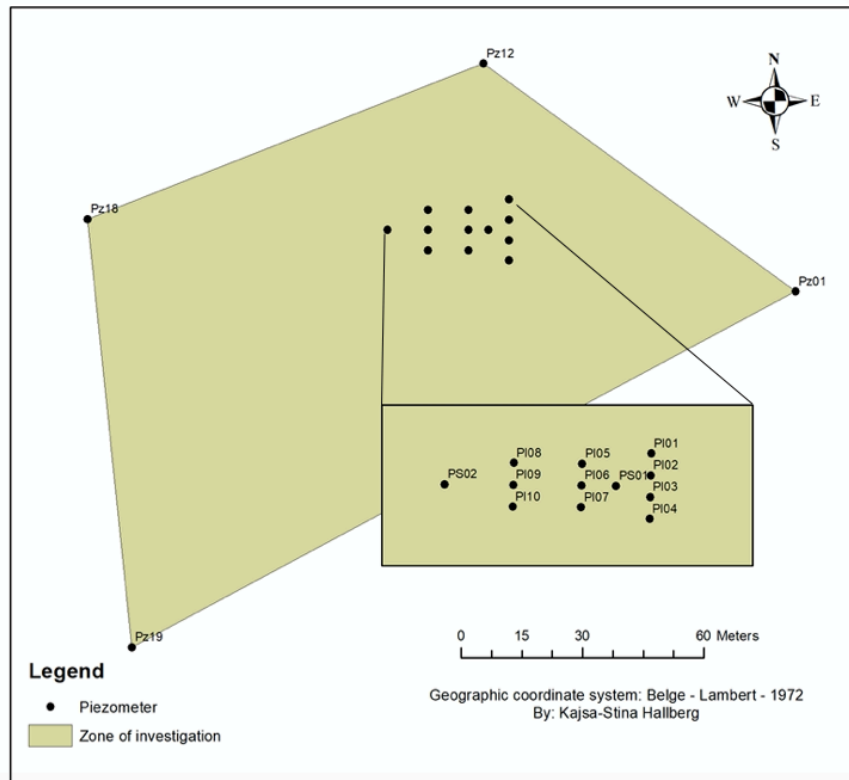


Figure 2. A zoom in image of the area of investigation together with the 12 piezometers drilled within the assumed source zone of pollution.

1.2.2 HISTORY OF THE SITE

The Bois Saint-Jean site (Figure 1) was used as a slag heap between the years 1920 – 1987 for a steel industry, and as a dump for the municipality of Ougrée together with private companies but also for clandestine deposits. At the time it was owned by the company Ougrée-Marihayel until 1999 (SPAQuE, 2017).

From the municipality, household waste was sent to the site together with molten slag and tar-based products. Additional companies also used the site as a dumping ground. The following timeline of the site as a slag heap, was done by SPAQuE (2017) in their investigation.

- **1920** - First waste deposits by the company Ougrée-Marihayel and municipality of Ougrée,
- **1935, 1941, 1942** - Official authorization from the Provincial Government allowing the company Ougrée-Marihayel to use the site as a deposit site
- **1952** - Authorization from the Permanent Deputation allowing the municipality of Ougrée to dump waste on the site for 10 years
- **1964** – Suspension of waste transport going to the site due to maintenance of the private road extending Biez-du-Moulin Street
- **1968** - The road closed to the public due to illegal dumping,
- **1970** - Request for renewal of the authorization to dump waste on the site by the municipality of Ougrée, without trace of official authorization from the inspectorate of hygiene,
- **1973** - Authorization for the following companies to use the site as a slag heap: Air Liquide, Isobelec, Linalux, Phénix Works, Société Belge de l'Azote, Tensia, Tubes de la Meuse,

- **1973, 1975** - Request for authorization, without any trace of response, for the waste deposit of packages of toxic products (phytopharmaceutical products) with the Provincial Government. by the Société Belge de l'Azote,
- **1976** - Cancellation, of a large part of the waste deposits authorized to private companies in 1973
- **1986** - According to a testimony to the DGRNE, the deposits are exclusively composed of gas scrubbing sludge from blast furnace B of Ougrée and blast furnace n°6 of Seraing and are only dumped in a large excavation present on the site,
- **1987** - Final dumping, without authorization, of gas scrubbing sludge, but also blast furnace sludge and solid and liquid residues from the chemical industry, since the publication of the Walloon Regional Executive Order on controlled landfills put a definitive end to deposits on the site

In 1999, the site was bought by SOGEPA from Usinor, and later in 2007 bought by SPAQuE. Some pieces of land were further sold to the company SPI in 2013. The above-mentioned activities, have resulted in large quantities of trash, garbage and contaminants contributing to the polluted situation at the site. Investigation of pollution first took place in 2000 and has ever since been going through additional investigations together with remediation of both soil and groundwater contamination (SPAQuE, 2017).

1.2.3 REGIONAL GEOLOGY

The *Bois Saint-Jean* site is located within the geological formations of the Ardenne Anticlinorium, on the border to the northern flank of the Dinant Synclinorium. Geological deposits corresponding to these regional geological units were formed during the Palaeozoic era. More precisely, sediments corresponding to the Ardenne Anticlinorium originate from the Lower Devonian period, while those of the Dinant Synclinorium were deposits later during the Lower Carboniferous period (Pirson *et al.*, 2008).

Mainly sandstone and shale sedimented during the Lower Devonian era (Godefroid *et al.*, 1994 from Pirson *et al.*, 2008), corresponding to the bedrock found within the Ardenne Anticlinorium. The Dinant Synclinorium can be seen in Condroz South of the Seraing, consisting a series of Famennian core anticlines (terrigenous input, constituting of Famenne shales and Condroz sandstone (Pirson *et al.*, 2008)) and Carboniferous synclines (Boulvain, 2021).

1.2.4 SITE GEOLOGY

The lithology of the site consists of a backfill layer ranging from 0 – 28m in thickness, mostly composed of ash and slag, with addition of some construction- and household waste, together with detergent compounds. This is followed by a compact red weathering clay ranging from 0 – 3 m in thickness. Shale in the colour of red, green and grey altered with sandstone in the tone of purple have been discovered in the western part of the site. Yellow-brown and black sand have been found in local clusters. The thickness of the weather rocks has been found locally to go down to 12m. Sandstone and shale have only been detected in the deep channels created by the stream Biez-du-Moulin and the creek Renory, during the installation of the drainage system (ECOREM, 2000 from SPAQuE, 2017). The information also led to the conclusion that the geological layers of the site was oriented East to West with a dip of 60 to 90° South. (SPAQuE, 2017)

1.2.5 AREA OF INVESTIGATION – GEOLOGY

Studying the drilling logs of the area of investigation from East to West (orientation of the geological layers, concluded by ECOREM, 2000 from SPAQuE, 2017), the succession consists of a back fill ranging between 0 to 10.0 m thickness. No backfill was found in the drilling log of Pz01 (East) were as for Pz18 (West) it ranged down to 10 m of thickness. This is followed by a silt, silty-sand layer ranging from 1 m in Pz01, to 4.70 m in P301 down to 0.5 m in Pz18. Underneath, local variation of particles size occurs. In the centre of the area, the injections wells display a 3 m layer of sand, clay and pebbles. This is followed by a ~1.2 m layer of earth and pebbles before starting to reach the bedrock consisting of shale at ~7.3 m. In the monitoring wells, similar lithology prevails with the shale layer slightly deeper, starting at 8.7 m. In the East (Pz01), the sandstone bedrock is reached at 3 m depth with a thickness of 4 m, followed by shale.

1.2.6 HYDROGEOLOGY

Investigation carried out by SGS concluded that on the Eastern part of the site, a groundwater table is found within the fractures and weathering sandstone top of the Lower Devonian formations. Their investigation also established that the groundwater flow within the site prevails almost everywhere in the natural terrain, with little influence from the backfill. The drawn piezometric map, indicates that groundwater is naturally drained by the Biez-du-Moulin stream to the West and the North and by the Renory stream to the East (Appendix B Figure 1). It has also been stated that the subsurface is influenced by an old draining valley (Vieux Moulin brook) flowing from the South, crossing under the slag heap. The hydraulic conductivity was estimated to 10^{-5} m/s for the fractured sandstone and to 10^{-7} m/s for the compact upper layer of the sandstone and shale (ECOREM, 2000 from SPAQuE, 2017). At the very local scale of the area investigated in this thesis, groundwater flows towards the North-West. The direction of the groundwater flow within the area of investigation (purple quadrangle in Figure 3), further explains that the source of the benzene pollution must be located within the area of investigation, hydrogeologically downgradient from Pz01, since this piezometer has never been contaminated with high concentrations of benzene.

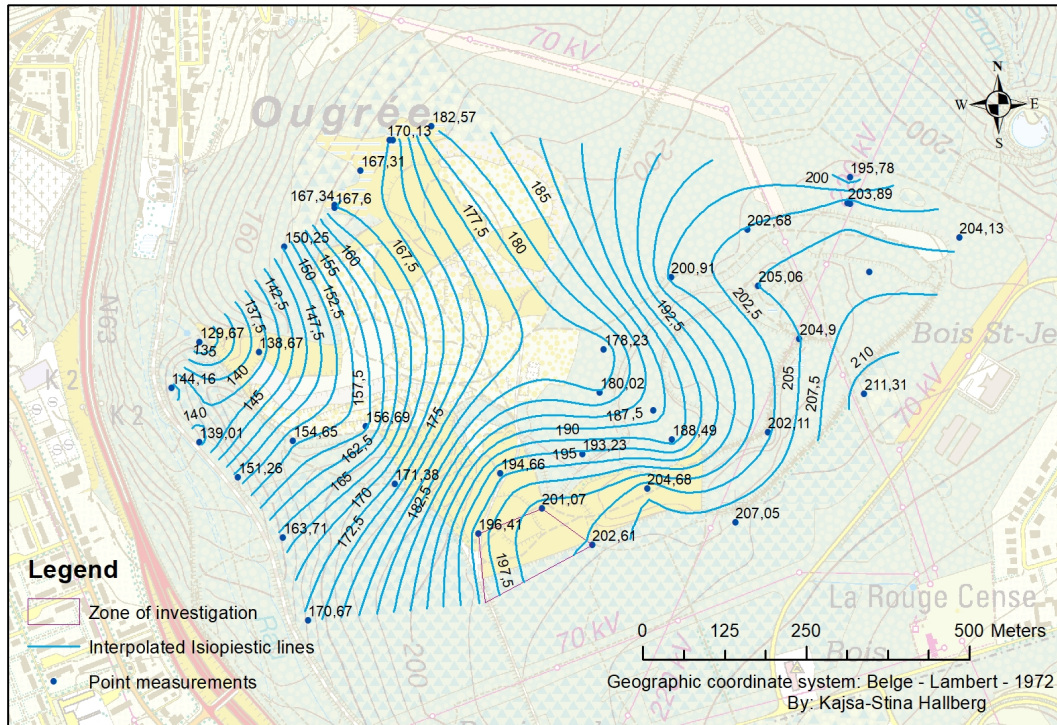


Figure 3. Piezometer map of the upper layer of the Lower Devonian sandstone and shale formation, interpolated through isopiestic lines from water level measurements [m] from piezometers within the site taken on the 8th and 9th of May in 2017. The distances between the isopiestic lines = 2.50 m. Together with the zone of investigation.

1.2.7 EARLIER REMEDIATION WORK

The site was first investigated for contamination in 2000 by ECOREM, followed by further investigation by SGS supervised by SPAQuE between 2003 – 2008 (SPAQuE, 2017). Continuous monitoring of groundwater took place between 2003 and 2016, with additional investigation of the area identified as “zone d’investigation 2017” in Figure 1 (SPAQuE, 2017), which will also be the investigated zone for this master thesis.

Through the early investigations, areas heavily contaminated by cyanide were detected, which led to excavation and backfilling with clean soils in 2002 as a first step in the remediation work. This was followed by the creation of controlled storages areas of contaminations/ contaminated zones of former household waste dumps and a former hydrocarbon hot spot, where contaminated surface materials were grouped together in relation with their pollution (SPAQuE, 2017). The area was sealed in different layers and a drainage network was installed to collect leachate water from the landfill. This was done between 2003 to 2004 (SPAQuE, 2017). A third step carried out between 2004 – 2005 consisted in controlling and securing the spontaneous burning of the spoil tip (accumulation of waste material removed during coal mining) due to oxidation of residual coal (SPAQuE, 2017). A capping bio filter system was installed. Additional remediation work involved the installation of a wastewater treatment plant in 2008, with the aim of collecting and treating highly basic water leaching from the spoil tip (pH>10). In 2009, Miscanthus was planted in order to produce biomass (SPAQuE, 2017).

Regarding groundwater contamination related to the landfill, heavy metals, mineral oils, monocyclic aromatics, polycyclic aromatics hydrocarbons, phenols, heavy metals and detergents were found (SPAQuE, 2017). Downgradient the landfill, cyanides compounds,

chloride and sulphate together with heavy metals were found. In the western part of the site, a hot spot contamination by mineral oils, hydrocarbons, monocyclic aromatics, polycyclic aromatic hydrocarbons, phenols, heavy metals and detergents was detected together with cyanides (SPAQuE, 2017). Through groundwater sampling, it was concluded that leaching of meteoric water from the landfill was the main process responsible for the pollution of groundwater below the site. Piezometer Pz18 was proven to show the most critical residual contamination at the site due to benzene concentration above $1000 \times VI_{\text{nappe}}^1$ (intervention threshold in the former “Décret sols” of the Walloon Region) and $100 \times VS_{\text{nappe volatilisation}}^2$ (SPAQuE, 2017). Pz18 is located next to a sidewalk (Figure 1), which is regularly used for outdoors activities such as walking, cycling and jogging by the public. In addition, the area around is expected to be used in the future for the expansion of the Liège Science Park, located in the neighbourhood of the site Bois Saint-Jean (SPAQuE, 2017). This led to further investigations in 2017 to locate the source of benzene pollution and to define remediation measures (Figure 2).

Investigations in 2002 and 2003 indicated that piezometers Pz01 and Pz19 located upgradient from Pz18 were not contaminated with benzene (SPAQuE, 2017). Soil samples taken in the vicinity of the Pz18 also revealed low concentrations of benzene, resulting in the assumption by SPAQuE that the source of benzene is likely located in the polygon formed by the Pz01, Pz12, Pz18 and Pz19 (Figure 2). The source of pollution was further assumed to be located within the embankment. Since the area formed by the polygons was heavily vegetated at the time, areas accessible for investigation were located, and can be seen in Figure 4.

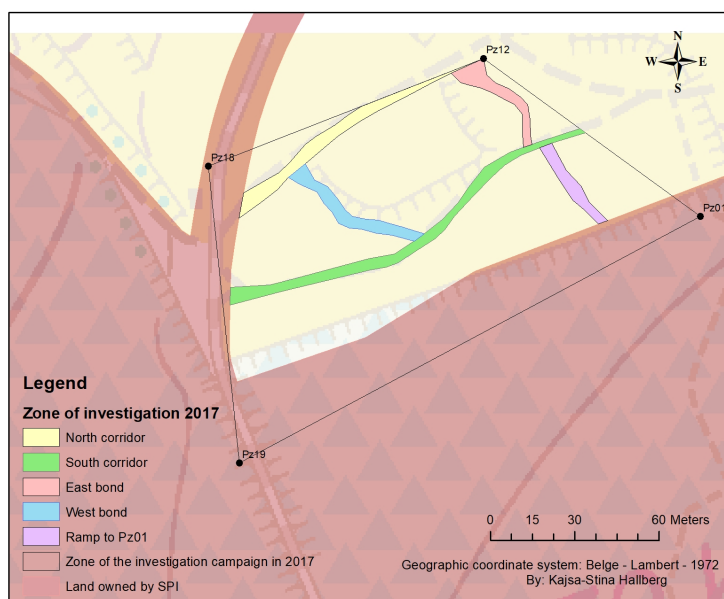


Figure 4. Locations of areas accessible for the investigation campaign in 2017.

¹ VI_{nappe} stands for « Valeur d’Intervention » for groundwater in the former “Décret sols” of Walloon Region i.e. concentration threshold above which an intervention is mandatory for groundwater because of heavy pollution evidence.

² $VS_{\text{nappe volatilisation}}$ stands for « Valeur Seuil » for pollutant volatilization from groundwater surface in the former « Décret sols » of Wallon Region i.e. concentration threshold above which there is a risk of volatilization from groundwater surface inducing a risk for human health by inhalation.

Soil and groundwater were investigated through the following actions: 12 drillings, 16 trenches, 2 piezometers, 136 soil samples and one groundwater sample from the bottom of the southern trench (south corridor, Figure 4). The drilling was performed by SMET G.W.T. and the sampling and interpretation of the results were made by SPAQuE. For the groundwater investigations, samplings were conducted by Almadius and analysed by SPAQuE, from 5 piezometers. Results indicated that soils in the entire zone were heavily contaminated by benzene (concentrations of $2250 \times VI_{UsageV}^3$) with highest measured concentrations of 1800 mg/kg_{m.s.} Other pollutants such as toluene, xylene, naphthalene, mineral oils (>C5-C8, >C8-C10) and some heavy metals (arsenic, copper and lead) above VS_{UsageV}^4 or VI_{UsageV} were also observed, however benzene was pointed out as the main pollutant measured in the soil. Concerning groundwater, sample indicated severe contamination of benzene at a maximum of 15000 µg/L ($375 \times VI_{nappe}$) upgradient (source zone). In Pz18, downgradient, the concentrations of benzene were measured to 3500 µg/L downgradient. This led to the excavation of hot spots of the soil with volatile compounds for ex-situ treatment. During the fall of 202, in-situ treatment of the groundwater took place by chemical oxidation (ISCO) of benzene. This was done by injecting Sodium Persulfate ($Na_2S_2O_8$) into the groundwater through the 10 injection wells, seen in Figure 2. Table 1 displays the measured values of benzene before and after the injection of ISCO. Even if a significant decrease of benzene concentrations was observed, benzene concentration remained above the groundwater limit of 10 µg/L (VS_{nappe}) still prevails.

It is also interesting to notice the large decrease of benzene concentrations in Pz18 measured between the 18th on July 2020 (3500 µg/L) and the last measurement before the ISCO treatment took place on the 14th of October the same year (6 µg/L). During this time, the excavation of benzene hot spots was undertaken, which resulted in the fact that the trenches stayed open for several weeks potentially inducing benzene volatilization and/or re-oxygenation of the aquifer to stimulate intrinsic biodegradation.

Table 1. Measured benzene concentrations in the study are of the Bois Saint-Jean site before the injection of Sodium Persulfate (14/10) for the ISCO treatment and two months after (16/12).

| <i>Sample location</i> | <i>P230</i> | <i>P301</i> | <i>P302</i> | <i>Pz12</i> | <i>Pz17</i> | <i>Pz18</i> |
|------------------------|---------------|---------------|---------------|---------------|---------------|---------------|
| <i>Sample date</i> | <i>[µg/L]</i> | <i>[µg/L]</i> | <i>[µg/L]</i> | <i>[µg/L]</i> | <i>[µg/L]</i> | <i>[µg/L]</i> |
| 14/10 - 2020 | <0.2 | 130 | 800 | 10.19 | <0.2 | 6 |
| 16/12 - 2020 | <0.2 | 39 | 320 | - | <0.2 | 4.5 |

³ VI_{UsageV} stands for « Valeur d'Intervention » for soil for industrial use in the former “Décret sols” of Walloon Region i.e. concentration threshold above which an intervention is mandatory for soil because of heavy pollution evidence.

⁴ VS_{UsageV} stands for « Valeur Seuil » for soil for industrial use in the former “Décret sols” of Walloon Region i.e. concentration threshold above which full investigation, including risk analysis, is mandatory for soil because of pollution evidence.

II. SECTION 2: AN OVERVIEW OF THE INVESTIGATION

The natural attenuation of benzene through microbial degradation will be investigated through push-pull tracer tests. To do so, different reactive tracers have been chosen as potential electron acceptors in the process of microbial degradation of benzene in groundwater. Through the push-pull tracer tests, the relative evolution of the reactive tracers will be compared to that of a conservative tracer (bromide), to account for the other hydrodynamic and hydrodispersives processes such as dispersion and dilution. The ratio between the normalized reactive tracer concentrations and the normalized conservative tracer concentration will be used as an indication of biodegradation. Changes in isotopic fractionation of different compounds involved in the biochemical reactions will also help to distinguish and additionally demonstrate if microbial degradation has occurred.

Prior to the push-pull tracer experiments itself, several measurements were needed to dimension the tracer tests. The sequences of the experiments of the investigation is illustrated in Figure 5.

The first part of the investigation involved groundwater sampling to get an overview of the hydrogeochemical conditions prevailing in groundwater. This involved the analysis of major ions, dissolved metals, benzene-, sulphate- and nitrate concentrations. In situ measurements were also performed to assess pH, dissolved oxygen (DO), redox potential (Eh) and electrical conductivity (EC). Additionally, groundwater samples were taken to measure the isotopic ratios of benzene, sulphate and nitrate. The information also gave an idea of the biodegradation conditions and was used as a reference point to the results of the push-pull tracer tests.

The second part involved slug test measurements, to assess the hydraulic conductivity of subsurface geological materials at the site. Knowing this has helped in the dimensioning of the injection and extraction rates of the push-pull experiments together with assessing the time frame for the resting phase of the experiments.

The final and third step of the investigation consisting in undertaking the push-pull experiments and to analyze the data for demonstrating microbial degradation.

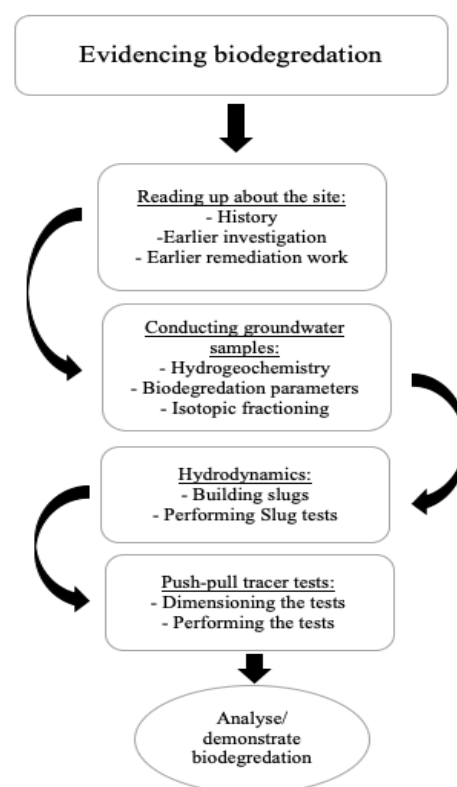


Figure 5. A flowchart of the method sequences involved in the investigation.

III. SECTION 3: BACKGROUND

3.1 SLUG TESTS

3.1.1 HISTORY

The origin and application of slug tests arose from the need of geotechnical engineers to assess parameters of shallow subsurface conditions and dewatering. Also pore pressure distribution factors were of importance in the conduction of buildings, bridges and dams (Bouwer, 1978).

Determine the hydraulic conductivity of a soil has been done through either field test such as, aquifer test. It is executed through pumping. Tracer studies can describe the estimation of travel direction and groundwater flow velocity. Slug-tests, or laboratory tests is another way to assess hydraulic conductivity of soil (Campbell *et al.*, 1990). However, it has been concluded by number of scientists that field measurements of hydraulic conductivity for fine-grained sediments with lower hydraulic conductivity is preferred (Melby, 1989 through Campbell *et al.*, 1990; Herzog and Morse, 1989; Cleary, 1990 through Campbell *et al.*, 1990; Olson and Daniel, 1981). It was stated that in situ measurements would allow a larger volume to be tested in relation to laboratory studies. It would by that include a more heterogeneous structure of macrostructures, macropores from example root openings and fissures (Olson and Daniel, 1981).

Different methods of slug tests have been developed with regards to different subsurface conditions. Today, different methods exist for estimating the hydraulic conductivity of the subsurface (Campbell *et al.*, 1990). The methods developed by Hvorslev (1951) have been described to be the pioneer of the slug tests (Campbell *et al.*, 1990; Hyder *et al.*, 1994). Other slug test methods involve the one developed by Cooper *et al.* (Butler, 1997) and the Approximate Deconvolution Method (Butler, 1997) for confined aquifer formations. Slug tests methods for unconfined aquifer formations include the Bouwer and Rice Method (Butler, 1997), The Dagan Method (Butler, 1997) and The KGS Model (Butler, 1997).

It has been stated that slug tests measurements of estimating and assessing the hydraulic conductivity have increased in popularity, and these have become well-known and used techniques (Butler, 1997; Campbell *et al.*, 1990; Kruseman and de Ridder 1989). The advantages of slug tests measurements have been stated to be the low cost connected to it, that it is simple to execute, relative rapid test procedure, useful in tight formation with low hydraulic conductivity, no water needs to be handled and taken care of, provide information of the special variation of the hydraulic conductivity and the analysis is stated to be straightforward (Butler, 1997). Since no water need to be handled or treated after the test have been done, it is a suitable method for contaminated groundwater. Drawbacks on the other hand includes the fact that the volume of geological material investigated around the tested well is very small, resulting in that the results may be strongly influenced by the filter pack, screening of the well and the constructions of the well. The hydraulic conductivity recovered from the tests therefor only represents the very local geology.

3.1.2 FUNCTION AND EXECUTING

The procedure of a slug test has been described as: “measuring the recovery of head in a well after near- instantaneous change of head/water level at that well” (Butler, 1997; Hyder *et al.*, 1994). In practice a known volume, usually a constructed “slug” (heavier than the same volume of water) is inserted in a piezometer/ well as instantaneously as possible. Meanwhile the change of head/ groundwater level is measured usually through a pressure transducer. Often it recalculates the change in pressure in the piezometers to a change in groundwater levels. The slug test is performed by inserting a slug in the investigated piezometer. This leads to a rise in head and groundwater level before recovery and stabilization, Figure 6a. The procedure is followed by the extraction of the slug, creating a drop in head and groundwater level before the groundwater is recovered to initial head and level, Figure 6b. This data can then be used in combination of mathematical formulas, in order to assess and estimate the hydraulic conductivity of the geological material adjacent to the piezometers investigated with the slug test.

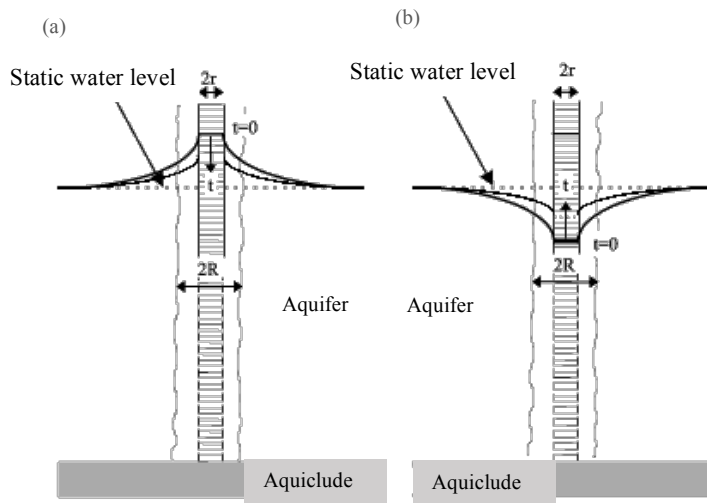


Figure 6. The slug test procedure is illustrated where (a) represents the insertion phase of the slug, while (b) represent the extraction phase of the slug in the piezometer investigated. Image taken from Waterloo hydrogeologic (n.d).

3.2 PUSH-PULL TRACER TESTS

3.2.1 HISTORY

Push-pull tracer tests have been mentioned by Istok *et al.* (1997) and Istok (2013) to potentially first be applied and used by Sternau *et al.* (1967) for investigating the mixing of injected water with the already existing groundwater. The same year it was also used in assessing the dispersion in radial flow from a recharge well by Hoopes and Harleman (1967). Nonetheless, the method has mostly been reported to be used in the oil industry until the late 1990s to determine residual oil saturation in petroleum reservoirs (Tomich *et al.*, 1973). Additional use of push-pull tracer tests has been proposed to assess some physical characteristics of an aquifer (Istok *et al.*, 1997; Hebig *et al.*, 2015). An equation was proposed by Gelhar and Collins (1971) to determine the longitudinal dispersivity of aquifer materials from the break through curves (BTC). Mass transfer processes has also been investigated with this technique by Beauheim

(Bauhheim, 1987 from Istok *et al.*, 1997), while an additional equation have been derived to determine the regional groundwater velocity and effective porosity of the volume of aquifer investigated (Hall *et al.*, 1991). Trudell *et al.* (1986) might have been the first to use push-pull tracer tests to try to assess and quantify microbial degradation in groundwater. Additional uses of the push-pull tracer techniques can also be found in the field of geothermal energy research (Herfort and Sauter, 2003; Pauwels, 1997)), but also for assessing and quantify degradation rate of phytoremediation of groundwater (Pitterle *et al.*, 2005). The technique has also been used in deeper settings to study the effects of salinization through cation exchange and oxidation-reduction (Vandenbohede *et al.*, 2008), together with trying to assess the anomalous dispersion from the BTC tailing (Gouze *et al.*, 2009). Today several studies have used push-pull tracer tests in order to assess and quantify microbial degradation (Istok *et al.*, 1997; Langenhoff *et al.*, 2009; Cho *et al.*, 2013; Burbery *et al.*, 2004; Scroth *et al.*, 2001; Vogt *et al.*, 2007; Hebig *et al.*, 2015).

3.2.2 FUNCTION AND EXECUTING

Push-pull tracer tests includes two phases: “push” and “pull”. The “push” corresponds to the injection phase of a known volume of a solution with known concentrations of tracers. The tracer solution is injected into a piezometer and further into the aquifer as illustrated in Figure 7a. The injection phase is assumed to be flowing radially from the screening of the piezometer, creating a hypothesis of approximate cylindrical formation of the injected test solution in the aquifer (Istok *et al.*, 1997). This is followed by the “pull” phase, where the injected solution is extracted from the aquifer through the same piezometer (Figure 7b). During the extraction phase, water samples are collected and analysed. The concentrations of the tracers are later interpreted in relation to the extraction time. In between the phases a “resting phase” or a “drift” is sometimes included for a given period of time, during which the injected tracer solution is allowed to drift in line with the regional groundwater flow downgradient (Istok *et al.*, 1997) and the tracers are allowed to react in the aquifer material. A resting phase is particularly recommended when trying to assess the microbial degradation in the groundwater (Istok *et al.*, 1997; Burbery *et al.*, 2003). The resting time should be long enough for microbial activity to take place, but short enough to avoid that all the tracer is being consumed (Istok *et al.*, 1997). It is also important to remember that the groundwater flow allows the test solution to drift. High groundwater velocity and high hydraulic conductivity could potentially flush the tracer away if left too long in the aquifer, resulting in no detection of the tracer during the extraction phase (Istok *et al.*, 1997).

The use of push-pull tracer tests for assessing the microbial degradation rate have been stated to present several advantages to other methods (Istok *et al.*, 1997). Istok *et al.* (1997) concluded that compared to laboratory test, a larger volume of the aquifer material can be investigated (on the order of tens to hundreds of litres). The in-situ test is also performed in a more representative environment compared to laboratory measurements, particularly in the presence of microbial communities prevailing in the aquifer materials. They also concluded that a series of push-pull tests can be successively performed in the same well to both assess the response of different microbial communities to different incentives and to quantify the microbial activity rate. Gouze *et al.*, (2009) also stated that additional advantages of the technique, is the reversal of flow which results in an optimal tracer mass recovery. The techniques also allow to cancel out the reversible dispersion (spreading) during the extraction phase that takes place during the injection and drift (Gouze *et al.*, 2009).

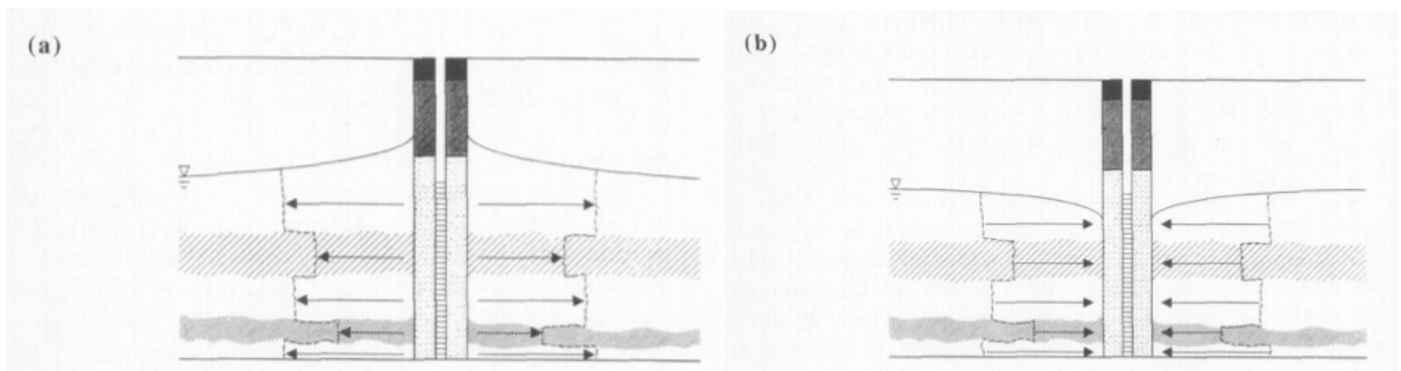


Figure 7. Figure (a) displays the “push” phase where figure (b) shows the “pull” phase of the push-pull tracer tests (Istok *et al.*, 1997).

3.2.3 TRACERS

The test solution is generally added with one or several tracers in order to be able to distinguish the test solution from the original groundwater. Reactive tracers to determine microbial degradation of a groundwater generally function either as an electron acceptor or an electron donor (Istok *et al.*, 1997). A conservative tracer is generally used in combination with the reactive tracers. This is done in order to separate the physical processes effecting the loss of active tracers such as dispersion and dilution (Istok *et al.*, 1997). The most classical conservative tracer used during push-pull tracer test are bromide and chloride (Istok *et al.*, 1997; Bombach *et al.*, 2010; Pitterle *et al.*, 2005; Cho *et al.*, 2013; Langenhoff *et al.*, 2009). When choosing a reactive tracer, a prerequisite is that the tracer used does either not exist in the investigated aquifer or at very low concentrations only. The reason for this is to be able to distinguish the injected tracers from the background concentrations (Bombach *et al.*, 2010). However, for remediation purposes the compound of interest to investigate for potential microbial degradation often exist in high concentrations, which makes the question of tracer more difficult. A way to solve this is to use an isotope of the compound of interest as a reactive tracer. In this way, it can be distinguished through its specific isotopic signature from the compound already existing in the aquifer. However, it has been stated that isotopes of compounds can be relatively expensive and, in some cases not available (Bombach *et al.*, 2010).

IV. SECTION 4: THE INVESTIGATION OF BOIS SAINT-JEAN SITE

4.1 HYDROCHEMICAL CHARACTERIZATION OF GROUNDWATER

4.1.1 METHOD

4.1.1-1 FILED MEASUREMENTS

To get an overview of the hydrochemistry of the groundwater and to have first insights on biodegradation mechanisms, a first sampling campaign took place on the 2021-03-03 at the Bois Saint-Jean site. The biodegradation mechanisms were evaluated based on redox-sensitive species and different types of stable isotopes. 7 piezometers were sampled during this campaign: piezometers Pz12, Pz18, the observation wells P301 and P302 (both still contaminated) and the injection wells PI02, PI06 and PI10.

The equipment used involved a HANNA Multiparameter (HI9829) measuring pH, EC, temperature and Eh. An additional HANNA Dissolved Oxygen (HI9828) device was used to measure DO in groundwater. A 2-inch pump (PP45) was used to pump groundwater up to the surface, using a low flow sampling procedure to limit drawdown in the piezometers.

Sampling at each piezometer began with measuring the depth to groundwater and to the bottom of the piezometer using a piezometric probe. The sampling flowrate ranged overall between 0.5 and 1.0 L/min. Groundwater samples were taken after stabilization (<5% change) of the in-situ parameters (EC, pH and temperature). The maximum waiting time for stabilization was 45 min, a time limit set by SPAQuE. The bottles for heavy metals and ammonium had to be filtered through a 0.45µm filter before being filled in order to remove solid particles. The bottles for organic compounds, DO and volatile compounds had to be sampled without any bubbles remaining in the bottles. In total, 18 different vials were filled for each piezometer and pH, EC, DO, Eh and temperature were measured in the field.

4.1.1-2 LABORATORY ANALYSES

16 of the groundwater vials were analysed by the company SGS on behalf of SPAQuE, for dissolved metals, ammonium, major ions, EC, pH, sulphate, nitrate, benzene, DO and organic compounds. This was done in order to have a first idea of the general chemical and biological composition of the groundwater. The total list of analyses available can be seen in Appendix A. The remaining two vials were analysed for stable isotopes of benzene by Prof. Dr. Christoph Schüth at the Technische Universität Darmstadt.

4.1.1-3 PROCESSING THE DATA

A first analysis was made based on in-situ measurements of pH, EC and Eh. Statistics on the major ions were further explored through min, median and max values, together with the ionic balance (IB), seen in Eq 1, where the molar weight and electron charge, of the ions in the water

samples are considered (cations: Fe^{2+} , Ca^{2+} , Mg^{2+} , Mn^{2+} , K^+ , Na^+ , NH_4^+ and anions: Cl^- , NO_3^- , SO_4^{2-} , HCO_3^-).

$$IB [\%] = \left(\frac{\Sigma \text{Cations} - \Sigma \text{Anions}}{\Sigma \text{Cations} + \Sigma \text{Anions}} \right) * 100 \quad \text{Eq 1}$$

Different graphs such as the Piper-, Schöeller-Berkloff-, Stiff- and Stabler diagrams were also produced using the software Diagrammes to explore the hydrochemical data. Additionally, saturation indexes (SI) were also calculated for different secondary mineral phases through the use of PHREEQc in Diagrammes. This was essentially done in order to evaluate if the ISCO treatment, based on sodium persulfate, could have led to the precipitation of sulphate as gypsum.

4.1.2 RESULTS AND DISCUSSION

4.1.2-1 PH, DO, EC AND EH ANALYSES

The first result in Table 2, indicate that the injection wells (PI02, PI06 and PI10) show very high EC, on the order of a thousand of $\mu\text{S}/\text{cm}$ to above 13000 $\mu\text{S}/\text{cm}$. They also show lower DO than the remaining piezometers. Nonetheless, all samples indicate anoxic conditions, since oxygenated groundwater are stated to be above $\sim 1\text{mg}/\text{L}$ (Søndergaard, 2009; USGS, 2016). The pH is in general around neutral with the exception of P301 which shows a more acidic character ($\text{pH} < 5.0$) and PI02 which shows a more basic character ($\text{pH} \sim 9.3$). Highly positive Eh values are indicative of oxidation conditions, usually corresponding to well oxygenated water and negative Eh values display a reducing environment, and an Eh even down to -300mV has been stated to potentially be an indication of microbial processes (Søndergaard, 2009). Here, The Eh values show intermediate to low results, which confirms the low DO values measured in the same wells.

Table 2. In-situ measurements at the Bois Saint-Jean site on the 3th of March 2021. The Piezometers in orange indicate that these were the inject wells during the ISCO treatment.

| <i>Pz</i> | <i>pH</i> | <i>DO</i> [mg/L] | <i>EC</i> [$\mu\text{S}/\text{cm}$] | <i>Temp.</i> [°C] | <i>Eh</i> [mV] |
|-----------|-----------|---------------------|--|----------------------|-------------------|
| Pz12 | 7.41 | 0.64 | 1168 | 12.18 | -291.6 |
| P301 | 4.69 | 0.19 | 1841 | 13.83 | 362.2 |
| PI02 | 6.63 | 0.00 | 13260 | 14.69 | -216.0 |
| PI06 | 9.33 | 0.00 | 4420 | 15.33 | -103.1 |
| PI10 | 5.91 | 0.00 | 3034 | 15.07 | 155.6 |
| P302 | 6.51 | 0.03 | 1623 | 15.36 | -62.7 |
| Pz18 | 5.85 | 0.56 | 1940 | 13.61 | 100.0 |

4.1.2-2 BENZENE CONCENTRATIONS

The benzene concentrations are presented in Table 3. The highest concentrations are observed in the area where the source of pollution is estimated to have been located ($54\text{--}8500\text{ }\mu\text{g}/\text{L}$). Piezometer Pz12 again do not show sign of benzene contamination. Pz18 downgradient shows lower, still above threshold, benzene concentrations. All results except Pz12 are above the $\text{VI}_{\text{UsageV}}$ of $10\text{ }\mu\text{g}/\text{L}$.

Table 3. Measured benzene concentrations at the Bois Saint-Jean during the sampling campaign taking place on the 2021-03-03.

| <i>Sample location</i> | <i>Pz12</i> | <i>PI02</i> | <i>PI06</i> | <i>PI10</i> | <i>P301</i> | <i>P302</i> | <i>Pz18</i> |
|------------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| <i>Sample date</i> | [$\mu\text{g/L}$] | [$\mu\text{g/L}$] | [$\mu\text{g/L}$] | [$\mu\text{g/L}$] | [$\mu\text{g/L}$] | [$\mu\text{g/L}$] | [$\mu\text{g/L}$] |
| 03/03 - 2020 | <0.2 | 580 | 8500 | 23 | 170 | 54 | 17 |

4.1.2-3 ANALYSES OF MAJOR IONS

The laboratory result of the major and minor ions can be seen in Table 4. From calculating the ionic balance (IB), with the excepted deviation of 10% (ALS, n.d), the IB do not indicate any anomalous results in the chemical dataset.

Table 4. Major and minor ions from the first sampling campaign at the Bois Saint-Jean site for the piezometers P301, P302, PI02, PI06, PI10, Pz12 and Pz18.

| <i>Ions</i> | <i>P301</i> | <i>P302</i> | <i>PI02</i> | <i>PI06</i> | <i>PI10</i> | <i>Pz12</i> | <i>Pz18</i> |
|--------------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| | [mg/L] | [mg/L] | [mg/L] | [mg/L] | [mg/L] | [mg/L] | [mg/L] |
| Ca^{2+} | 21 | 39 | 430 | 100 | 66 | 110 | 130 |
| Mg^{2+} | 8.7 | 3.5 | 180 | 48 | 32 | 46 | 61 |
| Mn^{2+} | 8.7 | 2.2 | 29 | 0.87 | 13 | 0.089 | 16 |
| K^+ | 5.7 | 19 | 110 | 77 | 26 | 70 | 70 |
| Na^+ | 360 | 310 | 3090 | 980 | 540 | 55 | 180 |
| NH_4^+ | 1.8 | 0.4 | 2.1 | 2.7 | 0.6 | <0.2 | 1.4 |
| Cl^- | 25 | 26 | 54 | 30 | 30 | 18 | 54 |
| NO_3^- | <0.75 | <0.75 | <0.75 | <0.75 | <0.75 | 6.7 | <0.75 |
| NO_2^- | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 |
| SO_4^{2-} | 860 | 530 | 8100 | 1900 | 1400 | 200 | 750 |
| Fe^{2+} | 0.3 | 15 | 2.7 | <0.2 | 0.4 | 0.6 | 3.8 |
| HCO_3^- | <20 | 250 | 970 | 280 | 130 | 530 | 280 |

A first analysis of the ions in the water samples, Table 5, indicate that almost all samples (except Pz12) show very high SO_4^{2-} concentrations, far above the water portability limit of 250 mg/L (Wallonie, 2004). No NO_3^- was detected in the samples, except at Pz12. On the contrary, ammonium levels are relatively high with most concentration values above the portability limit of 0.5 mg/L (Wallonie, 2004). Elevated concentrations of Mn^{2+} and Fe^{2+} are also observed in comparison to the Directive 98/83/EC of drinking water, respectively of 0.05 mg/L and 0.2 mg/L (EU Groundwater Directive 2006/118/EC – Annex 3, 2006).

Table 5. Minimum, median and maximum values of the ions analysed in the water samples. The red numbers indicate that the values are either above the portability limit of the Wallonie region or above the Directive 98/83/EC.

| <i>Ions</i> | <i>Min</i> | <i>P50</i> | <i>Max</i> |
|------------------|------------|--------------------|------------|
| | [mg/L] | (Median) [mg/L] | [mg/L] |
| Fe^{2+} | 0 | 0.6 | 15 |
| Ca^{2+} | 21 | 100 | 430 |
| Mg^{2+} | 3.5 | 46 | 180 |
| Na^+ | 55 | 360 | 3090 |
| K^+ | 5.7 | 70 | 110 |
| NH_4^+ | 0 | 1.1 | 2.1 |
| Mn^{2+} | 0.09 | 8.7 | 29 |

| | | | |
|-------------|-----|-----|------|
| Cl^- | 18 | 30 | 54 |
| NO_3^- | 0 | - | 6.7 |
| HCO_3^- | 0 | 280 | 970 |
| SO_4^{2-} | 200 | 860 | 8100 |

Elevated concentrations of SO_4^{2-} and Na^+ observed in the sampled piezometers is explained by the ISCO treatment where peroxydisulfate ($Na_2S_2O_8$), after oxidation reaction delivered both ions in groundwater (Wilson *et al.*, n.d). Lower SO_4^{2-} concentrations were measured before the treatment (400 and 300 mg/L for P301 and P302 respectively) than after (1900 and 6700 mg/L respectively). Additional effects of the ISCO treatments is also related to the high EC measured in the injection wells (PI02, PI06 and PI10), Table 2.

4.1.2-4 ANALYSIS OF THE PIPER, SCHÖELLER BERKALOFF, STIFF AND STABLER DIAGRAMS

The Piper diagram, Figure 8, indicates that the groundwater samples show difference compositions. Pz12 has not been exposed to neither the benzene contamination nor the ISCO treatment due to its upgradient position with regards to the groundwater flow direction. In this way, the corresponding groundwater could be assumed to be representative of the “natural composition” (still, Pz12 has been reported being contaminated by other compounds). In the Piper diagram, Pz12 shows a calcium -magnesium and bicarbonate type of groundwater. Pz18, downgradient from the contamination zone, displays a calcium-magnesium and chloride-sulphate type water. The rest of the piezometers (PI02, PI06, PI10, P301 and P302), show sodium-potassium and chloride-sulphate type of water.

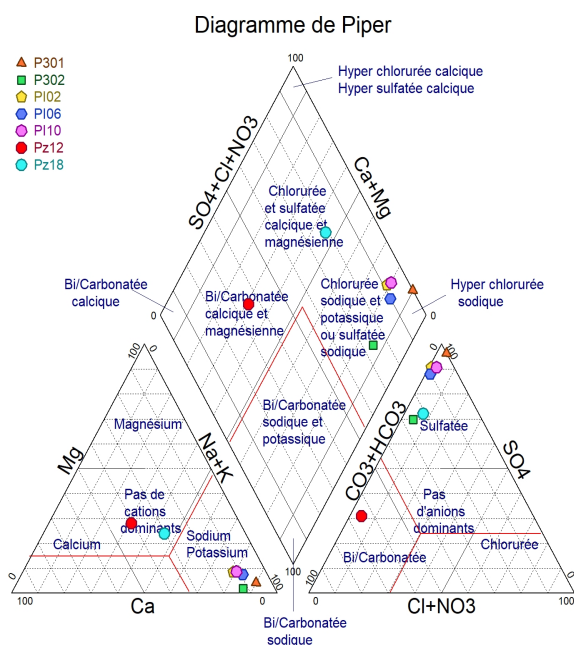


Figure 8. Show the hydrochemical facies of the water samples through a Piper diagram.

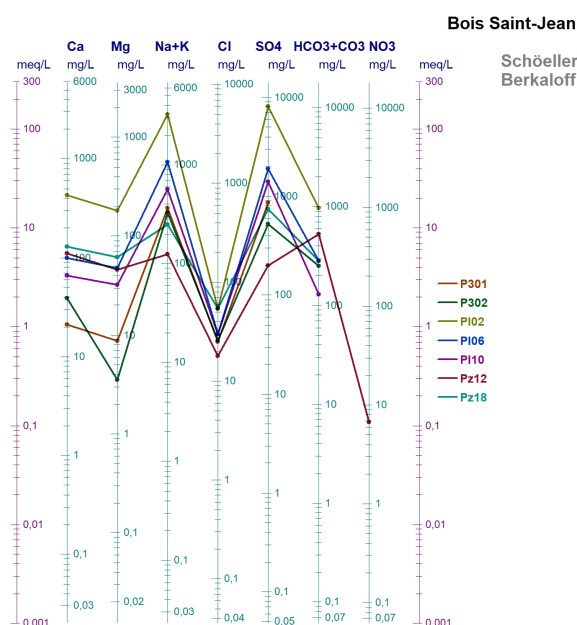


Figure 9. The hydrochemical facies of the water samples through a Schöeller Berkaloﬀ diagram.

The Schöeller Berkloff diagram, Figure 9, shows that PI02 stands out from all the water samples, with highest sodium, potassium and sulphate concentrations. Pz18, hydrogeologically downgradient shows the lowest magnesium concentrations. For Pz12, groundwater shows the lowest concentrations of sodium, potassium, chloride and sulphate, while being the only groundwater showing traces of nitrate.

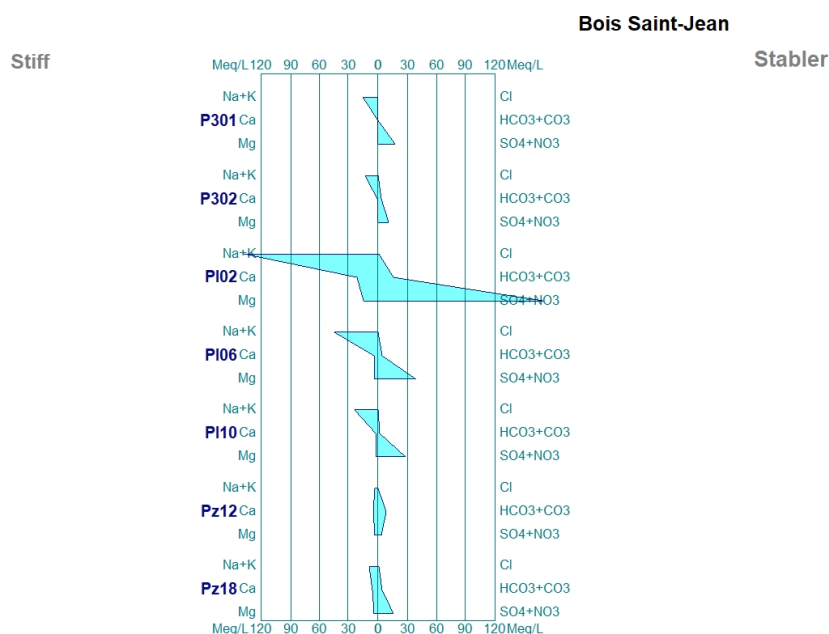


Figure 10. The mineralisation and hydrochemical facies of the water samples through a Stiff diagram.



Figure 11. The mineralisation of the water samples, with their respectively cation and anion composition.

The Stiff diagram, Figure 10, clearly shows that even though the samples located in the potential pollution source zone have similar mineralization characteristics, PI02 deviates from the others with very elevated concentrations as seen also in the Schöeller Berkloff diagram, Figure 9. The high mineralization could be linked to the efficiency of the ISCO treatment, since the piezometers is not the most polluted one with benzene, Table 3. Pz18 indicate though the Stiff diagram a mineralisation somewhere between the piezometers located in the potential source zone and Pz12, with higher sulphate concentrations like the piezometers in the potential source zone, however with bicarbonate facies towards the magnitude of Pz12.

In the Stable diagram in Figure 11, it clearly displays that Na^{2+} is the dominated cation, and not both Na^{2+} and K^{+} as Schöeller Berkloff and Stiff diagram indicated (Figure 9 and 10). It also shows that for the piezometers effected by the ISCO treatment, high concentration of Na^{2+} corresponds to high concentrations of SO_4^{2-} .

The chemical composition observed for injection wells reflect residuals of the ISCO treatment rather than the intrinsic groundwater characteristics.

4.1.2-5 ANALYSIS OF THE SATURATION INDEXES (SI)

The SI is in equilibrium when $SI = 0$, meaning when calcite and gypsum is in equilibrium. Equilibrium is also assumed/ accepted with the deviation of $SI = \pm 0.5$ (Haile-Meskale, 2017). The potential source zone of contamination, displays mixed results, Table 6. In general, the

samples show below saturation levels for both calcite and gypsum. Pz12, which is assumed to best represent the intrinsic groundwater characteristics, indicate an equilibrium of calcite, with an under saturation of gypsum. PI06 shows oversaturated with calcite ($SI > 0/ \pm 0.5$). Oversaturation could be a sign of CO₂ degassing (Neal, 2002), this would then mean that the sample has been in contact with the atmosphere, which could have happened during sampling or during the analyse. PI02 show equilibrium with calcite and a slight over saturation of gypsum. This is linked to the very mineralization produced by the ISCO treatment.

Table 6. Saturation index for the water samples. The number marked as green indicate that equilibrium occurs $SI = 0$ and ± 0.5 .

| <i>Pz</i> | <i>SI (Calcite)</i> | <i>SI (Gypsum)</i> |
|-------------|---------------------|--------------------|
| <i>Pz12</i> | 0.45 | -1.06 |
| <i>P301</i> | - | - |
| <i>PI02</i> | 0.18 | 0.70 |
| <i>PI06</i> | 1.93 | -0.33 |
| <i>PI10</i> | -1.96 | -0.58 |
| <i>P302</i> | -1.19 | -1.11 |
| <i>Pz18</i> | -1.37 | -0.51 |

4.1.2-6 FIRST ASSESSMENT ON POTENTIAL MICROBIAL ACTIVITY

Following the redox sequence ($O_2 \rightarrow NO_3^- \rightarrow Mn/Fe \rightarrow SO_4 \rightarrow CH_4$) for the assessment on potential microbial activities (USGS, 2016), no DO were observed, indicating anaerobic conditions. The Eh indicated reducing conditions, with values that has been linked to biological degradation. The absence of NO_3^- in groundwater indicates that nitrification have occurred, depleting the oxygen and nitrate levels in groundwater (AWWA, 2002). An increase in Mn^{2+} and Fe^{2+} concentrations along a groundwater flow path would indicate manganese- and iron reducing conditions. Elevated concentrations of Mn^{2+} and Fe^{2+} were observed in the groundwater. Nonetheless no direct indication of this can be seen along the hydrogeological flow patterns. The data indicate that the reducing conditions in the aquifer is below denitrification conditions, following the redox sequence.

The high SO_4^{2-} could function as an electron acceptor for biodegradation of benzene due to the reducing conditions in the aquifer (Lovley *et al.*, 1995). Methane was also measured in samples taken in the source area (0.01-0.3mg/L), an additional sign of microbial activities (Beeman and Suflita, 1990; Kleikemper *et al.*, 2005).

4.2 ISOTOPIC ANALYSES OF $\delta^{34}S$ - SO_4 / $\delta^{18}O$ - SO_4 AND $\delta^{13}C$ -BENZENE

4.2.1 METHOD

Looking at the evolution of the isotopic signature of different chemicals during the push-pull experiments is expected to be a way of highlighting the benzene biodegradation processes, through changes in the isotopic ratios of specific compounds in benzene ($\delta^{13}C$) and in electron acceptors involved in the oxidation reactions (most probably NO_3^- or SO_4^{2-}).

A first isotopic sampling campaign took place on the 29th (Pz18, P301, P302, PI10) and 30th (Pz12) of March 2021 in order to have the background signature of the stable isotopes of benzene ($\delta^{13}\text{C}$) and sulphate. The procedure of the sampling followed the same as described in section 4.1.1-1. A pinch of Zn Acetate was added in each bottle to be analysed for stable isotopes of SO_4^{2-} , in order to precipitate any free hydrogen sulphide. PI02 and PI06 were both excluded from the isotopic sampling since the chemical composition seems to be more representative of the residuals from the ISCO treatment than the groundwater composition.

Analysis of stable isotopes of benzene ($\delta^{13}\text{C}$) were done by Prof. Dr. Christoph Schüth at the Technische Universität Darmstadt. The stable isotopes of sulphate on the other hand were analysed by Dr. Kay Knoeller at the Helmholtz Centre for Environmental Research – UFZ.

4.2.2 RESULTS AND DISCUSSION

4.2.2-1 STABLE ISOTOPE $\delta^{13}\text{C}$ -BENZENE

Unfortunately, the analyses undertaken for the stable isotope $\delta^{13}\text{C}$ -Benzene indicated that benzene concentrations were below detection limit for all the samples, even though the previous samples collected at the same piezometers had indicated high concentrations of benzene, Table 3. CO_2 was also measured and the laboratory concluded that the samples must have contained oxygen. This suggests that biodegradation under oxidizing conditions had probably occurred in the samples in the period of time between their collection in the field and analysis in the lab (only 3 or 4 days), resulting in no detection of benzene. The laboratory also suggested that the next samples collected in the field should be poisoned in order to prevent precipitation.

4.2.2-2 STABLE ISOTOPES $\delta^{34}\text{S}$ - SO_4 AND $\delta^{18}\text{O}$ - SO_4

Through isotopes and dual isotope ratios in this case $\delta^{34}\text{S}$ - SO_4 and $\delta^{18}\text{O}$ - SO_4 , the original isotopic signature of sulphate can be determined and any subsequent isotopic fractionation process connected to microbial degradation evidenced (Hosono *et al.*, 2014). An increase in the ratio of $\delta^{34}\text{S}$ - SO_4 / $\delta^{18}\text{O}$ - SO_4 over time, would be a sign of biodegradation where SO_4^{2-} works as an electron acceptor (Sageman *et al.*, 2014). The current measured isotopic ratio in Figure 12, therefore work as background signatures of the SO_4^{2-} isotope composition for future analysis.

Due to time limitations of this thesis, the additional isotopic results on SO_4^{2-} could not be incorporated in the results.

Even so, a first “guess interpretation” of the results in Figure 12 was done. Comparing the fractioning of Pz18 to Pz12, (Pz12) which represents the background isotopic signature of SO_4^{2-} , a relatively significant increase in both isotopes is observed. This might reflect SO_4^{2-} reduction, even though the concentrations of SO_4^{2-} are higher at Pz18, which in turn could be indicating benzene degradation at plume scale. The remaining piezometers (P301, P302 and PI10) represent the isotopic signature of the zone treated with the ISCO treatment, probably influenced by the initial isotopic signature of $\delta^{34}\text{S}$ in S_2O_8 , with a strong enrichment in $\delta^{18}\text{O}$ (around 10) and low $\delta^{34}\text{S}$ (around 0). This mean that the background isotopic signature of the zone investigated with the push-pull tracer tests could be considered: $\delta^{18}\text{O} = 10$ and $\delta^{34}\text{S} = 0$, Figure 12.

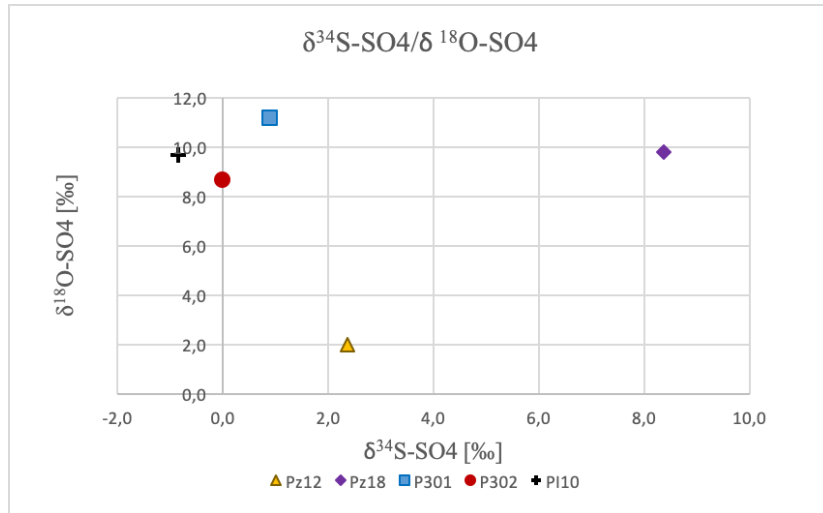


Figure 12. The dual isotope ratios of $\delta^{34}\text{S-SO}_4$ and $\delta^{18}\text{O-SO}_4$ is plotted.

4.3 SLUG TESTS

4.3.1 METHOD

4.3.1-1 CONSTRUCTION OF THE SLUGS

8 slugs were constructed for the slug tests, in two different lengths (1m and 2m). 4 for the piezometers with 4" diameter and 4 for the 2" diameter. PVC pipes were used, as suggested by Butler (1997). The PVC pipes were filled with sand, were the 2" and 4" slugs were constructed according to the sketch in Figure 13. The 2" slugs resulted in weights of 2 kg (1m slugs) and 4kg (2m slug). The 4" slugs resulted in weights of 8kg (1m slugs) and 13.5 kg (2m slugs). Several slugs were used to be able to test several piezometers at the same time. Since the slug test are assumed only to investigate the area in the vicinity of each piezometer, interference between test was not assumed. However, to exclude any possibility of interference slug test were never done at the same time for piezometers next to each other. The use of slugs with different volumes was suggested by Butler (1997), to be able to separate and exclude the effects of the dynamic well skin (zone closest to the well).

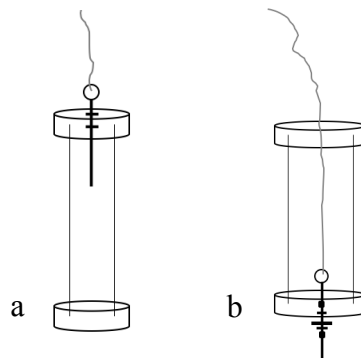


Figure 13. The 2 different slug constructions used for the slug tests. The construction of image **a**, was used for the 2" inch piezometers, for both 1 and 2 m length, but also for the 1m long 4" inch piezometers. The construction of image **b** was used for the 2m long 4" inch piezometers.

4.3.1-2 FIELD PROCEDURE

The slug tests were conducted on the 29th of March 2021. In each piezometer the groundwater levels were measured with a measurement tape for water, to have a reference point of the stabilization of the groundwater. A barometer was used, in order to correct the pressure data from the Diver pressiometric probes, so that any change in atmospheric pressure on the measurements is excluded. Each slug test began with a “push” phase where the slugs is inserted. Due to the weight of slugs for the 4” piezometers, it was lowered instead of dropped into the piezometers. After stabilization of the groundwater level, or with an excepted deviation of 5% (Butler, 1997), the “pull” phase of the slug test took place.

After the first pull phase undertaken in the injection wells, little displacement of groundwater/ changing of head was observed in combination with a very fast stabilization (after only a few seconds). Due to the fact that the Diver pressiometric probes measured at every 5s, no representative data was assumed to be collected. The rapid groundwater recovery was most probably an indicator of the filter pack then the adjacent geology, and these wells were afterwards excluded from further tests. All tested wells showed the same behaviour. For the Pz12, the recovery of the groundwater level was several hours longer then for the P301 and P302. Since it also is located outside the source zone of pollution, the measurements of this piezometer was also excluded.

The procedure of the slug test, as described above, was repeated three times for each of the 4” piezometer by changing the volume of the slug during the second repetition, resulting in that the same volume of the slugs were used to begin and end the slug tests, as recommended by Butler (1997).

4.3.1-3 ANALYSIS OF THE SLUG TEST RESULTS

The Bouwer and Rice Method (Bouwer and Rice, 1976; Bouwer, 1989), with the modification of Zlotnik (Zlotnik, 1994), was chosen to analyse the slug tests and to calculate the hydraulic conductivity. This is justified by the fact that the slug tests were performed in an unconfined aquifer and that the slugs were lowered down and not dropped near-instantaneous (Butler, 1997). Butler (1997) also stated that the Bouwer and Rice method is most often used doing slug tests in wells screened across the water table (Butler, 1997), which is the case of Pz18 and P302. However, it is also used for wells screened below the water table (Butler, 1997), as for P301. Two assumptions are made for the mathematical model, and Butler (1997) conclude it as being (1) “the effect of elastic storage mechanisms can be neglected”. Secondly (2), “the position of the water table, and thus the saturated thickness of the formation, does not change during the course of the test”. Additionally, a fully penetrating well is assumed since no information exist on the depth to any impermeable layer below the piezometers ($L_w = H$, Figure 14). The following steps were used to calculate the hydraulic conductivity from the slug tests data:

1. The slug tests data from the Diver pressiometric probes were modified with regards to the barometer data.
2. The natural logarithmic normalized head data ($\ln(H_{(t)}/H_0)$) was plotted over time, where $H_{(t)}$ is the change of head.
3. A trendline was adjusted to fit the increase or decrease of the change in head in the groundwater, and the slope of the trendline was calculated.
4. The parameters r_e , r_w , L_w and L_e can be seen in Figure 14, and corresponds to the following parameters:

r_c = (the well diameter/2 + the filter pack diameter/2) * the porosity of the filter pack [m]

r_w = the well diameter/2 + the filter pack diameter/2 [m]

L_w = distance between water table and bottom of the piezometer [m]

L_e = length of the screening [m]

5. The assumption of fully penetrating well leads to the calculation of the parameter C through Eq 2, and the additional Eq 3 of the term: $\ln \left(\frac{R_e}{r_w} \right)$. Since all the $\ln \left(\frac{R_e}{r_w} \right)$ values for the piezometers were below 6.0, the actual values were used (Butler, 1997; pp 108).
6. A mean hydraulic conductivity was calculated through Eq 4, for the six different slug tests at each piezometer [m/s].

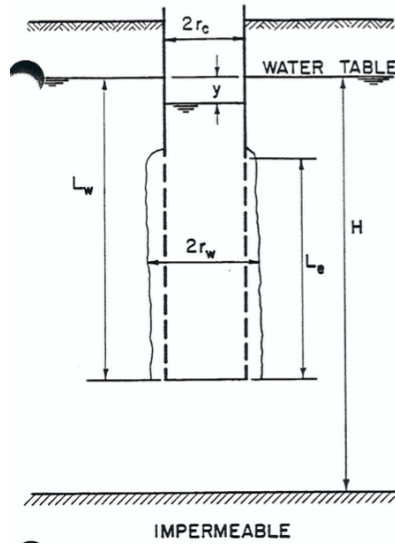


Figure 14. A theoretical well with the geometry and symbols used to calculate the hydraulic conductivity from a slug test (Bouwer, 1989).

$$C = 0.7920 + 3.993 \times 10^{-2} \times \left(\frac{L_e}{r_w} \right) - 5.743 \times 10^{-5} \times \left(\frac{L_e}{r_w} \right)^2 + 3.858 \times 10^{-8} \times \left(\frac{L_e}{r_w} \right)^3 - 9.659 \times 10^{-12} \times \left(\frac{L_e}{r_w} \right)^4 \quad \text{Eq 2.}$$

$$\ln \left(\frac{R_e}{r_w} \right) = \left(\frac{1.1}{\ln \left(\frac{L_w}{r_w} \right)} + \frac{C}{\left(\frac{L_e}{r_w} \right)} \right)^{-1} \quad \text{Eq 3.}$$

$$K = \frac{r_c^2 \ln \left(\frac{R_e}{r_w} \right)}{2 * L_e} * \ln \left(\frac{H_0}{H_t} \right) = \frac{r_c^2 \ln \left(\frac{R_e}{r_w} \right)}{2 * L_e} * \text{slope of the trendline} \quad \text{Eq 4.}$$

4.3.2 RESULTS AND DISCUSSION

The values used for the calculation of the hydraulic conductivity were taken from the drilling logs of the piezometers and can be seen in Table 7. The porosity of the filter pack was estimated by measuring the porosity of 3-5 mm gravels.

The change of pressure head in the piezometers during the slug tests for the piezometers Pz12, P301 and P302 can be seen in Figure 15-17. Slug tests results indicate that the conductivity values range can from 4.8×10^{-6} m/s in P301 to 2.5×10^{-4} m/s at Pz18, Table 8. From the drilling

logs, it can be seen that the layer of embankments increases downgradient hydrogeological, which is probably why the hydraulic conductivity increases.

Table 7. The values used for each of the piezometers P301, P302 and Pz18 in order to calculate the hydraulic conductivity from Eq 2-4.

| <i>Pz</i> | <i>r_c</i> [m] | <i>r_w</i> [m] | <i>L_w</i> [m] | <i>L_e</i> [m] | Porosity filter pack [%] |
|-----------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| P301 | 0.046 | 0.12 | 5.7 | 5.0 | 38 |
| P302 | 0.046 | 0.12 | 5.9 | 6.0 | 38 |
| P18 | 0.046 | 0.12 | 5.1 | 9.0 | 38 |

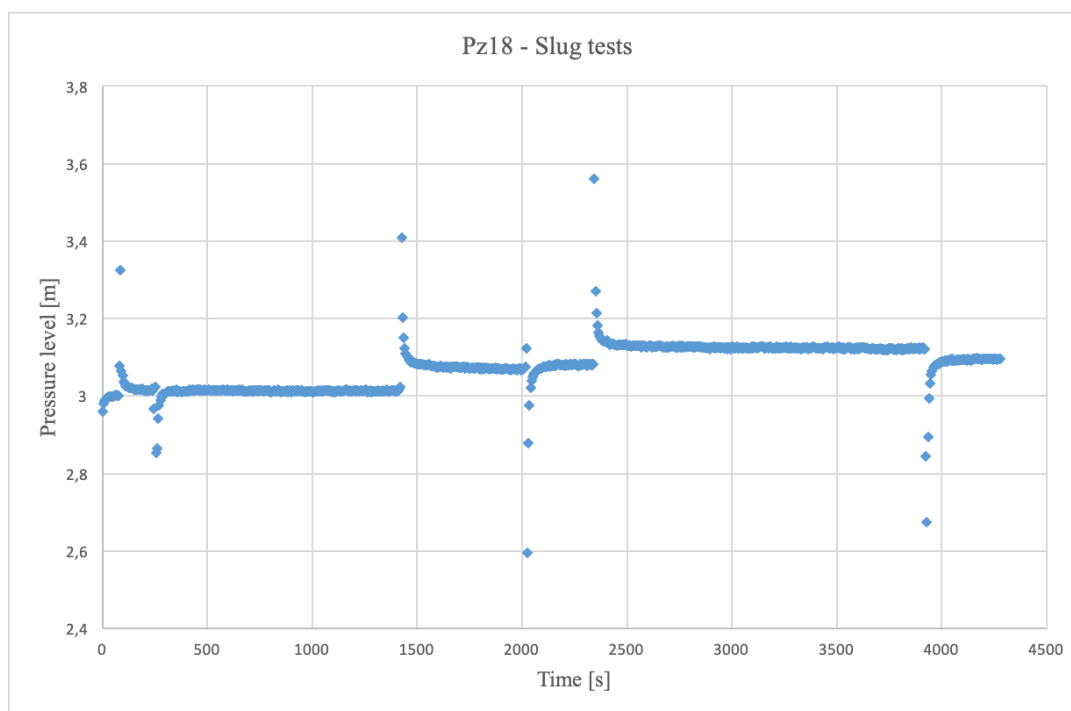


Figure 15. The injection and extraction phases of the slug test in Pz18 with change of pressure head over time.

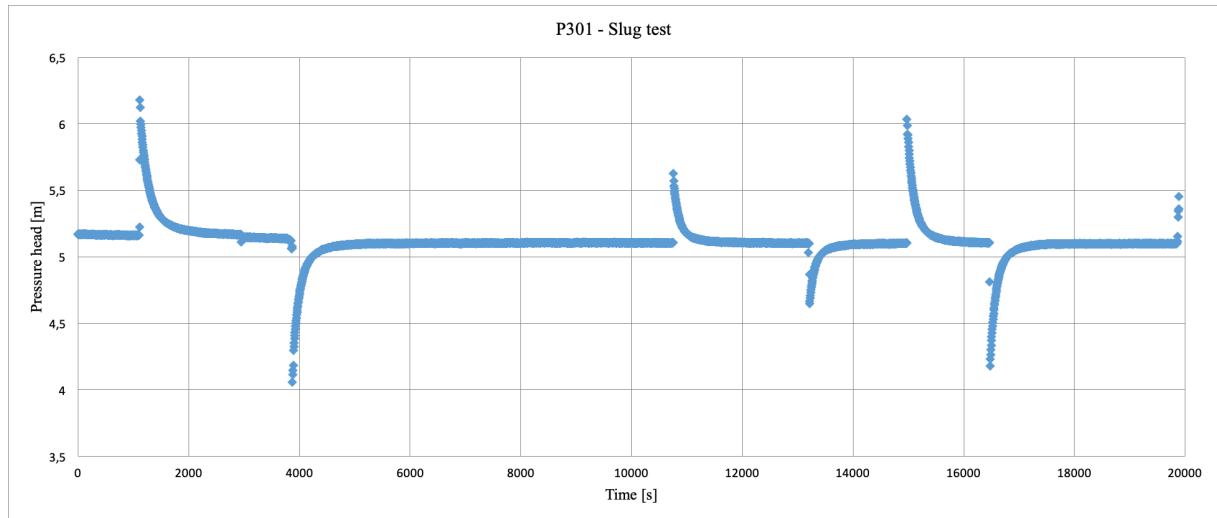


Figure 16. The injection and extraction phases of the slug test in P301 with change of pressure head over time.

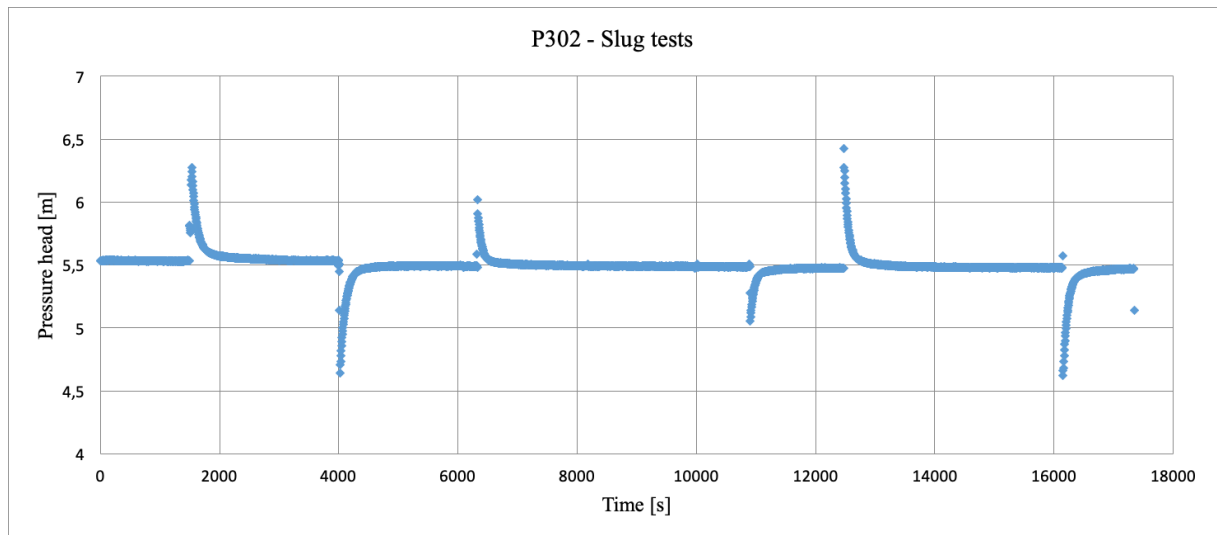


Figure 17. The injection and extraction phases of the slug test in P302 with change of pressure head over time.

Table 8. The estimate hydraulic conductivity [m/s] for each of the adjacent area of Pz18, P301 and P302.

| Piezometer | <i>Pz18</i> | <i>P301</i> | <i>P302</i> |
|------------------------------|----------------------|----------------------|----------------------|
| Hydraulic conductivity [m/s] | 2.5×10^{-4} | 4.8×10^{-6} | 1.7×10^{-5} |

4.4 PUSH-PULL TRACER TESTS

4.4.1 METHOD

4.4.1-1 SELECTION OF TRACERS

Three tracers were used during the reactive push-pull tracers tests in the forms of salts. Bromide (Br^-) was chosen as the conservative tracer, in the form of KBr. For the reactive tracers/ electron acceptors both SO_4^{2-} in form of Na_2SO_4 and NO_3^- in the form of KNO_3 were used. Due to the assumption of SO_4^{2-} reducing conditions in the aquifer, SO_4^{2-} might work as an electron acceptor. Nonetheless, NO_3^- was also assumed to function as electron acceptor, since NO_3^- was almost not detected in the groundwater samples. Due to the fact that microbial communities generally do not co-exist, in practice, only one of the two active tracers should be functioning as an electron acceptor. This would result in drop of concentration for that one compared to bromide. The corresponding isotopic ratios should also be affected if biodegradation occurs, with an enrichment in the heavier isotopes (Hunkeler *et al.*, 2001). The isotopes $\delta^2\text{H}$ and $\delta^{13}\text{C}$ of benzene should increase as well.

Br^- was chosen since it has been used in number of push-pull tracer tests and is not assumed to react or degrade (Istok *et al.*, 1997; Bombach *et al.*, 2010; Pitterle *et al.*, 2005; Cho *et al.*, 2013; Schroth *et al.*, 2001; Pitterle *et al.*, 2005; Langenhoff *et al.*, 2009). Dassargues (2019) even wrote in his book that Bromide is “*known to be one of the most conservative anions*”. In former experiments, reported concentrations of bromide were between 40-100 mg/L, and the lower concentration of 40 mg/L was chosen for the tracer tests within this thesis.

NO_3^- from the salt NaNO_3 has often been used in push-pull tracer tests (Cho *et al.*, 2013; Istok *et al.*, 1997; Langenhoff *et al.*, 2005). However due to access of KNO_3 at the University of Liège, this was used instead. Nitrate concentrations classically used in former push-pull tracer test varied from 5-30mg/L (Cho *et al.*, 2013; Istok *et al.*, 1997; Langenhoff *et al.*, 2005). In order to secure that nitrate would be above detection limit a concentration of 50 mg/L was chosen.

Because of the already high SO_4^{2-} concentrations in the aquifer, its stable isotopes were sent for laboratory analysis. Due to long expected time for the laboratory analysis, and the limited time frame of this thesis, the results will be outside the scope of this thesis. A higher concentration of SO_4^{2-} (2x the measured background levels in the GW), was used in order to distinguish the injected test solution from the background concentration. Due to a misreading, the background concentrations got mixed resulting in that the test solution for P301 got a concentration of 1060 mg/L SO_4^{2-} (background concentration 860 mg/L). For P302 the concentration ended up being of 1720mg/L (background 530 mg/L).

Fluorescein is a fluorescent dye that is commonly used as a tracer all around the world (Dassargues, 2019). It has also been previously used during push-pull experiments (Shakas *et al.*, 2017; Kang *et al.*, 2015). In our case, fluorescein was added to allow monitoring directly in the field the evolution of concentrations of the recovered tracers during the pull phase, with the assumption is that all the tracers in the test solution are recovered almost at the same time. For P302 180 mg of fluorescein was used, resulting in a concentration of 435 $\mu\text{g/L}$. For P301 117 mg was used, with the same concentration as for P302.

4.4.1-2 FIELD PROCEDURE

The experiments started on the 5th of May 2021, with piezometer P302 hydrological downgradient to avoid interference between the two experiments. Two inflatable tanks “Reserveo Eau non-Potable Volume 500L”, were used to store the water for the test solution and the flushing water. The tracers were poured in one of the tanks and the tanks were further

vacuumed of air by the use of a Watson Marlow 520S air pump. Groundwater was further pumped into the tanks, which was used to maintain the anoxic conditions of groundwater. Site groundwater was used for the tracer solution to maintain as similar chemical composition, as in groundwater itself (Istok *et al.*, 1997; Hebig *et al.*, 2015; Langenhoff *et al.*, 2009; Burberry *et al.*, 2004; Scroth *et al.*, 2001). Groundwater was pumped with a Grundfos MP1 submersible pump, which was both connected to a Honda EU Inverter 20i generator for energy and to a flowmeter. The groundwater was pumped at a pumping rate of around 8L/ min for the P302. The volume of groundwater in the tank with the tracers corresponded to three times the estimated volume of water in the piezometer and its filter pack together, as suggested by Istok *et al.* (1997), Table 9. In the other tank, one times the volume of the piezometer and filter pack was pumped and stored in the other inflatable tank, to subsequently flush out the remaining test solution in the filter pack (Istok *et al.* 1997; Burberry *et al.*, 2004). The tracer solution was then injected into the tested piezometer, with a pumping rate of 5L/min, as done by Hebig *et al.* (2015), followed by the “flushing volume” at the same pumping rate. The injection was done by the use of a Kärcher BP3 Home & Garden pump that was connected to the same generator and to the inflatable tank connected to the flowmeter.

The same procedure was supposed to be applied for the P301. However, during the extraction phase of the tracer solution, a strong drop of the groundwater level was noticed after a short time of pumping. This resulted in a pumping rate ranged between 0-6L/min. The test solution of three times the volume as for P302, was not feasible within the time frame. This resulted in a test solution of ~2.6 time the volume in the piezometer and filter pack, Table 9. The flushing volume was also affected, resulting in a low flush volume of 60L. During the injection phase of the test solution the injection pump went on and off of its own. Therefore, only 269L of test solution was injected in the piezometer. This also effected the “flushing volume” which then was done by tapping water from the inflatable tank into a bucket which was further emptied in the piezometer. A flushing volume of 15L was used, Table 9.

For both piezometers, a resting phase followed, to give time to biodegradation to take place (Istok *et al.*, 1997; Bombach *et al.*, 2010). Since the test solution of P302 was injected several hours earlier (started 12:29PM) then P301 (injection started 17:05PM), they were left with different resting times. The time period was originality chosen to be ~24h. It was reported by Burberry *et al.* (2004) that 8h of resting was not sufficient, while a resting time of 35 hours showed degradation results. The relative low hydraulic conductivity in the adjacent area of the piezometers (Table 8) also effected the length of the resting phase. This led to the assumption that 24h would be sufficient to indicate potential biodegradation without risking that the test solutions would be transported away with the hydrogeological flow. However, due to logistics the resting phase for the test solution in P302 was ~21h. The test solution for P301 was given longer resting time, ~64h. This was of course a risk, with concern to the hydraulic conductivity and potential degradation.

The extraction phase for the P302 was done with the same rate as during the injection (5L/min) (Istok *et al.*, 1997; Gouze *et al.*, 2009). The volume extracted was estimated to be ~3x the injection volume, as done by Pitterle *et al.* (2005) to improve the possibility to retrieve all the test solution. However, since the fluorescein concentration was directly measured, it gave an indication of the evolution of concentration of the tracers. A volume more than 4 times the injection solution was recovered, Table 9. The tail of the recovery curve did not yet completely stabilize. However due to time limit the extraction phase had to be stopped. It was estimated that additionally 2% of the mass of the tracer was retrieved every hour. During the pull phase,

groundwater samples were collected every 5 min during the first 80 min, then every 10 min for around 160 min, and finally every 20 min until the end of the extraction phase.

The extraction procedure for P301 followed the same pattern, with a groundwater sampling frequency every 5 min during the first 75 min, then every 10 min for 30 min, and finally every 20 min until the extraction phase was done during a 160 min. Because of the drop in groundwater level seen during the first extraction phase, a flow rate of ~2L/min was used. The aim was to extract 3x the injection volume (Table 9), nonetheless a clear plateau was seen during the retrieved fluorescein. This led to the stop of the extraction phase, and little more than 2x the injection volume was extracted, Table 9. Due to some technical problem with the connection of the field fluorometer Scheng GGUN FL30 and the field data, the data set of the fluorescein concentration is not complete for the extraction phase, however the concentration recovery can still be seen clearly.

Table 9. The volumes used for the push-pull tests for the piezometers P301 and P302. V_{pz+fp} indicate the volume of the piezometer and the filter pack.

| Volumes | P301 | P302 |
|---|-------------|-------------|
| Flushing volume (V_{pz+fp}) | ~15 L | ~141 L |
| Injection volume (V_{pz+fp}) | ~269 L | ~423 L |
| Extraction volume ($V_{injection\ volume}$) | ~586 L | ~1975 L |

The tracers salt used in the push-pull tracer tests, where poured into the inflatable tanks in dry condition. When water was added progressively into the tanks, this seemed to have created “clumps” of tracers in the tanks. Even with external physical movement in order to try to dilute the tracers, the assumption is that still not all the tracer where diluted to a homogenous liquid. Therefore, a difference can be seen between the theoretical mass and the actual mass and concentrations measured by CILE in the test solution, Table 10. For the analysis of the result the theoretical mass was excluded.

Table 10. The final masses and concentrations measured in the test solutions by CILE of the tracer ions Br^- , NO_3^- and SO_4^{2-} for P301 and P302 used for the push-pull tracer tests, together with the theoretical mass.

| Tracer ions | P301 | | | P302 | | |
|--------------------|----------------------|-------------------|-----------------------|----------------------|-------------------|-----------------------|
| | Theoretical mass [g] | Measured mass [g] | Measured conc. [mg/L] | Theoretical Mass [g] | Measured mass [g] | Measured conc. [mg/L] |
| Br^- | 10.8 | 12.9 | 48.5 | 22.6 | 18.2 | 43.0 |
| NO_3^- | 13.5 | 16.7 | 62.0 | 28.2 | 23.3 | 55.2 |
| SO_4^{2-} | 285.1 | 297.7 | 1991.4 | 970.1 | 1573.0 | 3718.7 |

The background concentration of SO_4^{2-} measured in the push pull experiments for P302, shows a large difference in comparison to the ones measured during the first sampling campaign in section 4.1.2-2 (289 and 530 mg/L respectively). This might be as a result of the large volume pumped for the injection solutions, mobilizing SO_4^{2-} concentrations in the test solutions while leaching the remaining groundwater of SO_4^{2-} in the adjacent area. This indicates that the SO_4^{2-} concentration in the aquifer might not be as homogeneous and uniformed as was expected. It rather shows that patches of larger concentrations might exist in the aquifer.

4.4.1-3 LABORATORY ANALYSES

The groundwater samples to be analysed for major ions, dissolved metals, NO_3^- , SO_4^{2-} and Br^- concentrations were sent to the CILE company in Liège. The major ions were analysed for some

samples in order to have the possibility to look at the evolution of groundwater chemistry during the tracer test and to be able to evaluate if any mass loss of sulphate could not be explained by the precipitation of gypsum (see section 4.4.2-2).

The analysis of the stable isotopes of benzene ($\delta^{13}\text{C}$ and $\delta^2\text{H}$) and stable isotopes of SO_4^{2-} ($\delta^{34}\text{S}$ - SO_4 and $\delta^{18}\text{O}$ - SO_4) were as done as in section 4.2.1, with the modification that the samples to be analysed for stable isotopes of benzene were spiked with mercury in order to preserve them. Samples were also taken for the stable isotopes of NO_3^- ($\delta^{15}\text{N}$). However, these were further frozen to be analysed later when the required staff of the Helmholtz Centre for Environmental Research – UFZ, would be available. For this reason, the analyses and results of these isotopes lies outside the scope of this master thesis. Nonetheless, they were conducted to further clarify the potential biodegradation in the aquifer.

4.4.2 RESULTS AND DISCUSSION

4.4.2-1 TRACER RECOVERY

The fluorescein concentrations recovery curve, measured in the field for P301 and P302 can be seen in Figure 18 and 19 respectively. Due to the technical problem during the sampling as described in section 4.4.1-2, the graph seen in Figure 18, is the approximated manually corrected curve from the recovery curve seen in Appendix B Figure 3. In total 11 samples from P301 were analysed for SO_4^{2-} isotopic ratios and will be analysed for NO_3^- isotopic ratios. They were also analysed for dissolved metals and NO_3^- , SO_4^{2-} and Br^- concentrations, Figure 18. Out of these, 10 samples were analysed for benzene concentrations and isotopic fractioning of benzene. Additionally, 5 samples were analysed for major ions Figure 18.

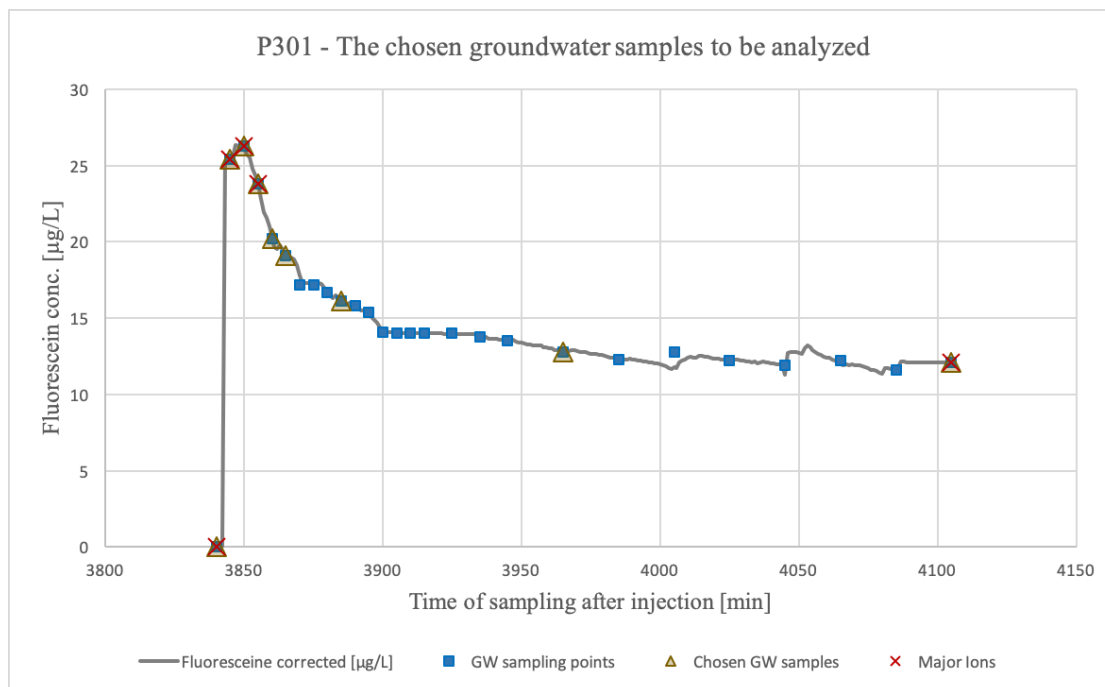


Figure 18. The approximated manually corrected fluorescein concentration recovery curve in relation to the time of sampling after injection, together with the chosen groundwater sampling points for further laboratory analysis.

For P302, 32 were analysed for SO_4^{2-} isotopic fractioning, dissolved metals, concentrations of NO_3^- , SO_4^{2-} and Br^- concentrations, Figure 19. The same samples will also be analysed for

NO_3^- isotopic fractioning. 28 samples were analysed for benzene- concentrations and isotopic fractioning.

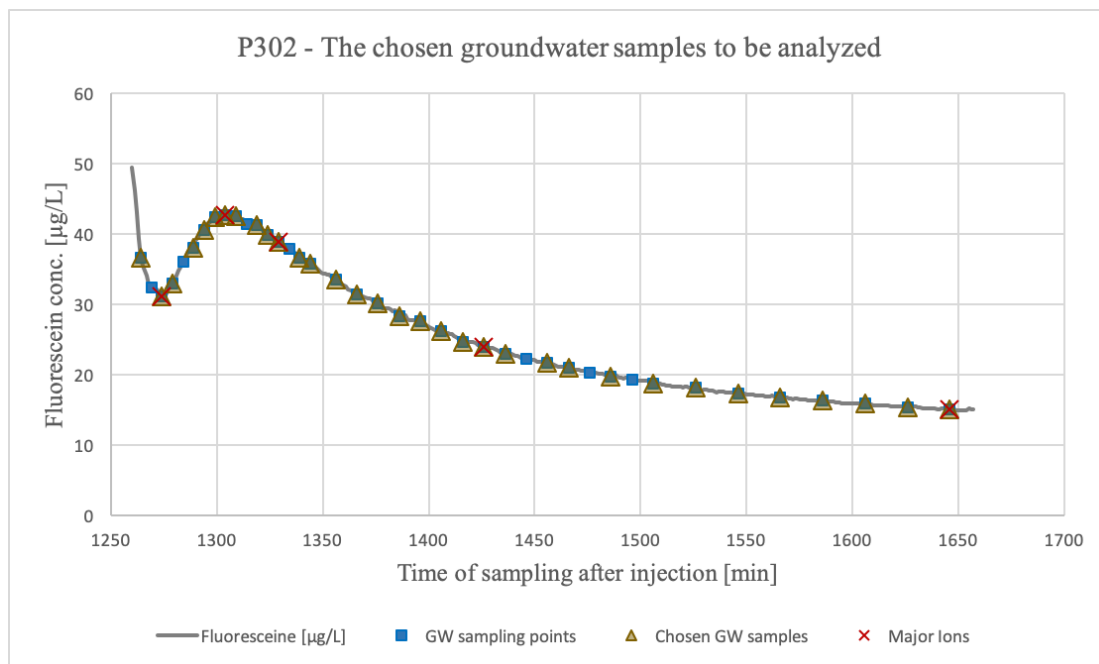


Figure 19. The fluorescein concentration recovery curve in relation to the time after injection, together with the sampling points chosen for further laboratory analysis.

From IB, with the expected deviation of 10% for the groundwater samples, a deviation was only observed for the last groundwater sample in the dataset for P301 (IB = 16.7%). For P302, the IB did not indicate any anomalous results in the chemical dataset.

The recovery curves for SO_4^{2-} , NO_3^- and Br^- for the push-pull tracer test performed in P301 can be seen in Figure 20. The concentration peaks seem to be happening at the same time, approximately at the 3:de sampling point, considering the first concentration measured as an outlier. The recovery curves for Br^- and NO_3^- have an exponential decline after the peak of 11.9 mg/L and 8.7 mg/L respectively. The concentration of SO_4^{2-} fluctuates more before declining, with a peak of 1205 mg/L.

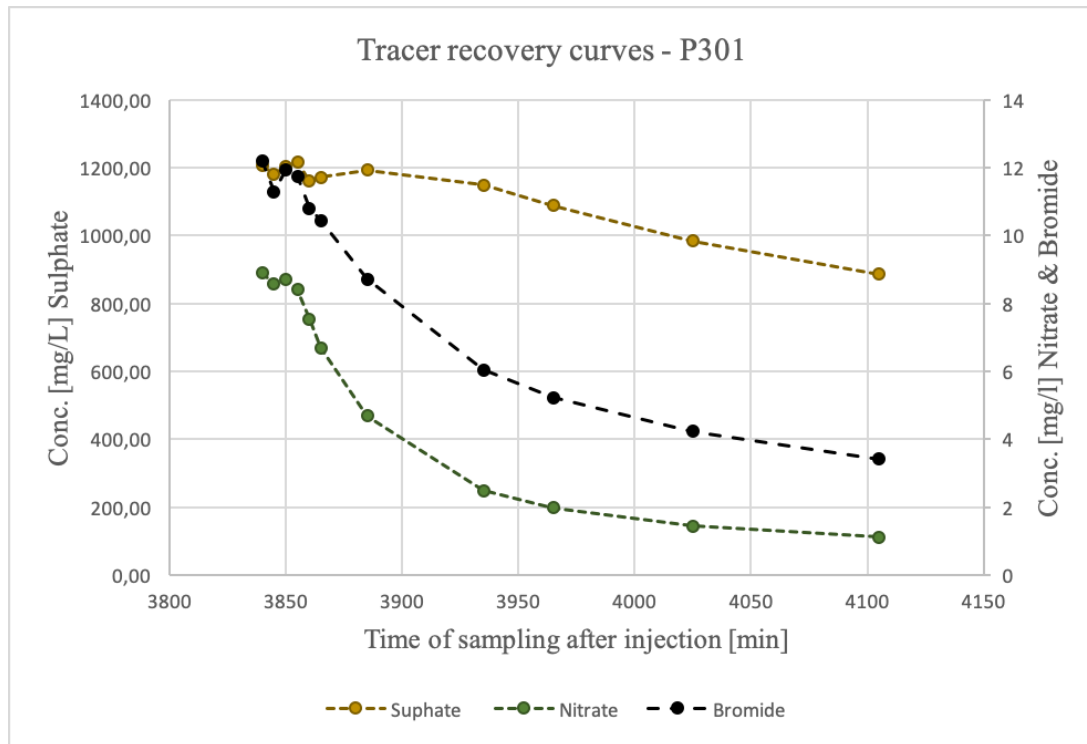


Figure 20. The concentration recovery curves of the tracers SO_4^{2-} , NO_3^- and Br^- are shown from the time of injection to time of extraction. The y-axis of the left side corresponds to the SO_4^{2-} concentrations, were as the right y-axis corresponds to the remaining two.

The breakthrough curve obtained at P302 can be seen in Figure 21. The peak for all three tracer seems to occur at the same time. Br^- has a peak of 9.4 mg/L, while NO_3^- has a peak concentration of 5.2 mg/L recovered and for SO_4^{2-} the peak is at 733 mg/L.

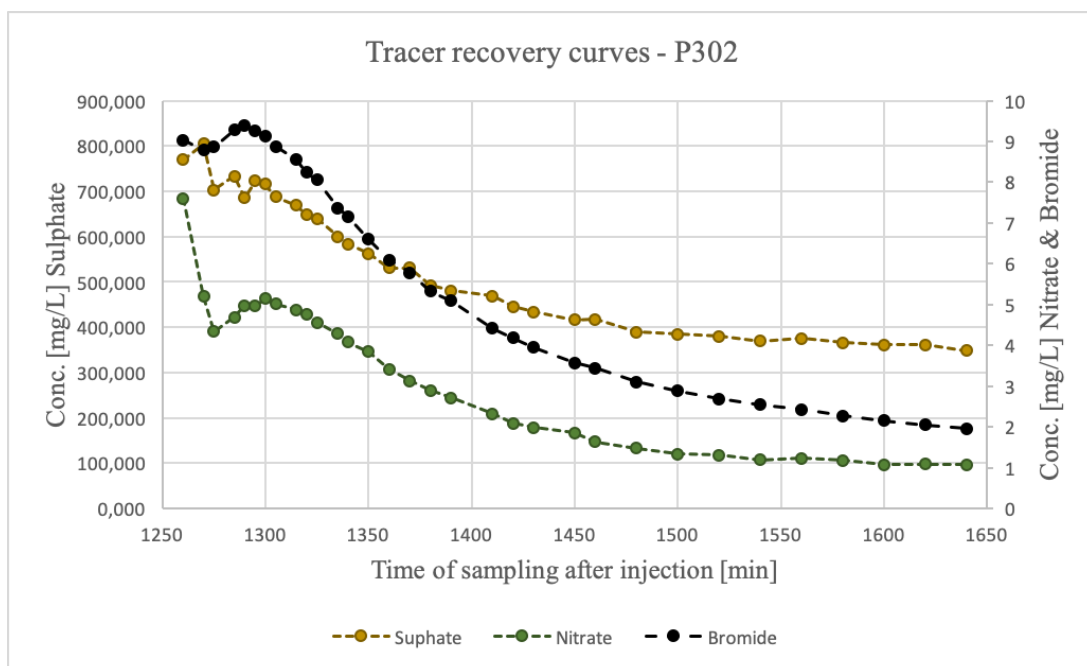


Figure 21. The concentration recovery curves of the tracers SO_4^{2-} , NO_3^- and Br^- are shown from the time of injection to time of extraction. The y-axis of the left side corresponds to the SO_4^{2-} concentrations, were as the right y-axis corresponds to the remaining two.

The tracer mass recovery can be seen in Table 11. The conservative tracer recovery factor is ~13% for P301 and ~42% for P302. In both cases (P301 and P302), the recovery of NO_3^- is less than this. For SO_4^{2-} , more mass is recovered compared to the conservative tracer at both piezometers.

More mass is overall recovered from the tracer in P302 then for P301. Since the resting phase of the tracer in the aquifer differs ~2days between the piezometers, the tracers in P301 had longer time to be affected by abiotic processes.

Table 11. The normalized tracer mass recovery with background mass recovery in the groundwater, for the two piezometers (P301 and P302) in relation to the mass of each tracer injected.

| Tracer | P301 Mass tracer recovery [g] | P301 Mass of tracer injected [g] | % Recovery | P302 Mass tracer recovery [g] | P302 Mass of tracer injected [g] | % Recovery |
|--------------------|--|--|---------------|--|--|---------------|
| Br^- | 1.7 | 13.0 | ~13 | 7.7 | 18.2 | ~42 |
| NO_3^- | 1.0 | 16.7 | ~5.8 | 4.3 | 23.3 | ~18 |
| SO_4^{2-} | 257.0 | 535.7 | ~48 | 797.8 | 1573.0 | ~51 |

4.4.2-2 ANALYSIS OF BIODEGRADATION

In order to assess the potential biodegradation of benzene from the tracer concentrations recovered during the push-pull tracer tests, the concentrations were further analyzed. The concentrations were normalized to the concentrations measured in the test solution injected for each tracer, over the cumulative volume extracted in relation to the volume injected. This is shown in break through curves (BTC) in Figure 22 and 23 for the piezometers. For both piezometers lower percentage of tracer is being recovered for NO_3^- compared to Br^- throughout the pull phase. Indeed, indicating biodegradation of NO_3^- through denitrification. The percentage of tracer mass recovery in Table 11, further strengthen the theory of denitrification.

For SO_4^{2-} the results look a bit different. In P301 higher recovery of SO_4^{2-} is observed throughout the pull phase compared to that of Br^- , indicating no biodegradation. The overall percentage of tracer mass recovered of SO_4^{2-} additionally strengthens the theory of no biodegradation, Table 11. An explanation to the much larger tracer recovery compared to Br^- , could be linked to the already elevated background concentrations (885 mg/L) measured around the piezometer and the hydraulic conductivity measured in the aquifer material (4.8×10^{-6} m/s). The hydraulic conductivity and the necessary low pumping rate used during the experiment, indicate that the groundwater flow in this part of the aquifer is low, “trapping” the water. SO_4^{2-} shows lower dilution at the beginning of the pull phase (large difference to Br^-) because the elevated background concentration in the aquifer around P301 keeps the concentrations relatively high. Later on, the concentrations of SO_4^{2-} goes progressively back to background levels (which is high), as observed in Figure 20. Since NO_3^- and Br^- are barely observed in the background of the groundwater, the same is not observed for these.

The same reasoning can be applied for P302, Figure 23. Groundwater flow is higher in the aquifer around P302 (hydraulic conductivity = 1.7×10^{-5} m/s). Because of higher fluxes, there is more dispersion and downgradient drift of the tracer in the aquifer. During the pull phase, globally, lower percentage of the different tracer are observed compared to P301 (Figure 22 and 23), because of the plume has migrated further downgradient and mixed with the intrinsic aquifer water. At the beginning of the pull phase, Figure 23, similar tracer recovery is observed

for SO_4^{2-} and Br^- which indicates that there is most probably no reduction of SO_4^{2-} . Compared to P301, SO_4^{2-} at P302 does not show any excess concentrations because the difference in $\text{Conc.}_{\text{injected}}$ (3719 mg/L) and $\text{Conc.}_{\text{background}}$ (289 mg/L) is large to what is observed at P301 (1991 mg/L and 885 mg/L respectively). Later on in the BTC (tailing), SO_4^{2-} concentration recovery shows a slower decline compared to the other tracers just because it turns back to around initial concentrations in the aquifer, as seen in Figure 21.

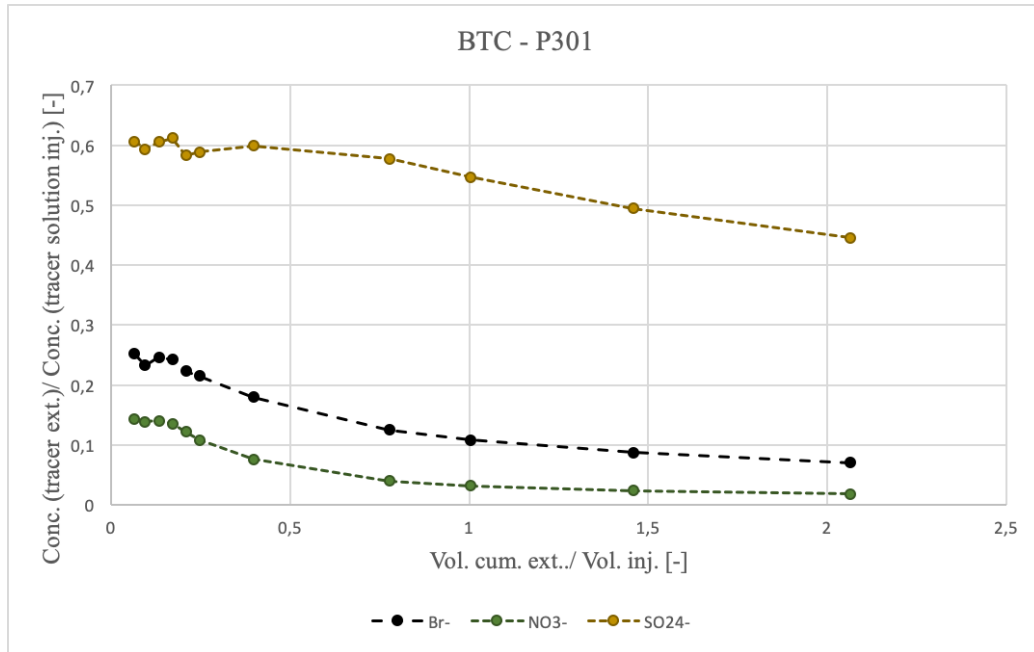


Figure 22. The concentration of each tracer extracted in relation to the concentration of the test solution injected for the tracer over the cumulative volume extracted in relation to the volume injected, are shown in BTCs for P301.

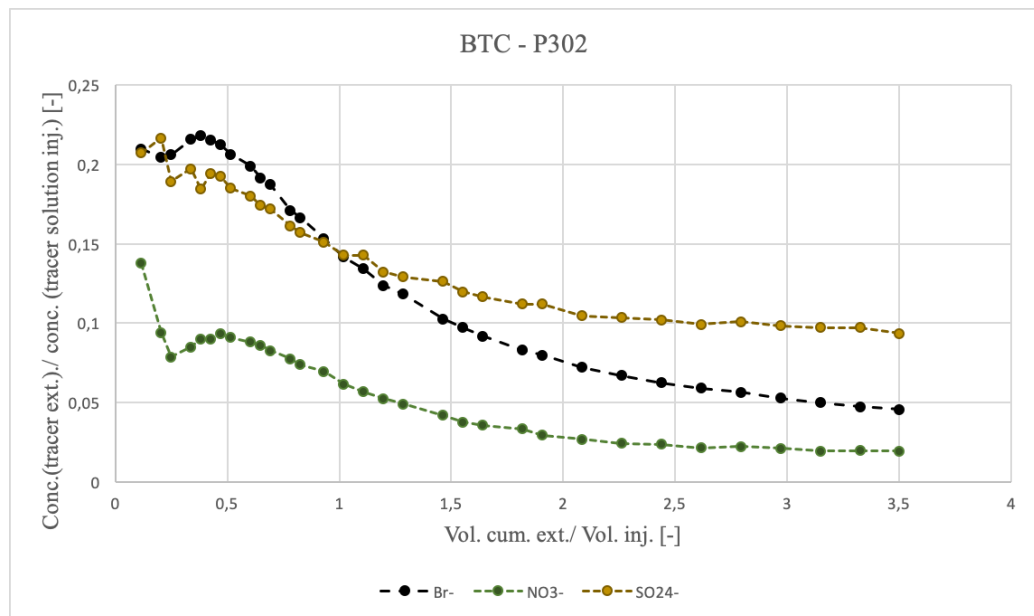


Figure 23. The concentration of each tracer extracted in relation to the concentration of the test solution injected for the tracer over the cumulative volume extracted in relation to the volume injected, are shown in BTCs for P302.

The benzene concentrations measured in the samples collected during the pull phase, shows similar trend for both P301 and P302, Figure 24-25. The results indicate that lower concentrations are measured during the beginning of the pull phase, then in the end of it. This would indicate that biodegradation of benzene has occurred.

The last samples collected from P301 seems to be characterised by the background concentrations (885 µg/L, measured in the beginning of the push-pull tracer test). A plateau can be seen in the end of the extraction phase of P302, which also seems to correspond to the background concentrations (289 µg/L, also measured in the beginning of the tracer test). This could potentially be as a result of mixing of the tracer solution with the background concentration, due to dispersion and groundwater flow movement.

The first samples collected would correspond to the tracers that remained close to the piezometer. This would further indicate that biodegradation have occurred in the vicinity to each piezometer, explaining why lower concentrations of benzene are observed at the beginning of the pull phase.

The background concentrations of benzene measured during the push-pull tracer test was much higher, then during the first sampling campaign in section 4.1.2-2, were concentrations of 170 µg/L and 54 µg/L was measured for P301 and P302 respectively. This rises the questions of the accuracy and representative of the low-flow sampling technique, but also if residual benzene is not trapped in the aquifer materials (residual NAPL phase?).

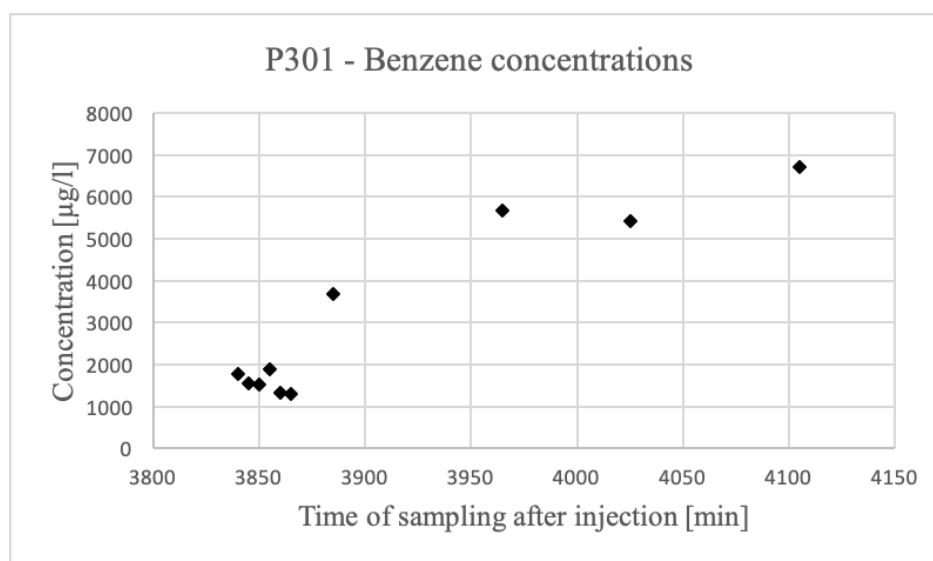


Figure 24. Benzene concentrations of the samples conducted during the extraction phase of the push-pull tracer tests for P301.

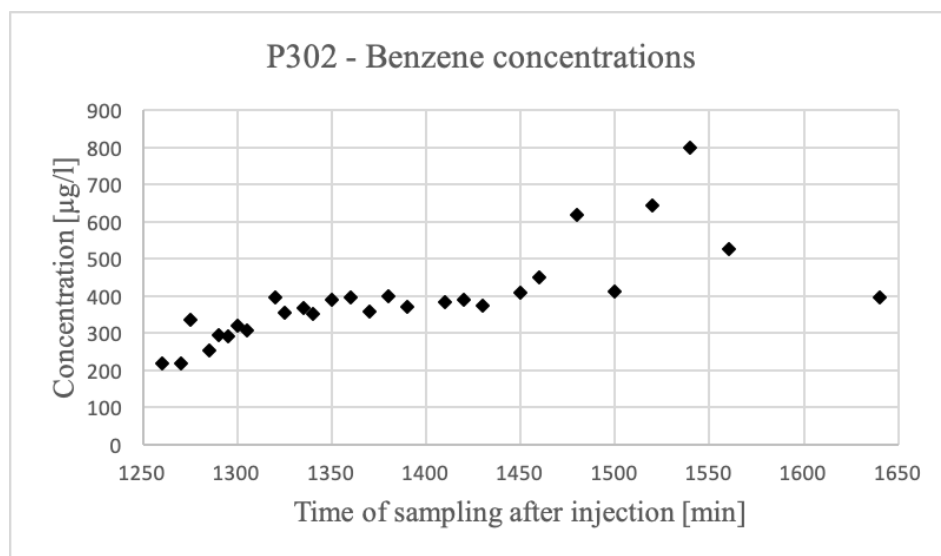


Figure 25. Benzene concentrations of the samples conducted during the extraction phase of the push-pull tracer tests for P302.

The isotopic ratios $\delta^{13}\text{C}$ and $\delta^2\text{H}$ of benzene can be seen in Figure 26-27 for the two piezometers. The same trend is observed for the $\delta^{13}\text{C}$ ratios for both piezometers. Heavier isotopes (less negative values) are measured in the beginning of the extraction phase, compared to the last samples extracted (more negative values corresponding to lighter isotopes). The evolution of $\delta^{13}\text{C}$ ratio for P301 is around 2‰, and around 2.5‰ to 3‰ for P302. Such enrichment factors have already been linked to biodegradation of benzene during anoxic conditions (Meckenstock *et al.*, 2004; Fischer *et al.*, 2008). Isotopic enrichment factors of $\sim -2.0\text{‰}$ to -2.4‰ , have further been stated to correspond to biodegradation of benzene through the reduction of NO_3^- (Meckenstock *et al.*, 2004). This would strengthen the theory that biodegradation of benzene occurs through denitrification. The result simultaneously show that biodegradation takes place in the vicinity of each piezometer, since heavier isotopes are found early on in the extraction phase. Indeed, the push-pull tracer tests also have a limited radius of influence, outside which there is no more nitrate present in the aquifer. Degradation of benzene with SO_4^{2-} as electron acceptor under anoxic conditions was reported to be seen with as isotopic fractioning of -3.6‰ (Meckenstock *et al.*, 2004). This is not seen for either of the piezometers, which indicate that such reducing conditions have not been reached.

The isotopic fractioning of the $\delta^2\text{H}$ of benzene has also been analyzed, Figure 26-27. The same trend is spotted as for the $\delta^{13}\text{C}$ fractioning, which would additional indicate biodegradation of benzene (Hunkeler *et al.*, 2001). The isotopic enrichment factor of $\delta^2\text{H}$ for the two piezometers are around -15‰ at P301 and around -25‰ at P302. An enrichment factor of -29‰ to -35‰ have also been linked to benzene degradation due to NO_3^- reduction (Meckenstock *et al.*, 2004), which further indicate that biodegradation of NO_3^- might occur in P302. If degradation of benzene with SO_4^{2-} would have occurred, much larger enrichment factor would be observed (-79‰), indicating that such reducing conditions most likely do not occur in the aquifer at this point.

Interesting is that heavier isotopes are observed in P301 compared to P302. This could either be a sign that biodegradation has been occurring longer around P301 or that the composition of the benzene pollution might be slightly different.

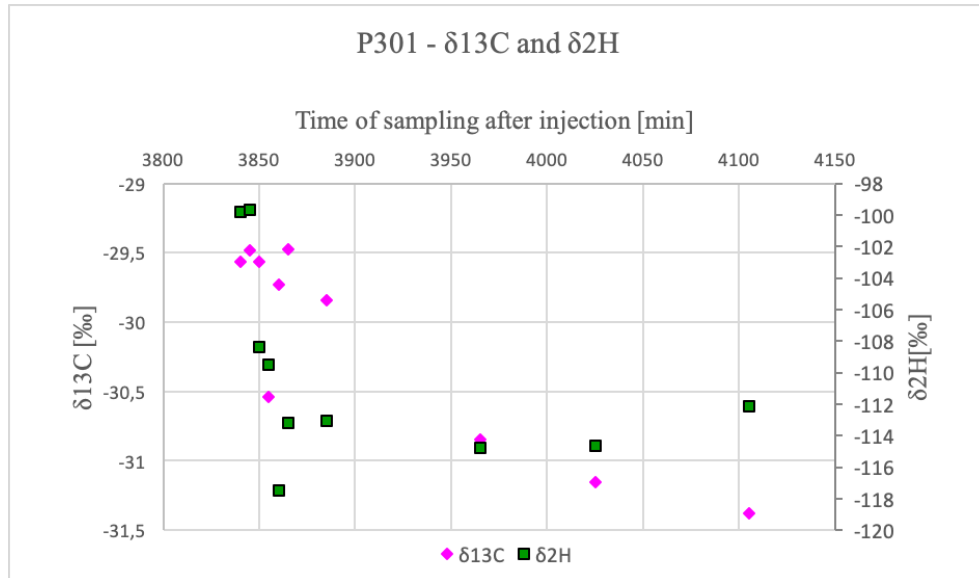


Figure 26. Isotopic fractionation of carbon and hydrogen from benzene, of the samples conducted during the extraction phase of the push-pull tracer tests for P301.

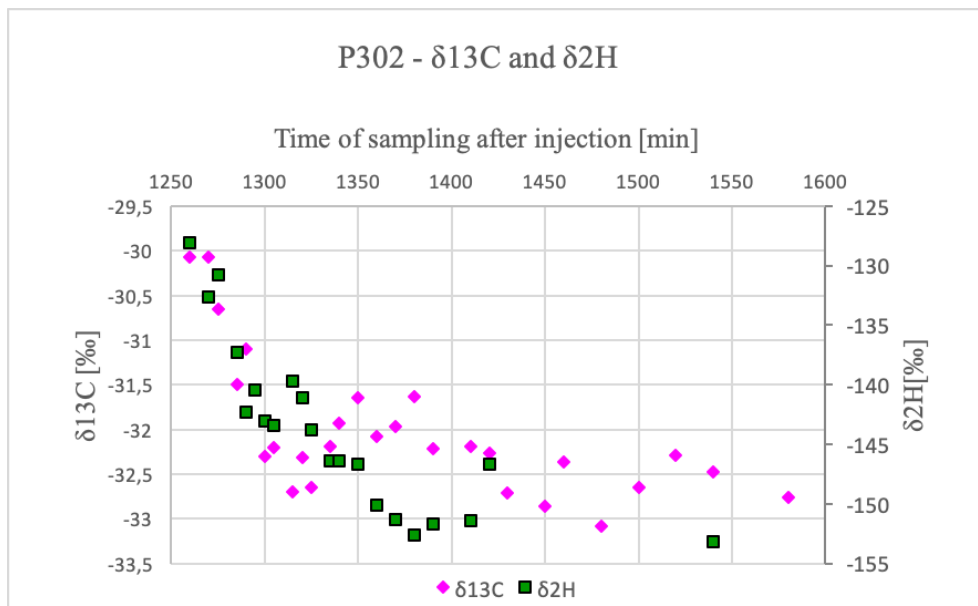


Figure 27. Isotopic fractionation of carbon and hydrogen from benzene, of the samples conducted during the extraction phase of the push-pull tracer tests for P301.

The degradation rate has been roughly estimated by using the change in benzene concentration between the start and end of the extraction phase, for the two piezometers (C. Schüeth, personal communication May 2021). Since the duration of the resting phase differed for the two tested piezometers, if one assumes that the degradation processes follow the same kinetics, the results of the two experiments can be combined into some calculations. Based on these hypotheses, approximate first-order degradation curve can be plotted, as seen in Figure 28, displaying that the benzene concentrations are decreasing over time. The degradation rate results in $0.000364 \text{ min}^{-1}$ and 0.524 day^{-1} . This would mean that ~52% benzene is degraded per day. This is very high and most probably corresponds to maximal estimate of the degradation rate.

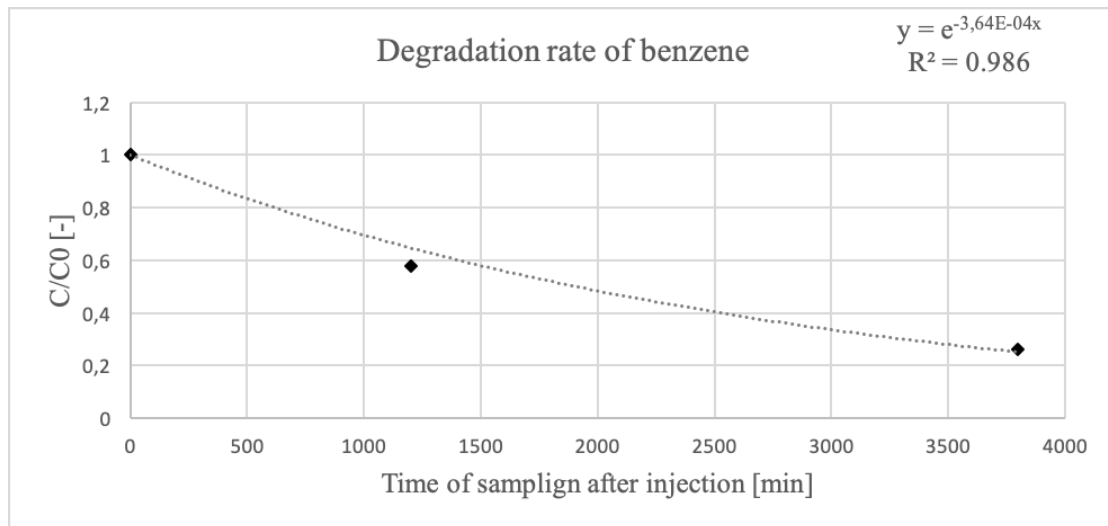


Figure 28. A rough estimation of the degradation rate from combining the results of the two piezometers, where the change in benzene concertation at the start of the extraction phase with the end of the extraction phase of the push-pull experiments for the two piezometers.

V. SECTION 5: CONCLUSIONS AND PERSPECTIVES

The main objectives of this thesis was to develop an integrated experimental protocol and to evaluate the potential of using reactive push-pull tracer experiments to evidence biodegradation of organic chemicals in groundwater. In practice the approach was used to demonstrate biodegradation of benzene in groundwater at the Bois Saint-Jean site in Liège, Belgium.

A first groundwater sampling campaign demonstrated that anaerobic reducing conditions prevails in the aquifer (from DO and Eh). NO_3^- was additionally not observed, indicating that the redox sequence had most likely passed the denitrification state, if microbial bacterial exists. Elevated concentrations of SO_4^{2-} were observed, which was linked to the previously performed ISCO treatment. Nonetheless, in theory SO_4^{2-} could work as an electron acceptor of benzene degradation, if the redox sequence of SO_4^{2-} is taking place.

Push-pull tracer tests were performed for piezometers P301 and P302, where both result for the tracer recovery shows that NO_3^- were reduced. Decreased benzene concentrations were also observed in the beginning of the pull phase, corresponding to the adjacent area of the tested piezometers. The tailing of the recovery curves seems to reflect the background concentrations of benzene around each piezometer, which could be as a result of dilution and flow movement, since it corresponds to the tracer that remained longest in the aquifer. Isotopic fractionation of benzene additionally demonstrated biodegradation, with an enrichment factor of -2‰, as observed in previous studies.

Overall, the investigations have demonstrated that push-pull tracer tests can be used to assess biodegradation of benzene with resting times of ~21h and ~64h for aquifer materials with hydraulic conductivity of 1.7×10^{-5} m/s and 4.8×10^{-6} m/s respectively. Biodegradation under denitrifying conditions have been evidenced by the lower recovery of the nitrate tracer compared to bromide. For the sulfate tracer, the interpretation is less evident because of the elevated background concentration of sulfate in the aquifer. Results also indicate that the isotopic fractionation results of $\delta^{13}\text{C}$ and $\delta^2\text{H}$ in benzene are also very helpful to confirm its biodegradation. Isotopic fractionation data on sulfate and nitrate would probably also be very helpful but the results could not be obtained in the timeframe of the MSc thesis.

In the end, push-pull tracer test results have demonstrated that NO_3^- has acted as electron acceptor to stimulate biodegradation of benzene, with a first rough estimate of 0.524 day^{-1} for the first-order degradation constant (most likely representing maximal biodegradation rate), and that it can be used to decrease benzene concentration in the groundwater at the Bois Saint-Jean site.

To answer the larger question if biodegradation from natural attenuation is sufficient to decrease the remaining benzene concentrations in the aquifer at the Bois Saint-Jean site, a few points needs to be considered further. The results from the push-pull tracer test clearly indicate denitrification bacteria in the groundwater, nonetheless, NO_3^- seems to be completely depleted in the aquifer. This would then indicate that it is unlikely that natural attenuation with NO_3^- would be sufficient to remove remaining quantity of benzene. SO_4^{2-} on the other hand, has been observed in large quantities in the source area, as a result of the ISCO treatment. It has been shown that SO_4^{2-} reducing conditions can be developing after ISCO treatment with persulfate (Arai, 2019). The results from the push-pull tracer test do not indicate that such reducing conditions have developed. Nonetheless, the first isotopic analysis of SO_4^{2-} show a significant

increase of $\delta^{18}\text{O}\text{-SO}_4$ and $\delta^{34}\text{S}\text{-SO}_4$ in Pz18 (downgradient from the source zone), both compared to the source zone and the Pz12 (assumed to represent the “original” groundwater composition). Which in turn might be a sign that benzene degradation under SO_4^{2-} reducing conditions is starting to take place. The result of isotopic sampling conducted during the push-pull tracer tests, will hopefully give a better view on this.

To further conclude on the possibility of natural attenuation of benzene, drilling additionally one or two piezometer hydrogeologically downgradient from the source zone (between P302 and Pz18) and perform a new sampling campaign, would help to assess the evolution on residual compounds. The sampling campaign is suggested to focus on redox sensitive parameter, and residuals of the biodegradation on NO_3^- and SO_4^{2-} together with the isotopic fractioning of these.

Through the investigation, questions have been rising concerning the actual benzene concentrations in the aquifer and the accuracy and reliability of the low flow sampling procedure, to represent the actual hydrochemical conditions in groundwater. Further evaluation of the sampling technique would be of interest, when testing different flow rates and comparing the results. Nonetheless, the elevated concentrations of benzene observed from the pull phase of the experiments (885 $\mu\text{g/L}$ and 289 $\mu\text{g/L}$ for P301 and P302 respectively), indicate that further investigation on the actual benzene concentrations in the aquifer is needed.

Throughout the analysis of the result, the notion of how much SO_4^{2-} actually was injected with the test solution has been problematic in explaining the result, and to be able to separate the injected test solution from the background concentrations. Diluting the tracer salt in some water before pouring them into the inflatable tanks, is an improvement that is assumed to minimize the risk of the “clumps” observed during the injection phase, and give better accuracy. The assumption and hope, is that the isotopic result might help in distinguish the isotopic signature of the tracer injected compared to the intrinsic one in the groundwater, however this might not be the case. The direct use of a tracer with different isotopes have been suggested, however since it often very expensive and sometimes not even available, therefore other alternatives should be evaluated. An alternative would be prior to the push-pull tracer tests, to analyze the tracer for the test solution (in this case Na_2SO_4) and the compounds from the ISCO treatment separately for their isotopic signature. This would help knowing if they can be distinguished from each other, if not, another tracer could be tested in order to assure difference.

The inflatable tanks, which was used during the push-pull tracer tests to keep the water in anoxic conditions, were proven to be very difficult to empty in muddy conditions. When dry, they could be folded in order to increase the pressure of the water leaving the tanks, something that was almost impossible in muddy conditions. Using gravity, by placing the tanks on higher elevation then the opening of the piezometer would have helped to maintained the water pressure when emptying the tanks. Additionally, attaching handles on the tanks would have made them easier to move and handle.

With additional time for the investigation, the push-pull tracer test could have been performed several times in the same piezometers. This would have helped to account for the natural fluctuations in the groundwater, but also to better evaluate the degradation rate for the piezometers individually. It could also have been used to try to assess the degradation rate for the piezometers separately over a longer period of time, where different resting time would have been tested for each push-pull experiment. From the investigation, the area around the piezometers show different flow velocity and fluxes. The piezometers additionally have different hydrogeological position (P302 downgradient and P301 upgradient), which could have

effect on the separate degradation rate for each piezometer, and therefore it would be better to further investigate the degradation rate separately to obtain a more reliable result.

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APPENDIX A

| Cadre 3. Analyses d'eau | |
|---|---|
| Poste n° | Désignation |
| 3.1 | Flaconnage |
| 3.1.01 | Flaconnage, stockage et destruction d'un échantillon NON analysé |
| 3.2 | Prétraitements |
| 3.2.01 | Prétraitement d'un échantillon de produit en phase libre |
| 3.3 | Propriétés physico-chimiques |
| 3.3.01 | Carbone organique dissous (COD) |
| 3.3.02 | Carbone organique total (C.O.T.) |
| 3.3.03 | Conductivité et pH |
| 3.3.04 | Potentiel rédox |
| 3.4 | Analyses individuelles |
| 3.4.01 | AOX (Composés organo-halogénés solubles dans l'eau et adsorbables sur charbon actif) |
| 3.4.02 | Chrome (VI) |
| 3.4.03 | Cyanures libres |
| 3.4.04 | Cyanures totaux |
| 3.4.05 | Indice phénols |
| 3.4.06 | Méthyl-Tert-Butyl-Ether (MTBE) |
| 3.5 | Analyses groupées |
| 3.5.01 | BTEXS |
| 3.5.02 | Hydrocarbures aliphatiques halogénés (17) |
| 3.5.03 | Hydrocarbures aromatiques polycycliques - HAP (16) |
| 3.5.04 | Hydrocarbures pétroliers EC5-EC11 |
| 3.5.05 | Hydrocarbures pétroliers EC10-EC40 |
| 3.5.06 | Caractérisation des hydrocarbures pétroliers : Fractions aliphatiques et aromatiques |
| 3.5.07 | Paquet Eau 1 - Décret sols pH; Conductivité; Métaux lourds (8); BTEXS; Hydrocarbures pétroliers EC5-EC11; Hydrocarbures pétroliers EC10-EC40; HAP (16); Hydrocarbures aliphatiques halogénés (17); Phénol; Cyanures libres |
| 3.5.08 | Paquet Eau 2 - Complet pH; Conductivité; Screening minéral (22); BTEXS; Hydrocarbures pétroliers EC5-EC11; Hydrocarbures pétroliers EC10-EC40; HAP (16); Hydrocarbures aliphatiques halogénés (17); Chlorobenzènes; PCB (7); Cyanures libres; Cyanures totaux; Phénols et chlorophénols; Méthyl-Tert-Butyl-Ether (MTBE); Chrome VI |
| 3.5.09 | Paquet Eau 3 - Décharge pH; Conductivité; Screening minéral (22); BTEXS; Hydrocarbures pétroliers EC5-EC11; Hydrocarbures pétroliers EC10-EC40; HAP (16); Hydrocarbures aliphatiques halogénés (17); Cyanures libres; Cyanures totaux; Azote Kjeldahl; Azote ammoniacal; Nitrates; Nitrites; Sulfates; Sulfites; DBO5; DCO; C.O.T.; Chlorures; Fluorures; Indice phénols; Fraction soluble |
| 3.5.10 | Paquet EAU Anions Chlorures; Sulfates; Sulfites; Nitrites; Nitrates; Carbonates; Bicarbonates; Phosphates |
| 3.5.11 | Paquet EAU Cations Ammonium; Calcium; Magnésium; Potassium; Sodium; Manganèse |
| 3.5.12 | Paquet EAU Cyanures pH; Cyanures libres; Cyanures totaux; Cyanures non oxydables au chlore; Thiocyanates |
| 3.5.13 | Paquet EAU Déchloration réductrice du PCE PCE; TCE; DCE; CV; Ethène; Ethane |
| 3.5.14 | Paquet EAU Paramètres biodégradation Carbone organique dissous; Oxygène dissous; Nitrates; Sulfates; Méthane; Fer(II); Mn(II) |
| 3.5.15 | Phénols et chlorophénols |
| 3.5.16 | Screening minéral (22) |
| Total | |
| Cadre R3. Analyses d'eau (Prestations en régie) | |
| Poste n° | Désignation |
| 3.6 | Analyses |
| 3.6.01 | Thiocyanates |
| 3.6.02 | PCB - 7 congénères de Ballschmiter |
| Total | |

APPENDIX B



Figure 1. Sketch of the piezometers in the East part of the site Bois Saint-Jean (ECOREM, 200 from SPAuE, 2017).

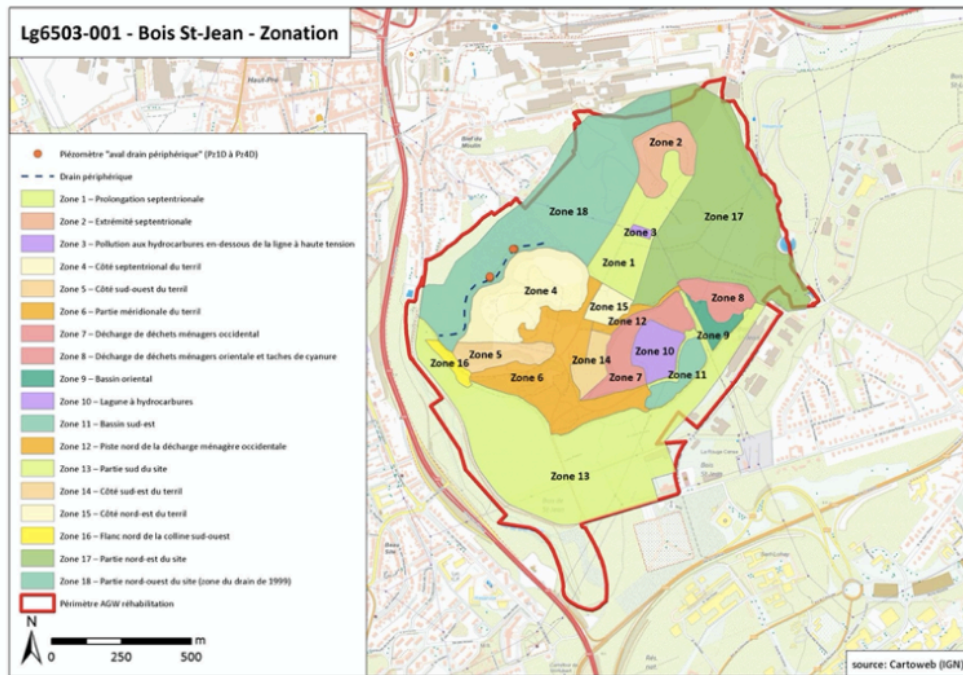


Figure 2. The different zones of the Bois Saint-Jean site (ECOREM, 2000), from SPAQuE (2017).

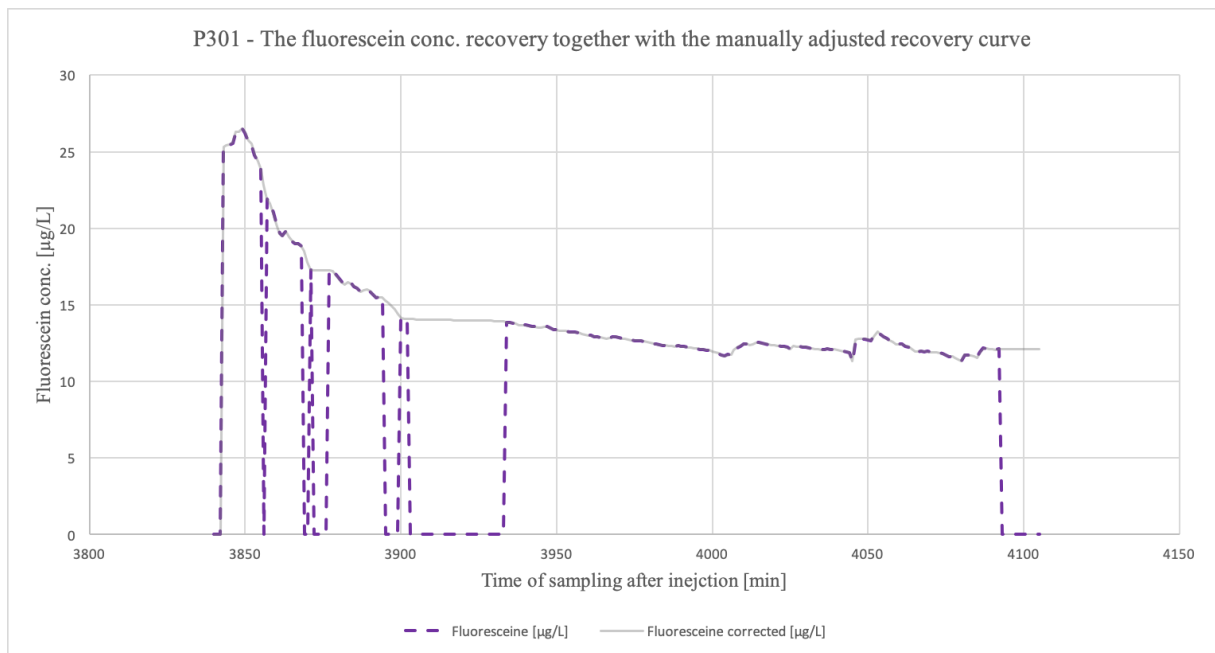


Figure 3. The fluorescein concentrations recovery measured in field with the field fluoreometer in grey, where the zero values most likely do not represent actual zero values, but the time steps where no concentrations were logged due to technical problem with the field fluoreometer. The grey line is the approximated manually fitted retrieved fluorescein concentrations from the extraction phase.