

Hydraulic and geochemical processes controlling the impact of urban runoff infiltration through loess during Managed Aquifer Recharge

Application to the Hesbaye chalk aquifer in Belgium

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HYDRAULIC AND GEOCHEMICAL PROCESSES CONTROLLING THE IMPACT OF URBAN RUNOFF INFILTRATION THROUGH LOESS DURING MANAGED AQUIFER RECHARGE

Application to the Hesbaye chalk aquifer in Belgium

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Abstract

In the context of climate change, increasing water demand, and continuous anthropogenic pressure on groundwater resources, many aquifers are experiencing long-term declines in groundwater levels, threatening the sustainable state of these freshwater systems. Notably, a persistent groundwater deficit has been observed over recent decades in the Hesbaye chalk aquifer (Liège, Belgium), which plays a strategic role in drinking water production. In response to this situation, it is essential to evaluate mitigation measures aimed at limiting the impacts of climate change on groundwater resources. In this regard, managed aquifer recharge (MAR) has emerged as a promising adaptation strategy to enhance groundwater resilience by artificially increasing recharge during periods of water availability. However, setting-up effective and sustainable MAR operations requires a careful assessment of site-specific constraints, as its technical feasibility depends not only on target recharge volumes, but also on subsurface infiltration capacity and the chemical quality of the recharge water.

Urban runoff is increasingly considered as an alternative water source for MAR, as it provides significant and spatially distributed volumes that are often already collected by existing infrastructures. However, these waters may contain a wide range of contaminants originating from traffic, industrial, and operational activities, raising concerns regarding groundwater protection. While water quality considerations are commonly integrated in MAR studies, most investigations focus primarily on nutrients, metals, or conventional organic pollutants. Contaminants of emerging concern (CECs), and notably per- and polyfluoroalkyl substances (PFAS), are relatively less documented in the context of MAR, despite their persistence, mobility, and toxicity. As a result, the potential impact of MAR operations on the transfer of contaminants from runoff toward groundwater remains insufficiently studied, highlighting the need for a more comprehensive qualitative assessment of runoff-based recharge.

From a hydraulic efficiency perspective, most existing MAR studies focus on highly permeable geological settings such as alluvial or sandy aquifers, where infiltration capacity is not a limiting factor. Fine-grained sediments such as loamy soils are therefore generally excluded from classical MAR schemes due to their low permeability. In practice, MAR operations in regions dominated by such sediments rely on infiltration through low-permeability surface materials, whose hydraulic behaviour under MAR conditions is still insufficiently documented at the field scale. This limits the applicability of existing MAR concepts in fine-grained sediments settings and requires dedicated investigations of recharge processes in such geological background.

This thesis aims to address these gaps by evaluating the feasibility of MAR in the Hesbaye region from both quantitative and qualitative perspectives, with a particular focus on urban runoff as a potential recharge water source. An integrated approach combining field investigations, hydrogeochemical analyses, laboratory experiments, and numerical modelling was developed to assess recharge potential, contaminant occurrence, attenuation mechanisms, and associated risks.

From a quantitative perspective, infiltration rates through loess deposits representative of the Hesbaye plateau were assessed at a pilot infiltration basin. Field experiments combining conventional monitoring techniques and distributed temperature sensing with fiber optics (DTS-FO) allowed the estimation of infiltration rates under operational conditions, demonstrating that effective recharge can be achieved in loess sediments. At the regional scale, potential recharge

water sources were identified and quantified, highlighting stormwater as a significant and spatially distributed resource, particularly in relation to traffic and airport infrastructures.

From a qualitative perspective, an extensive hydrochemical characterization of selected stormwater basins was conducted across multiple seasons to capture climatic and activity-related variability. Results reveal that runoff water quality is highly variable and reflects the influence of both traffic and other site-specific operational activities. Classical pollutants were generally present at moderate concentration levels, while CECs — including benzotriazoles, alkylphenols, and PFAS — were frequently detected and exhibited clear seasonal patterns linked to site-specific operational activities.

To investigate the fate of these contaminants during infiltration through loess sediments, laboratory batch experiments were performed using representative Hesbaye loess samples. The results demonstrate contrasting attenuation behaviours between contaminant families. Benzotriazoles and alkylphenols showed partial attenuation through sorption and biodegradation processes, whereas PFAS showed strong persistence and limited attenuation, with sorption potential decreasing for short-chain compounds.

Finally, a two-dimensional numerical model coupling variably saturated groundwater flow and reactive solute transport was developed to simulate MAR operations under realistic wetting–drying scenarios, while integrating field and laboratory results. Modelling results confirm that MAR can significantly enhance groundwater recharge even through fine-grained sediments but also demonstrate that contaminant transfer is strongly controlled by unsaturated zone processes, CECs hydrogeochemical properties, and MAR operational conditions. In particular, short-chain PFAS emerge as the most critical contaminants in terms of groundwater vulnerability under MAR operations due to their persistence and high mobility.

Overall, this thesis demonstrates that MAR using urban runoff could contribute to the mitigation of groundwater depletion in the Hesbaye region, including in geological contexts traditionally considered unfavourable for recharge. At the same time, although the results indicate that natural attenuation processes during the infiltration through the loess layer is effective for many contaminants, they may be inefficient for persistent and weakly sorbing compounds, such as short-chain PFAS. These findings motivate the need to integrate appropriate pre-treatment strategies into MAR schemes when urban runoff is used, to avoid any groundwater contamination risks. By addressing underexplored geological settings and emerging contamination risks in the context of MAR, this work provides new insights to inform the safe design of MAR while explicitly accounting for associated groundwater quality risks, therefore contributing to sustainable groundwater management under future climatic conditions.

Résumé

Dans un contexte de changement climatique, de hausse de la demande en eau et de pression anthropique continue sur les ressources en eaux souterraines, de nombreux aquifères connaissent une baisse durable de leurs niveaux, menaçant la pérennité de ces systèmes d'eau douce. Un déficit persistant a notamment été observé au cours des dernières décennies dans l'aquifère crayeux de Hesbaye (Liège, Belgique), qui joue un rôle stratégique dans la production d'eau potable. Dans ce contexte, il est essentiel d'évaluer des mesures d'atténuation capables de limiter les effets du changement climatique sur les eaux souterraines. Parmi celles-ci, la recharge maîtrisée des aquifères (MAR) apparaît comme une stratégie prometteuse, en augmentant artificiellement la recharge pendant les périodes de disponibilité en eau. Sa mise en œuvre exige toutefois une évaluation rigoureuse des contraintes locales, car sa faisabilité dépend à la fois des volumes visés, de la capacité d'infiltration du sol et de la qualité chimique de l'eau de recharge.

Les eaux de ruissellement urbain sont de plus en plus envisagées comme source alternative pour la MAR, car elles représentent des volumes importants, spatialement répartis et souvent déjà collectés par des infrastructures existantes telles que des bassins d'orage. Cependant, elles peuvent contenir de nombreux contaminants issus du trafic, des activités industrielles ou d'autres activités spécifiques aux sites, ce qui soulève des questions quant à la protection des eaux souterraines. Si la qualité de l'eau est généralement prise en compte dans les études sur la MAR, celles-ci portent surtout sur les nutriments, les métaux et les polluants organiques conventionnels. Les contaminants d'intérêt émergent (CECs), et en particulier les PFAS, restent encore peu étudiés dans ce contexte malgré leur persistance, leur mobilité et leur toxicité. L'impact potentiel de la MAR sur leur transfert vers les eaux souterraines demeure donc insuffisamment documenté, ce qui justifie une évaluation qualitative plus approfondie de la recharge à partir des eaux de ruissellement urbain.

Du point de vue de l'efficacité hydraulique, la plupart des études consacrées à la MAR portent sur des contextes géologiques très perméables, comme les aquifères alluviaux ou sableux, où l'infiltration ne constitue pas une contrainte majeure. À l'inverse, les sédiments plus fins, comme les limons, sont généralement écartés des schémas classiques de MAR en raison de leur faible perméabilité. Dans les régions où ces formations dominent, la recharge repose pourtant sur l'infiltration à travers des matériaux peu perméables, dont le comportement hydraulique en conditions opérationnelles de MAR reste encore insuffisamment documenté. Cette limite réduit l'applicabilité des concepts actuels de MAR dans ce type d'environnement et souligne la nécessité d'études spécifiques sur les processus de recharge dans ces contextes géologiques.

Cette thèse vise à combler ces lacunes en évaluant l'impact de la MAR sur l'aquifère crayeux de Hesbaye d'un point de vue quantitatif et qualitatif, en mettant particulièrement l'accent sur les eaux de ruissellement urbain comme source potentielle d'eau de recharge. Une approche intégrée combinant des études de terrain, des analyses hydrogéochimiques, des expériences en laboratoire et de la modélisation numérique a été développée pour évaluer le potentiel de recharge, la présence de contaminants, les mécanismes d'atténuation de ces derniers au cours de leur infiltration et les risques associés pour la masse d'eau souterraine sous-jacente.

D'un point de vue quantitatif, les taux d'infiltration à travers les dépôts limoneux représentatifs du plateau hesbignon ont été évalués sur un site pilote. Des expériences de terrain combinant des techniques de suivi conventionnelles ainsi qu'innovantes, telles que les mesures distribuées de température par fibre optique (DTS-FO), ont permis d'estimer les taux d'infiltration en conditions

opérationnelles, démontrant qu'une recharge effective est possible au travers de ces sédiments fins. À l'échelle régionale, les sources potentielles d'eau de recharge ont été identifiées et quantifiées, mettant en évidence les eaux de ruissellement comme une ressource importante et spatialement distribuée, en particulier en lien avec les infrastructures routières et aéroportuaires.

D'un point de vue qualitatif, une caractérisation hydrochimique approfondie de plusieurs bassins d'orage a été réalisée au cours de différentes saisons. Les résultats montrent que la qualité des eaux de ruissellement est très variable et reflète l'influence à la fois du trafic et des activités spécifiques à chaque site. Les polluants classiques ont été généralement quantifiés à des concentrations modérées, tandis que les CEC — notamment les benzotriazoles, les alkylphénols et les PFAS — ont été fréquemment détectés et présentaient des variations saisonnières nettes en lien avec des activités opérationnelles propres à chaque site.

Afin d'étudier le devenir de ces contaminants lors de l'infiltration au travers des loess, des expériences batch ont été réalisées en laboratoire sur base d'échantillons représentatifs du loess de Hesbaye. Les résultats mettent en évidence des comportements d'atténuation contrastés selon les familles de contaminants. Les benzotriazoles et les alkylphénols ont montré une atténuation partielle par des processus de sorption et de biodégradation, tandis que les PFAS ont présenté une forte persistance et une atténuation limitée, avec un potentiel de sorption décroissant pour les composés à chaîne courte.

Enfin, un modèle numérique 2D couplant l'infiltration des eaux de ruissellement en milieu variablement saturé et le transport réactif des contaminants associés a été développé afin de simuler les opérations de MAR dans des conditions réalistes, tout en intégrant les résultats des campagnes de terrain et de laboratoire. Les résultats de modélisation confirment que la MAR peut accroître significativement les volumes de recharge, même au travers de sédiments fins, mais montrent également que le transfert des contaminants est fortement contrôlé par les mécanismes de transport au sein de la zone non saturée, les propriétés hydrogéochimiques des CECs et les conditions de mise en œuvre de la MAR. En particulier, les PFAS à chaîne courte apparaissent comme les contaminants les plus critiques en termes de vulnérabilité des eaux souterraines dans le cadre des opérations de MAR, en raison de leur persistance et de leur forte mobilité.

Dans l'ensemble, cette thèse démontre que la mise en œuvre de la MAR utilisant des eaux de ruissellement urbain peut contribuer à limiter l'épuisement des eaux souterraines, y compris dans des contextes géologiques généralement considérés comme défavorables à la recharge. Toutefois, si l'infiltration à travers la couche de loess permet une atténuation naturelle efficace pour de nombreux contaminants, elle reste limitée pour les composés persistants et faiblement retenus, comme les PFAS à chaîne courte. Ces résultats soulignent la nécessité d'intégrer des traitements adaptés avant recharge afin de prévenir tout risque de contamination des eaux souterraines. En intégrant à la fois les contraintes géologiques et les risques liés aux contaminants d'intérêt émergents, ce travail apporte des éléments utiles pour concevoir des opérations de MAR sûres et adaptées aux conditions climatiques futures.

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List of acronyms

ADAF : aircraft deicing and anti-icing fluids

ADE : advection–dispersion equation

ADTS : active distributed temperature sensing

AFFF : aqueous film forming foam

APEO : alkylphenol ethoxylates

AWI : air-water interface

BDOC: biodegradable dissolved organic carbon

BOD: biochemical oxygen demand

BPA : bisphenol A

BZT : benzotriazole

BTEX : benzene, toluene, ethylbenzene, and xylenes

CECs : contaminants of emerging concern

CILE : Compagnie Intercommunale Liégeoise des Eaux

DO : dissolved oxygen

DOC : dissolved organic carbon

DTS : distributed temperature sensing

EC : electrical conductivity

EFA : European Food Agency

EPA: Environmental Protection Agency

EQS : environmental quality standards

ER : exceedance ratio

EU : European Union

FNRS : The Funds for Scientific Research

FO : fiber optic

FTOHs : fluorotelomer alcohols

6:2 FTS : 1H,1H,2H,2H-perfluorooctanesulfonic acid

HPLC-MS/MS: high performance liquid chromatography – tandem mass spectrometry

IPCC : Intergovernmental Panel on Climate Change

IRM : Royal Meteorological Institute

LOD : limit of detection

LTM : Leverett thermodynamic model

MAR : managed aquifer recharge

MARWAL : managed aquifer recharge in Wallonia

MILS: moving instantaneous line source

MPs: microplastics

NAPL : Non-Aqueous Phase Liquid

NP : nonylphenol

NPEO : nonylphenol ethoxylates

NP₂EO : nonylphenol diethoxylate

OP : octylphenol

OPEO : octylphenol ethoxylates

OPFR : organophosphate flame retardants

ORP : oxidation–reduction potential

PAH : polycyclic aromatic hydrocarbons

PBDE : polybrominated diphenyl ethers

PCB : polychlorinated biphenyls

PFAS : per- and polyfluoroalkyl substances

PFBA : perfluorobutanoic acid

PFCA : perfluoroalkyl carboxylic acids

PFECHS : perfluoroethylenecyclohexanesulfonate

PFHxA : perfluorohexanoic acid

PFOA : perfluorooctanoic acid

PFOS : perfluorooctane sulfonate

PFPeA : perfluoropentanoic acid

PMT : persistent, mobile, toxic

PPCP : pharmaceuticals and personal care products

QPSR : quantitative structure-property relationships

RCM : regional climate model

RMSE: root mean square error

RPFs: relative potency factors

SAT : soil aquifer treatment

SPW-MI : Service public de Wallonie – Mobilité et Infrastructures

SWRC : soil-water retention curve

TLT : tolyltriazole

TOC : total organic carbon

TP : total phosphorus

TRWP: tire and road wear particles

TSS : total suspended solids

VOC : volatile organic compounds

WWTP : wastewater treatment plants

Chapter 1

Introduction and objectives

1. General background and scientific context

Groundwater constitutes an essential component of freshwater resources, as it supplies drinking water, supports agricultural and industrial activities, and sustains river baseflows and associated ecosystems. In many regions worldwide, groundwater systems have often been considered as reliable and stable resources, as their subsurface storage provides a natural buffering capacity against short-term climatic variability. However, over the last decades, this apparent stability has been increasingly challenged. Climate change is progressively disturbing the hydrological cycle through shifting in precipitation patterns, increased evapotranspiration, and higher frequency of extreme events such as prolonged droughts and intense rainfall. Beyond their impact on surface water dynamics, these climatic changes alter both the magnitude and efficiency of groundwater recharge. In addition, anthropogenic pressure on groundwater resources continues to increase due to population growth, urban expansion, and abstraction rates that are often driven by water demand rather than adapted to changing recharge conditions. The combined anthropogenic and climatic pressures on groundwater resources have led to persistent groundwater deficits in many aquifers, characterized by declining water levels and reduced resilience during dry conditions.

This situation is particularly concerning for aquifers that play a strategic role in regional water supply. In Wallonia (Belgium), some major groundwater bodies have shown increasing sensitivity to climate variability combined with sustained exploitation (Brouyère *et al.*, 2021; Hutzemakers *et al.*, 2024). Among these, the Hesbaye chalk aquifer constitutes one of the most important freshwater resources in the region, supplying drinking water to the Liège area through pumping wells and drainage galleries. Long-term observations have indicated a persistent decline in groundwater levels over recent decades, reflecting an imbalance in the groundwater budget (Goderniaux *et al.*, 2023; Andriamialisoa, 2024). Although groundwater response to precipitation is buffered in time, the Hesbaye chalk aquifer remains sensitive to sustained variations in effective recharge. It is therefore critical to ensure sustainable groundwater management for this aquifer (Brouyère, 2023, 2024), especially in a context where alternative water sources are limited and possibilities for reducing groundwater abstraction remain restricted.

In this context, Managed Aquifer Recharge (MAR) is increasingly considered as a promising strategy to address groundwater depletion and improve the resilience of water supply systems. MAR operations consist in intentionally increase groundwater recharge by infiltrating alternative water sources during periods of availability, thereby enhancing subsurface storage and buffering the effects of climate variability on groundwater resources. In terms of water management perspective, MAR offers a response to groundwater deficits by relying on the aquifer itself as a storage subsurface reservoir that can be integrated into existing supply infrastructures. In addition, when MAR is implemented through surface infiltration systems, the percolation of water through the soil and unsaturated zone may contribute to water quality improvement through natural filtration and attenuation processes.

Nevertheless, implementing such a system as a viable water management option remains complex. When MAR is considered for a highly exploited aquifer such as the Hesbaye chalk aquifer in the region of Liège, several fundamental questions emerge. First, MAR technical feasibility depends on the availability of suitable water recharge sources. In many areas, conventional sources such as surface water or excess river flows are limited by hydrological constraints or ecological requirements. Alternative water sources, such as runoff generated in urban or other impervious-

dominated environments, may represent significant water volumes but are characterized by strong temporal variability and uncertain chemical quality. Second, ensuring groundwater quality during MAR operations is critical, especially when recharge waters originate from urban and anthropogenic influenced areas. The assumption that soils and the unsaturated zone systematically act as an effective protection barrier in MAR schemes remains insufficiently quantified for many contaminants, especially persistent, mobile and toxic compounds. Finally, MAR implementation requires infiltration rates that can be sustained over time and compatible with operational constraints. This is not a condition easy to achieve in geological settings dominated by fine-grained sediments such as loess, which are often excluded for MAR schemes involving surface infiltration systems.

All together, these considerations indicate that the technical feasibility of MAR is strongly case-specific and cannot be transferred from one hydrogeological context to another. Instead, it requires an integrated evaluation explicitly accounting for local hydrogeological conditions, recharge water characteristics, soil properties, and groundwater protection objectives. In the Hesbaye context, the implementation of MAR requires an assessment adapted to local conditions, addressing the key scientific and technical constraints that govern recharge feasibility, contaminant attenuation, and long-term infiltration performance. This PhD thesis aims to address these aspects to determine whether such an approach can be realistically and safely integrated into groundwater management practices in the Hesbaye chalk aquifer.

2. Objectives of the thesis and methodological framework

As emphasized in the introduction, assessing MAR feasibility in a given hydrogeological context requires an integrated assessment combining both quantitative and qualitative aspects. In this thesis, the quantitative dimension refers to all elements related to the amount of water that can be potentially recharged, including the availability of recharge water sources, the volumes that can be mobilized for MAR operations, and the soil infiltration capacity. In contrast, the qualitative perspective refers to the chemical quality of the recharge water and encompasses both its overall composition and the behaviour of the detected contaminants during infiltration.

Based on this distinction, the overall objective of this PhD thesis is to quantify the potential contribution of MAR to groundwater replenishment in the Hesbaye chalk aquifer while evaluating the implications for groundwater quality under local conditions. More specifically, the thesis aims to determine whether MAR could contribute significantly to groundwater recharge and thus constitute an effective mitigation measure against the impacts of climate change on groundwater resources, or whether it could instead represent a potential source of groundwater contamination under local hydrogeological conditions. To address this question, MAR operations are numerically reproduced under realistic conditions by combining the quantitative and qualitative information gathered throughout the work.

2.1. Quantitative assessment

From a quantitative perspective, the objective is to evaluate whether MAR could provide recharge volumes sufficient to reduce the imbalance in the hydrogeological budget of the Hesbaye chalk aquifer. Achieving this objective requires both the identification of potential recharge water sources and the assessment of the soil infiltration capacity under realistic operating conditions.

The first component of the quantitative assessment therefore focuses on evaluating the availability of alternative recharge water sources (runoff and wastewater, among others) and estimating the volumes that could realistically be mobilized for MAR operations. Before considering qualitative constraints, it is indeed necessary to determine whether these sources could provide sufficient water volumes for their use in MAR to significantly contribute to groundwater replenishment. To this end, data analyses are carried out using information provided by several institutional and technical partners, including “*Service public de Wallonie – Mobilité et Infrastructures (SPW-MI)*”, Raisô, “*Société wallonne des Aéroports (SOWAER)*”, and “*Centre d'Expertise en Traitement et Gestion de l'eau (CEBEDEAU)*”. As available datasets do not always allow a direct quantification of harvestable recharge volumes, these data are complemented by assumptions related to runoff generation and to the fraction of runoff that can be collected and stored in stormwater basins, which are considered as potential recharge water sources.

A second objective of the quantitative assessment is to evaluate the infiltration capacity of the loess deposits that cover a large part of the Hesbaye chalk aquifer. Since infiltration performance directly controls the efficiency of MAR operations, field-scale investigations are required to assess whether infiltration through fine-grained sediments can realistically sustain MAR operations. To address this objective, infiltration tests are conducted at a pilot infiltration basin connected to a groundwater production well operated by the “*Compagnie Intercommunale Liégeoise des Eaux (CILE)*” public water distribution company. Infiltration through the loess layer is monitored using conventional instruments such as pressure sensors, as well as an innovative approach based on distributed temperature sensing (DTS) with fiber-optic cables. This combination allows characterization of both spatial and temporal variability in recharge dynamics, rather than relying solely on average infiltration rates.

2.2. Qualitative assessment

From a qualitative perspective, the objective is to assess whether the selected recharge water sources may pose a risk to groundwater quality during MAR operations. This requires a detailed characterization of recharge water chemistry as well as an evaluation of the fate of identified contaminants during infiltration through the unsaturated zone.

The qualitative assessment therefore begins with the evaluation of the physicochemical quality of potential recharge waters. Following a literature review of contaminants commonly reported in urban runoff, target-screening sampling campaigns were conducted to quantify the presence of expected compounds and to identify potential additional contaminants. These sampling campaigns were performed during different seasons to capture potential seasonal variability in water quality related to climatic conditions and site-specific activities. Both conventional water quality parameters and selected contaminants of emerging concern are included in the analytical strategy.

Based on this characterization, the most relevant contaminants are selected for further investigation. A second objective of the qualitative assessment is to evaluate whether these compounds may represent a risk to groundwater quality if recharge waters are infiltrated without adequate pre-treatment. To address this question, laboratory batch experiments were carried out at IDAEA-CSIC (Barcelona, Spain) to investigate the physicochemical behaviour of selected contaminants when being in contact with loess sediments, with a particular focus on sorption and biodegradation processes. Key parameters describing these processes were estimated through chemical modelling approaches designed to reproduce the experimental observations.

2.3. Final integrated assessment

The final step of the thesis is to integrate the information obtained from both quantitative and qualitative assessments to assess MAR impacts under realistic operating conditions while ensuring groundwater quality protection. This integration is necessary to assess whether recharge efficiency and water quality constraints can be jointly satisfied.

To achieve this objective, numerical modelling of MAR operations is performed to couple recharge dynamics and contaminant transport altogether within a coherent framework. Simulations are conducted using the HYDRUS software to represent infiltration processes and solute transport under variably saturated conditions. Different modelling scenarios are explored to account for uncertainties in the parameters related to each studied contaminant and in the representation of key transport and attenuation processes. Risk assessment is then conducted by evaluating the potential transfer of contaminants associated with MAR operations under environmentally relevant concentration levels.

3. Thesis structure

The present doctoral thesis is organized as summarized in the organigram presented in Figure 1. It is structured around a progressive framework that addresses MAR in the Hesbaye chalk aquifer from both quantitative and qualitative perspectives, before integrating these aspects into a risk-oriented assessment.

Chapter 1 introduces the general background that motivates this research. It provides the scientific and environmental context of the study, presents the main objectives of the thesis, and outlines the overall structure of the manuscript.

The necessary background to contextualize the research questions addressed in this thesis is provided throughout chapters 2 and 3. As the work covers a broad range of interconnected topics, these chapters aim to ensure a clear understanding of the environmental context and of the scientific background framing the study. **Chapter 2** presents the environmental setting of the thesis, with a particular focus on the impacts of climate change on groundwater resources in Wallonia (Belgium), and more specifically in the Hesbaye region. The Hesbaye chalk aquifer is introduced as a relevant case study for assessing MAR suitability, as it represents a strategic freshwater resource for the region of Liège that has experienced declining piezometric trends over recent decades. It also describes the different potential recharge water sources available in the study area and justifies the selection of urban runoff as a particularly relevant option for MAR operations. In this context, the potential use of alternative recharge water sources for MAR raises important questions related to groundwater quality protection. **Chapter 3** is therefore dedicated to a state-of-the-art review of contaminants that may be present in urban runoff, identified as a potential recharge water source for MAR operations, and presents their origin, occurrence, and physicochemical behaviour within groundwater. This chapter provides the scientific basis for the qualitative assessments developed in the subsequent chapters.

Chapter 4 addresses the qualitative dimension of the study by presenting the sampling campaigns carried out to characterize runoff water quality for the selected stormwater basins, including the identification of detected contaminants, their concentration ranges, and their temporal variability in relation to seasonal conditions and site-specific activities.

Following the identification of contaminants in alternative recharge water sources, **Chapter 5** focuses on their behaviour during infiltration through loess deposits. This chapter presents laboratory batch experiments conducted at IDAEA-CSIC (Barcelona, Spain) to investigate contaminant attenuation processes under controlled conditions. The experimental setup is described, and the fate of selected contaminants is analysed with respect to sorption and biodegradation mechanisms. Chemical models are also introduced and calibrated to reproduce experimental observations and to estimate key parameters governing contaminant behaviour in loess sediments. Chapter 5 is presented in the form of a peer-reviewed publication in *Journal of Contaminant Hydrology* (Glaude *et al.*, 2026)¹.

Chapter 6 then investigates the quantitative dimension by focusing on infiltration processes at the field scale. It presents infiltration tests conducted at a pilot infiltration basin connected to a groundwater production well. These experiments are monitored using both conventional instrumentation and advanced monitoring techniques based on active and passive distributed temperature sensing (DTS) with fiber optic (FO) cables. By analysing temperature responses along the FO cable installed within the infiltration basin, this chapter provides insights into spatial and temporal variations in infiltration rates under realistic MAR operating conditions. Chapter 6 is presented in the form of a peer-reviewed publication in the *Journal of Hydrology* (Glaude *et al.*, 2025)².

Chapter 7 integrates the qualitative and quantitative findings through numerical modelling. It introduces a variably saturated flow and solute transport model developed using the HYDRUS software to reproduce MAR operations at the pilot site. This modelling framework is used to assess the potential transfer of contaminants from recharge water toward the Hesbaye chalk aquifer, while accounting for uncertainties associated with key parameters controlling contaminant transport and attenuation during percolation through the unsaturated zone dominated by loess deposits.

Finally, **Chapter 8** presents the main conclusions of the thesis. It summarizes the key findings, discusses the limitations of the study with transparency, and outlines perspectives for future research related to MAR implementation in Hesbaye.

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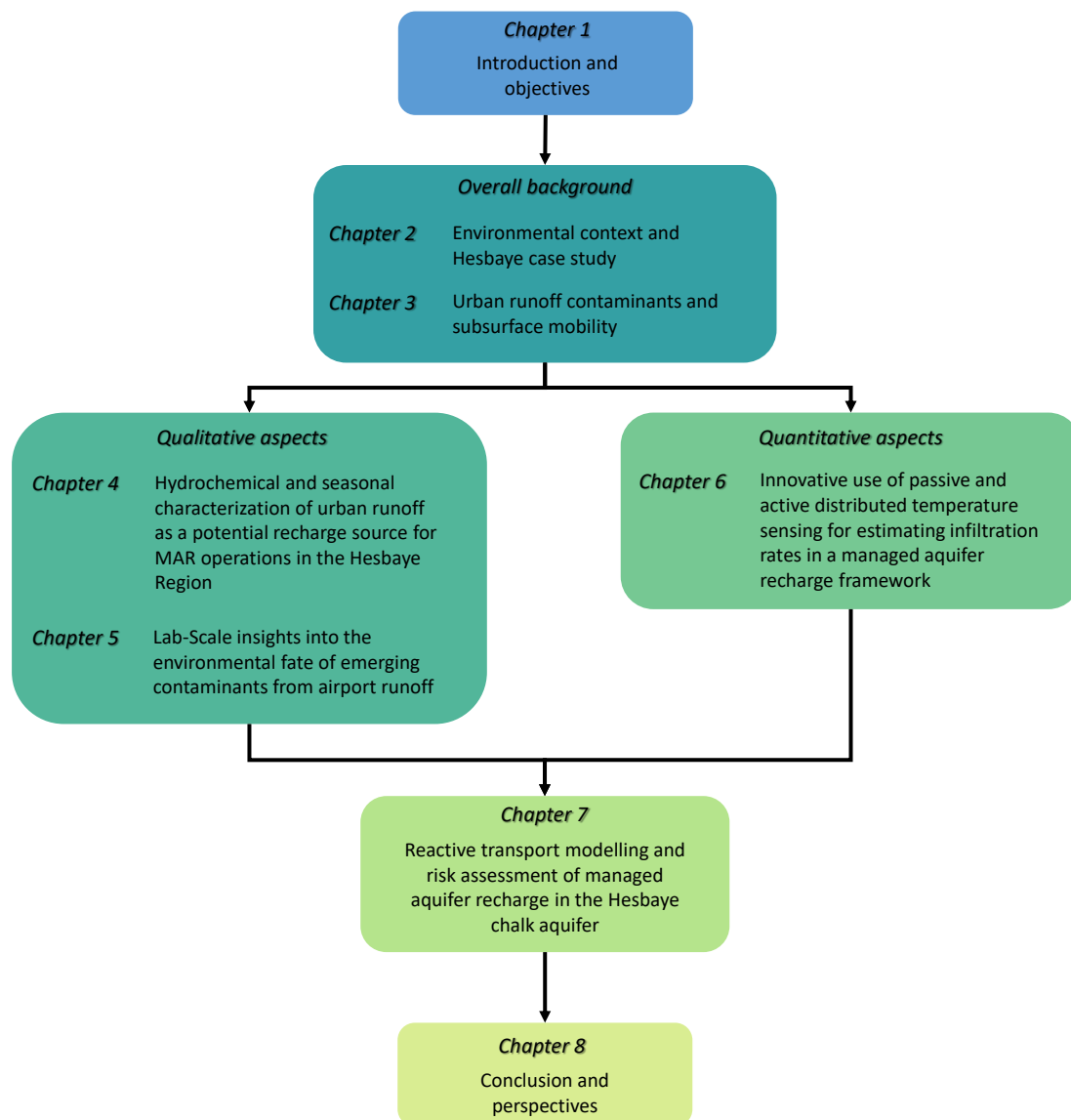


Figure 1. PhD thesis structure.

Chapter 2

Environmental context and Hesbaye case study

1. Climate change mechanisms affecting groundwater recharge

Groundwater resources, which supply approximately half of the volume of water abstracted globally for domestic use and around 25% for irrigation, are becoming increasingly vulnerable to the effects of climate change (UN Water, 2022). Notably, rising global temperatures and shifting precipitation patterns are altering the balance between aquifer recharge and groundwater abstraction in many regions of the world (Taylor *et al.*, 2013; Scanlon *et al.*, 2023). In this chapter, the general mechanisms by which climate change influences groundwater recharge are first briefly described. The discussion then progressively shifts to climate observations and projections in Belgium and Wallonia, before focusing on the Hesbaye chalk aquifer which constitutes the main case study of this thesis.

According to the Intergovernmental Panel on Climate Change (IPCC, 2023), climate change is expected to have an impact on groundwater through several mechanisms. In temperate regions such as Belgium, these are notably reflected through (i) changes in precipitation and evapotranspiration patterns, (ii) increasing frequency and severity of extreme hydrological events, and (iii) modifications in land use and vegetation cover.

1.1. Changes in precipitation and evapotranspiration patterns

These climate-driven trends significantly influence groundwater recharge, especially in semi-arid and temperate regions where water balances are particularly sensitive to climate variability. A decrease in recharge can often be attributed to reduced infiltration resulting from declining precipitation (Doll and Fiedler, 2008). Furthermore, shifts in rainfall seasonality and intensity can alter the timing and efficiency of infiltration, potentially reducing groundwater recharge by increasing evapotranspiration losses or shortening the window during which percolation is possible (Thomas *et al.*, 2016; Zheng *et al.*, 2023). In parallel, higher temperatures intensify evapotranspiration, removing more moisture from soils and vegetation and further reducing the water available for infiltration (Taylor *et al.*, 2013; Condon *et al.*, 2020). Drier soils also reduce recharge efficiency by initially retaining rainfall to restore soil moisture, thereby delaying or preventing percolation (Song and Wang, 2019). These effects are particularly pronounced in semi-arid zones, where groundwater recharge is episodic and highly dependent on infrequent, high-intensity rainfall events (Boas and Mallants, 2022).

1.2. Rise in the frequency and severity of extreme hydrological events

Extreme hydrological events, such as droughts and floods, are projected to be more frequent and severe under climate change, with direct and indirect implications for groundwater systems (IPCC, 2023). Droughts can considerably reduce groundwater recharge by limiting precipitation and increasing soil dryness, which leads to lower infiltration efficiency (Peters *et al.*, 2006). Dry soils absorb the initial rainfall to moisten the soil layers, raising the maximum amount of precipitation required for percolation, and can lead to runoff once soils become less permeable after prolonged dryness (Reinsch *et al.*, 2024). Moreover, groundwater abstraction typically increases during drought periods to compensate for reduced surface water availability and meet irrigation or domestic needs, placing additional stress on aquifers and often leading to significant declines in groundwater levels (Famiglietti, 2014; Wendt *et al.*, 2020). If aquifers experience repeated drought

events over consecutive years, they may not have sufficient time to recover to their pre-drought conditions, leading to cumulative groundwater depletion and persistent declines in groundwater storage (Famiglietti, 2014).

On the other hand, although flooding may seem to offer an opportunity for recharge due to the large volumes of water involved, its contribution to aquifer replenishment is highly context-dependent. Some studies report that intense floods result in surface runoff that is rapidly evacuated downstream when soils are already saturated or severely dried, thereby limiting its contribution to groundwater recharge (Bronstert *et al.*, 2023). In urban areas, impervious surfaces prevail and further limit water infiltration, causing the excess water to bypass natural recharge pathways (O'Connell *et al.*, 2007; Fletcher *et al.*, 2013). Conversely, other studies in Swiss urban catchments report the opposite behaviour, with urbanization locally increasing groundwater recharge through water drainage and sewer network leakage (Minnig *et al.*, 2018). In addition, in some alluvial plains, karst systems, or managed recharge areas, floods can enhance recharge if water remains ponded or if it is diverted to infiltration zones (Luo *et al.*, 2025; Wang *et al.*, 2025).

1.3. Transformation of land use and vegetation cover

Changes in land use and vegetation induced by climate change or human activities can significantly affect groundwater recharge by altering key hydrological processes such as interception, evapotranspiration, surface runoff, and infiltration (Adams *et al.*, 2012). For example, prolonged droughts or rising temperatures can lead to vegetation decline, changes in plant species composition, or increased wildfire frequency, which reduce canopy interception and root water uptake (Xu *et al.*, 2017; DeSoto *et al.*, 2020; Wasserman, 2023). These changes may initially increase infiltration in some cases but often lead to soil degradation, reduced organic matter, and crust formation (Reinsch *et al.*, 2024). This situation leads to a decrease in soil infiltration capacity and an increase in surface runoff. On the other hand, transformation of land use such as deforestation, agricultural intensification, or urban expansion result in reduced vegetation cover, soil compaction, or the growth of impervious surfaces, which altogether prevent infiltration and accelerate runoff (Peña-Arancibia *et al.*, 2019; Pasquier, Vahmani and Jones, 2022; Frene, Pandey and Castrillo, 2024). Therefore, both climate-induced changes in vegetation cover and anthropogenic land-use transformations can significantly influence groundwater dynamics, often leading to reduced recharge potential.

2. Climatic and land-use evolution in Belgium

2.1. Climate observations and projections

Although groundwater resources are generally better protected from the effects of climate change than surface water, they remain vulnerable to a range of direct and indirect pressures as mentioned in section 0. Notably, climate projections for Belgium indicate a marked increase in average temperatures, a shift in seasonal precipitation patterns and a rise in the frequency of hydrological extremes, such as droughts and floods.

According to the Royal Meteorological Institute (IRM, 2020), seasonal temperatures have shown a clear and significant warming trend across all seasons since 1981. From 1954 to 2019, summers have warmed the most, with an average increase of 0.36°C per decade, followed by spring

(+0.34°C/decade), winter (+0.29°C/decade) and autumn (+0.20°C/decade). This warming is evident across the country and particularly pronounced in Uccle, where the warmest years on record have all occurred after 2005. Heatwaves have become more frequent, longer, and more intense in recent decades. In terms of precipitation, trends are more variable and it is difficult to draw conclusions about a statistically significant trend for the country. Nevertheless, climate projections for 2100 agree that winters will generally be wetter and summers drier (Tabari *et al.*, 2015). In addition, the frequency and intensity of heavy rainfall events (> 20 mm/day) have increased over the last 40 years. Since 1981, there has been a significant average increase (+2%/decade) in the contribution of these heavy rainfall events to the annual total.

Hydrological extremes are also projected to intensify. In particular, meteorological droughts—defined only based on reduced precipitation—are expected to become significantly more frequent and intense by the end of the century under high-emission scenarios such as RCP 8.5. For example, extreme droughts like that of 1976 could occur up to five times more often compared to the historical period (1951–2005), especially due to the projected decline in summer precipitation (Zamani *et al.*, 2016; Van De Vyver and Van Den Bergh, 2018; IRM, 2020).

In contrast, extreme rainfall events and flooding are also expected to increase in frequency and intensity. The devastating floods that hit Belgium in July 2021 offer a clear illustration of this trend. In the Meuse basin, record-breaking cumulative rainfall over 48 hours, reaching nearly 300 mm in some places, led to disastrous floods, particularly in the Vesdre catchment. The consequences were devastating, with 39 fatalities, thousands of homes destroyed or severely damaged, and extensive damage to public infrastructure (Dewals *et al.*, 2021). Although flood impacts were less severe than in the Vesdre catchment, flooding also affected parts of the Hesbaye region, where the aquifer investigated in this thesis is located. Estimated return periods for the observed rainfall totals in some areas exceeded 200 years, underscoring the exceptional nature of the event. A recent study by Brajkovic *et al.* (2025) using the high-resolution regional climate model projects that extreme daily precipitation in Belgium will increase in intensity by approximately 7% per degree of global warming. By the end of the 21st century, the 20-year return level for daily rainfall is expected to rise by 25–30%, reaching or exceeding 100 mm/day in flood-prone areas such as the Vesdre valley and southern Ardennes. Furthermore, the frequency of these extreme events will increase significantly: in a +2 °C scenario, what was historically a 20-year event could occur every 9 years on average, and as frequently as every 4 to 7 years in local hotspots.

2.2. Land-use and soil sealing

In addition to climate change, land use dynamics significantly influences the response of water resources and flood risk. In Belgium, the landscape has undergone profound transformations over recent decades, with urbanisation and soil impermeabilization emerging as major pressures on both surface and subsurface hydrological processes

According to the CORINE Land Cover data and European Environment Agency (EAA, 2023), land take between 2000 and 2018 reached approximately 104 km² in Belgium. Over the same period, land take reached about 2154 km² in France, 1381 km² in Germany, and 642 km² in the Netherlands. When expressed as a percentage of national territory, land take represents a similar proportion in Belgium, France, and Germany (around 0.3–0.4% of total area), whereas it is significantly higher in the Netherlands (1.8% over the same period). Moreover, by 2000, Belgium was already one of the

most densely populated countries in Europe and already had one of the highest proportions of artificial surfaces compared to France or Germany, leaving relatively limited rural land available for further urban expansion. This expansion is particularly concentrated around urban agglomerations such as Brussels, Liège, Charleroi, and Antwerp. Urban expansion is also noticeable in peri-urban and rural zones, particularly in Wallonia where low-density urban expansion is widespread. In Wallonia, artificialized land reached 1823 km² by 2021 (10.8% of the region's surface), differing from the 1260 km² in 1985 (Etat de l'environnement wallon, 2022). Although the rate of land conversion has slowed down in recent years, residential development remains the main driver of this growth. This growth is often accompanied by increased soil sealing, with impermeable surfaces such as roads, buildings, and parking lots replacing natural or agricultural land. This urban expansion is notably depicted in Figure 2.

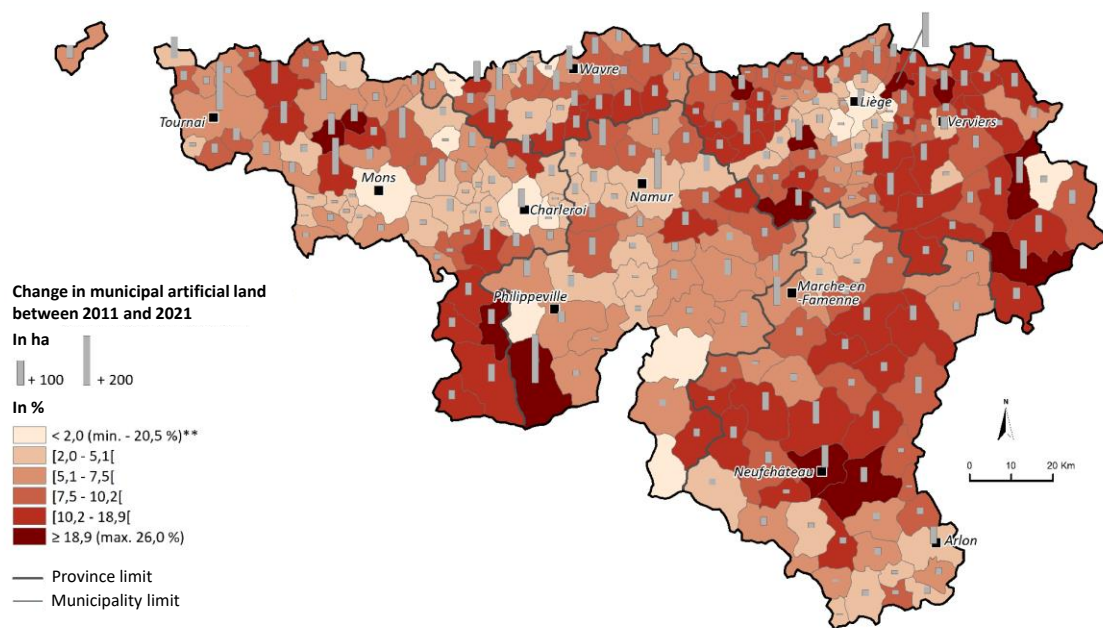


Figure 2. Land artificialization evolution in Wallonia between 2011 and 2021 (modified from Etat de l'environnement wallon, 2022)

In Wallonia, agricultural practices and land consolidation have also played a role in modifying runoff and recharge dynamics. Notably, Evrard et al. 2007) documented that land consolidation projects carried out in the Belgian loess belt in the 1970s, which includes field size expansion and landscape buffer removal, resulted in approximately 33% increase in peak stream discharge and 19% in total runoff volume. These changes, combined with intensive cropping practices such as deep tillage in fine-grained soils, have reduced infiltration and accelerated surface runoff, often leading to muddy floods frequently observed in the region (Ryken et al., 2018).

3. Groundwater resources in Wallonia

3.1. Groundwater use and hydrogeological setting

Groundwater plays a dominant role in ensuring water security in Wallonia, where it is predominantly used for public water distribution. In 2022, a total of 372.8 million cubic metres of groundwater were abstracted in the region, of which 78.5% was intended for public water supply. The remaining proportions were associated with mines and quarries (11.3%), other industrial uses such as cooling (6.8%), agriculture (1%), and other minor uses (SPW, 2025). This strong reliance on groundwater is explained by the overall availability, accessibility, and generally good quality of water stored in Walloon aquifers (Dassargues and Walraevens, 2014). In addition to meeting regional needs, groundwater resources in Wallonia also contribute to water supply beyond regional boundaries, with approximately 34% of the abstracted volumes exported to Brussels and Flanders

Wallonia's subsurface hosts a diverse range of aquifers that vary greatly in productivity depending on geological characteristics. Wallonia's aquifers are typically grouped into seven main units. First, Carboniferous limestone aquifers extending along the Meuse valley represent the region's primary source for large-scale abstraction. Another significant groundwater bodies are the Cretaceous chalk aquifers, notably in Hesbaya region and the Mons Basin, which often present confined conditions and support substantial public supply, notably to the city of Liège and Mons respectively. In Brabant wallon, the Tertiary sand aquifers, such as the Bruxellian and Landenian sands, also represent important local resources, particularly for the Brussels region. In contrast, the Devonian sandstone-schist massifs of the Ardenne and the Cambro-Silurian basement rocks of eastern and southern Wallonia offer limited yields, yet remain essential for decentralized supply, particularly in more rural or topographically constrained areas (SPW, 2025). Figure 3 depicts the different aquifer main units as well as abstracted water volumes data from groundwater and surface water bodies for public distribution.

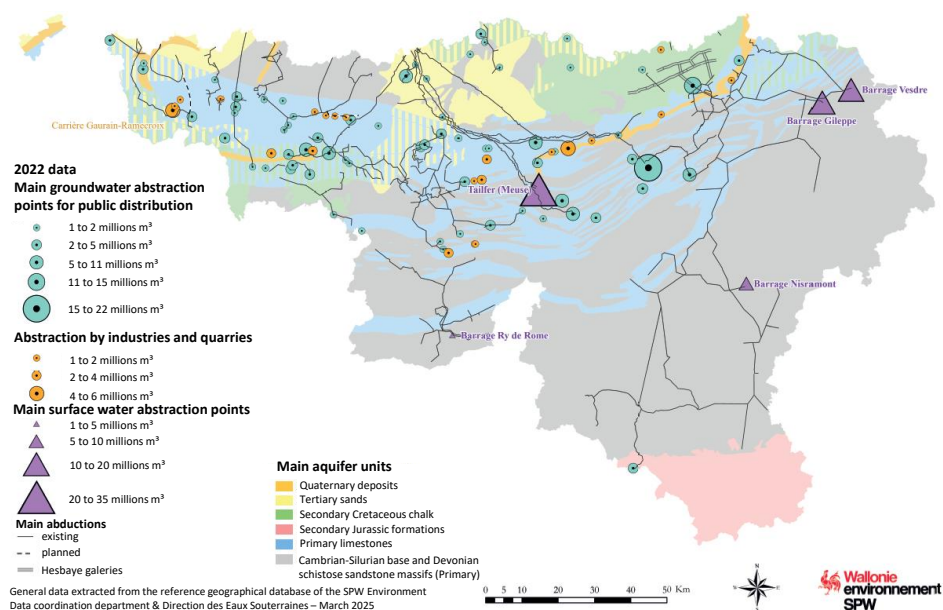


Figure 3. Groundwater and surface water abstraction data in Wallonia (2022) and main hydrogeological units (modified from SPW, 2025)

3.2. Pressure on chalk groundwater systems

3.2.1. Observed groundwater stress

Several studies conducted in Belgium have demonstrated the impact of climate change on groundwater systems, particularly in chalk aquifers, which represent strategic water resources in Wallonia. A detailed analysis is provided by Goderniaux et al. (2023), who investigated long-term groundwater level evolution in the chalk aquifers of the Mons Basin and Hesbaye region over the past six decades in the context of climate change.

By comparing two 30-year periods (1960–1990 and 1990–2020), the authors identified a clear decline in groundwater levels in both aquifers, with the most pronounced decrease observed in the Hesbaye chalk aquifer. In this aquifer, mean groundwater levels decrease by approximately 6 m between the two periods, a trend that is consistently observed across most of the basin (Goderniaux *et al.*, 2023). This long-term decline contrasts with the limited seasonal variability typically observed in chalk aquifers and reflects a long-term imbalance between recharge and outflows.

This groundwater level decrease is primarily attributed to climate-driven changes affecting recharge processes. Goderniaux et al. (2023) reported an increase in air temperature across all months of the year with respect to the reference period of 1960–1990, reaching up to +2 °C in summer, combined with a reduction in precipitation during recharge periods in late autumn and winter. As a result, the mean annual groundwater recharge in the Hesbaye aquifer decreased from approximately 207 mm year⁻¹ during the 1960–1990 period to only 117 mm year⁻¹ during 1990–2020, corresponding to a reduction of about 45% (Goderniaux *et al.*, 2023).

The impact of reduced recharge on groundwater levels is further amplified by the hydrogeological setting of the Hesbaye chalk aquifer. Due to the presence of thick loess deposits and a deep unsaturated zone, the response time between precipitation and groundwater level variations can range from several weeks to more than one year depending on the location. This delayed response leads to short-term recovery during wet periods and increases the persistence of groundwater deficits during successive dry years.

3.2.2. Projected impacts

To better quantify how groundwater systems will respond to future climate change, several groundwater modelling studies have been conducted in Belgium using a range of climate scenarios. A notable example is the study by Goderniaux et al. (2015), which focused on the Geer catchment, a chalk aquifer system in eastern Belgium. They developed a fully integrated surface–subsurface hydrological model (HydroGeoSphere) coupled with multiple regional climate model (RCM) projections under the SRES A2 emission scenario. Their results indicated a projected decline in groundwater levels of 7 to 20 meters and a reduction of 44% to 70% in streamflow by the end of the 21st century, depending on the climate scenario used. Similarly, Dams et al. (2012) applied a high-resolution set of 28 climate change scenarios on groundwater system for a Flemish lowland catchment. Their results for the end of 21st century indicated an average decrease in annual recharge of 7%, with projections ranging between a 20% decrease and a 7% increase, in comparison with the reference period 1960–1990.

However, it is important to note that the climate scenarios used in these studies are now more than a decade old. Since then, climate projections have evolved, and more recent models reflect a greater complexity in future precipitation patterns. While the ongoing increase in mean temperatures is broadly accepted, precipitation trends are more difficult to predict due to increased variability, seasonal shifts, and a higher likelihood of hydrological extremes such as intense rainfall events or prolonged droughts. Nevertheless, higher temperatures, more frequent and intense droughts, and growing urbanisation pressures will likely exacerbate groundwater stress, which reinforces the urgent need to preserve and manage groundwater resources sustainably.

4. The Hesbaye chalk aquifer

4.1. General background

In the framework of this PhD thesis, the focus is placed on the Hesbaye chalk aquifer, a transregional groundwater body that extends across Wallonia and Flanders in eastern Belgium (Figure 4). The aquifer underlies the Geer basin and plays a fundamental role in regional water supply. In Wallonia, the aquifer is notably exploited by the CILE, supplying approximately 15 million cubic meters of water annually to the city of Liège through pumping wells and drainage galleries (CILE, 2022), making it one of the most significant chalk aquifers in Belgium in terms of both spatial extent and abstraction volumes.

The unconfined portion of the aquifer covers approximately 350 km² in the southeastern Hesbaye plateau. It is bounded to the south and east by the Meuse valley, to the west by the Mehaigne catchment, and to the north by the Geer River. North of the Geer, the aquifer becomes confined beneath Cenozoic formations of lower permeability. The topography of the plateau gently slopes northward, with altitudes ranging from 206 m in the southwest to 80 m in the northeast (Orban *et al.*, 2014a).

The hydrological network interacting with the aquifer is relatively sparse, particularly in the unconfined southern parts, leading to the naming “Hesbaye sèche” (dry Hesbaye) for the region.

Land use in the Geer basin is mostly agricultural, accounting for approximately 68.5% of the total surface area (Orban *et al.*, 2014a). This is largely a result of the highly fertile loess-derived soils that cover much of the plateau (CFDT, 2009). The combination of productive soils and relatively flat terrain has encouraged intensive farming practices, which has consequently introduced increasing pressures on groundwater quality through nitrate and pesticide leaching (Batlle Aguilar *et al.*, 2007; Hakoun *et al.*, 2017a). These pressures are particularly significant in the unconfined part of the aquifer, where direct infiltration is more likely due to limited low-permeability soil cover.

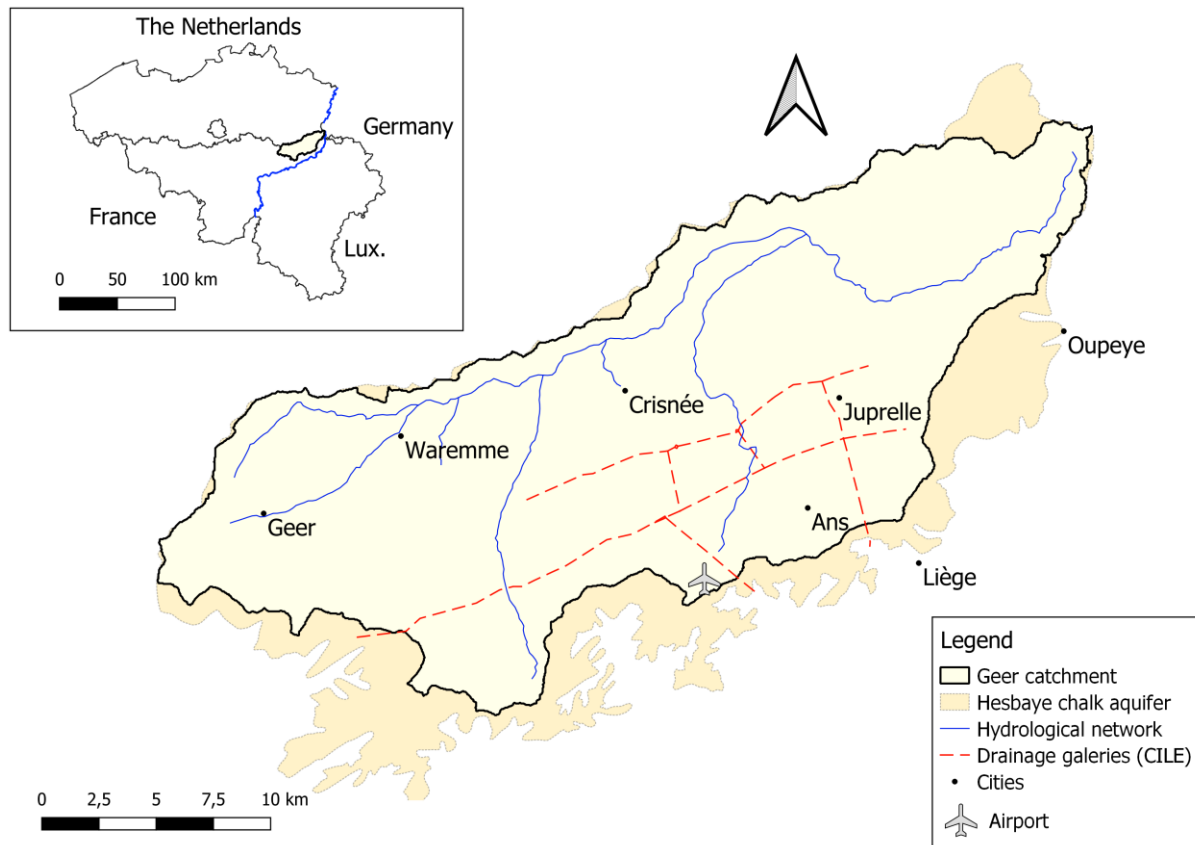


Figure 4. Location of the Geer basin at the national and regional scale.

4.2. Geological setting

The Hesbaye chalk aquifer is hosted within a sedimentary sequence dipping gently to the north, and composed of Upper Cretaceous to Cenozoic formations that overlay a Paleozoic basement (Orban *et al.*, 2014a). The geological structure of the Hesbaye Plateau results from the post-Variscan peneplanation of the Paleozoic basement, followed by a major Cretaceous marine transgression progressing from northeast to southwest, which led to the deposition of carbonate formations that now constitute the main aquifer system (Orban *et al.*, 2014a).

The geological formations underlying the Hesbaye Plateau are classically described from bottom to top as follows:

- At the base of the sedimentary sequence lies the Vaals formation, of Lower Campanian age, that consists of glauconitic marls and smectite-rich clays with variable carbonate content (20–35% CaCO_3). Due to its very low hydraulic conductivity, this formation constitutes the impermeable low boundary of the Hesbaye chalk aquifer and limits vertical groundwater flow toward the Paleozoic basement.
- The Upper Campanian white chinks, belonging to the Gulpen Formation, form the main body of the chalk aquifer. These white and fine-grained chinks occur in regular bedding and reach an average thickness of approximately 20 m, representing nearly two-thirds of the total chalk thickness in the region. They are characterised by high matrix porosity, which

provides significant groundwater storage capacity, while permeability remains low such that groundwater flow is mainly controlled by fractures and fissures.

- Within the upper part of the Gulpen Formation, the Campanian chalks are overlain by a persistent indurated chalk level, commonly referred as *hardground*, indicating the transition toward the Maastrichtian. This horizon exhibits reduced permeability and may act as a semi-confining layer between the underlying Campanian chalks and the overlaying units, except where locally fractured.
- Above this transition level, the Maastrichtian chalks that are also attributed to the upper part of the Gulpen Formation, consist of grey and slightly marly chalks. These units are generally more fractured than the underlying Campanian chalks and therefore display higher effective hydraulic conductivity. As a result, they play a key role in controlling groundwater flow within the aquifer system.
- At the top of the Cretaceous sequence, the chalk formations are locally affected by intense weathering, leading to the development of altered calcareous facies enriched in residual flints.
- The Upper Cretaceous chalks are overlain by Paleogene sands and clays, which are discontinuous across the Hesbaye Plateau. These deposits consist mainly of fine sands with intercalated clayey layers and contribute to the confinement of the chalk aquifer in the northern part of the Hesbaye region.
- Finally, the Hesbaye Plateau is covered by widespread Quaternary loess deposits, with thicknesses typically ranging from 2 to 20 m. These loam-rich soils originate from aeolian processes during the last glaciation and contribute significantly to the agricultural fertility of the region (CFDT, 2009). From a hydrogeological perspective, although loess exhibits relatively low permeability, it promotes slow, diffuse infiltration toward the underlying chalk formations and acts as an effective natural filter for percolating water.

4.3. Hydrological setting

The aquifer is exploited via a network of approximately 45 km of draining galleries and pumping wells developed within the fractured chalk layers. Hydrologically, the aquifer is largely unconfined in the central and southern parts of the basin but becomes progressively confined in the northern part beneath Cenozoic formations, especially north of the Geer River. Loess sediments that cover most of the Hesbaye plateau also exert a strong control on infiltration dynamics. In the southern and eastern *dry Hesbaye*, loess thickness is thinner and infiltration into the chalk is more direct. Conversely, in the northern *wet Hesbaye*, thicker loess layers reduce soil permeability, leading to more surface runoff and a denser fluvial network. The hydrographic network is relatively sparse and primarily composed of the Geer River and its tributaries such as Roua and the Yerne. Its connexion with the Hesbaye chalk aquifer is limited, except locally along lower reaches of the Geer where piezometry reveals hydraulic connection (Orban *et al.*, 2014a).

Hydraulic gradients are directed northwards, following the structural dip of the geological layers, ranging from 0.01 in the south to 0.003 near the Geer. This overall groundwater flow direction is notably depicted on Figure 5, which presents the piezometric map of the Hesbaye chalk aquifer during low-water conditions (SPW, 2025). The aquifer is characterized by dual porosity: a 40 %

porous matrix that stores water and a fracture network ($\sim 1\%$ effective porosity, $K \approx 10^{-4} \text{ m s}^{-1}$) that governs groundwater flows.

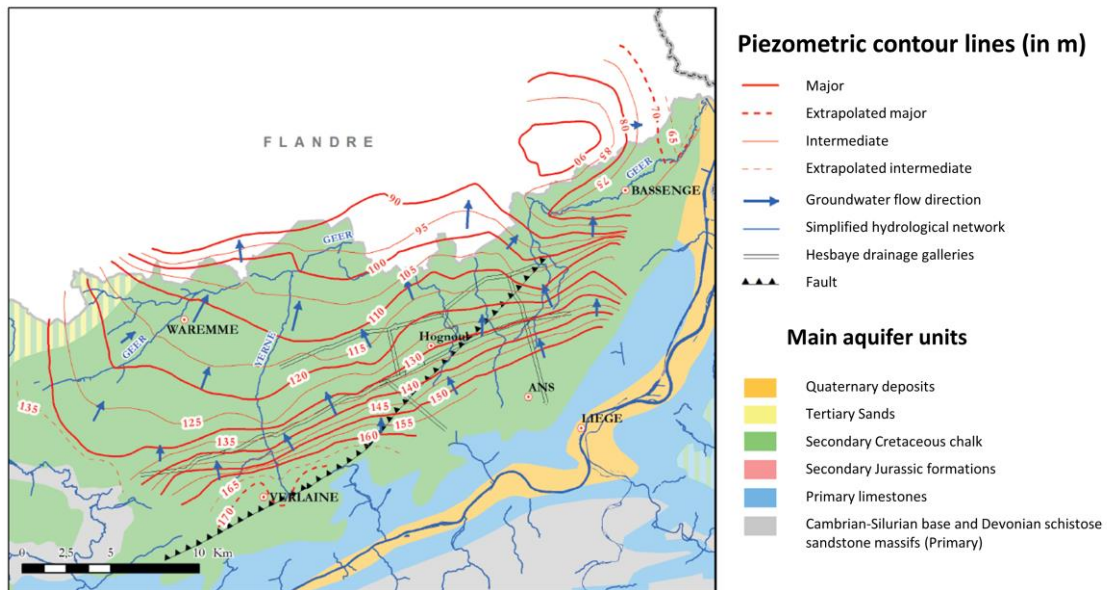


Figure 5. Piezometric map of the Hesbaye chalk aquifer (2008). Modified from SPW (2025)

However, as already extensively explained in section 3.2.1, a significant decline in groundwater levels has been documented when comparing 1990-2020 period to 1960-1990 (Goderniaux et al., 2023). This decreasing tendency is largely attributed to a decrease in mean annual recharge, reflecting the impact of climate change on the groundwater resources. The declining trend is also reflected in the evolution of the hydrological balance in the Geer basin between 2000 and 2021 (Figure 6). During this period, annual precipitation shows a clear decreasing trend, while actual evapotranspiration remains relatively steady. As a result, a greater proportion of the incoming water is lost through evapotranspiration, leaving less effective water available for recharge. In parallel, potential evapotranspiration increases in response to the overall rise in temperature. The combined effect of these climatic changes leads to a progressive decline in groundwater recharge, while outlet annual discharges diminished from nearly half of its volume between 2000 and 2021. Given that groundwater abstraction volumes have remained relatively constant over this period, the observed decline in groundwater levels is primarily attributed to climatic factors rather than to anthropogenic. It is however important to interpret these findings with caution, as a 20-year observation window remains relatively short for assessing long-term climatic trends. However, while some uncertainty remains regarding the future evolution of precipitation patterns, the increase in evapotranspiration is inevitable as a direct consequence of rising temperatures.

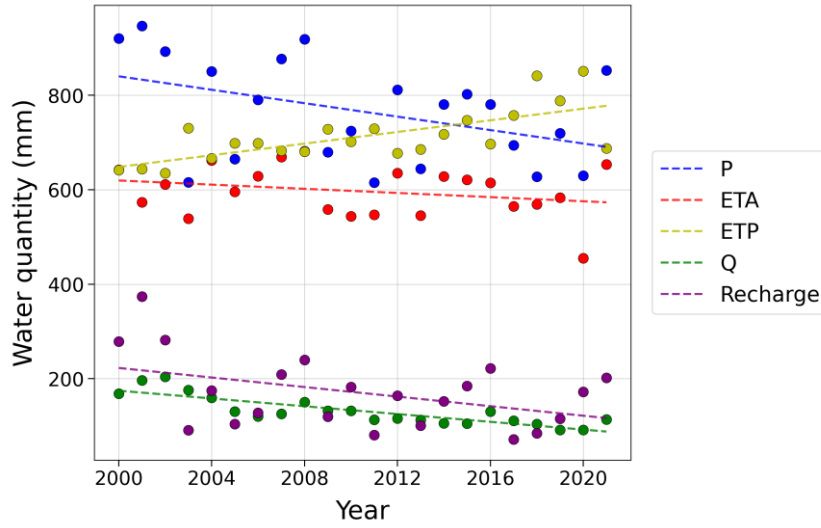


Figure 6. Evolution of the hydrological balance in the Geer basin from 2000 to 2021. Annual pumping rates and groundwater storage variations are not included. P refers to precipitation, ETA to actual evapotranspiration, ETP to potential evapotranspiration, Q to outlet discharge, and Recharge to effective water. The effective water is considered equivalent to groundwater recharge, assuming negligible surface runoff in the Geer basin due to its flat topography.

4.4. Groundwater deficit

The persistent decline in piezometric levels observed across the Hesbaye chalk aquifer highlights the need to quantify the groundwater storage deficit that has developed over recent decades. In general terms, groundwater storage variations (Δres) over a given period can be expressed through a hydrogeological balance written as:

$$P = ETA + Q_e + Q_p + \Delta Res \quad (1)$$

Where P refers to precipitation, ETA to actual evapotranspiration, Q_p the total abstracted volumes, and Q_e the discharge measured at the outlet of the hydrological basin.

Based on the work of Andriamialisoa (2024), three independent and complementary approaches were used to estimate Δres in the Hesbaye chalk aquifer over the period 2000-2020: (i) the water table fluctuation method, (ii) a basin-scale hydrogeological balance, and (iii) baseflow recession analysis of the Geer river.

A synthesis of the results obtained using the three methods is presented in Table 1. Despite relying on different assumptions and datasets, all approaches consistently indicate a significant groundwater storage deficit over the study period. Estimated deficits range between approximately 50 and 80 million cubic meters (Mm^3) over 20 years. On average, the magnitude of the groundwater deficit is equivalent to approximately two years of groundwater abstraction in the region.

Table 1. Summary of groundwater storage deficit estimates in the Hesbaye chalk aquifer over the period 2000–2020 based on three complementary methods defined in Andriamialisoa (2026) study. ω refer to effective porosity, ΔH to piezometric level differential, P to precipitation, ETA to actual evapotranspiration, Q_p the total abstracted volumes, Q_e the discharge measured at the outlet of hydrological basin, Q_b the baseflow and t to the time.

Method	Governing equation	Estimated deficit (Mm ³)	Main assumptions and remarks
Water table fluctuation	$\Delta Res = \omega \times \Delta H$	24 to 61	Effective porosity $\omega = 2\text{-}5\%$; Higher values reflect locally fractured chalk.
Hydrogeological balance	$\Delta Res + \varepsilon = P - ETA - Q_e - Q_p$	74	Basin-scale estimate; ε includes groundwater outflows toward neighbouring basins
Baseflow recession analysis	$\Delta Res = \int_{t_1}^{t_2} Q_b dt = \frac{Q_{b1} - Q_{b2}}{\alpha}$	57	Based on long-term baseflow decline of the Geer river

Although uncertainties remain regarding assumptions taken between selected methods and lateral groundwater outflows toward neighbouring basins, the convergence of results across methods provides a robust indication of a groundwater deficit rather than short-term climatic variability. These findings are consistent with long-term recharge reductions reported by Goderniaux *et al.* (2023) and confirm that climate-driven changes are already impacting groundwater storage in the Hesbaye chalk aquifer.

From a groundwater management perspective, the magnitude of the observed deficit is significant. Although the aquifer maintains its considerable storage capacity and buffering potential, the persistence of negative storage trends implies that current abstraction levels may be difficult to sustain under future climate conditions. This highlights the need to consider adaptive groundwater management strategies aimed at stabilising groundwater levels under evolving climatic conditions.

4.5. Managed aquifer recharge as a mitigation measure in Hesbaye

4.5.1. Definition and objectives

In this context, managed aquifer recharge (MAR) appears as a potential mitigation measure against groundwater deficits, that aims in actively enhancing recharge rather than relying on natural recharge replenishment alone. The Hesbaye chalk aquifer therefore constitutes a particularly relevant case study for assessing the feasibility and limitations of MAR as part of a broader climate adaptation strategy for groundwater management.

MAR is defined as “the purposeful recharge of water to aquifers for subsequent recovery or for environmental benefit” (Dillon, 2009). MAR can be used to meet a variety of objectives depending on the hydrogeological context, socio-environmental pressures, and water availability. These include notably: (i) securing water availability in a changing climate, (ii) restoring or maintaining the

quantitative status of aquifers, (iii) improving groundwater quality, (iv) supporting baseflow maintenance, (v) countering seawater intrusion in coastal aquifers, (vi) reducing flood risks, and (vii) mitigating subsidence. Note that real MAR case studies are often associated with multiple objectives, rather than one.

The Hesbaye chalk aquifer presents a valuable case study for examining the implementation of MAR as a measure to mitigate the effects of climate change. Given that the aquifer is not overexploited and pumping rates have remained relatively constant, enhancing recharge is likely to be more effective than solely reducing abstraction rates, which are necessary for public water distribution. The primary objective of a MAR project in this context would be to secure the long-term groundwater supply and reduce the aquifer's vulnerability to droughts, rather than to restore groundwater levels or address an environmental issue.

In Wallonia, the growing interest in managed aquifer recharge as a potential response to groundwater stress has also been reflected in recent regional initiatives. Among these, the MARWAL project aimed to explore the technical, regulatory, and economic feasibility of using alternative water sources for MAR in Wallonia, with the objective of enhancing groundwater resilience at the regional scale. While the present thesis is not limited to the scope of this project, it builds on the same regional context and contributes a detailed hydrogeological and water-quality-oriented assessment of MAR feasibility in the Hesbaye chalk aquifer.

4.5.2. MAR methods

A wide variety of MAR methods can be used to enhance groundwater storage, depending on the local hydrogeological setting, water availability, water quality, and recharge objectives (seasonal storage, water quality improvement, and counter seawater intrusion, among others). MAR techniques are generally classified into water spreading methods, well-based techniques, bank filtrations and in-channel modifications. Moreover, each method is suited to specific conditions and their performances depends heavily on factors such as soil permeability, aquifer transmissivity, water quality, land availability, economical constraints. Figure 7 depicts most existing MAR methods that are divided into:

- **Water spreading methods:** these consist in promoting the gravitational percolation of the recharge water from the surface down to the aquifer thanks to structures at ground level, such as infiltration ponds or trenches, that retain recharge water for infiltration. These techniques are commonly used to replenish shallow unconfined aquifers and provide the advantage to naturally filter and purify the water as it infiltrates through the soil, notably through soil aquifer treatment (SAT).
- **Well-based techniques:** these methods directly introduce recharge water into the aquifer via wells, bypassing the vadose zone. These techniques are especially suited to deep or confined aquifers, when the surface has low permeability, or when surface land is too scarce for surface infiltration. Infiltration rates can be much higher than for spreading methods as the water is injected under pressure through a screened borehole.
- **Riverbank filtration:** this technique involves the indirect abstraction of water from a river or lake via abstraction wells located near the water body. As water moves laterally through the riverbank sediments towards the well, it undergoes natural filtration that removes

particulates, pathogens, and some chemical contaminants. Bank filtration is most effective in areas where rivers are hydraulically connected to shallow, permeable aquifers, and where river stage is relatively stable.

- **In-channel modification:** to a lesser extent, in-channel modifications turn a riverbed into a natural area where surface water can percolate into the subsurface. Small dams are built across the channel to slow floodwater and create temporary pools. While surface water is collected in the pond, it slowly infiltrates through the sandy riverbed, filling up the shallow aquifer beneath. Later, well located further downstream recover the recharge water mixed with the native groundwater.

In the context of this study, the Hesbaye chalk aquifer presents distinct advantages such as its relatively high matrix porosity ($\approx 40\%$), enabling significant storage of water. Additionally, the presence of fractures in the chalk allows efficient drainage toward wells, allowing for effective recovery of the recharge water. In the Walloon region, the aquifer is primarily unconfined but becomes progressively confined northward. Despite its unconfined nature, the aquifer is not necessarily shallow. Depending on the thickness of the loess and the flint/conglomerate layers overlying the chalk, the water table may occur at depths ranging from 20 to 30 meters.

Direct injection methods could technically bypass the loess layer and allow rapid recharge of the chalk aquifer. However, their implementation would require recharge water of very high quality and chemical compatibility with native groundwater to avoid direct contamination of this strategic drinking water resource. Moreover, when such water quality is already achieved, it would in most cases be more suitable for direct distribution rather than subsurface injection. In addition, bypassing the natural protective role of the loess layer would increase the vulnerability of the aquifer to contamination. For these reasons, direct injection methods are not addressed further in this thesis.

In-channel modification techniques are also not considered viable in the Hesbaye context due to the extremely limited hydrographic network within the Geer basin. In contrast, infiltration methods based on surface spreading are well suited to the local hydrogeological setting. The relatively fine texture and clay mineral content of the loess promote effective filtration of recharge water and provide an additional protective barrier against groundwater pollution. Consequently, surface spreading is retained as a relevant MAR method and is further examined in this thesis.

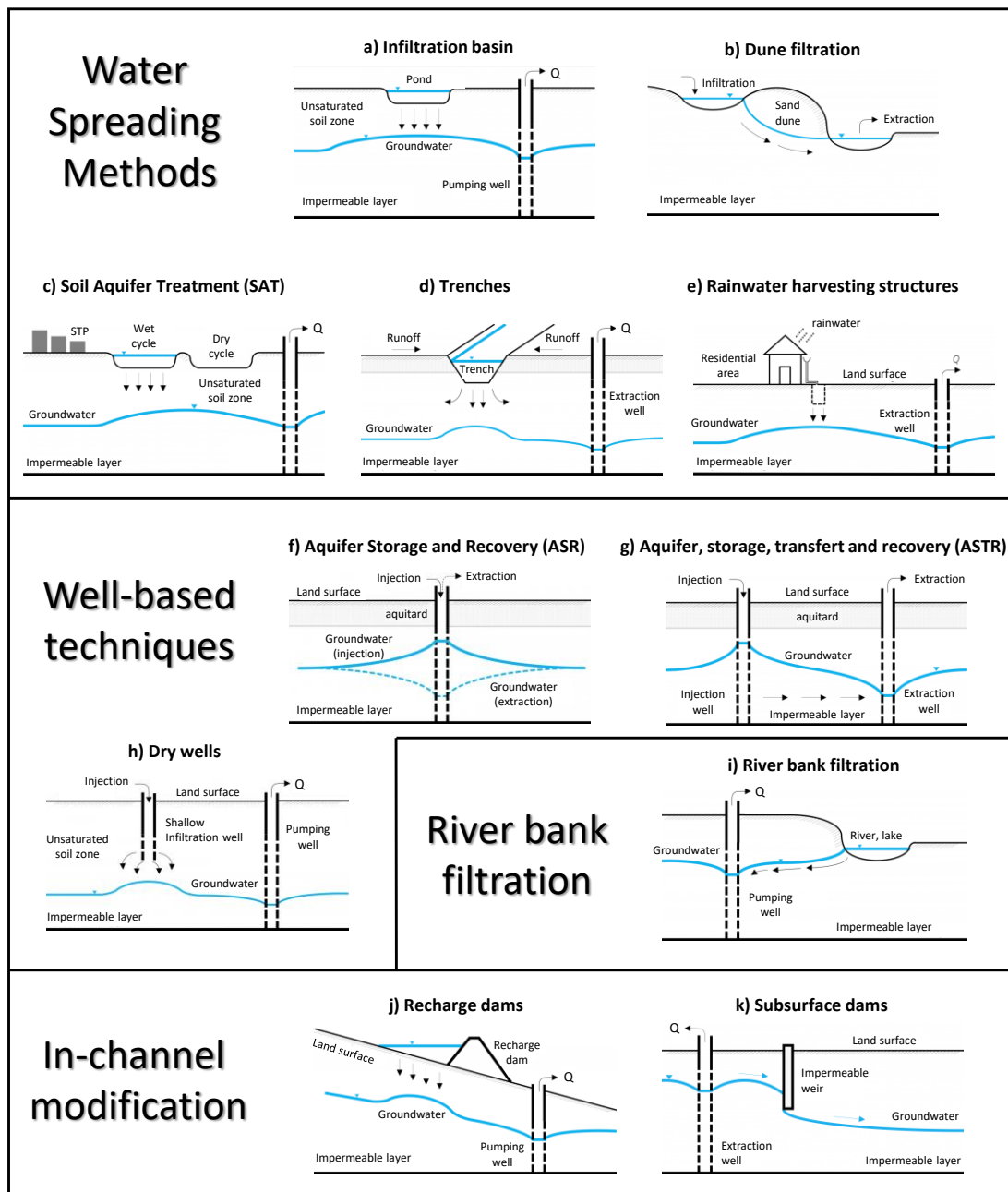


Figure 7. MAR methods separated in water spreading methods, well-based techniques, riverbank filtration, in-channel modification (adapted from INOWAS).

4.5.3. Recharge waters

In a MAR project, the water source is just as critical as the recharge method, even though both are correlated. The system's efficiency and sustainability depend mainly on the quality of the recharge water. Therefore, the chosen water source determines how much water is available, what pre-treatment is needed, and the long-term effects on both the infiltration system and the target aquifer. Around the world, many types of recharge water are used, each with its own advantages, limitations and suitability depending on the local hydrogeological conditions and socio-economic setting. The three main categories of potential recharge waters include:

- **Excess surface water** from rivers, lakes, or flood events is commonly used for MAR in regions with distinct wet and dry seasons. It is typically diverted during high-flow periods to infiltration systems when it would otherwise be lost as runoff. This water is generally abundant and cost-effective, but it typically carries suspended solids, organic matter, and microbial contaminants that can clog infiltration surfaces or degrade water quality if not properly managed. Furthermore, careful monitoring is required when surface water is taken from ecological sensitive areas or where downstream users depend on the river flow.
- **Stormwater/runoff** collected from urban areas is increasingly considered for MAR, as it can contribute both to reducing flood risk and to supporting groundwater recharge. Large volumes may be available during storm events, particularly in highly urbanised catchments where impervious surfaces promote rapid runoff. However, stormwater availability depends on rainfall patterns. In addition, its quality is highly variable and strongly influenced by land use.
- **Treated wastewater** is increasingly used for MAR, and particularly in water-scarce regions. Its main advantage lies in its continuous availability, independently of seasonal hydrological variability. When adequately treated, reclaimed water can provide a reliable and controlled source for groundwater recharge. However, treated wastewater may still contain residual organic micropollutants that require advanced treatment and long-term monitoring. In addition to technical constraints, the use of treated wastewater for MAR is often limited by public perception and regulatory acceptance.

In the context of the Hesbaye chalk aquifer, the selection of recharge water sources strongly depends on local conditions. The limited density of the surface water network within the Geer basin excludes surface water as a viable recharge option in this study. Treated wastewater represents a potential alternative, given the presence of several wastewater treatment plants in the area that produce relatively stable volumes throughout the year. The following section therefore presents a quantitative assessment of the different potential recharge sources in the Hesbaye region, with the objective of identifying waters that could be infiltrated as part of MAR operations.

4.6. Sources of alternative recharge water in Hesbaye

To design MAR operations in the Hesbaye region, it is essential to identify and characterize potential recharge water sources. Indeed, the spatial distribution and the quality of available waters will determine the technical feasibility and long-term sustainability of the infiltration system. As outlined earlier, different sources of water could be harvested such as excess surface water, stormwater, treated wastewater, and to a lesser extent desalinated water and rainwater.

Naturally, desalinated water is excluded from this study, as the Hesbaye region is located inland and far from any coastal area. Similarly, rainwater harvesting is not considered in this study since rooftop collection is typically suited for small-scale MAR operations, and the land use in the Geer basin is not predominantly residential. Finally, surface water is not retained as a viable option neither. Indeed, the hydrographic network of the Hesbaye plateau is not very dense, particularly in the unconfined southern part of the chalk aquifer (see section 4.3). Furthermore, most streams exhibit low flows regimes, which limits the reliable availability of excess water for infiltration. In addition, ecological constraints (baseflow maintenance) would also restrict the diversion of these already limited flows toward MAR systems.

As a result, wastewater and stormwater present alternatives of interest. These different water resources were identified and characterized in the context of this thesis, in collaboration with the MARWAL project (Brouyère, 2023, 2024). Figure 8 depicts the location and the annual exploitable volume of these potential water sources. The spatial distribution of these water sources exhibits a contrast within the Geer basin. WWTPs are mainly located near urban centres while stormwater basins are more dispersed and directly associated to impervious surfaces such as traffic or airport infrastructures. No WWTPs or stormwater basins were identified in the southwest where land use is predominantly agricultural and villages too small to have a WWTP. Finally, the inventory was restricted to the southern part of the Geer basin, which corresponds to the unconfined part of the Hesbaye chalk aquifer and therefore to the area where surface-based MAR is technically relevant and expected to have a direct effect on groundwater recharge. Consequently, potential sources located in the northern part of the basin were not integrated in this assessment.

Wastewater can be split up in two categories: treated effluents from wastewater treatment plants (WWTPs) and discharges from industries. Annual outflow volumes were compiled directly from measured wastewater flowrates at the outlets of the industries or WWTPs. The WWTPs that operate within the Geer basin have the advantage to provide continuous volumes throughout the year. However, their use remains sensitive due to public perception, potential regulatory restrictions and the need for advanced monitoring of residual organic micropollutants. Industrial wastewater discharges pose an even greater challenge, as their treatment level and composition are highly variable depending on the industrial process and on-site treatment capacity. For these reasons, it has been decided to focus primarily on urban runoff in this thesis.

Urban runoff emerges as a strong recharge water candidate for MAR operations. Even though a large proportion of land use is dedicated to agriculture in the Hesbaye region, large impervious surfaces are present due to urban, industrial and transport infrastructures. These infrastructures include the dense highway network as well as industrial zones in the southeast of the Geer basin, that include an airport which represents one of the largest impervious areas in the region. Following rainfall events, the generated runoff from these surfaces is systematically collected through stormwater management infrastructures, providing an operational basis for harvesting significant volumes for MAR. In some cases, these infrastructures also integrate preliminary treatment units such as sedimentation basins or hydrocarbon separators, which represents an additional advantage for recharge applications. Finally, the proximity of these stormwater basins to the production galleries would facilitate the recovery of recharged groundwater resources but also requires greater preventive measures to limit potential contamination. The next subsections therefore focus on the quantification of exploitable volumes and on the characterization of stormwater basins representative of both airport activities and road-traffic infrastructures.

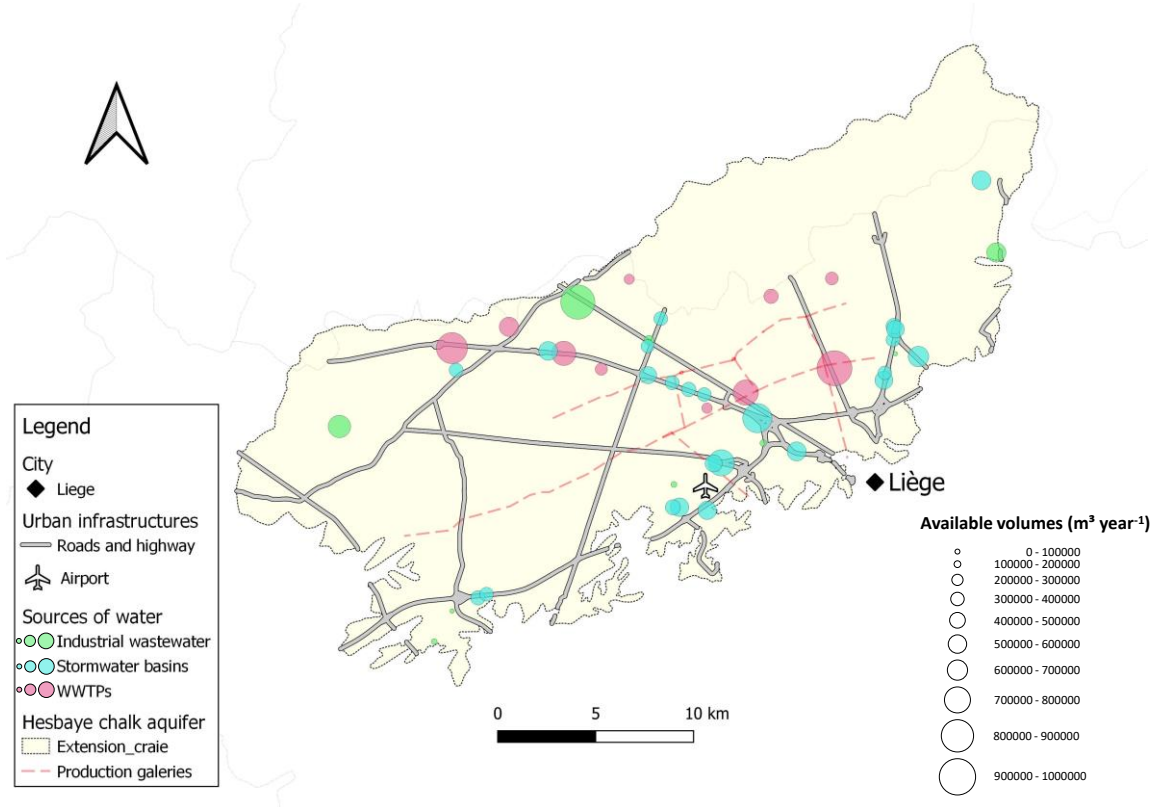


Figure 8. Location of potential recharge water sources in the Hesbaye region and their annual exploitable volumes. Annual volumes in this map were represented using the Flannery method, which applies a perceptual scaling factor to adapt circle sizes in proportional symbol maps, ensuring that differences in volumes are visually comparable across the different sources.

4.6.1. Exploitable runoff volumes

Urban runoff has been identified as a promising source of recharge water for MAR operations in the Hesbaye region. To assess its quantitative potential, it is necessary to estimate the annual exploitable volume that can be collected from each stormwater basin. This requires the knowledge of hydrological characteristics of the catchment area (runoff surface, runoff coefficient), rainfall statistics (annual average precipitation, extreme precipitation events) and basin design (storage capacity, outflow rate). In theory, the exploitable runoff volume can be estimated by:

$$V_{exp} = P \times S_r \times C_r - V_{loss} = P \times S_w - V_{loss} = V_{runoff} - V_{loss} \quad (2)$$

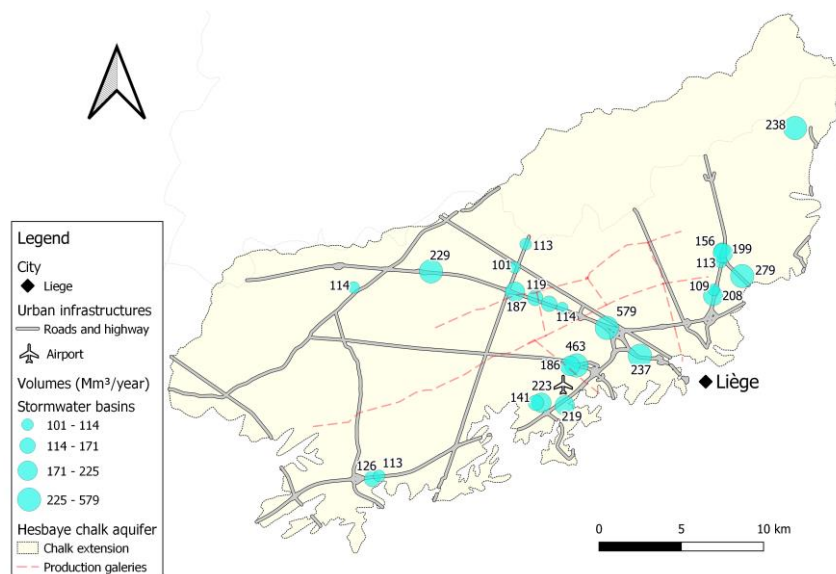
where V_{exp} is the exploitable runoff volume [L³], S_r the runoff surface or catchment area [L²], C_r the runoff coefficient [-], P the precipitation [L], S_w the weighted runoff surface [L²], V_{runoff} the raw runoff volume [L³], and V_{loss} = water losses [L³] that are mainly associated to evapotranspiration and negligible contribution of small rainfall events to generated runoff. Table 2 depicts classical runoff coefficient values depending on the associated land cover (SPW, 2023).

Table 2. Runoff coefficients per surface category (SPW, 2023)

Surface category	Runoff coefficient
forests, woods	0.05
meadows, gardens, grassy areas, lawns, parks	0.15
cultivated fields, moors, scrubland, green roofs, cemeteries, stone slabs	0.25
grass pavers	0.4
compacted earth surface, dirt roads	0.5
open-joint pavers, permeable pavers	0.7
paved driveways, paved sidewalks, parking lots, impermeable surfaces	0.9
roofs, roads, water bodies	1

When these parameters are available, the annual exploitable volume can be calculated directly. In practice however, the situation is more complex as detailed design parameters such as catchment area or outflow rates are not available for most documented stormwater basins in Wallonia. A relationship that links the mean annual precipitation quantity and stormwater basin storage volume with the exploitable runoff volume has therefore been developed by Raisô (Durieux *et al.*, 2024), one of the different collaborators of the MARWAL project (Brouyère, 2023, 2024). This methodology is explained in further detail in Annex A and had been employed at the scale of Wallonia to include different annual precipitation ranges depending on the geographical position.

Using this approach, the annual runoff volume that could realistically be captured for MAR can be estimated from just two inputs: the stormwater basin storage capacity and the mean annual precipitation at the site. This is a key advantage, since these are typically the only consistently available data, whereas detailed design and operational information for stormwater basins are rarely reported. Despite the uncertainties inherent to such a simplified method, it provides a solid first-order estimate of exploitable annual volumes for stormwater basins across the Hesbaye region. The resulting estimates were computed for each stormwater basin and are represented on the map in Figure 9.

Figure 9. Annual exploitable runoff volumes in $\text{Mm}^3 \text{ year}^{-1}$ in the Hesbaye region (adapted from Durieux *et al.* (2024)).

4.6.2. Selected stormwater basins

After the quantitative evaluation of the potential recharge sources for MAR, it is necessary to identify a limited number of stormwater basins that are representative of urban runoff in the Hesbaye region. From a logistical and financial perspective, it is indeed not feasible to sample all available basins in the region. This selection allows for a more detailed qualitative assessment, focusing on chemical quality of the collected runoff water. As depicted in Figure 8 and Figure 9, stormwater basins are mainly concentrated around road infrastructures and the airport. Representative basins were therefore chosen for each category of runoff: traffic- and airport-related. For anonymity reasons, the different basins will not be presented under their real names but instead using identifiers: T1 and T2 for traffic-related basins, and A1, A2, and A3 for airport-related basins.

Traffic-related basins

Stormwater basins associated with road infrastructures are managed by the *Service public de Wallonie – Mobilité et Infrastructures* (SPW-MI). For each basin, SPW-MI provides a descriptive sheet that includes an overall quality score. This score is based on several criteria: maintenance of vegetation, visible pollution, operational performance of the basin, completeness of the equipment, and the condition of associated hydraulic structures.

In the Hesbaye region, only two achieved a global quality score above 75%. These were therefore selected for qualitative analysis. Their characteristics are summarized in Table 3. Both collect runoff from the national roads, which is then discharged into a nearby stream.

Based on their storage capacity and following the methodology described in section 4.6.1, the estimated annual exploitable runoff volume for each basin is approximately 100,000 m³. Field visits and noticeable odours further suggest that in addition to stormwater, the basins may also receive unregistered wastewater discharges. As a result, the analysed water is likely more representative of runoff-wastewater mixture than of pure runoff. Figure 10 shows illustrative photographs of the two basins.

Table 3. Parameters associated to the selected traffic-related basins. Lambert 72 refers to the geographical coordinate system in Belgium.

Parameters		Stormwater basin	
		T1	T2
Basin design (m)	Length	55	71
	Width	38	35
	Length bottom	50	63
	Width bottom	30	29
	Height	5	4.65
Volumes (m ³)	Basin	8934	9986
	Exploitable annual runoff	101000	113000
Water network	Upstream	Runoff from national road	
	Downstream	Nearby stream	



Figure 10. Photos of selected traffic-related stormwater basins.

Airport-related basins

Liège airport also represents a vast impervious area in the Hesbaye region, where large volumes of runoff water are generated during rainfall events. Airport runoff is managed through an extensive drainage network that conveys water towards stormwater retention basins designed to temporarily store and regulate flows before being released to downstream receiving bodies. Among the existing facilities, three basins are particularly relevant for our study:

- 1) A1 stormwater basin is the largest and most significant stormwater retention facility on the airport site. It drains a surface area of approximately 345 hectares. The basin offers a storage capacity of around 41,000 m³ and discharges to the Meuse River via a regulated outlet. Unlike traffic-related stormwater basins, its design parameters are well documented, including the contributing catchment, land cover and runoff coefficients. In Liège, average annual precipitations above 1mm day⁻¹ reach 627.5 mm year⁻¹. Accounting for approximately 30% evaporation losses, an effective rainfall of about 439.25 mm year⁻¹ is available for runoff generation. Applying runoff coefficients to the contributing surfaces and the effective rainfall (Eq. 2), the exploitable annual runoff volume is estimated at 1038.8 thousand m³. Given its scale and strategic location, A1 stormwater basin serves as the airport's primary stormwater outlet.
- 2) A2 stormwater basin is smaller but plays a key role in managing airport runoff, by draining an area of roughly 80 hectares, which includes both airport areas as well as sections of the nearby highway, covering both road surfaces and embankments. With an estimated storage volume of 19,000 m³, the basin discharges runoff water into a nearby stream, following preliminary treatment through sedimentation and hydrocarbon separation. Applying a similar methodology than for basin A1, an exploitable runoff volume of 276.5 thousand m³ is estimated.
- 3) A3 stormwater basin also receives airport runoff but is not considered in this study. It covers a small catchment (62.8 ha) and is logistically less accessible for monitoring.

If airport runoff from A1 and A2 stormwater basins can be captured and used for MAR, the best scenario would allow the infiltration of over 1 million m³ of water annually into the chalk aquifer. This represents more than half of the annual estimated groundwater deficit in the Hesbaye chalk aquifer (see Section 4.4) and would reduce the hydric stress of its exploitation. However, beyond these promising quantities, the feasibility of MAR ultimately depends ultimately on the quality of available airport runoff, which requires accurate assessment.

5. Synthesis

The elements presented in this chapter establish the framework within which managed aquifer recharge is examined for the Hesbaye chalk aquifer. The hydrogeological characteristics of the aquifer, the documented groundwater deficit, and the brief review of MAR techniques and recharge water sources together define the scope of the approaches considered in this study. Within this context, the analysis conducted here leads to a focus on surface infiltration methods, which allow recharge water to percolate through the loess cover and benefit from its natural filtering capacity, ensuring a first level of protection for this strategic groundwater resource.

Among the potential recharge waters, urban runoff is retained as the primary water source investigated in this thesis. At the scale of the Geer basin, runoff generated on large impervious surfaces (road infrastructures and major transport platforms) represents a locally available resource that is already actively managed through stormwater collection networks and retention basins. These infrastructures provide operational sites for capturing and quantifying the mobilized runoff volumes. The thesis therefore focuses on selected stormwater basins representative of the dominant urban runoff contexts in Hesbaye, with emphasis on runoff collected from large impervious areas associated with road-traffic and airport-related catchments.

Building on this contextual framework, chapter 3 addresses the nature and behaviour of contaminants potentially present in urban runoff, with particular attention to their origin and mobility in subsurface environments. This provides the scientific basis required to assess groundwater quality risks associated with runoff-based managed aquifer recharge in the Hesbaye chalk aquifer.

Chapter 3

Contaminants in urban runoff

1. Introduction

As introduced in Chapter 2, runoff water generated on impervious surfaces represents a potential alternative resource for MAR, particularly in peri-urban environments where large volumes can be mobilised during rainfall events. However, the use of such waters in surface infiltration systems raises important questions regarding water quality and the possible transfer of contaminants to subsurface environments. These concerns are especially critical in regions where aquifers constitute a major source of drinking water, such as the Hesbaye chalk aquifer supplying the Liège area.

Urban runoff is characterised by a highly heterogeneous chemical composition, resulting from the accumulation and wash-off of pollutants originating from a wide range of diffuse and point sources. These include traffic-related emissions and abrasion products (e.g. tyre and brake wear), atmospheric deposition, weathering of construction materials, and operational activities associated with transport and urban infrastructures. In addition, runoff may contribute to the remobilisation of contaminants previously deposited on surfaces, particularly in historically industrialised regions. Understanding the nature of these contaminants and the processes governing their transfer during infiltration is therefore essential when evaluating the suitability of runoff waters for MAR practices.

Within the Hesbaye region, urban runoff constitutes a relevant point of attention for MAR feasibility, particularly in the south-eastern area where land use is strongly influenced by urban development and transport-related infrastructures. Among these, large transport platforms such as airports represent specific settings characterised by extensive impervious surfaces and distinct operational activities, which can result in runoff waters with a chemical composition that differs from those typically observed in residential or industrial urban areas. The large paved areas associated with runways, taxiways, and aprons can generate significant runoff volumes during rainfall events. Capturing and infiltrating this water could reduce flooding risks on the airfield during intense precipitations while contributing to groundwater recharge. At the same time, operational, safety, maintenance, and seasonal activities carried out on such infrastructures may introduce specific contaminants into runoff waters. Pollutants associated with these activities, are therefore also considered within the broader framework of urban runoff contamination addressed in this chapter.

In this context, the present chapter provides an overview of contaminants commonly reported in runoff waters, with particular attention to organic micropollutants relevant to groundwater protection. The chapter further discusses the key physicochemical processes controlling the mobility, attenuation, and persistence of these contaminants during infiltration through the unsaturated zone. This synthesis provides the relevant basis required for the interpretation of field observations and experimental investigations presented in the following chapters.

2. Contaminants commonly reported in urban runoff

2.1. Inorganic contaminants

2.1.1. Heavy metals

Heavy metals such as zinc (Zn), copper (Cu), lead (Pb), cadmium (Cd), and nickel (Ni) are among the most well-documented pollutants in urban runoff (Nabizadeh *et al.*, 2005; Brown and Peake, 2006; Aryal *et al.*, 2010; Helmreich *et al.*, 2010; Zgheib *et al.*, 2012; Gunawardena *et al.*, 2013; Chen *et al.*, 2016; Masoner *et al.*, 2019; Müller *et al.*, 2020). These predominantly originate from road traffic and related infrastructure. Zn is mainly released from tyre deterioration as it is used as a vulcanisation

activator in tire rubber (McKenzie *et al.*, 2009; Alam *et al.*, 2022). Cu is largely derived from brake pad abrasion, where it is used to improve heat dissipation to prevent wear (Österle *et al.*, 2010). Common sources of Ni include lubrication oil, diesel exhaust, asphalt paving, and metal plating (Duke *et al.*, 1998; Singh *et al.*, 2006; Fiala and Hwang, 2021). On the other hand, Pb in urban runoff is commonly associated with the weathering of Pb-containing paints applied to buildings, infrastructure, and vehicles (Davis and Burns, 1999; Müller *et al.*, 2020). While lead (Pb) was historically a key additive in gasoline, its use has been strictly prohibited in the European Union since 1993 (Thomas, 1995), leading to the universal adoption of lead-free fuel (Müller *et al.*, 2020). Finally, Cadmium is present as a trace metal in brakes and tyres at very low concentrations (McKenzie *et al.*, 2009; Helmreich *et al.*, 2010). In airports, Component degradation and corrosion during maintenance may release metals such as Cd, Pb, Ni, Cr, Cu and Zn (Sulej-Suchomska *et al.*, 2024). Although these metals are often particle-bound, metal transport is facilitated with fine particulates that are washed off during high-intensity rainfall (Jartun *et al.*, 2008a). In addition, aircraft engines and ground support vehicle emit fine particulates enriched in heavy metals (Zn, Cu, Pb, Ni, Cr, Cd) (Sulej *et al.*, 2012; Sulej-Suchomska *et al.*, 2024). The subsequent wash-off of these enriched particles during rainfall may mobilize these pollutants into the drainage system.

The concentrations of heavy metals in urban runoff exhibit significant variability, often spanning several orders of magnitude depending on traffic density and land use. Typically reported Event Mean Concentrations (EMCs) for the most common metals include 50 to 1500 $\mu\text{g L}^{-1}$ for Zn, 5 to 200 $\mu\text{g L}^{-1}$ for Cu, 5 to 150 $\mu\text{g L}^{-1}$ for Pb, 2 to 50 $\mu\text{g L}^{-1}$ for Ni, and 0.1 to 5 $\mu\text{g L}^{-1}$ for Cd (Helmreich *et al.*, 2010; Zgheib *et al.*, 2012; Gunawardena *et al.*, 2013; Masoner *et al.*, 2019; Müller *et al.*, 2020). In specific settings like airports or high-traffic highways, concentrations of Zn and Cu can occasionally reach the upper limits of these ranges due to the high frequency of mechanical wear.

In addition to direct traffic-related emissions, atmospheric deposition represents an important diffuse pathway for all these metals (Müller *et al.*, 2020). Metals emitted by exhaust gases, industrial activity, or dust resuspension can be deposited onto impervious surfaces, where they accumulate and are washed off during rainfall events (Wicke *et al.*, 2012). Other sources of pollution include weathering and leaching from metal roofs, gutters, and façade materials (Charters *et al.*, 2025). This is especially the case in older buildings where anti-corrosion paints and coatings may contain high concentrations of metal-based additives such as Pb or Zn (Davis and Burns, 1999; Kszos *et al.*, 2004). In historically industrialised regions such as in Liège surroundings, atmospheric emissions from former industrial activities may have led to the accumulation of metals in soils, dust, and surface materials (Liénard *et al.*, 2014), which can subsequently be remobilised during rainfall events and contribute to runoff contamination (Hill *et al.*, 2023).

Due to their persistence, potential toxicity, and occurrence in both dissolved and particulate phases, these metals are of particular concern in urban runoff, especially if this water is intended to be recharged via MAR systems (Masoner *et al.*, 2019). However, while their presence must be carefully monitored, their actual transport to the aquifer is generally limited, as most heavy metals tend to exhibit strong sorption onto soil particles during percolation through the unsaturated zone (Stone and O'shaughnessy, 2005; B *et al.*, 2021).

2.1.2. Salts

During winter conditions, urban runoff frequently contains elevated concentrations of inorganic salts, primarily as a result of cold road and pavement maintenance practices (Haake *et al.*, 2022). De-icing and anti-icing operations constitute the dominant source of salts in urban environments, with sodium chloride (NaCl) being the most widely applied compound due to its low cost and high efficiency (Cruz *et al.*, 2022; Gruber *et al.*, 2023). As a consequence, runoff generated during and following winter periods often exhibits increased concentrations of sodium (Na^+) and chloride (Cl^-) (Rivett *et al.*, 2016).

The concentration of salts in urban runoff varies significantly across seasons. While background chloride (Cl^-) levels in non-winter urban runoff typically range from 10 to 100 mg L^{-1} , concentrations during de-icing periods can increase up from 500 to 5000 mg L^{-1} (Müller *et al.*, 2020; Haake *et al.*, 2022; McQuiggan *et al.*, 2022). Sodium (Na^+) concentrations follow similar seasonal trends, often ranging from 100 to 2500 mg L^{-1} during peak winter maintenance (Rivett *et al.*, 2016).

In addition to chloride-based de-icers, alternative organic products are increasingly used in contexts where corrosion control or operational constraints limit NaCl application (Giebson *et al.*, 2010; P. Li *et al.*, 2023). These alternatives include acetate- and formate-based salts such as potassium acetate, sodium acetate, and potassium formate, which are commonly applied on transport infrastructures such as highways, bridges, and airport pavements (P. Li *et al.*, 2023). Pavement de-icers based on these compounds are designed to reduce corrosion of concrete and metallic structures (P. Li *et al.*, 2023). Urea-based de-icers were widely applied in the past but are now subject to restrictions, although they may still be used in some facilities (Jia *et al.*, 2018). In airport environments in particular, where these compounds are widely used to reduce corrosion, concentrations in runoff can reach several hundreds to over 1000 mg L^{-1} during active winter operations (Giebson *et al.*, 2010; P. Li *et al.*, 2023). Unlike chloride, these compounds contribute significantly to the Chemical Oxygen Demand (COD) of runoff due to their organic nature (Corsi *et al.*, 2012).

Salts introduced through de-icing practices are highly soluble and are therefore predominantly transported in the dissolved phase (Lund *et al.*, 2018). In particular, chloride exhibits conservative behaviour in the subsurface as it is not subject to significant sorption or degradation processes (Lund *et al.*, 2018; Cruz *et al.*, 2022). As a result, chloride derived from road salting can accumulate in soils and shallow groundwater beneath urbanised catchments (Ludwikowski and Peterson, 2018; Mackie *et al.*, 2022).

2.1.3. Nutrients

Urban runoff may also contain relatively high concentrations of nutrients, coming primarily from nitrogen and phosphorus species that originate from a range of diffuse anthropogenic sources (Hobbie *et al.*, 2017; Yang and Lusk, 2018). Common sources include atmospheric deposition, soil and decomposing plant materials (e.g. leaf litter), fertiliser application in urban green spaces and animal waste (Yang and Lusk, 2018). In addition, local leakage or illicit connections between stormwater and wastewater networks may contribute to elevated nutrient concentrations in runoff (Ruihua Zhang *et al.*, 2023).

Nitrogen is present in runoff in multiple forms, including nitrate (NO_3^-), ammonium (NH_4^+), and organic nitrogen (Li and Davis, 2014; Jani *et al.*, 2020). Where urea-based de-icing agents are applied, urea represents a direct source of dissolved nitrogen, as it is rapidly hydrolysed to ammonium and subsequently oxidised to nitrate under aerobic conditions (Jia *et al.*, 2018). Phosphorus in urban runoff occurs in both dissolved and particulate forms, often associated with suspended solids, organic matter, or fine mineral particles (Wei *et al.*, 2013).

Nutrient concentrations in urban stormwater exhibit considerable variability, typically ranging from 0.5 to 5 mg L⁻¹ for total nitrogen (TN) and from 0.01 to 1.5 mg L⁻¹ for total phosphorus (TP) (Li and Davis, 2014; Jani *et al.*, 2020; Müller *et al.*, 2020). Within the nitrogen pool, nitrate (NO₃⁻) concentrations commonly fluctuate between 0.2 and 2 mg L⁻¹, though values exceeding 10 mg L⁻¹ can be observed in catchments characterized by intensive landscape management or significant urea-based de-icer application (Jia *et al.*, 2018; Yang and Lusk, 2018).

Compared to many other contaminant groups, nutrients (particularly nitrate) exhibit relatively high mobility in subsurface environments due to weak sorption to mineral surfaces (Rivett *et al.*, 2008; C. Yang *et al.*, 2022). Their fate during infiltration depends strongly on local biogeochemical conditions, including redox state and microbial activity, which may promote transformation processes such as nitrification and denitrification (Kolbe *et al.*, 2019; C. Yang *et al.*, 2022). As a result, nutrient inputs from runoff represent a potential pressure on groundwater quality in areas where infiltration occurs, depending on attenuation capacity within the unsaturated zone (C. Yang *et al.*, 2022).

2.2. Conventional organic contaminants

2.2.1. Petroleum hydrocarbons (BTEX, PAHs)

Petroleum hydrocarbons are ubiquitous contaminants in urban runoff and are commonly reported among conventional organic pollutants (Latimer *et al.*, 1990; Hasani Moghaddam *et al.*, 2021). They originate primarily from the use, handling, and degradation of fossil fuels and petroleum-derived products, including vehicle traffic, fuel storage and distribution systems, and industrial activities (Latimer *et al.*, 1990). In urban environments, hydrocarbons are introduced to impervious surfaces through fuel spills and leaks, lubricating oil losses, exhaust residues, and atmospheric deposition of combustion-related particles (Stenstrom *et al.*, 1984; Latimer *et al.*, 1990; Hasani Moghaddam *et al.*, 2021).

The concentration of total petroleum hydrocarbons in urban runoff typically ranges from 1 to 10 mg L⁻¹, though concentrations exceeding 20 mg L⁻¹ are often recorded in high-traffic areas or during first-flush events (Stenstrom *et al.*, 1984; Lau *et al.*, 2002). Among these, individual PAHs are found at much lower levels, with total PAH concentrations generally ranging from 1 to 50 µg L⁻¹ (Zgheib *et al.*, 2012; Gasperi *et al.*, 2022). BTEX compounds, being highly volatile, are often detected at trace levels between 0.1 and 10 µg L⁻¹, although localized spills can lead to significantly higher concentrations in the immediate runoff (Sulej *et al.*, 2012; Hasani Moghaddam *et al.*, 2021).

In areas characterized by intense transport activities connected by dense road networks and associated infrastructures, petroleum hydrocarbons accumulate progressively on pavements during dry periods and are subsequently mobilised during rainfall events, often leading to noticeable first-flush effects (Hunter *et al.*, 1979; Lau *et al.*, 2002; Vaze and Chiew, 2002; Mangani *et al.*, 2005; Aryal *et al.*, 2006). In airport environments, additional inputs may occur through aircraft refuelling operations, fuel handling, and maintenance activities, where accidental spills or leaks can locally increase hydrocarbon loads in runoff waters (Sulej *et al.*, 2012; Jia *et al.*, 2018; Sulej-Suchomska *et al.*, 2024). In addition, aircraft engines and ground support vehicles emit fine particulates enriched in unburned hydrocarbons, which may be deposited on surfaces and subsequently mobilised during rainfall events (Sulej *et al.*, 2012; Sulej-Suchomska *et al.*, 2024).

Petroleum hydrocarbons are present as complex mixtures comprising a wide range of compounds, including monoaromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylenes (BTEX), as well as polycyclic aromatic hydrocarbons (PAHs) (Williams *et al.*, 2006; Logeshwaran *et al.*, 2018).

These compounds exhibit contrasted physicochemical properties, which strongly influence their behaviour during transport and infiltration processes (Williams *et al.*, 2006; Wang *et al.*, 2021). BTEX compounds and lighter PAHs are relatively soluble and are therefore predominantly transported in the dissolved phase, resulting in higher mobility (Mzoughi and Chouba, 2011; Kalmykova *et al.*, 2013). In contrast, higher-molecular-weight PAHs are generally less soluble and more hydrophobic (Mzoughi et Chouba, 2011; Kalmykova *et al.*, 2013; Brown *et al.*, 2017). They are thus preferentially associated with suspended particles, organic matter, and sediments (Mzoughi and Chouba, 2011). Consequently, the transport and attenuation of petroleum hydrocarbons in the subsurface depend on the relative proportions of dissolved and particulate-associated fractions, and are strongly influenced by soil properties, organic matter content, and redox conditions (Totsche *et al.*, 2006).

While many petroleum hydrocarbons are biodegradable under aerobic conditions, their degradation may induce local oxygen depletion due to high biochemical oxygen demand (BOD) (Grishchenkov *et al.*, 2000; Miles and Doucette, 2001; Das and Chandran, 2011; Wartell *et al.*, 2021). In addition, petroleum-derived compounds are toxic to aquatic and terrestrial organisms, and their persistence in soils and sediments raises concerns regarding long-term accumulation in surface and subsurface environments (Fakinle *et al.*, 2022; Gasperi *et al.*, 2022).

2.2.2. Biocides and urban pesticides

Biocides and urban pesticides are frequently detected in urban runoff and represent an important group of conventional organic contaminants associated with urban environment (Hensen *et al.*, 2018; Masoner *et al.*, 2019; Md Meftaul *et al.*, 2020; Bork *et al.*, 2021; Zhang *et al.*, 2024). Their presence in runoff is primarily linked to the widespread use of treated construction materials and the routine application of herbicides and insecticides in urban areas, combined with their mobilisation by rainfall from impervious surfaces (Burkhardt *et al.*, 2012; Hensen *et al.*, 2018; Paijens *et al.*, 2020).

Biocides are additive compounds that control growth of unwanted microorganisms to prevent construction material deterioration by microbial activity (Burkhardt *et al.*, 2007, 2011; Gasperi *et al.*, 2014). They include fungicides and algaecides that are found in resin-based paints for the protection of façades from organic coating (Burkhardt *et al.*, 2012). In addition, herbicides are applied for pathways and terraces maintenance while insecticides serve for pest control (Md Meftaul *et al.*, 2020; Myers *et al.*, 2022). They reach runoff through washoff from impervious surfaces or leaching from treated materials after rainfall events (Burkhardt *et al.*, 2011, 2011, 2012). Pesticides encompass a diverse range of chemical classes, including triazines (terbutryn, cybutryn), phenylureas (diuron, isoproturon), and carbamates (carbendazim), which function as algaecides and fungicides in facade coatings (Bollmann *et al.*, 2014). Furthermore, urban runoff often contains isothiazolinones (OIT, BIT, MIT) used as preservatives, triazoles (tebuconazole, propiconazole) from wood protection, and the phenoxy acid mecoprop, which is primarily leached from root-resistant roof membranes (Burkhardt *et al.*, 2012; Bollmann *et al.*, 2014; Paijens *et al.*, 2021).

Several of these compounds are associated with potential human-health risks, ranging from endocrine-disrupting effects to moderate carcinogenicity, while their environmental behaviour depends on their solubility and mobility. For instance, carbendazim has been reported as a reproductive and developmental toxicant, with moderate persistence and mobility in soil and water (Jin *et al.*, 2013; Zhou *et al.*, 2023). Diuron is generally persistent in all environmental matrices (soils, surface water, groundwater) and exhibits moderate toxicity to aquatic species (Giacomazzi and Cochet, 2004). More generally, hydrophilic compounds (such as mecoprop) are mobilized faster and remain in the water, whereas hydrophobic ones (such as terbutryn) tend to adsorb to soils and persist longer, leading to higher environmental persistence (Hensen *et al.*, 2020).

The concentrations of individual biocides and pesticides in urban runoff are generally observed at a magnitude close to nanogram to low microgram per liter. Typical reported concentrations for common urban pesticides such as diuron, mecoprop, and terbutryn range from 10 to 1000 ng L⁻¹ (Burkhardt *et al.*, 2011; Gasperi *et al.*, 2014; Paijens *et al.*, 2021). Isothiazolinones and wood preservatives (e.g., tebuconazole) are usually found at slightly lower concentrations, typically between 5 and 200 ng L⁻¹ (Bollmann *et al.*, 2014; Hensen *et al.*, 2018).

2.2.3. Glycols from de-icing and anti-icing fluids

In airport environments, glycols are often found in runoff waters as a direct consequence of the use of aircraft de-icing and anti-icing fluids (ADAFs) during winter operations (Toscano *et al.*, 2014; Yakovlieva *et al.*, 2022). In temperate climate where cold conditions prevail, winter safety operations require the use of ADAFs to remove and prevent ice accumulation on aircraft and pavement surfaces (Switzenbaum *et al.*, 2001; Freeman *et al.*, 2015). Numerous studies documented the presence and impact of ADAFs on airport runoff and connected water systems (Cancilla *et al.*, 1998; Breedveld *et al.*, 2002; Cancilla *et al.*, 2003; Corsi *et al.*, 2006a; Giger *et al.*, 2006a; Harris *et al.*, 2007; Kiss and Fries, 2009a; Jia *et al.*, 2018; Pressl *et al.*, 2019; Sulej-Suchomska *et al.*, 2024). ADAFs are typically composed of 20-50% of glycols (propylene glycol, ethylene glycol or diethylene glycol), 20-50% of water, and 1-4% of additives such as corrosion inhibitors and surfactants (Breedveld *et al.*, 2002). Glycols are easily biodegradable but impose a high BOD during oxidation, causing hypoxic conditions in receiving waters (Fazliev *et al.*, 2024).

Because ADAFs are applied in large volumes, glycol concentrations in airport runoff during winter events can be extremely high, typically ranging from 100 to 10000 mg L⁻¹ (Corsi *et al.*, 2006b; Jia *et al.*, 2018). Close to de-icing areas or during periods of intense application, concentrations of propylene or ethylene glycol can increase to over 20000 mg L⁻¹ (Switzenbaum *et al.*, 2001; Pressl *et al.*, 2019).

2.2.4. Plasticizers and phenolic compounds

Urban runoff may also contain significant levels of plastic-related compounds such as phthalates and Bisphenol A (BPA) (Clara *et al.*, 2010). These compounds are regularly used as plasticizers in building materials, packaging and consumer products (Lamprea *et al.*, 2018; Spahr *et al.*, 2020; Gasperi *et al.*, 2022).

The concentrations of these compounds in urban runoff typically range from 0.1 to 10 µg L⁻¹ (Clara *et al.*, 2010; Gasperi *et al.*, 2022). Within this category, phthalates and specifically Di(2-ethylhexyl) phthalate (DEHP), are often the most abundant with concentrations frequently reported between 1 and 5 µg L⁻¹ (Lamprea *et al.*, 2018; Müller *et al.*, 2023). Bisphenol A is generally detected at lower levels, typically ranging from 0.05 to 2 µg L⁻¹, although higher localized peaks can occur in catchments with high proportions of urban litter or industrial wastes (Spahr *et al.*, 2020; Gasperi *et al.*, 2022).

As a result, the degradation of plastics, urban litter, or construction residues may result in the release of plasticizers into runoff after rainfall events (Müller *et al.*, 2023). The endocrine-disrupting potential of BPA and several phthalates is well-known (Ma *et al.*, 2019; Sree *et al.*, 2023). Their presence in runoff is therefore considered problematic, especially when MAR systems are intended to contribute to potable water supply.

2.2.5. Polychlorinated biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) were banned or severely restricted in most countries since the late 20th century (Gilbreath and McKee, 2015). However, soil and water contamination by these compounds is still on-going due to their historical uses in industrial products such as fire-resistant transformers and insulating capacitors, as well as consumer products such as ink, paper and paints, plasticizers (Rossi *et al.*, 2004). Their presence in runoff water is mostly explained by poor management or incomplete removal from old materials, equipment or waste, as well as from atmospheric deposition and from oil/fuel leakages (Washington State Department of Ecology, 2023). In addition, they might still be emitted from waste incineration plants that do not filtrate fumes properly (Rossi *et al.*, 2004).

Because of their low water solubility and historical phase-out, PCBs are typically detected in urban runoff at ultra-trace levels, with dissolved concentrations generally ranging from 1 to 50 ng L⁻¹ (Rossi *et al.*, 2004; Zgheib *et al.*, 2012; Gasperi *et al.*, 2022). However, total concentrations (including particle-bound concentration) can be significantly higher, reaching up to 500 ng L⁻¹ in historically industrialized areas or catchments with aging infrastructure (Gilbreath and McKee, 2015; Washington State Department of Ecology, 2023).

PCBs are highly hydrophobic, resulting in a strong tendency to adsorb to organic matter and fine sediments in aquatic systems (National Research Council, 2001; Werner *et al.*, 2010). Their chemical stability and resistance to degradation make them persistent in the environment, enabling long-range atmospheric transport (National Research Council, 2001). Their mobility in the unsaturated zone is generally low due to strong sorption (Vitale *et al.*, 2018). In addition, PCBs pose significant health risks, being linked to carcinogenic, neurotoxic, immunotoxic, and endocrine-disrupting effects (National Research Council, 2001).

2.3. Contaminants of emerging concerns

Over the past two decades, a growing amount of research has highlighted the presence of Contaminants of Emerging Concern (CECs) in urban stormwater (Zgheib *et al.*, 2012; Gasperi *et al.*, 2014, 2022; Burant *et al.*, 2018; Fairbairn *et al.*, 2018; Lamprea *et al.*, 2018; Tran *et al.*, 2018; Müller *et al.*, 2020; Zhang *et al.*, 2024). This broad category includes synthetic compounds that are not routinely monitored but are known or suspected to cause ecological or human health effects (Wilkinson *et al.*, 2016; Department of Ecology (State of Washington), 2020). They are often detected at trace concentrations, yet they exhibit biological impact, persistence, and complex environmental behaviour (Pal *et al.*, 2010; Richardson and Kimura, 2020). Given their overall low degradability and potential for subsurface transport, CECs pose potential risks that must be carefully considered in the design and monitoring of MAR systems.

2.3.1. Alkylphenols and ethoxylate derivatives

Alkylphenols such as nonylphenol (NP) and octylphenol (OP), and their ethoxylate derivatives (NPEOs and OPEOs), are frequently detected in urban runoff (Bressy *et al.*, 2011; Lamprea *et al.*, 2018). These substances are commonly used as surfactants and emulsifying agents in industrial detergents, coatings, paints, concrete additives, and polymer production (Bennie *et al.*, 1997; Lamprea *et al.*, 2018). These compounds can be washed-off after rainfall events from treated surface and construction materials and enter stormwater systems (Bressy *et al.*, 2011). Due to their endocrine-disrupting properties, hydrophobicity, and tendency to accumulate in sediments, these compounds are considered as

concerning contaminants for both surface and infiltrating water (Cailleaud *et al.*, 2007). In urban stormwater, concentrations of NP and OP typically range from 0.1 to 5 $\mu\text{g L}^{-1}$, while their parent ethoxylates are often detected at higher levels, ranging from 1 to 20 $\mu\text{g L}^{-1}$ (Bressy *et al.*, 2011; Gasperi *et al.*, 2022).

In airport environments, alkylphenol ethoxylates (APEOs) can occur as additives in aircraft de-icing and anti-icing fluids, where they act as non-ionic surfactants within the additive package (Corsi *et al.*, 2003, 2006a). APEOs are of concern because they can degrade into more persistent and endocrine-disrupting by-products such as NP and OP (Sulej *et al.*, 2012). During de-icing/anti-icing operations, a fraction of applied fluids can be transferred to the airport drainage network through dripping, overspray losses, and subsequent mobilisation during rainfall or snowmelt events (Switzenbaum *et al.*, 2001; Freeman *et al.*, 2015). As a result, airport runoff can act as a vector for alkylphenols towards soil and potentially groundwater systems, which requires particular attention when considering the use of runoff as a recharge water source for managed aquifer recharge (MAR) operations.

Some EU Directive limit the use of alkylphenols and their derivatives, such as the EU Directive 2003/53/EC that limits NPEOs concentration to less than 0.1% in chemical formulation and EU Directive 2020/2184 that included NP in the list of hazardous substances to be monitored in drinking water, with a guideline value of 300 ng L^{-1} (REWE Group, 2015; INERIS, 2022). However, despite these regulatory restrictions, these compounds are still widely detected in urban runoff. This persistence is associated to their continued use in specific sectors (e.g., paints and plastics, among others) and their environmental stability (Lamprea *et al.*, 2018).

2.3.2. Pharmaceuticals and Personal Care Products (PPCPs)

Pharmaceuticals and personal care products (PPCPs) include a wide range of compounds such as analgesics, antibiotics, antidepressants, hormones, psycho-stimulants, fragrances, UV filters, and preservatives (Li, 2014). Their main sources in urban runoff include leakage from sewer systems or mixing with wastewater, improper waste disposal, and washing of treated skin or textiles outdoor (Masoner *et al.*, 2019; Zhang *et al.*, 2024). In particular, UV filters used in sunscreens and cosmetics are frequently detected in stormwater due to direct wash off during outdoor activities in sunny days (Tijani *et al.*, 2016; Damikouka *et al.*, 2024).

The concentrations of PPCPs in urban runoff are generally low, typically occurring in the nanogram per liter range. Common pharmaceuticals like carbamazepine or ibuprofen are often found between 10 and 500 ng L^{-1} , while UV filters (e.g., benzophenones) and stimulants such as caffeine can reach higher concentrations ranging from 100 to 2000 ng L^{-1} (Masoner *et al.*, 2019; Zhang *et al.*, 2024). In catchments where urban runoff is impacted by significant sewer leakage or illicit cross-connections, concentrations of individual PPCPs can occasionally occur at the microgram per liter range (Tijani *et al.*, 2016; Damikouka *et al.*, 2024).

PPCPs are known for their persistence and biological impacts (Ortúzar *et al.*, 2022). Antibiotics and endocrine-disrupting hormones can affect microbial communities and aquatic life even at trace concentration (Hu *et al.*, 2025). Furthermore, these bioaccumulative compounds persist in sediments and organisms (Yamamoto *et al.*, 2009). Therefore, their environmental fate in the vadose zone and groundwater may pose potential long-term risks if present in the recharge water applied in MAR settings.

2.3.3. Flame retardants (PBDEs, OPFRs)

Polybrominated diphenyl ethers (PBDEs) are brominated flame retardants that were historically incorporated into plastics, textiles, polyurethane foams, and electronic equipment until their production was progressively phased out (Gilbreath and McKee, 2015; Wu *et al.*, 2019). Despite the stop of their production and ban of use, PBDEs remain in the environment due to their persistence and continued release from in-use products and waste materials (Abbasi *et al.*, 2019; Kostenko *et al.*, 2024; Shakil *et al.*, 2025). In urban areas, they are mobilized into runoff primarily through the wash-off of contaminated dust and particles during rainfall events while atmospheric deposition and wastewater effluent act as secondary sources (Kim et Kannan, 2018; Müller *et al.*, 2020; Liu et Folk, 2021; Yao *et al.*, 2021). PBDEs are persistent, bioaccumulative, and toxic with documented neurodevelopmental, endocrine, and reproductive effects (Gao *et al.*, 2024). Furthermore, their degradation can yield to carcinogenic by-products such as hydroxylated or methoxylated PBDEs (Zhang *et al.*, 2022; Gao *et al.*, 2024). Their low water solubility and high affinity for particulate phase limit dissolved-phase transport but promote accumulation in sediments and soils (Zhang *et al.*, 2016; Khairy and Lohmann, 2017; Motamedi *et al.*, 2022).

Organophosphate flame retardants (OPFRs) have increasingly replaced PBDEs to prevent the risk of fire in applications such as electronics, building materials, furniture, and textile, leading to their widespread presence in the environment (Cristale *et al.*, 2013; Kim and Kannan, 2018; Pantelaki et Voutsas, 2019; Spahr *et al.*, 2020). They can be released during product use and disposal through volatilisation, abrasion, and leaching during rainfall events (Chupeau *et al.*, 2020). Due to their relatively high solubility, OPFRs are frequently detected in surface water and stormwater runoff (Kim and Kannan, 2018; Yang *et al.*, 2019). This physico-chemical behaviour facilitates their transport in the dissolved phase (Regnery and Püttmann, 2010; Kim and Kannan, 2018), making them concerning in case of their presence in recharge water in MAR systems. Furthermore, OPFR exposure has been associated with neurotoxicity, endocrine disruption, and carcinogenic effects, raising concerns about their potential risks to human health (Doherty *et al.*, 2019; Chupeau *et al.*, 2020; Patisaul *et al.*, 2021; Pyambri *et al.*, 2025).

Similarly than for PCBs, the low water solubility and historical phase-out of PBDE lead to dissolved concentrations in urban runoff that are typically very low, ranging from 0.1 to 10 ng L⁻¹ (Kim and Kannan, 2018; Müller *et al.*, 2020). However, total concentrations that include particle-bound concentrations, can range from 10 to 100 ng L⁻¹, reflecting their high affinity for particulates (Gilbreath and McKee, 2015; Yao *et al.*, 2021). In contrast, the more soluble OPFRs are found at significantly higher levels. Typical concentrations for OPFRs in urban stormwater range from 100 to 5000 ng L⁻¹, with certain compounds like TCPP or TCEP occasionally exceeding 10000 ng L⁻¹ in densely urbanized catchments (Kim and Kannan, 2018; Spahr *et al.*, 2020).

2.3.4. Triazole-based corrosion inhibitors

Triazole-based corrosion inhibitors, mainly benzotriazole (BT) and its methylated derivatives (4- and 5-methylbenzotriazoles, i.e. tolyltriazoles), are widely used to protect metals against corrosion in industrial and domestic applications (Pillard *et al.*, 2001; Janna *et al.*, 2011; Fateh *et al.*, 2020; Olds *et al.*, 2022; Soman and Vaidya, 2026). In airport environments, these compounds are notably associated with aircraft de-icing and anti-icing operations, as they are included in additive packages of ADAFs that are widely applied during winter periods (Breedveld *et al.*, 2002; Giger *et al.*, 2006; Olds *et al.*, 2022).

Beyond airports, benzotriazoles are also common in urban settings due to their use in dishwasher formulations, cooling systems, antifreeze and metal-working fluids (Giger *et al.*, 2006; Soman and Vaidya, 2026). This results in frequent detection in municipal wastewater and WWTP effluents (Reemtsma *et al.*, 2010). Consequently, their occurrence in stormwater can reflect both direct surface wash-off and indirect inputs linked to wastewater mixing, sewer leakage or cross-connections (Giger *et al.*, 2006; Reemtsma *et al.*, 2010; Gu *et al.*, 2021).

The concentrations of benzotriazoles in urban runoff generally range from 0.5 to 10 $\mu\text{g L}^{-1}$, often reflecting background inputs from domestic or industrial sources (Giger *et al.*, 2006c; Reemtsma *et al.*, 2010). However, in airport environments, these concentrations can increase by several orders of magnitude. During winter de-icing operations, tolyltriazoles concentrations in airport runoff have been reported to range from 100 $\mu\text{g L}^{-1}$ to over 5000 $\mu\text{g L}^{-1}$ (Cancilla *et al.*, 2003; Corsi *et al.*, 2006a; Kiss and Fries, 2009a).

Benzotriazoles are typically soluble and poorly biodegradable, and they generally exhibit low sorption onto mineral soils, which favours their persistence in the dissolved phase and promotes mobility during infiltration (Breedveld *et al.*, 2002; Jia *et al.*, 2007; Kiss and Fries, 2009a). Their transfer through the subsurface has been reported at airport sites impacted by de-icing-related contamination, where benzotriazoles were detected in groundwater (Cancilla *et al.*, 2003). Benzotriazoles have been associated with ecotoxicological effects in aquatic environments, and their frequent detection driven by continuous emissions supports considering them as relevant micropollutants in water quality assessments (Seeland *et al.*, 2012; Alotaibi *et al.*, 2015; Shi *et al.*, 2019). Overall, their high solubility, limited biodegradability, and relatively low sorption favour persistence in the dissolved phase and facilitate transport through the vadose zone, increasing the potential for transfer toward groundwater systems (Jia *et al.*, 2006, 2007; Shi *et al.*, 2019; Ruiling Zhang *et al.*, 2023a).

2.3.5. Per- and polyfluoroalkyl substances (PFAS)

Per- and polyfluoroalkyl substances, commonly referred as PFAS, are a large family of fluorinated compounds that have been widely used in commercial and industrial applications (Kissa, 2001). The C-F bond present in the moieties $\text{C}_n\text{F}_{2n+1}$ of these compounds make them extremely persistent and bioaccumulative, leading to a global environmental contamination after their widespread use (Buck *et al.*, 2011). In addition to their extreme chemical stability, the amphiphilic nature of PFAS (hydrophobic tail and hydrophilic head) makes them extremely useful for polymers and surfactants application (Kissa, 2001). Common polymer applications involve coatings and surface treatment that provide stain and soil repellence to textiles and carpets, grease resistance to food packaging paper, and protective layers to cookware, construction materials, and electronic components (Buck *et al.*, 2011; Glüge *et al.*, 2020; Gaines, 2023). Surfactants that take advantage of the low surface tension attributed to PFAS in their formulation include aqueous firefighting films (AFFFs) used in firefighting foams to extinguish fire, drilling and oil recovery fluids, cleaning and degreasing solvents, and various industrial wetting and emulsifying applications (Buck *et al.*, 2011; Glüge *et al.*, 2020; Gaines, 2023).

In urban and industrial areas, the runoff generated after rainfall events on impervious areas (roads, rooftops, parking lots, and sidewalk, among others) can mobilize PFAS deposited on those surface from various sources (Xiao *et al.*, 2012; Wee and Aris, 2023). These include residues from AFFF used in firefighting training sites, degradation of PFAS-treated materials (surface coatings on building, fabric, treated textiles, and paints, among others), atmospheric deposition (wet and dry), and leaching from landfills and industrial wastes exposed to rainfall, among others (Shimizu *et al.*, 2021; Pfothner *et al.*

al., 2022; Schellenberger *et al.*, 2022; Capozzi *et al.*, 2023; Coffin *et al.*, 2023; Aeterra, 2024; Li, 2024; Wang and Good, 2024; Pritchard *et al.*, 2026). The contaminated runoff may act thereafter as an important pathway for PFAS to enter receiving waters. For example, Kali *et al.* (2025) reported an increase in PFAS concentration in urban streams during wet weather, with strong contribution of stormwater discharges.

At airport, firefighting activities represent a major and well-documented source of PFAS contamination, particularly during routing training and equipment testing (Milley *et al.*, 2018; Liu *et al.*, 2022, 2023). To ensure the rapid suppression of real fuel fires, these training often involve the use of AFFF, which contain high concentrations of PFAS (Høisæter *et al.*, 2019). Historically, AFFF contained long-chain perfluoroalkyl sulfonates and carboxylates (notably PFOS) at non-negligible concentrations in the foam concentrate. Although their production and use is phased out in many countries, past contamination remains with PFAS leaching from soils at training sites decades after use (Liu *et al.*, 2022). Current AFFF formulations often contain short-chain PFAS replacements (e.g., PFHxA, PFBS) as well as fluorotelomer compounds such as 6:2 fluorotelomer sulfonate (6:2 FTS), which can degrade into other PFAS (Yang *et al.*, 2022). Although the short-chain analogues are less bioaccumulative, they are equally persistent and more mobile in the environment (Brendel *et al.*, 2018).

Besides the use of AFFF, there are some other sources of PFAS contamination in airport areas that are less documented. In particular, the presence of perfluoroethylenecyclohexanesulfonate (PFECCHS) as a corrosion inhibitor in aircraft hydraulic fluids leads to the contamination of nearby waters through runoff transport (Wang *et al.*, 2016a). Besides being a cyclic PFAS, PFECCHS shares similar physicochemical properties with PFOS: it is persistent and moderately bioaccumulative (MPART, 2020). However, its toxicological profile remains poorly understood and requires further investigation (Mahoney *et al.*, 2022, 2023).

The concentrations of total PFAS in urban runoff typically range from 10 to 200 ng L⁻¹, with individual compounds such as PFOS and PFOA often found between 1 and 50 ng L⁻¹ (Xiao *et al.*, 2012; Wee and Aris, 2023; Kali *et al.*, 2025). However, in specific areas impacted by the historical or current use of AFFF such as airport firefighting training grounds, concentrations in runoff can be significantly higher, with total PFAS levels frequently exceeding 1000 ng L⁻¹ (Milley *et al.*, 2018; Høisæter *et al.*, 2019; Liu *et al.*, 2022).

2.3.6. Microplastics

Microplastics (MPs), defined as plastic particles smaller than 5 mm, have recently been recognized as a ubiquitous component of urban stormwater (Werbowski *et al.*, 2021). In urban environments, they originate from a variety of primary and secondary sources, including the fragmentation of larger plastic litter, atmospheric deposition of synthetic fibres, and the wear of construction materials (Ross *et al.*, 2023). A particularly dominant source in transport-related runoff is tire and road wear particles (TRWP), defined as black rubber fragments generated by the abrasion between tires and pavement, which can constitute up to 85% of the total anthropogenic microparticles found in urban stormwater (Werbowski *et al.*, 2021). In addition to ecological risks (Thacharodi *et al.*, 2024), MPs pose a potential threat to human health. They have been detected in various human tissues and are associated with oxidative stress, inflammatory responses, and the potential translocation of chemical additives into the circulatory system (Prata *et al.*, 2020; Vethaak and Legler, 2021).

Microplastic concentrations in urban runoff are characterized by extreme heterogeneity, influenced by storm intensity, prior dry periods, and catchment imperviousness (Ross *et al.*, 2023). Studies

mentioned by Ross et al (2023) report concentration typically covering several orders of magnitude, ranging from 1.3 to 6000 particles per liter (pcs/L) in urban stormwater. These concentrations are typically higher than those found in WWTP effluents (Wang *et al.*, 2022).

3. Synthesis of sources and associated contaminants

As described in section 2, urban runoff integrates contaminants originating from numerous sources that operate simultaneously at the hydrological catchment scale. Pollutant loads in urban runoff result from the accumulation of substances on impervious surfaces during dry periods and their subsequent mobilisation during rainfall or snowmelt events, but also from indirect inputs such as atmospheric deposition and interactions between stormwater and wastewater networks. In this context, the occurrence of contaminants in runoff can be interpreted by associating each source category to specific contaminant families. This provides a useful synthesis of the contaminants susceptible to pose a risk for groundwater quality during MAR operations.

In urban settings, traffic-related activities represent one of the dominant sources. They contribute primarily through abrasion products (tyre and brake wear) and fuel/oil residues, leading to the presence of heavy metals (e.g., Zn, Cu, Pb, Ni), petroleum hydrocarbons (BTEX and PAHs), and fine particles acting as carriers for hydrophobic organic contaminants. Urban infrastructures and building materials constitute a second major source category. Weathering, leaching, and wash-off from roofs, façades, coatings, sealants, and treated construction materials can introduce metals, plasticizers and phenolic compounds (e.g., phthalates, BPA), and biocides/pesticides commonly used for material preservation into urban runoff. In addition, atmospheric deposition further acts as a diffuse input pathway. It supplies both recently emitted pollutants (combustion-related particles, metals, PAHs) and legacy contaminants associated with historically contaminated dusts and soils, including persistent organic pollutants such as PCBs and brominated flame retardants (PBDE). Finally, interactions with wastewater systems can locally exert a strong influence on runoff quality. Sewer leakage, cross-connections, or overflows may contaminate urban runoff with nutrients and a range of polar organic micropollutants typically associated with domestic and industrial wastewater. These include PPCPs and corrosion inhibitors such as benzotriazoles.

Within this general urban framework, large transport platforms such as airports represent specific environments where additional operational sources can influence runoff composition. Winter maintenance activities involve the use of ADAFs, which contribute to the presence of glycols and organic compounds as additives such as triazole-based corrosion inhibitors and alkylphenol ethoxylates within runoff. In addition, firefighting training and equipment testing activities are documented sources of PFAS through the use of AFFFs. Aircraft hydraulic fluids represent another potential source, as certain formulations may contain specific PFAS additives. Finally, airport traffic and refuelling operations (aircraft and ground-support vehicles) can contribute petroleum-derived contaminants and combustion-related particles, leading to inputs of PAHs and trace metals in runoff. Figure 11 illustrates the contaminant groups associated with airport activities that may be present in runoff.



Figure 11. Airport activities and associated contaminants encountered in runoff water.

Overall, this synthesis highlights that runoff contamination is controlled the combination of multiple source pathways, with chemical signatures varying according to land use and operational practices. This synthesis between sources and contaminant families provides a structured basis for the discussion of fate and transport processes during infiltration through the vadose zone.

4. Subsurface mobility of urban runoff contaminants

When runoff water is applied to surface-based MAR systems, contaminants may be transferred from the surface to the subsurface and migrate through the unsaturated zone toward groundwater (Voisin *et al.*, 2018; Mumberg *et al.*, 2024). The extent of this transfer depends on the combined effect of hydrological conditions (infiltration rate, soil moisture, wetting–drying cycles), soil properties (texture, organic carbon content, mineralogy), and geochemical conditions (pH, ionic strength, redox state) (Schotanus, 2013; Sarkar *et al.*, 2021). These factors control the partitioning of contaminants between dissolved and particulate phases, their residence time in the reactive zone, and their attenuation through sorption, degradation, and transformation processes (Schotanus, 2013; Bahar *et al.*, 2021; Ćwieląg-Piasecka, 2023). Accordingly, the contaminants described above can be grouped into categories reflecting their physico-chemical behaviour and expected mobility during subsurface transport. In addition, Figure 12 presents a conceptual scheme of the mobility potential and persistence expected in the vadose zone for the main contaminant classes commonly encountered in urban runoff. This scheme aims to be general as some classes, such as pesticides and PPCPs, include compounds with a wide range of behaviours depending on their polarity and hydrophobicity.

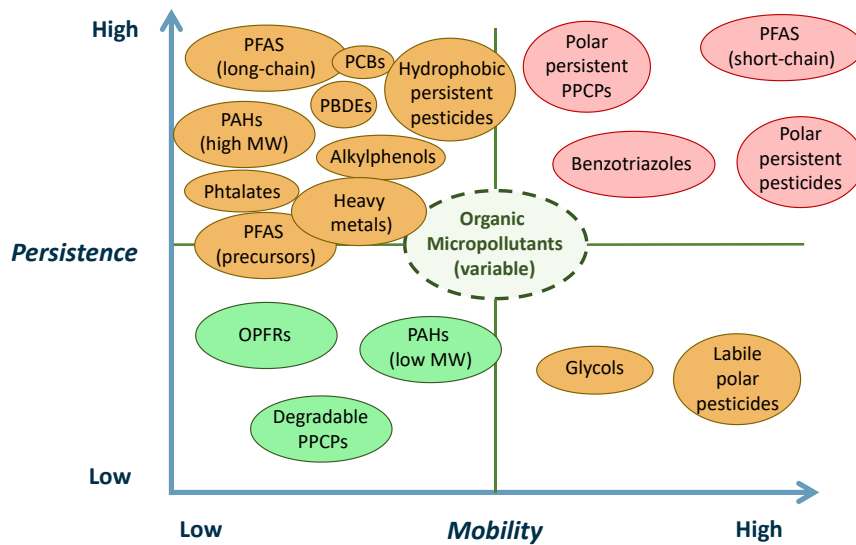


Figure 12. Conceptual scheme of mobility potential and persistence of contaminant classes commonly encountered in urban runoff, as expected in the vadose zone.

4.1. High-mobility constituents

A first category includes contaminants that are predominantly transported in the dissolved phase and that exhibit limited attenuation through classical sorption processes. This is particularly the case for de-icing-derived salts (Baraza and Hasenmueller, 2021; McQuiggan *et al.*, 2022). Chloride generally behaves conservatively in subsurface environments, with negligible sorption and no degradation (Stutter *et al.*, 2005; Baraza and Hasenmueller, 2021; McQuiggan *et al.*, 2022). This conservative tracer is thus prone to migrate rapidly with percolating water and to potentially reach groundwater if infiltration volumes are significant (Stutter *et al.*, 2005; Baraza and Hasenmueller, 2021; McQuiggan *et al.*, 2022). Other major ions such as sodium, calcium or potassium may undergo cation exchange reactions with negatively charged soil minerals, which can slightly delay their transport and modify groundwater hardness (Wodschow *et al.*, 2018; Baraza and Hasenmueller, 2021). However, it does not completely prevent their transfer at the scale of repeated recharge events.

Nutrients can also be efficiently transported in the dissolved phase, but their behaviour is more reactive and therefore more dependent on local biogeochemical conditions (Notodarmojo, 1991; Szymczycha *et al.*, 2017). Nitrate (NO_3^-) generally shows high mobility due to weak sorption to mineral surfaces and can rapidly migrate under oxic conditions (Szymczycha *et al.*, 2017; Abdelwaheb *et al.*, 2019). However, nitrogen species can still undergo strong transformations along the infiltration pathway depending on redox conditions (Szymczycha *et al.*, 2017; Tesoriero *et al.*, 2021; Waterhouse *et al.*, 2025). Ammonium (NH_4^+) can be temporarily retained by cation exchange in fine-textured soils and may subsequently be oxidised to nitrate through nitrification when oxygen is available (Alshameri *et al.*, 2018). Conversely, nitrate can be reduced through denitrification under anoxic conditions, provided that electron donors are present (Szymczycha *et al.*, 2017; Pang and Wang, 2021). As a result, the potential for nutrient transfer to groundwater is strongly controlled by redox conditions and by the residence time of infiltrating water within reactive zones of the unsaturated profile.

4.2. Particle-bound contaminants

A second category integrates contaminants that are associated with suspended solids and fine particles mobilised during runoff events (Jartun *et al.*, 2008a). In this case, contaminant transfer is not only governed by dissolved-phase transport but also by the behaviour of particles and colloids during infiltration (Flury and Qiu, 2008; Cheng and Sayers, 2010; Sharma and Paswan, 2023). At the soil surface, natural filtration can retain a significant part of particulate matter, particularly in fine-textured materials, leading to accumulation within the upper soil layers (Jartun *et al.*, 2008b). This physical retention process can significantly limit deep contaminant migration, but it may also promote clogging at the infiltration interface leading to a reduction in infiltration efficiency in the case of MAR systems (Tedoldi *et al.*, 2016a; Zaidi *et al.*, 2020). In parallel, the progressive accumulation of pollutants in shallow soil layers may later act as a secondary source of contamination through leaching during wet periods or high-infiltration events (Tedoldi *et al.*, 2016a; Gong *et al.*, 2023).

Heavy metals often occur as a mixture of particulate and dissolved fractions (Maniquiz-Redillas and Kim, 2014). Their mobility is commonly controlled by particle dynamics because metals can bind efficiently to mineral surfaces, iron and manganese oxides, and organic matter (Covelo *et al.*, 2007; Li *et al.*, 2022). During infiltration, particle-bound metals tend to be retained in the upper soil layers, while the dissolved fraction may be attenuated through sorption and precipitation reactions depending on pH and redox conditions (Esfandiar and McKenzie, 2022). Similarly, hydrophobic organic contaminants such as PAHs, as well as legacy pollutants like PCBs and PBDEs, generally show low water solubility and preferentially partition to suspended solids and soil organic matter (Maxin and Kögel-Knabner, 1995; Chiou *et al.*, 1998; Durjava *et al.*, 2007). Their dissolved-phase mobility is therefore usually limited, but they may accumulate in shallow sediments and near-surface soils under repeated infiltration (DiBlasi *et al.*, 2009; Cao *et al.*, 2019; Esfandiar and McKenzie, 2022; Yuan *et al.*, 2023). This can thus lead to the creation of persistent reservoirs that may remobilise them through colloid transport.

Finally, MPs represent a specific class of particle-bound contaminants whose subsurface transfer is governed by their physical size and surface chemistry (Yang *et al.*, 2025). Because they are predominantly particulate, a significant fraction is retained in upper soil layers through physical filtration and straining (Yang *et al.*, 2025). However, their mobility can be enhanced by several factors. First, migration through macropores or fractures can facilitate the transport of small particles (< 100 µm) deeper into the vadose zone (Yang *et al.*, 2025). Second, environmental weathering, such as UV radiation or oxidation, can increase the hydrophilicity and surface charge of MPs, altering thus potentially their affinity for soil particles (Jingya *et al.*, 2025).

4.3. Organic micropollutants

Organic micropollutants include diverse compound families (e.g., biocides, plasticizers, alkylphenols, PPCPs, triazole-based inhibitors) showing contrasted behaviours during infiltration (Wołowicz *et al.*, 2025). Their subsurface mobility is mainly controlled by the balance between sorption and biodegradation, with soil organic matter acting as a central driver (Rauch-Williams *et al.*, 2010; Patterson *et al.*, 2011; Regnery *et al.*, 2017). Compounds with higher hydrophobicity typically exhibit stronger sorption, which increases retardation and promotes accumulation in the upper soil layer (Wen *et al.*, 2012). This sorption can reduce aqueous concentrations and limit transport, but it may also decrease bioavailability and slow biodegradation (Ren *et al.*, 2018). Conversely, more polar compounds show weaker affinity for mineral soils and can remain predominantly in the dissolved phase, leading to higher mobility unless degradation becomes effective (Wen *et al.*, 2012; Reemtsma *et al.*, 2016).

Biodegradation represents a key attenuation pathway for many organic micropollutants, but its efficiency is strongly dependent on local conditions. Oxygen availability, temperature, microbial activity, and residence time in biologically active zones are all controlling factors (Hellauer *et al.*, 2018; Guillemoto *et al.*, 2022; Hübner *et al.*, 2022; Mueller *et al.*, 2022). Under well-aerated infiltration conditions, aerobic degradation can be significant for biodegradable compounds (Patterson *et al.*, 2011). However, infiltration systems may also develop locally reducing conditions, especially when organic matter inputs are high or when clogging layers form at the surface (Regnery *et al.*, 2015; Filter *et al.*, 2023; Pedretti *et al.*, 2024). In such cases, degradation pathways may slow down or shift toward alternative redox processes. Overall, organic micropollutants illustrate the strong variability of vadose-zone attenuation capacity: some compounds may be efficiently transformed within the upper soil, whereas others remain persistent and can migrate over larger distances (Filter *et al.*, 2021).

4.4. PFAS

PFAS constitute a specific group due to their extreme persistence and their complex transport behaviour in unsaturated porous media (Sharifan *et al.*, 2021). Their mobility depends strongly on molecular properties, notably chain length and functional group (i.e., carboxylates, sulfonates), which govern both aqueous solubility and sorption affinity (Sharifan *et al.*, 2021; Sadia *et al.*, 2024; Loganathan *et al.*, 2025). In general, long-chain PFAS sulfonates exhibit stronger sorption to organic matter and certain mineral phases, showing higher bioaccumulation potential, whereas short-chain PFAS carboxylates are less sorptive and therefore more mobile in water (Campos Pereira *et al.*, 2018; Fabregat-Palau *et al.*, 2021). This combination of high persistence with potentially high mobility for persistent short-chain compounds is particularly concerning for subsurface transfer (Kannan *et al.*, 2026).

In addition to classical solid–water interactions, PFAS are surface-active compounds and may accumulate at interfaces (Brusseau *et al.*, 2021; Fang *et al.*, 2025). Under vadose-zone conditions, adsorption at the air–water interface (AWI) can contribute to retardation beyond what would be expected from solid-phase sorption alone (Lyu *et al.*, 2018; Brusseau *et al.*, 2019a; Guo *et al.*, 2020; Brusseau *et al.*, 2021). This mechanism becomes more important when soils are partially saturated and when the interfacial area is large, meaning that PFAS transport can be sensitive to soil moisture dynamics (Lyu *et al.*, 2018; Brusseau and Guo, 2021, 2022a). Wetting–drying cycles may therefore influence PFAS retention and release, potentially leading to delayed transport or concentration pulses during rewetting conditions. Finally, the presence of PFAS precursors adds another layer of complexity (Stockwell *et al.*, 2026). Some polyfluoroalkyl precursors can progressively transform into terminal perfluoroalkyl acids, modifying PFAS signatures over time and potentially generating more mobile end-products depending on their chain length (Wang *et al.*, 2005; Liu *et al.*, 2010; Liu and Mejia Avendaño, 2013; Yang *et al.*, 2014; Mejia Avendaño and Liu, 2015; Stockwell *et al.*, 2026). As a result, PFAS behaviour cannot be reduced to a single partitioning mechanism, but rather reflects the combined influence of persistence, sorption, interfacial processes, and possible precursor transformation (Fabregat-Palau *et al.*, 2021). This will be further developed in the following chapters.

5. Summary

This chapter highlighted that urban runoff, although attractive from a quantitative point of view as a recharge source in urban and peri-urban settings, is characterized by a highly heterogeneous contaminant signature resulting from multiple diffuse and point sources. Major contaminant groups commonly reported in runoff include inorganic constituents (heavy metals, salts, nutrients) and organic pollutants ranging from conventional compounds (petroleum hydrocarbons,

pesticides/biocides, glycols, plasticizers) to contaminants of emerging concerns (e.g., alkylphenols, PPCPs, flame retardants, triazoles, PFAS). The relative importance of these groups depends strongly on land use and associated activities, with transport infrastructures representing specific environments where winter maintenance (use of ADAFs), refuelling and traffic, and firefighting operations may introduce characteristic compounds.

The chapter further emphasized that the potential risk for groundwater quality, if such waters are infiltrated, is not only controlled by contaminant presence, but also by their behaviour during infiltration through the unsaturated zone. Conservative solutes such as chloride and other de-icing-related ions show high mobility and limited natural attenuation, while nutrient exhibit mobility that is strongly conditioned by redox conditions and microbial transformation. Conversely, many metals and hydrophobic organic contaminants (e.g., PAHs, PCBs, PBDEs) are often retained near the infiltration interface through sorption processes, leading to a limited deep transfer but potential long-term accumulation in shallow layers. By contrast, organic micropollutants display more variable behaviour governed by the balance between sorption and biodegradation, with polar and persistent compounds being particularly mobile in the aqueous phase. PFAS stand out due to their extreme chemical stability and their contrasted mobility, with short-chain compounds being prone to transport, and with additional retention mechanism linked to AWI adsorption in variably saturated media.

This synthesis shows that evaluating runoff suitability for MAR requires moving from a generic inventory of contaminants towards a site-specific understanding of (i) which contaminant families could occur in the investigated mobilized sources under local conditions, and (ii) how infiltration settings may attenuate or transfer them toward groundwater. Chapter 4 therefore builds directly on this framework by presenting the sampling campaigns of runoff water, carried out to characterize local runoff quality and identify relevant contaminant fingerprints.

Chapter 4

Hydrochemical characterization of urban runoff in the Hesbaye Region

1. Introduction & objectives

As shown in Chapter 3, runoff generated during rainfall events in urban environments acts as a mobilisation pathway for contaminants previously deposited on impervious surfaces. Pollutants accumulate through a range of anthropogenic inputs (e.g., traffic-related emissions, industrial and airport activities, maintenance practices) and are subsequently washed off during precipitation. As a result, urban runoff becomes enriched in dissolved and particulate chemical compounds and may exhibit a distinct chemical signature depending on local land use and dominant emission sources. This chemical fingerprint is particularly relevant when runoff is considered as a potential source for MAR, because the chemical composition of recharge water ultimately governs both operational constraints and potential impacts on groundwater quality.

In the context of increasing pressure on groundwater resources, urban runoff collected in stormwater infrastructures represents an attractive alternative recharge source for MAR operations. However, the quality of such water cannot be assumed a priori. Indeed, Runoff may contain conventional pollutants such as trace metals, hydrocarbons, and nutrients, but also a range of organic micropollutants and CECs such as PFAS, alkylphenols, or benzotriazoles. Many of these substances fall within the PMT category (persistent, mobile, toxic) and their presence, even at trace concentrations, may be critical when assessing the compatibility of runoff water with recharge into groundwater systems.

This chapter therefore aims to characterize the chemical quality of urban runoff collected in stormwater basins relevant to the study area. Sampling campaigns have been carried out at different seasons to capture temporal variability and to document the occurrence of expected pollutants under contrasting climatic conditions (e.g., deicing period in winter). Samples were analysed using a combination of conventional physico-chemical measurements and targeted screening approaches for organic micropollutants. This allows the identification of compound families characteristic of the main anthropogenic emission sources.

2. Description of the sampling campaigns

2.1. Sampling campaign design

The availability of recharge water for MAR operations does not necessarily guarantee their suitability for MAR operations. Poor-quality water with excessive turbidity may rapidly clog infiltration systems. Conversely, low turbidity or an apparent “clean” water does not exclude the presence of dissolved contaminants, including organic micropollutants. Depending on their physicochemical properties (e.g., persistence, solubility, and sorption potential), such compounds may be transported through the unsaturated zone and potentially reach groundwater. To address these concerns, a sampling campaign was carried out on the four stormwater basins identified in Chapter 2: two associated with road infrastructure (*T1* and *T2*) and two connected to the airport (*A1* and *A2*).

Sampling was conducted across three different seasons to capture intra-annual variability, both from a climatic perspective (see Figure 13) and in terms of activity-specific inputs:

- **Spring (24th May 2022):** This campaign followed overall dry conditions, with around 10 mm of cumulative precipitations during the 15 preceding days. A single rainfall event occurred on 23rd May 2022, producing a first flush effect. This situation resulted in water reflecting a mixture of stagnant basin water and fresh runoff mobilising contaminants that had accumulated on impervious surfaces over several weeks.

- **Winter (1st February 2023):** This sampling event was preceded by wetter conditions, with approximately 23 mm of cumulative precipitation in the two weeks prior to sampling, mainly associated with a snowstorm on 20th January 2023 which deposited 20 mm of snow. The subsequent thaw contributed to runoff originating largely from snowmelt, combined with rainfall events throughout the month. This period also coincided with intense de-icing and anti-icing operations applied on both road infrastructures and airport surfaces, introducing winter-specific compounds into the drainage system.
- **Autumn (26th September 2023):** September 2023 was a relatively humid month, with around 50 mm over the 15 days prior to sampling associated to multiple moderate precipitation events. This campaign therefore captured more typical runoff dynamics, rather than first-flush behaviour. Only the airport basins were sampled, with the objective of providing representative values for the synthetic airport runoff waters later prepared in the IDAEA laboratory (Barcelona).

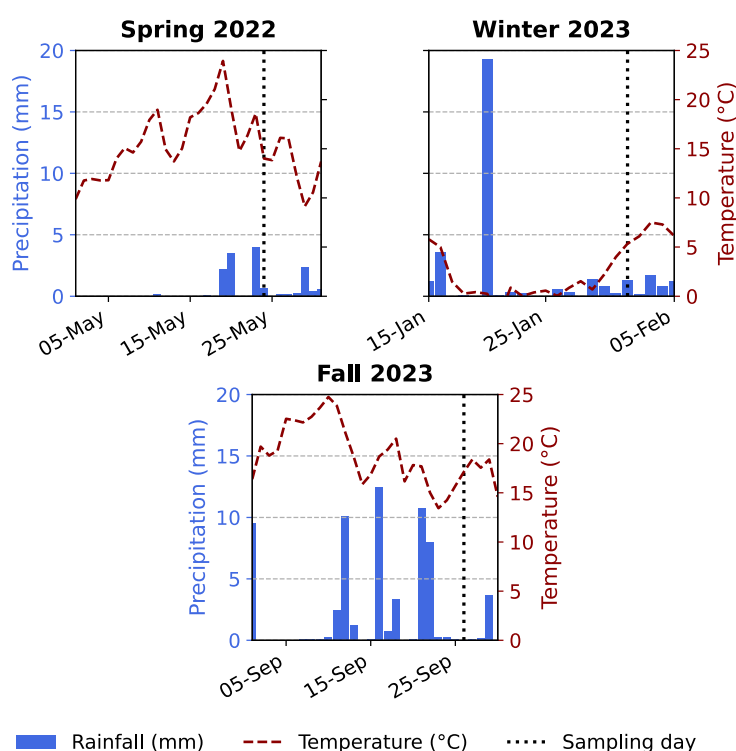


Figure 13. Rainfall events preceding the three sampling events.

For each campaign, grab samples were collected directly at the inlets of the stormwater basins shortly after rainfall events. This ensured that the sampled water reflected active runoff conditions rather than prolonged basin storage, except for the first campaign, which represented a mixed stagnant–runoff signal. At each site and sampling event, in situ measurements were performed for pH, electrical conductivity (EC), dissolved oxygen (O₂), oxidation–reduction potential (ORP), and temperature using a multiparameter probe.

2.2. Analytical methods and target compounds

To assess the chemical quality of runoff water, three categories of analyses were conducted by different laboratories: (i) general hydrochemistry, (ii) conventional pollutants typically associated with urban and transport-related runoff, and (iii) organic micropollutants, with an emphasis on PMT

substances that are relevant for subsurface transfer. Together, these analyses provide both a baseline description of runoff composition and a screening of expected CECs in the context of MAR and groundwater quality protection.

2.2.1. General hydrochemistry

General hydrochemical parameters were measured to (i) characterize the ionic composition and hydrochemical facies of runoff water, and (ii) enable comparison with the geochemical background of groundwater from the Hesbaye chalk aquifer. The groundwater dataset used for this comparison was compiled from the PhD work of O. Nikolenko and associated publications (Nikolenko *et al.*, 2018, 2019, 2021). These data were selected because they are relatively recent and provide coverage across the unconfined part of the Hesbaye chalk aquifer. The locations of the groundwater sampling points are shown in Annex B.

The major ion composition, defined by the main cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) and anions (HCO_3^- , CO_3^{2-} , SO_4^{2-} , Cl^-), provides a first order fingerprint of the sampled runoff waters and supports comparison with typical Hesbaye groundwater signature (e.g., ionic strength, dominant facies, chloride and sulfate levels, nutrients occurrence). In addition to major ions, selected minor ions (such as Li^+ , Sr^{2+} , Br^- , F^- , and NO_2^-) were measured to refine the geochemical signature of the runoff and detect potential influences from anthropogenic inputs. Furthermore, pH, alkalinity, and carbonate parameters were measured to assess buffering capacity and the potential for calcite precipitation or dissolution during infiltration (Appelo and Postma, 2010). Finally, Dissolved Fe and Mn were also analysed as part of the general water-quality assessment, as their concentrations can reflect reducing conditions and/or metal release within stormwater infrastructures (e.g., water–sediment interactions under stagnant conditions) and may contribute to operational and quality constraints (He *et al.*, 2023).

Analyses were performed at the Geological Laboratory of the University of Liège. Major ions and minor inorganic species were quantified by ion chromatography (Metrohm Professional 850 AnCat). Dissolved Fe and Mn were determined by atomic absorption spectrometry (Analytik Jena AA400). Alkalinity and related carbonate parameters were measured using titrimetric methods (Metrohm Titrando 905).

2.2.2. Conventional pollutants

A set of “conventional” contaminants was analysed by accredited laboratories (Celabor and ISSEP) to capture pollutant families commonly reported in runoff influenced by urbanized, airport and traffic-related environment, as described in Chapter 3. Heavy and trace metals were targeted because they are strongly associated with road and transport infrastructures, such as brake and tyre wear, vehicle-related abrasion, and/or corrosion of metallic surfaces. These include Al, Sb, Ag, As, Ba, Cd, Cr, Cu, Fe, Mg, Mn, Hg, Ni, Pb, Zn, which are frequently observed in particulate and dissolved fractions of urban runoff. In this thesis, only dissolved fractions were quantified. PAHs and volatile organic compounds (VOCs) were also included in the analyses due to their link with fuel combustion, petroleum products and traffic-related emissions. These are particularly relevant for runoff influence by road surfaces and traffic-related areas. Total phosphorus (TP) was analysed as a classical nutrient indicator reflecting overall enrichment and potential contribution to eutrophication pressure if discharge occurs, while also serving a general marker of runoff quality (Correll, 1998; Golubkov et Golubkov, 2025). In addition, total organic carbon (TOC) and total suspended solids (TSS) were determined to better characterize the amount of reactive organic matter and particulate transport, which are key parameters for assessing runoff quality and potential impacts during MAR operations (Chua *et al.*, 2009; Miguntanna

et al., 2010; Song *et al.*, 2019). Finally, total cyanides were included because cyanide has been reported among inorganic contaminants measured in airport runoff monitoring (Sulej *et al.*, 2012).

2.2.3. Organic micropollutants

To address the diversity of potential contaminants in urban runoff, organic micropollutants were investigated based on a suspect screening approach using liquid chromatography coupled to high-resolution mass spectrometry (LC-HRMS). This approach combines the quantitative determination of selected target compounds, with broader screening for additional substances expected from urban and transport-related sources. The suspect list was designed to prioritise PMT compounds, i.e. compounds that are persistent (P) and show limited natural attenuation, sufficiently mobile (M) to be transported with percolating water, and associated with toxicological (T) concern for drinking-water resources (e.g., endocrine-disrupting or carcinogenic properties). The compound classes included in the analyses were:

- **Per- and polyfluoroalkyl substances (PFAS)**, due to their well-known occurrence in AFFF used in firefighting trainings, which are regularly conducted in dedicated zones of the airport area for safety reasons. In addition, their ubiquitous presence in environmental matrixes justifies their inclusion within analyses.
- **Benzotriazoles and tolyltriazoles**, which are corrosion inhibitors commonly reported in urban waters and particularly relevant in settings affected by de-icing/anti-icing operations carried out in airport environment.
- **Alkylphenols and alkylphenol ethoxylates**, surfactants widely used in industrial detergents, coatings, paints, and concrete additives, that can be washed off from treated surface and construction materials. These compounds are also known to be used as additives in ADAFs and are therefore expected in airport runoff as well.
- **Organophosphate flame retardants**, which are also commonly applied on building materials and can be released when rainfall washes off degraded materials, leading to accumulation in urban runoff.
- **Polychlorinated biphenyls (PCBs)**, which are also included due to their historical use in industrial and consumer products. However, none were detected in any sample (all concentrations < LOD) and were therefore not discussed further.

This analytical strategy ensures that the most critical contaminants for MAR feasibility are identified and characterized, both in terms of occurrence and seasonal variability. These analyses were also carried out by the accredited laboratory Celabor and ISSEP.

3. Results

3.1. General water quality

3.1.1. Field physico-chemical parameters

During sample collection, physico-chemical parameters were measured *in situ* using a multiparameter probe positioned at the upstream inlet of each stormwater basin. This approach ensured that the recorded values were more representative of the runoff water entering the basins rather than of the mixed stagnant basin water itself. The measured parameters are displayed in Figure 14.

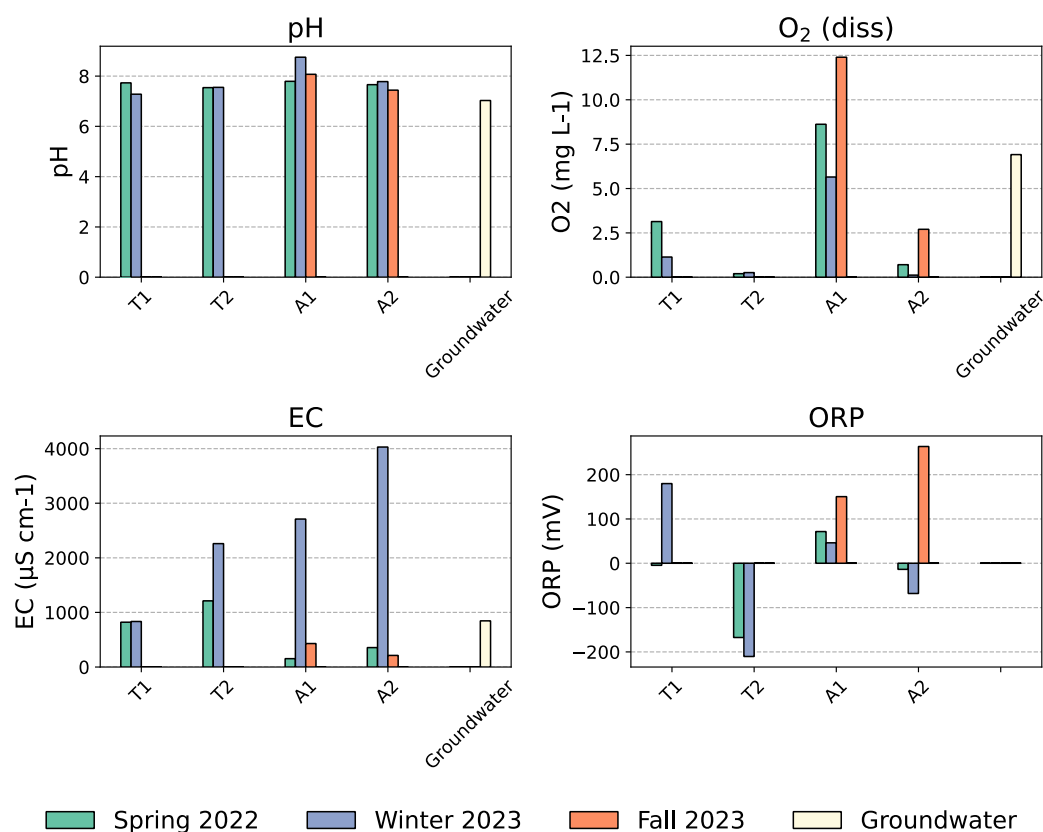


Figure 14. Field physico-chemical parameters (pH, dissolved oxygen, electrical conductivity, and oxidation–reduction potential) measured at the inlets of the four stormwater basins (T1, T2, A1, and A2) during the three sampling campaigns (Spring 2022, Winter 2023, and Fall 2023). For comparison, median pH, dissolved oxygen, and electrical conductivity values were computed for groundwater samples from the Hesbaye chalk aquifer.

Overall, the pH values were close to neutral across all sites and seasons, with most measurements ranging between 7.2 and 7.8. The only exception was observed at A1, which consistently showed higher pH, particularly in winter 2023 (pH ≈ 8.7). Such alkalinity is likely associated to the use of de-icing and anti-icing agents (such as acetate-based salts) applied on airport surfaces during the cold season. These compounds are known to increase alkalinity in runoff water (Fay et Shi, 2012) as they dissolve and are transported to the drainage system. The effect is thus accentuated at A1, which receives runoff directly from airport areas where de-icing operations are performed. In comparison, groundwater from the Hesbaye chalk aquifer shows a median pH of 7.03, indicating that urban runoff is slightly more alkaline than the aquifer. From a MAR perspective, this pH difference is not expected to be problematic for infiltration into the Hesbaye chalk aquifer as groundwater in chalk environment is well buffered by carbonate equilibria. Therefore, moderately higher pH should be rapidly neutralized, although the higher pH value observed for A1 in winter could favour carbonate precipitation.

Dissolved oxygen concentrations showed spatial and seasonal variability. Oxygen levels were generally low in the T2 and A2 basins, especially in winter (below 0.5 mg L⁻¹), indicating strongly reducing conditions that may result from the decomposition of organic matter and limited aeration within the basins. The persistence of low O₂ values in these sites may be linked to the continuous inflow of wastewater entering the drainage system, particularly at T1 and T2 basins which receive constant sewage water inputs even during dry periods. Such inflows typically contain biodegradable organic matter, leading to microbial oxygen consumption and maintaining reducing conditions in the basins. In contrast, A1 exhibited consistently higher O₂ concentrations, reaching 5.6 mg L⁻¹ in winter and 8.62 mg L⁻¹ in fall.

mg·L⁻¹ in spring, reflecting well-aerated conditions maintained by the slope-induced turbulent inflow at the sampling point. The peak value of 12.4 mg·L⁻¹ measured in winter is less reliable, as it would imply supersaturation of dissolved oxygen under typical field conditions. The *T1* site showed intermediate values (≈ 3 mg·L⁻¹ in spring, ≈ 1 mg·L⁻¹ in winter), suggesting moderate oxygen consumption and limited water renewal at the inlet. The overall increase in O₂ during fall, observed at *A1* and *A2*, is likely associated with the occurrence of more representative runoff events, which enhance runoff inflows and promote oxygen renewal at the basin inlets. From a MAR perspective, infiltrating water from *A1* would not necessarily deteriorate groundwater quality in terms of dissolved oxygen as it exhibits values similar to median data for groundwater (6.91 mg·L⁻¹). However, recharging water with low dissolved O₂ concentration could promote the mobilization of redox-sensitive components and may also affect nitrogen and organic carbon transformations. These potential impacts should therefore be evaluated by monitoring redox indicators (DO, ORP, Fe(II)/Fe(III), NH₄⁺/NO₃⁻, DOC) during MAR operations.

Electrical conductivity displayed significant contrasts between sites and seasons. The *T2* basin showed the highest EC values in spring (≈ 1200 μ S·cm⁻¹), likely reflecting solute concentrations under dry conditions and the effect of a continuous inflow of wastewater that maintains a relatively mineralized base inflow even in the absence of rainfall. In winter, the highest conductivities were recorded at *A1* (≈ 2700 μ S·cm⁻¹) and *A2* (≈ 4000 μ S·cm⁻¹), consistent with the application of de-icing and anti-icing salts on airport surfaces during cold weather. The increase observed at *T2* during the same sampling period (≈ 2200 μ S·cm⁻¹) may have a similar origin, as this basin is adjacent to a national road likely subject to road salting operations. The *T1* basin displayed much moderate conductivities (≈ 800 μ S·cm⁻¹) and limited seasonal variation, suggesting a stable but moderate mineralized inflow associated to continuous wastewater discharge. In contrast, EC values in the airport basins (*A1* and *A2*) were very low outside the winter period (typically below 400 μ S·cm⁻¹), reflecting less mineralized inflow and therefore potentially better water quality during non-winter conditions. By contrast, groundwater exhibits a median conductivity of 845 μ S·cm⁻¹, which is similar to the values measured in the basins outside the winter period. However, the much higher EC recorded in winter indicate a pronounced concentration in dissolved ions, which could pose risks to groundwater if such waters were infiltrated during MAR operations, as they would shift its baseline ionic composition.

The oxidation–reduction potential (ORP) values are the reflection of the dissolved oxygen patterns and confirmed distinct redox environmental across the basins. The *T2* and *A2* sites showed negative ORP values in spring and winter (-170 to -210 mV for *T2*; -10 to -70 mV for *A2*), indicating reducing conditions consistent with the observed oxygen depletion. In *A2*, a shift towards oxidizing conditions in fall (≈ 260 mV) coincided with the increase in O₂ concentrations, reflecting oxygen renewal through runoff inflows. The *A1* basin maintained positive ORP values across all seasons (ranging from 45 to 150 mV), in agreement with its higher oxygen content well-mixed inflow dynamics. In contrast, *T1* exhibited variable redox conditions, shifting from slightly reducing (-5 mV) to oxidizing in winter (180 mV). However, this evolution is not in adequation with measured O₂ and may reflect local environmental changes at the inlet or instrumental variability during field measurements, making its interpretation less certain.

Overall, these field physico-chemical parameters reveal clear spatial contrasts and seasonal dynamics among the stormwater basins. The airport basins (*A1* and *A2*) are particularly affected by winter operations, showing increased pH and electrical conductivity associated with the use of acetate- and chloride-based de-icing products, while non-winter periods are characterized by less mineralized and better-aerated waters. In contrast, the *T1* and *T2* basins, which receive continuous wastewater inflows display persistently higher mineralisation and reducing conditions, especially during dry or cold periods

when water renewal is limited. The combined evolution of O_2 and ORP indicates that aeration and hydrological renewal play a dominant role in controlling redox dynamics across sites. These *in situ* measurements provide a first insight into the hydrochemical conditions of each basin and set the framework for interpreting the chemical composition and contaminants profiles discussed in the following sections.

3.1.2. Major ions and nutrients

Similarly to the field physico-chemical parameters, the chemical composition of runoff is characterized by both spatial and seasonal variability across the studied basins. Detailed ionic concentrations are presented in the Section 2 of Annex B. The Piper diagram (Figure 15) indicates that most samples fall at the edge between bicarbonate-calcium/magnesium and bicarbonate-sodium/potassium facies, suggesting waters influenced by both natural background chemistry and anthropogenic inputs. This intermediate facies is consistent with observations from the MARWAL project, where surface waters generally displayed a bicarbonate-calcium facies, WWTP effluents were typically sodium-chloride dominated, and stormwater basins occupied an intermediate position between these two facies areas (Brouyère, 2023). However, distinct seasonal shifts are observed, particularly at airport basins during winter season.

In winter 2023, a significant increase in sodium (Na^+), potassium (K^+), and chloride (Cl^-) concentrations was observed in the airport basins A1 and A2, consistent with the application of de-icing and anti-icing products. At A2, the elevated chloride concentrations likely reflect combined input from airport de-icing operations and NaCl applied on the adjacent highway. At A1, the relatively higher contribution of potassium compared with sodium suggests a stronger influence of potassium-based de-icers (e.g., potassium formate) rather than NaCl alone. This interpretation is supported by the positive error (+38%) on the ionic charge balance at A1, suggesting the presence of unmeasured anions (most plausibly formate, $HCOO^-$). This difference is reflected in the Piper diagram (Figure 15), where winter samples from both basins clearly shift toward the Na–K–Cl domain, contrasting with the more balanced Ca– HCO_3 facies observed in spring. A similar but less pronounced increase in Na^+ , K^+ , and Cl^- concentrations is observed in the T1 basin, likely related to road salting along the nearby national road.

By contrast, the T1 and T2 basins display higher calcium (Ca^{2+}) and bicarbonate (HCO_3^-) concentrations, which can be attributed to the partial mixing of runoff water with domestic sewage water within the stormwater basin. In this area, sewage water likely contains elevated levels of Ca^{2+} and HCO_3^- because it ultimately derives from the public distribution network supplied by the Hesbaye chalk aquifer, which is naturally enriched in these ions.

By comparison, groundwater from the Hesbaye chalk aquifer shows a median Ca– HCO_3 dominated ionic composition, consistent with carbonate mineral dissolution in a chalk setting and buffering by the carbonate system. From a MAR perspective, the key issue is therefore the mixing of waters with contrasting ionic compositions. Recharge events shifting toward Na–K–Cl dominance (as observed in winter) could locally modify the ionic balance of the aquifer and lead geochemical changes such as cation exchange (e.g., Na^+ replacing Ca^{2+} on exchange sites) and modifications in carbonate equilibrium. These reactions may alter hardness, alkalinity and the relative proportions of major ions compared with initial groundwater composition. This underlines the need to manage and/or treat high-ionic-input events, and to monitor major ions during MAR operations.

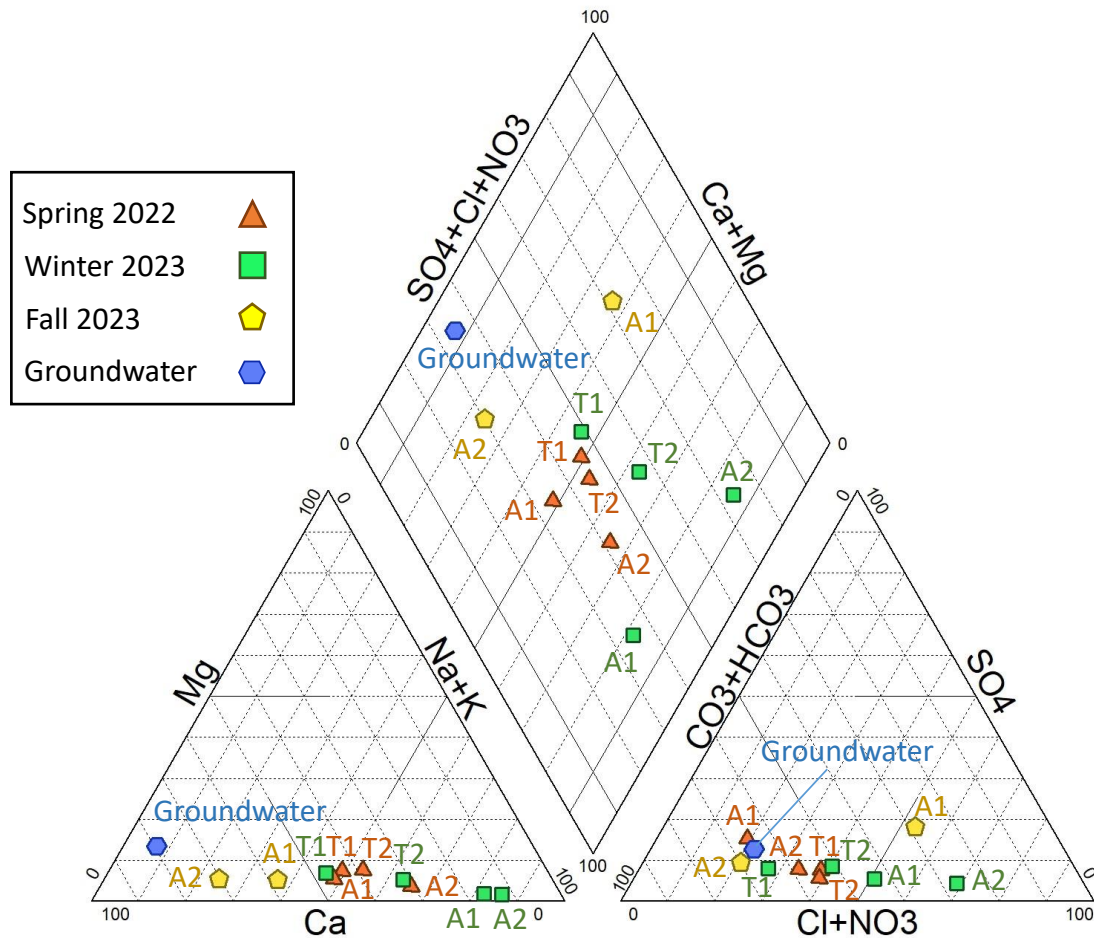


Figure 15. Piper diagram showing the hydrochemical facies of runoff samples collected from the different stormwater basins (T1, T2, A1 and A2) during spring 2022, winter 2023, and fall 2023, as well as the median relative ionic composition of groundwater from the Hesbaye chalk aquifer.

The Stiff diagrams (Figure 16a) clearly illustrate the spatial contrasts between the studied basins and the seasonal evolution of major ion composition. During winter, the A1 and A2 basins show strongly asymmetric shapes dominated by $\text{Na}^+ + \text{K}^+$ on the cationic side and Cl^- on the anionic side, reflecting the impact of de-icing salts applied at the airport. In A1, part of this ionic enrichment results from an incomplete charge balance, consistent with the plausible presence of formate anions (HCOO^-) that were not included in the ionic balance calculation, producing a positive imbalance of +38 % in winter 2023. In contrast, T1 and T2 display more symmetrical Stiff profiles throughout the year, with a chemical composition indicative of waters influenced by mixed runoff and domestic sewage rather than de-icing inputs. The spring and fall samples from all basins generally show more balanced shapes and are more representative of background hydrochemical conditions rather than affected by de-icing operations. By comparison, groundwater samples exhibit typical bicarbonate-calcium signature, with a symmetric pattern between Ca^{2+} on the cationic side and with $\text{HCO}_3^- + \text{CO}_3^{2-}$ on the anionic side. Outside the winter period, the Stiff diagrams also indicate that groundwater is generally more mineralized than the airport basins A1 and A2 in spring 2022 and fall 2023, whereas it is of similar order of magnitude to the traffic-related basins T1 and T2. This similarity likely reflects the additional ionic contribution from wastewater inputs at T1–T2, which increases overall mineralization compared with the airport basins(excluding winter conditions).

The Stabler diagrams (Figure 16b) complement these observations by showing the relative proportions of cations and anions for each sampling period. Similarly to Stiff diagrams, they highlight

a marked shift toward $\text{Na}^+ + \text{K}^+$ and Cl^- dominance during winter 2023 at the airport sites. In fall 2023, a reverse trend is observed for most basins, with the diagrams shifting back toward the bicarbonate domain, indicating both reduced anthropogenic inputs and increased dilution by rainfall. Finally, the elevated nitrate (NO_3^-) concentration observed at A1 during fall 2023 constitutes an isolated anomaly and could be related to localized nutrient-rich discharge water. Finally, groundwater samples exhibit a dominated proportion in calcium and bicarbonate ions, as expected for water derived from a chalk aquifer. Among the stormwater basins, A2 in fall 2023 shows the closest proportional signature to groundwater in the Stabler diagram, although it remains less mineralized overall (as indicated by associated Stiff diagram).

In summary, the hydrochemical composition of the runoff samples shows that runoff chemical signature generally falls within an intermediate position between the surface water and wastewater signatures, reflecting mixed anthropogenic and natural influences. De-icing operations represent the most plausible factor of ionic enrichment during winter, while the fall 2023 samples seem to indicate a return toward background conditions, consistent with reduced anthropogenic pressure and partial dilution by rainfall. Overall, these temporal and spatial contrasts underline the strong anthropogenic control on the hydrochemical signature of runoff water in the Geer basin.

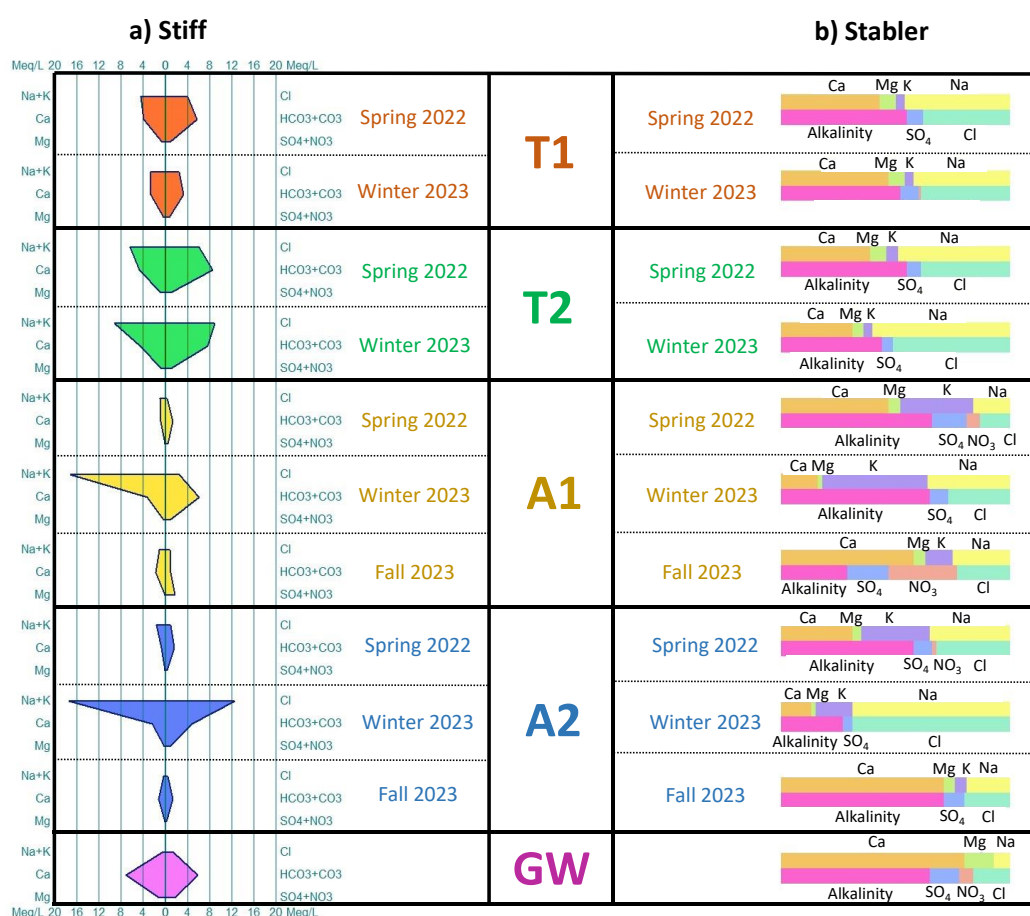


Figure 16. Seasonal evolution of cation and anion proportions for runoff (T1, T2, A1 and A2) and groundwater (GW) samples represented by: (a) Stiff diagrams and (b) Stabler diagrams. Note that alkalinity refers to HCO_3^- concentrations. Drinking water guideline

3.1.3. Metals and other parameters

The analysis of dissolved metals and additional parameters such as total cyanides, TOC, TP and TSS was performed selectively depending on the sampling campaign and analytical availability. TP was analysed during both spring 2022 and winter 2023, whereas metals were measured only in spring 2022, and cyanides, TOC, and TSS were determined in winter 2023. Therefore, seasonal comparisons remain limited, and the discussion rather focuses on observed ranges and potential sources.

Metals

In spring 2022, concentrations of dissolved metals were overall low across all basins. Most trace metals elements such as Cu, Pb, Ni, Cd, As, Sb and Hg were below detection limits. Aluminium (Al) and iron (Fe) ranged respectively from 0.4 to 1.1 mg·L⁻¹ and 0.4 to 1.2 mg·L⁻¹, while manganese (Mn) varied between 0.04 and 0.33 mg·L⁻¹ and zinc (Zn) between 0.05 and 0.15 mg·L⁻¹. Although Fe and Mn concentrations exceed the WHO drinking water guidelines (0.3 mg·L⁻¹ and 0.1 mg·L⁻¹, respectively; WHO, 2017), these thresholds are primarily based on aesthetic criteria, such as taste and staining, rather than health toxicity. These concentrations typically fall within the typical ranges reported for urban stormwater (Hubert et al., 2016; Djukić et al., 2016) and do not indicate significant metal contamination. Consequently, dissolved metals were not considered as target contaminants in the modelling work. The highest metal levels were recorded at T2 (for Al and Fe) and A2 (for Zn), both basins being located in the proximity of traffic roads, suggesting that vehicular emissions and road runoff constitute the main sources of metallic inputs.

Total cyanides

Cyanides were detected in winter 2023, with measurable concentrations at all sites ranging from 1.8 to 9.2 µg·L⁻¹. Their occurrence during winter is consistent with the presence of ferrocyanide compounds commonly added to road salts as anti-caking agents (Ohno, 1990). These additives can partially dissociate or degrade during their storage and application, leading to the release of total cyanides in runoff water at low concentration levels. Although detected, the measured concentrations remain well below the European environmental quality standard (EQS) for total cyanides (50 µg·L⁻¹; Directive 2013/39/EU), indicating a limited risk of toxicity in the studied runoff water.

Total organic carbon, total phosphorus, and suspended solids

TOC, TP, and TSS were measured in winter 2023 and exhibited clear differences between airport and traffic related basins. The highest TOC concentrations were indeed recorded at A1 (208 mg·L⁻¹) and A2 (140 mg·L⁻¹). This pattern may be explained by the potential contribution from organic ADAP (e.g., glycol-based fluids), which are readily biodegradable and rich in organic carbon (Revitt and Worrall, 2003; Corsi et al., 2006a; Sayin et al., 2024). T2 basin showed moderately high TOC (63 mg·L⁻¹), likely due to mixed runoff–sewage water.

For TP, the highest concentrations were observed in the traffic-related basins, with T1 and T2 runoff water exhibiting 3.6 and 5.5 mg·L⁻¹ respectively, in spring 2022. In winter 2023, slightly lower concentrations are measured, ranging from 1.6 to 4.3 mg·L⁻¹ for T1 and T2 respectively. These elevated values are consistent with the influence of sewage inputs, as phosphorus is a common constituent of household detergents and domestic effluents (Chen et al., 2022). In contrast, TP concentrations in the airport basins remained relatively low (0.2–0.7 mg L⁻¹) during both seasons.

TSS ranged from 7.6 mg L⁻¹ at T1 to 46 mg L⁻¹ at T2, and from 12.6 mg L⁻¹ at A1 and 34 mg L⁻¹ at A2, depicting spatial variability among the basins. The lowest values measured at T1 and A1 correspond to sites where runoff water is relatively clear (in terms of turbidity) and where flow conditions at the inlet

limit sediment resuspension. In contrast, the higher values observed at A2 and T2 likely reflect the mobilization of fine particulates, such as road dust, carried by runoff over impervious surfaces together with inlet flows that may favour the resuspension of previously deposited solid materials.

3.1.4. Polycyclic aromatic hydrocarbons (PAHs)

As already described in Chapter 3, polycyclic aromatic hydrocarbons (PAHs) are organic compounds primarily derived from the incomplete combustion of fossil fuels. They are typically released through traffic exhaust, fuel handling, and other industrial activities. Once emitted, PAHs adsorb on airborne particles and road dust, which can be later mobilized by surface runoff or snowmelt, leading to potential contamination of stormwater systems. In spring 2022 and winter 2023, sixteen priority PAHs were analysed in the different stormwater basins, with corresponding concentration results depicted in Figure 17. Each basin offers a distinct pattern in observed PAHs concentrations.

- **T1:** Naphthalene, phenanthrene, and pyrene were the only PAHs systematically detected, with concentration inferior to 25 ng L^{-1} . Other compounds were not detected and no significant seasonal variability was observed. The absence of clear seasonal patterns suggests a limited pollutant load and relatively homogeneous input across the sampling periods. In addition, the low detection frequency and concentration range suggest rather diffuse pyrogenic inputs (i.e. atmospheric deposition of combustion residues) than direct hydrocarbon contamination.
- **A1:** fluoranthene, phenanthrene, and pyrene were measured at concentrations all below 20 ng L^{-1} , along with a higher concentration of naphthalene in winter (47 ng L^{-1}). As described in the section 4.6.2 of Chapter 2, the basin collects runoff from impervious surfaces of the airside area, which includes aprons, taxiways, and service roads where aircraft and service vehicles circulate. Therefore, these surfaces are subject to fuel residues, exhaust particles, and combustion-related deposits. The higher winter concentrations likely reflect the mobilization of these PAHs during snowmelt, when pollutants deposited on paved surface during the cold season are flushed into the drainage system. Despite this seasonal difference, the concentrations remain very low and indicate only minor PAHs inputs from airside runoff.
- **A2:** As expected, the A2 basin which drains both highway and airport surfaces exhibits the largest number of detected PAHs (14 out of 16) and includes the highest individual concentration, with acenaphthene reaching 109 ng L^{-1} . Other compounds such as fluorene, fluoranthene, and pyrene, are also frequently detected but generally remain below 50 ng L^{-1} , at levels comparable to those observed in the T2 basin. The observed PAH profile (acenaphthene, fluorene, fluoranthene, pyrene) indicates a pyrogenic origin, consistent with traffic emissions and combustion residues. In terms of seasonal variability, it seems to be compound dependent. Indeed, some PAHs (acenaphthene, fluoranthene, fluorene) show higher concentrations in spring, likely due to dry deposition accumulation before being washed off during first rainfall events. On the other hand, other compounds (naphthalene, phenanthrene) exhibit higher values in winter. This increase may be linked to enhanced pollutant mobilization during snowmelt, when accumulated contaminants are released and transported with meltwater (Meyer *et al.*, 2011; Kuoppamäki *et al.*, 2014; Allan *et al.*, 2016; Parajulee *et al.*, 2017). This dual seasonal behaviour highlights the combined influence of deposition processes and hydrological conditions on PAH transport.
- **T2:** This basin also shows frequent detection, with most PAHs present at low to moderate concentration ($< 100 \text{ ng L}^{-1}$). Concentrations tend to be slightly higher in winter, except for acenaphthene and naphthalene. Similarly to T1, the concentration increase in winter may be attributed to enhanced pollutant mobilization after snowmelt (Meyer *et al.*, 2011; Kuoppamäki

et al., 2014; Allan *et al.*, 2016; Parajulee *et al.*, 2017). Phenanthrene shows the highest levels, with 75 ng L⁻¹ in spring 2022 and 89 ng L⁻¹ in winter 2023. Similarly to the compounds detected in A2 basin, these are also associated with fuel combustion and traffic emission, which is consistent with the basin collecting roadway runoff.

Across all basins, the PAH profiles are dominated by low molecular weight compounds (such as naphthalene, acenaphthene, fluorene, phenanthrene), which are more soluble and mobile in water, and typically associated to pyrogenic sources. High molecular weight PAHs (such as benzo[a]pyrene or indeno[1,2,3-cd]pyrene) were less frequently detected, which indicates that coarse particulate wash-off contribute less to runoff contamination.

Seasonal differences were observed at different sites, apart from T1. The data suggest that snowmelt preferentially mobilizes heavier particle-bound PAHs, such as benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene and benzo[g,h,i]perylene, which accumulate on sediments and snow due to their low solubility and strong sorption to particulates. In contrast, rainfall events following dry deposition tend to mobilize lighter and more soluble PAHs, such as naphthalene, acenaphthene, or fluorene. This behaviour reflects the influence of hydrological conditions on PAH transfer mechanisms to stormwater basins, with snowmelt enhancing the mobilization of particle-bound species while rainfall promotes rather the transport of surface deposited contaminants.

From a regulatory perspective, most of the detected PAHs remain below or close to the EQS established under the European Water Framework Directive (Directive 2013/39/UE). For reference, the current EQS maximum allowable concentration in surface waters apply to the group of carcinogenic PAHs and are of 27 ng L⁻¹ for benzo[a]pyrene, 17 ng L⁻¹ for benzo[b]fluoranthene and benzo[k]fluoranthene, and 0.82 ng L⁻¹ for benzo[g,h,i]perylene. In this case, while concentrations of light PAHs remain low, some heavy PAHs and particularly benzo[b]fluoranthene, benzo[a]pyrene, and benzo[g,h,i]perylene, reach or exceed these EQS thresholds in certain samples. These observations indicate that although PAH contamination in stormwater remains moderate, the occurrence of high molecular weight carcinogenic PAHs may present concerns depending on which stormwater basin is exploited for MAR operations.

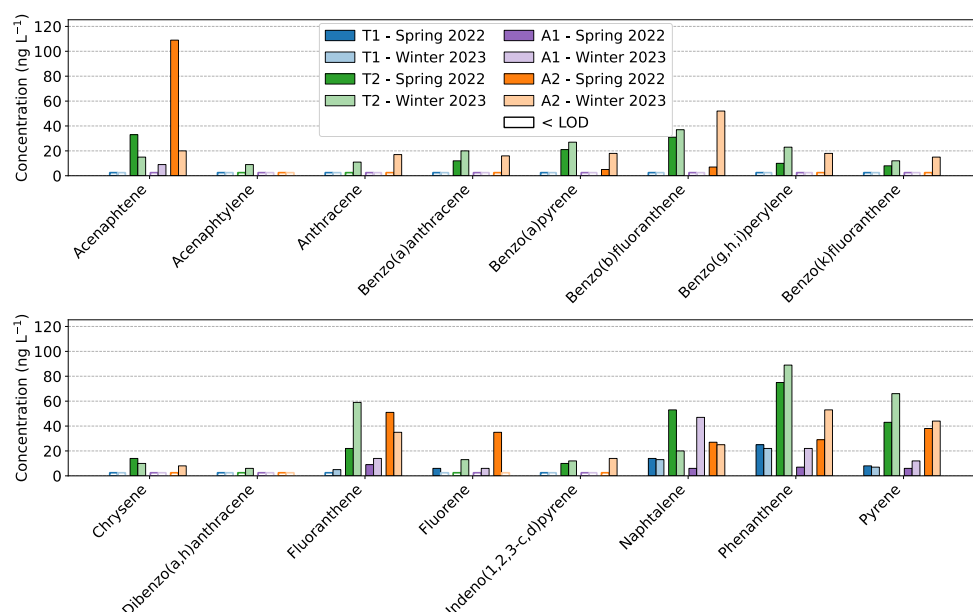


Figure 17. Concentration of sixteen priority PAHs in stormwater basins during Spring 2022 and Winter 2023. Bars represent the four basins (T1, T2, A1 and A2), with darker colours for spring and lighter tones for winter. Empty outlined bars indicate concentrations below the analytical limit of detection (< LOD).

3.2. Contaminants of emerging concerns (CECs)

3.2.1. Alkylphenols

As mentioned in Chapter 3, alkylphenols and bisphenol A are synthetic aromatic surfactants widely used in detergents, coatings, paints, concrete additives, and polymer production. Their environmental presence is mainly related to industrial discharges and wastewater effluents. Among these, nonylphenol (NP), octylphenol (OP), their ethoxylated derivatives (NP₁EO, NP₂EO, OP₁EO, OP₂EO) and bisphenol A (BPA) are of particular concern due to their persistence and endocrine-disrupting effects. In particular, twelve alkylphenol compounds were analysed and the concentration results are depicted in Figure 18.

- **T2**: This basin exhibits the highest concentrations of alkylphenols, with NP, OP, and their derivatives detected up to 466 ng L⁻¹, together with high concentrations of bisphenol A reaching 438 ng L⁻¹. These elevated values and frequent detection, in contrast with airport basins (A1 and A2), likely reflect a mixed input of sewage and runoff water, as wastewater effluents typically contain higher levels of alkylphenols than pure runoff.
- **T1**: Similarly to T2, this basin receives both sewage and runoff water. Therefore, alkylphenols were detected as well but in lower concentrations, ranging from 42 to 242 ng L⁻¹. This may be explained by a lower wastewater contribution associated to a smaller drainage network in contrast to T2.
- **A2**: In this basin collecting exclusively runoff water from airport and nearby highway areas, alkylphenols were detected only occasionally, with NP and OP concentrations below 50 ng L⁻¹, and NP₁EO, NP₂EO typically between 40 and 80 ng L⁻¹. These low concentrations probably originate from residues in road cleaning or maintenance agents used on paved surfaces. Bisphenol A, however, remains consistently detected at elevated concentrations, between 200 and 250 ng L⁻¹, indicating that its origin extends beyond wastewater inputs.
- **A1**: This basin shows almost no detection of alkylphenols, with only trace levels of 4-NP tech and NP₁EO (below 30 ng L⁻¹). Bisphenol A was nevertheless detected, with concentrations ranging from 120 to 130 ng L⁻¹.

Across all basins, bisphenol A appears as the most ubiquitous compound, with concentrations consistently reaching several hundreds of ng L⁻¹. On the other hand, alkylphenols display more spatial variability depending on the relative influence of wastewater and surface runoff. No clear seasonal pattern was observed, suggesting that alkylphenol inputs are mostly controlled by continuous anthropogenic discharges, occasionally reinforced by runoff events.

From a regulatory framework, nonylphenol and octylphenol are listed as priority hazardous substances under the European Water Framework Directive (Directive 2013/39/EU). Their recommended annual-average environmental quality standards (EQS) are 300 ng L⁻¹ for NP and 100 ng L⁻¹ for OP in surface waters, with no specific limits defined for their ethoxylated derivatives. In this study, all measured concentrations fall below these EQS values. Bisphenol A currently has no official EQS under the same directive, but its inclusion among regulated substances is under discussion in forthcoming European water legislation (European Food Agency (EFA), 2025).

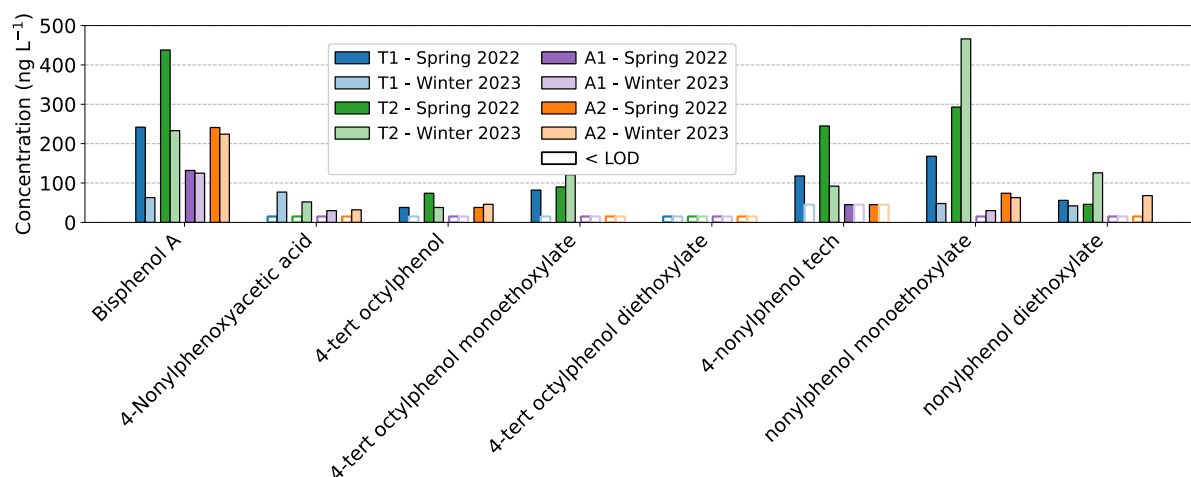


Figure 18. Concentration of alkylphenols measured in stormwater basins during Spring 2022 and Winter 2023. Bars represent the four basins (T1, T2, A1 and A2), with darker colours for spring and lighter tones for winter. Empty outlined bars indicate concentrations below the analytical limit of detection (< LOD).

3.2.2. Per- and polyfluoroalkyl substances (PFAS)

As a reminder from chapter 3, PFAS are synthetic fluorinated surfactants extensively used in industrial and commercial applications, including firefighting foams (AFFF), cleaning solvents, coatings, and hydraulic fluids. Their exceptional stability and resistance to degradation have led to their global environmental persistence and frequent detection. Among the PFAS compounds analysed, twelve were detected and quantified. They include fluorotelomer sulfonates (6:2 FTS, 8:2 FTS), perfluoroalkyl carboxylic acids (PFBA, PFPeA, PFHxA, PFHpA, PFOA), perfluoroalkyl sulfonic acids (L-PFBS, L-PFHxS, PFOS), and the cyclic compound perfluoroethylcyclohexane sulfonate (PFECHS). Concentration results per basin and per season are displayed in Figure 19.

- Airport basins (A1 and A2):** These two basins exhibit the highest PFAS concentrations, with 6:2 FTS reaching up to 590 ng L⁻¹, followed by PFECHS (490 ng L⁻¹), and PFOS (310 ng L⁻¹). The predominance of 6:2 FTS is consistent with its use in modern AFFF formulations historically applied during firefighting training at the Liège airport. Its degradation products which include PFHxA, PFHpA, PFPeA, and PFBA (Yan, Dong, Manz, *et al.*, 2024) were also detected, with higher concentrations during the winter 2023 campaign. This seasonal increase likely reflects both recent foam usage and enhanced mobilization during snowmelt. The detection of PFOS in the A2 basin, despite its restricted use since 2011, probably results from remobilization of residual contamination in the airport drainage system or soils during past AFFF applications. Finally, the compound PFECHS which is used as a corrosion inhibitor in aircraft hydraulic fluids (De Solla *et al.*, 2012), was also found at significant concentrations, confirming its strong link to airport operations (Wang *et al.*, 2016b).
- Traffic-related basins (T1 and T2):** Outside the airport influence, PFAS concentrations were generally much lower. In T2 basin, most of the PFAS were not detected, except for PFPeA reaching up extremely high concentration of 330 ng L⁻¹ in spring 2022. This PFAS compound is typically associated with wastewater sources and supports the hypothesis previously formulated for alkylphenols, suggesting that the T2 basin receives a larger share of domestic wastewater inputs. By contrast, more PFAS were detected in T1 (PFBA, PFPeA, PFHxA, PFHpA, PFOA and PFOS) at concentrations lower than 25 ng L⁻¹, except for 6:2 FTS detected at 63 ng L⁻¹. In terms of seasonality, PFAS were detected in spring 2022 but not in winter 2023, without an obvious explanation.

From a regulatory perspective, the assessment of PFAS in urban runoff must consider both the current category of the water and its eventual use as a resource for MAR. While the ultimate goal of recharge in the Hesbaye region is to support drinking water production, regulated by the EU Drinking Water Directive (DIRECTIVE (EU) 2020/2184) that sets a limit of 100 ng L^{-1} for the sum of 20 priority PFAS, the runoff itself is first evaluated against proposed Environmental Quality Standards (EQS). These standards set a restrictive threshold of 4.4 ng L^{-1} for the sum of 24 PFAS, expressed as PFOA equivalents (European Commission, 2022; EEA, 2024).

This approach uses relative potency factors (RPFs) to rank individual PFAS against PFOA (European Commission, 2022; Bil *et al.*, 2023). For example, PFOS is assigned an RPF of 2, meaning the 310 ng L^{-1} measured in the airport basin represents 620 ng L^{-1} in PFOA equivalents, which is two orders of magnitude above the designed EQS. Shorter-chain or replacement compounds often exhibit lower relative potencies. For instance, PFPeA (RPF 0.05; Bil *et al.* 2020) and 6:2 FTS (RPF 0.02; Bil *et al.* 2020) contribute to 16.5 ng L^{-1} and 11.8 ng L^{-1} respectively to the weighted sum. While a harmonized RPF for the cyclic PFAS PFECHS is not yet established in EU directives, recent studies rank its potency below that of PFOS but emphasize its high environmental persistence (Mahoney *et al.*, 2022).

Even when applying these weighting factors, individual concentrations of PFOS, PFPeA, and 6:2 FTS each independently exceed the cumulative 4.4 ng L^{-1} threshold. This underlines the widespread contamination in airport runoff and supports the transition toward PFAS-free firefighting foams at the airport. However, given the magnitude to which these levels exceed both environmental thresholds and long-term drinking water targets, continuous monitoring remains essential for the safe implementation of MAR operations.

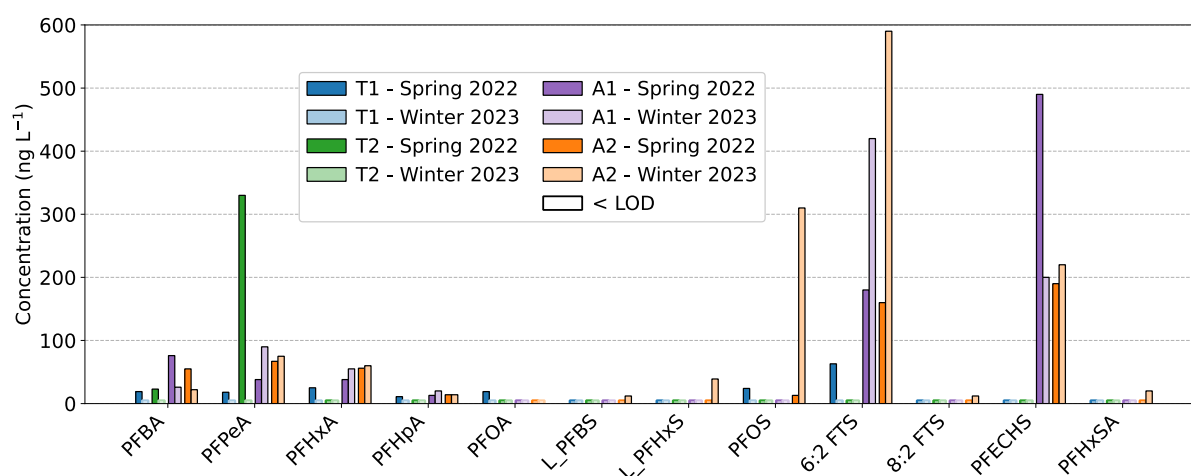


Figure 19. Concentration of detected PFAS measured in stormwater basins during Spring 2022 and Winter 2023. Bars represent the four basins (T1, T2, A1 and A2), with darker colours for spring and lighter tones for winter. Empty outlined bars indicate concentrations below the analytical limit of detection (< LOD).

3.2.3. Organophosphate flame retardants (OPFRs)

As explained in Chapter 3, OPFRs have increasingly replaced PBDEs in electronics, building materials, furniture and textiles. Because many OPFRs have relatively high solubility, they are frequently detected in surface waters. In this study, out of nine studied OPFRs, six were detected: TCEP, TCPP, TDCPP, TBEP, 2-ethylexyl diphenyl phosphate and tributyl phosphate. OPFRs were analysed in spring 2022 but subsequent campaigns did not include them unfortunately due to budget constraints. The measured concentrations in each basin are shown in Figure 20.

- **Airport basins (A1 and A2):** A1 presents the greatest diversity and magnitude of OPFRs detections (six compounds), with TCPP reaching 3200 ng L⁻¹, followed by TBEP (610 ng L⁻¹), tributyl phosphate (570 ng L⁻¹), and TDCPP (280 ng L⁻¹). On the other hand, A2 shows only two OPFRs: TCPP (410 ng L⁻¹) and 2-ethylhexyl diphenyl phosphate (250 ng L⁻¹). These elevated levels in airport basins make sense given that OPFRs are used in aircraft lubricating oils and hydraulic fluids (Li et al. 2019). The greater diversity and magnitude observed in A1 likely arises from its larger and more complex drainage area, which includes taxiways and runways where aircraft operations occur, whereas the A2 basin drains a smaller area with limited aircraft circulation and consequently lower contaminant inputs.
- **Traffic-related basins (T1 and T2):** In T1, only TCPP (1300 ng L⁻¹) and 2-ethylhexyl diphenyl phosphate (470 ng L⁻¹) were detected, with the latter being remarkably high compared to other basins. In T2, three OPFRs were quantified at more moderate levels: TCEP (340 ng L⁻¹), 2-ethylhexyl diphenyl phosphate (300 ng L⁻¹), and tributyl phosphate (320 ng L⁻¹). The sources in these traffic-related catchments may reflect urban and residential inputs, such as the use of OPFR-containing materials in household products, insulating foams, and textiles, as well as diffuse emissions from wastewater and atmospheric deposition which have been identified as common urban pathways for these compounds (Peter *et al.*, 2024).

To date, there are no existing EQS in Europe specifically for OPFRs. However, some regulatory steps have been taken such as the limitation of TCEP, TCPP and TDCP in toys to 5 mg kg⁻¹ (EC, 2014). In addition, the United States Environmental Protection Agency (US-EPA) has published its final risk evaluation of TCEP, concluding that it poses in an “unreasonable” risk as it has the potential to cause kidney cancer, damage the nervous system and kidneys and fertility issues (US-EPA, 2024).

Therefore, given the lack of published EQS thresholds, these results cannot yet be compared to regulatory limits. However, the high concentration observed indicate that OPFR contamination is occurring but is not trivial and deserves monitoring and further toxicity evaluation.

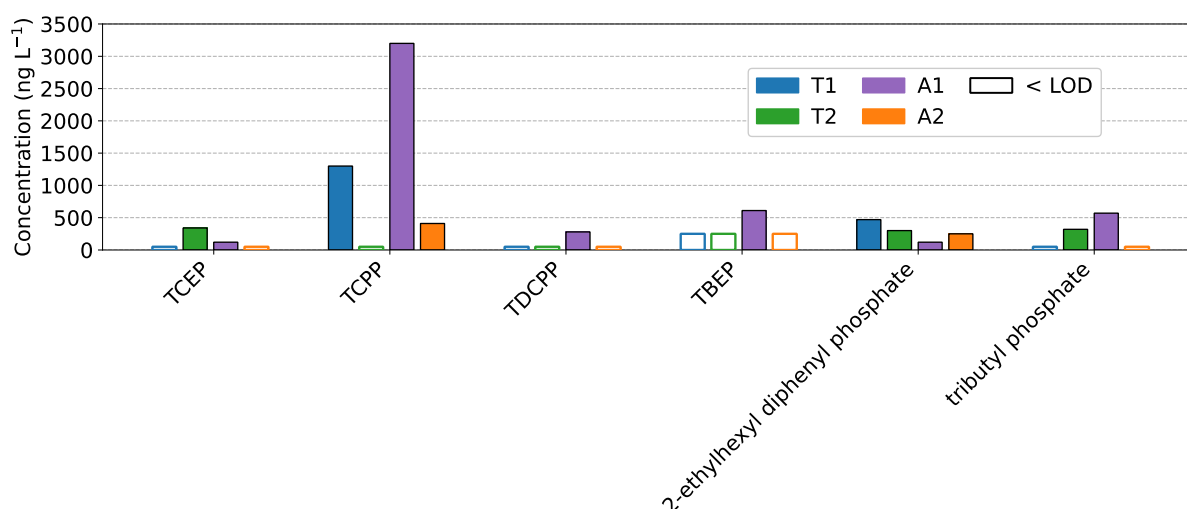


Figure 20 Concentration of organophosphate flame retardants (OPFRs) measured in stormwater basins during Spring 2022. Bars represent the four basins (T1, T2, A1 and A2), with darker colours for spring and lighter tones for winter. Empty outlined bars indicate concentrations below the analytical limit of detection (< LOD).

3.2.4. Benzotriazoles

Benzotriazoles (BTs) and their methylated derivatives (4- and 5-methylbenzotriazoles, also referred as tolyltriangles) were quantified only during the winter campaign in T2 and A1 basins. The restriction of

BT analysis to winter is justified by their primary use as corrosion inhibitors in aircraft and pavement de-icing fluids, which are applied exclusively during cold months (see Chapter 3). In *T2*, representative of a traffic-related stormwater basin, benzotriazole and 5-MeBT were detected at 1400 ng L^{-1} and 440 ng L^{-1} respectively. On the other hand, in *A1* which is characterized as an airport stormwater basin, BTs and 5-MeBT concentrations reached 390 ng L^{-1} and 360 ng L^{-1} respectively. Similar winter occurrences of benzotriazole compounds in airport areas have already been documented in different studies (Alotaibi *et al.*, 2015), relevant with our findings.

In traffic-related basins such as *T2*, the origin of triazoles is more likely related to domestic sources since these compounds are also widely used in household products such as dishwasher detergents, cooling and hydraulic fluids, and metal protection agents (Kiss and Fries, 2009b). Their presence in *T2* therefore suggests a predominant wastewater origin, consistent with the higher influence of sewage water discharge in this basin. On the other hand, the detections in *A1* are clearly associated to the use of ADAFs containing benzotriazoles as corrosion inhibitors in their formulation.

Unfortunately, seasonal influence could not be evaluated as the monitoring was limited to winter. Nevertheless, it is reasonable to assume that BTs concentrations in spring and summer would be significantly lower in airport basins, reflecting the absence of de-icing activities at that time of the year. Conversely, in traffic-related stormwater basins receiving both stormwater and wastewater discharges, inputs are expected to occur more continuously throughout the year rather than through episodic runoff events.

Although benzotriazoles are not currently regulated under the EU Water Framework Directive, they are increasingly recognized as contaminants of emerging concern due to their persistence, low biodegradability, and potential aquatic toxicity (Alotaibi *et al.*, 2015; Avagyan *et al.*, 2015). Reported concentrations in surface waters typically range from a few tens to several thousand ng L^{-1} (Alotaibi *et al.*, 2015; Molins-Delgado *et al.*, 2017; Ruiling Zhang *et al.*, 2023b). The concentration levels measured in this study fall within the same range as those previously reported, although some higher detected values such as in *T2* require particular attention for future monitoring.

3.3. Synthesis of the field campaigns

The identification and characterization of potential recharge water sources in the Hesbaye region highlighted stormwater as a promising alternative for MAR. Among the listed stormwater basins (see Chapter 2), four sites were selected for detailed investigation based on their representativeness, exploitable volume and accessibility: two mixed runoff-wastewater basins (*T1* and *T2*) and two airport stormwater basins (*A1* and *A2*). This selection enabled the distinction of contrasting hydrological and chemical conditions, ranging from runoff drainage network receiving continuous wastewater inflows to systems dominated solely airport runoff.

Overall, the hydrochemical analyses revealed moderate mineralization and close to neutral pH across most samples outside the winter period, with water compositions generally plotted close to the transition between a Ca-HCO_3 and a more mixed Na-K-HCO_3 facies. This pattern reflects the combined natural background influence and anthropogenic inputs. In contrast, winter conditions were marked by a pronounced increase in mineralization at several sites, likely associated with de-icing and road-salting practices. Clear differences nevertheless emerged between the two basin categories:

- The mixed runoff-wastewater basins (*T1* and *T2*) showed higher electrical conductivity, reducing conditions, elevated concentrations in nutrients (phosphorus and nitrate), and alkylphenols. This pattern probably reflects the influence of constant domestic wastewater

inputs within the drainage network, which results in a mixed chemical signature between urban runoff and sewage effluents.

- In contrast, the airport basins (A1 and A2) were characterized by an overall better chemical quality outside the winter period, with lower mineralization and higher dissolved oxygen levels. Nevertheless, they were affected by specific contaminants related to airport operations such as the use of firefighting foams, hydraulic fluids, and de-icing products. Accordingly, PFAS, benzotriazoles, and OPFRs were detected, highlighting operational fingerprints specific to the airport environment.

Seasonality further controlled these patterns. Winter conditions were characterized by a marked increase in mineralization and a shift in ionic dominance (Na^+ , K^+ and Cl^-) at the airport sites and near traffic-influenced locations, consistent with de-icing and road-salting practices. Autumn samples were generally more representative of baseline stormwater conditions, whereas spring samples more strongly reflected first-flush effects following dry periods.

4. Conclusion

The identification and characterization of potential recharge water sources in the Hesbaye region indicate that stormwater basins could provide exploitable volumes for MAR, but that water quality and chemical compatibility with the chalk groundwater remain the main constraints to address. The field campaigns show that the candidate waters are not chemically equivalent to the target groundwater and may introduce (i) redox perturbations, notably in T1–T2 where low dissolved oxygen and elevated organic matter indicate reducing conditions, (ii) ionic contrasts and seasonal pulses, notably in winter with Na–K–Cl signature, and (iii) a diverse mixture of micropollutants linked to wastewater inputs, traffic-associated contamination and airport-related activities. From a MAR perspective, these differences imply that recharge feasibility will depend on period selection and operational management. It implies notably to avoid winter high-ionic-input events, and to account for the stronger wastewater influence in T1–T2. Finally, the natural capacity of Hesbaye sediments to attenuate contaminants and to buffer geochemical changes during infiltration is a key aspect to consider for MAR feasibility assessment.

This chapter further demonstrates that the considered waters contain multiple contaminant families at concentrations that may represent a potential threat for groundwater quality if transferred conservatively without any effective attenuation processes. Therefore, assessing MAR suitability requires determining whether these substances are attenuated, transformed, or persistent upon contact with local sediments under relevant geochemical conditions.

Based on the field results and on their relevance for MAR, three contaminant groups were selected for further investigation: (i) alkylphenols, as markers of wastewater/detergent inputs representative of conditions in T1–T2, (ii) benzotriazoles, as characteristic airport-related compounds during winter conditions, and (iii) PFAS due to their ubiquitous occurrence and their well-known persistence and mobility for short-chain compounds. These target groups they exhibit potential PMT behaviour (persistence, mobility, and toxicity), making them particularly relevant for assessing groundwater protection in MAR contexts. Other contaminant families detected in the field (e.g., OPFRs and PAHs) were not prioritized for the experimental phase due to analytical/logistical constraints and/or because they were less central to the objectives of the present work. The following chapter therefore investigates the physico-chemical behaviour of the selected CECs upon contact with Hesbaye sediments, with the aim of quantifying attenuation processes and identifying potential risks for MAR.

Chapter 5

Lab-Scale insights into the environmental fate of emerging contaminants from urban runoff

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Abstract³

Contaminants of emerging concern (CECs) present in runoff pose risks to groundwater quality during their infiltration. Understanding the processes that control their attenuation is therefore essential for designing effective mitigation strategies. This research investigates the attenuation capacity of loess sediments overlaying a major Cretaceous chalky aquifer in Belgium, as part of a pre-feasibility study of soil aquifer treatment (SAT) system using airport runoff. In particular, the study aims to assess the natural ability of these sediments to filter and biologically degrade detected contaminants in airport runoff, thereby reducing their concentrations to levels compliant with water quality standards. Controlled batch experiments were thus conducted to analyse the sorption and biodegradability of key CECs, including PFAS, alkylphenols and benzotriazoles. The experiments were performed in triplicate using batch reactors filled with sediments and synthetic runoff. An abiotic control was included to distinguish between sorption and biodegradation. Results revealed distinct attenuation behaviours. Nonylphenol diethoxylate showed the highest removal, driven entirely by biodegradation with no contribution from sorption. Benzotriazole, tolyltriazole, PFOS, and 6:2 FTS showed moderate attenuation, primarily due to sorption for PFAS compounds. The remaining PFAS, — PFOA, PFHxA, and PFECHS — exhibited low attenuation, limited by sorption and no biodegradation. These findings confirm that loess sediments can reduce loads of certain CECs and also highlight the persistence of PFAS in water during infiltration. The results provide critical parameters for modelling CECs transport during SAT operations and support the safe management of airport runoff as a recharge source.

Keywords: PFASs, Emerging Contaminants, Runoff, Soil Aquifer Treatment, attenuation processes, chemical modelling, batch experiments

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Chapter context

Despite the promising potential of urban runoff as a recharge source from a quantitative perspective, the sampling campaigns results detailed in Chapter 4 revealed the presence of several organic micropollutants, including a range of CECs. These compounds are particularly important to address because of their persistence, mobility, and potential toxicity. Notably, alkylphenols, PFAS, and benzotriazoles were detected at significant concentrations (hundreds of ng L^{-1}). To assess the impact of MAR using such water sources, it was necessary to evaluate the physicochemical behaviour of the identified CECs when being in contact with the sediments of our study area⁴. Determining the key attenuation parameters of these contaminants, such as their sorption coefficients and biodegradation rates, is essential to predict their potential migration through the unsaturated zone and to evaluate whether they could reach the Hesbaye chalk aquifer if infiltrated without prior treatment.

This chapter, presented as an article published in the *Journal of Contaminant Hydrology*, reports batch experiments carried out at laboratory-scale under the supervision of Estanislao Pujades and Anna Jurado at IDAEA-CSIC (Barcelona). The experiments were designed to study the attenuation processes affecting selected CECs previously detected in the airport runoff. The target compounds included benzotriazole, 5-methylbenzotriazole (tolyltriazole), PFOA, PFOS, PFHxA, 6:2 FTS, PFECBS, and nonylphenol diethoxylate (NP_2EO). This study showed that the loess sediments of the Hesbaye region exhibit a moderate but measurable capacity to attenuate the target contaminants present in urban runoff. These findings therefore indicate that attenuation within the loess layer may mitigate the direct transfer of CECs toward groundwater but cannot be considered as a definitive purification process.

The parameters derived from these experiments were integrated into the two-dimensional transport model presented in chapter 7, which simulates contaminant migration through the unsaturated loess layer under infiltration conditions representative of MAR. This modelling work aims to evaluate the potential for natural attenuation within the vadose zone and to assess whether such processes are sufficient to prevent CECs from reaching the underlying chalk aquifer. To reliably simulate these processes, the model also requires a robust characterization of the flow dynamics controlling recharge beneath the infiltration basin. Chapter 6 therefore presents the field investigation carried out to quantify infiltration rates at the base of the pilot infiltration basin.

⁴ Loess covering the Hesbaye chalk aquifer.

1. Introduction

Managed Aquifer Recharge (MAR) is a promising strategy to address the increasing global water demand and groundwater depletion by artificially augmenting groundwater recharge, thereby enhancing storage capacity, groundwater quality and resource sustainability (Sprenger *et al.*, 2017; Dillon *et al.*, 2020). MAR also offers solutions to environmental challenges such as saltwater intrusion (Pyne, 2015) or land subsidence (Seidl *et al.*, 2024). In addition, MAR can improve the quality of recharge water through Soil Aquifer Treatment (SAT) systems that rely on natural physical, chemical and biological processes in the soil and subsurface (Ringleb *et al.*, 2016). Suitable water sources for MAR operations include treated wastewater, surface water and runoff water (Dillon *et al.*, 2019). In particular, urban runoff water is notably accessible in urban and peri-urban areas (Han *et al.*, 2022). Nevertheless, the use of runoff water as a recharge source necessitates rigorous quality assessment to prevent pollution risks to groundwater systems, as it frequently contains contaminants originating from anthropogenic activities (Masoner *et al.*, 2019). Thus, selecting suitable water sources for recharge is critical for SAT efficiency and environmental safety.

Urban runoff is a complex matrix containing conventional pollutants (Zgheib *et al.*, 2012; Gasperie *et al.*, 2014; Launay *et al.*, 2016; Spahr *et al.*, 2020) and contaminants of emerging concern (CECs) such as pharmaceuticals, personal care products, and industrial chemicals (Gasperi *et al.*, 2014, 2022; Pinasseau *et al.*, 2020). Airport runoff, which is generated by the extensive impervious surfaces, is of particular interest due to its high volume and potential for resource recovery (Jaiyeola, 2017). Capturing and recharging this water through MAR could help mitigate flooding risks in airport areas while contributing to groundwater resources. However, the chemical quality of airport runoff raises concerns regarding its suitability for direct infiltration into aquifers. Airport areas are routinely exposed to de-icing agents, hydraulic fluids, fuel residues, and other pollutants associated with aviation activities (Sulej *et al.*, 2011). This exposure results in a diverse range of contaminants on airport surfaces such as heavy metals, glycols, benzotriazoles, detergents, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, formaldehydes, phenols and PFAS (Jia *et al.*, 2018; Pressl *et al.*, 2019; Sulej-Suchomska *et al.*, 2021). During rainfall events, these contaminants are washed away and transported via runoff to stormwater basins. Recent studies, such as the review by Sulej-Suchomska *et al.* (2024), highlights the widespread occurrence of these contaminants in airport runoff. For instance, benzotriazoles and its derivatives have been detected at concentrations ranging from 0.083 to 156 $\mu\text{g}\cdot\text{L}^{-1}$. PFAS levels have also been found to be significant, with concentrations in runoff from Chinese airports ranging between 19 to 342 $\text{ng}\cdot\text{L}^{-1}$. Additionally, Ahrens *et al.* (2015) reported elevated concentrations of PFAS in a lake near a Swedish airport, with the sum of PFOA, PFHxA, PFOS and PFHxS ranging between 150 and 350 $\text{ng}\cdot\text{L}^{-1}$ during 2009–2013.

Understanding the factors that govern the fate and transport of CECs in soil during infiltration is thus crucial for assessing their potential impacts on groundwater quality. During infiltration, soil can act as a natural filtration barrier, attenuating pollutant concentrations through processes such as sorption, biodegradation and physical retention (Tedoldi *et al.*, 2016b). These mechanisms are central to SAT systems, where natural subsurface processes mitigate contaminants loads during MAR operations with surface-based infiltration systems (Sharma and Kennedy, 2017). The efficiency of these processes varies significantly depending on the physicochemical properties of CECs —such as solubility, polarity, and biodegradability (Lapworth *et al.*, 2012) —as well as soil characteristics, including porosity, organic matter content, mineral composition, and the presence of microbial communities (Boyd *et al.*, 1988;

Semple et al., 2007; Cheng et al., 2012). For example, hydrophobic contaminants tend to bind strongly to soil particles, reducing their mobility, while hydrophilic and polar compounds, such as pharmaceuticals and pesticides, are more prone to leaching, posing a greater risk of groundwater contamination. The persistence of PFAS highlights the need for an in-depth evaluation of their behaviour in SAT systems (Mumberg et al., 2024). Gaining insight into these interactions can inform the design of SAT systems to enhance natural attenuation and prevent groundwater pollution.

Laboratory studies on CEC behaviour are often based on kinetic sorption experiments, where contaminants are introduced into soil in controlled environments such as polypropylene bottles or falcon tubes (Zhang et al., 2015, Askeland et al., 2020, Barth et al., 2021; Dai et al., 2023; Hubert et al., 2023). These experiments primarily aim to quantify sorption processes by measuring the equilibrium distribution of contaminants between the solid and liquid phases. Sorption tests are valued for their simplicity, cost-effectiveness, and ability to provide detailed data on specific interactions between contaminants and soil particles, such as adsorption isotherms and partition coefficients (Zhang et al., 2015). These results are fundamental for understanding contaminant behaviour and for informing predictive models of their transport (Kret *et al.*, 2015). However, these simplified setups do not fully replicate the complexity of natural environments, as they often do not consider other attenuation mechanisms like biodegradation or chemical transformation, which can significantly reduce contaminant concentrations over time. Therefore, comprehensive batch experiments that incorporate multiple attenuation processes simultaneously are essential for a more accurate prediction of CEC behaviour in SAT settings.

This study is motivated by MARWAL project, which aims to assess the technical, regulatory, and economic feasibility of utilizing alternative sources like airport runoff for MAR in the Hesbaye chalk aquifer, with the goal of enhancing regional groundwater resilience (Brouyère, 2024). MAR through SAT systems is particularly relevant in Hesbaye, where the aquifer faced significant declines in groundwater levels and quality over the past decades (Hakoun *et al.*, 2017a; Goderniaux *et al.*, 2023). In this context, the study involved designing comprehensive batch experiments to evaluate the attenuation capacity of loess sediments overlaying the Hesbaye chalk aquifer in Belgium when exposed to airport runoff water. Sampling campaigns carried out as part of this study revealed the presence of PFAS, alkylphenols, and benzotriazoles in airport runoff, originating from airport-related activities. The experiments were conducted in a laboratory setting to simulate the interactions between the sediments and the identified CECs in airport runoff water. The primary goal was to quantify the overall attenuation of each contaminant after the experiment. A secondary objective was to identify which contaminants were most sorbed or attenuated in contact with loess sediments. Finally, the influence of redox conditions on CECs degradation was analysed. By simulating these soil-contaminant interactions in the laboratory, the study aimed to deepen our understanding of the natural attenuation potential of loess sediments. This is an essential consideration for evaluating the long-term safety and viability of SAT with airport runoff as a recharge source.

2. Materials and Methods

2.1. Sampling

2.1.1. Runoff water

To assess the chemical quality of runoff water in the study area, samples were collected from stormwater retention basins connected to roads and the Liège airport. These grab samples were collected following rainfall events in spring 2022 and winter 2023, ensuring that the water was representative of potential contaminants mobilized during stormwater runoff. The timing of sampling at different seasons was chosen to partially account for seasonal variability.

The selection of the contaminants was based on a target screening approach using literature data, prioritizing compounds commonly found in urban runoff (Zgheib et al., 2012; Burant et al., 2018; Spahr et al., 2020; Gasperi et al., 2022). Special attention was given to persistent, mobile, and toxic (PMT) organic contaminants (Mutzner *et al.*, 2023), which are of particular concern for groundwater contamination. Alkylphenol analyses were conducted by ISSEP (Belgium) using LC-MS/MS. Benzotriazoles and PFAS were analysed by Celabor (Belgium), also using LC-MS/MS.

In addition, samples were collected to determine major ion composition, electrical conductivity, and pH. Major ion analyses were performed by the Hydrogeology and Environmental Geology Laboratory at the University of Liège using a Metrohm Professional 850 IC AnCat - MCS system. All this information is essential for formulating a synthetic water solution in the lab that mimics the composition of the sampled runoff water.

2.1.2. Loess sediments

To assess the interactions between runoff water and the sediments, loess sediment samples were collected at a depth of 50 cm from an infiltration basin in the Hesbaye region using a hand auger. Grain size distribution analyses were carried out in the Building Materials Laboratory (LMC) at the University of Liège to characterize the sediment texture, with detailed results provided in Section 1 of Annex C. The remaining sediments were then transported in cold conditions to IDAEA-CSIC laboratory (Barcelona), where they were frozen before the start of the batch experiments.

Additional loess sediment samples from the region were collected similarly and analysed for their organic carbon content. These analyses were conducted by the BEAGx laboratory at the University of Liège using wet oxidation of humic substances.

2.2. Experimental set-up

2.2.1. Batch and control reactors

Batch experiments were conducted in triplicate to assess the attenuation of selected CECs present in airport runoff water when being in contact with loess sediments. The target compounds included benzotriazole, tolyltriazole, nonylphenol diethoxylate (NP2EO), PFOA, PFOS, PFHxA, PFECHS and 6:2 FTS. The experimental set-up consisted of three 3.5 L reactors, each operated for four weeks, as attenuation processes in static batch systems are expected to occur mainly during the initial phase of the experiment. Indeed, sorption equilibrates rapidly, and biodegradation is in principle most active under oxic conditions before slowing down significantly once oxygen is depleted. A volumetric ratio of

85:15 between the aqueous and the solid phases was selected to ensure sufficient water volume for repeated sampling during the experiment, while maintaining a stable solid–liquid balance (see Figure 21a). The solid to liquid ratio was also chosen as a compromise for being not too large to prevent the development of redox zoning within the sediments, and not too small to prevent a minimization of the effective surface available for sorption processes. This choice was made similarly to the approach employed by Villa *et al.* (2025) and Pujades-Garnes *et al.* (2025), where batch experiments were set-up to evaluate the fate of pharmaceuticals and gadolinium in groundwater, respectively. In practice, this ratio was approximated based on sediment density (grain density = $2.7 \text{ g}\cdot\text{cm}^{-3}$; wet density = $1.80 \text{ g}\cdot\text{cm}^{-3}$) and corresponds to an approximate liquid-to-solid mass ratio of 4:1. The aqueous phase comprised synthetic runoff water, formulated to mimic the chemical composition of the runoff water. The solid phase consisted of unconsolidated loess sediments collected from the Hesbaye region.

Each reactor bottle was equipped with a cap consisting of three screw connectors with ports (see Figure 21a). The first one was connected to the sampling tube, which was sealed between samplings events. The second one was connected to the nitrogen inlet, which was also closed between the collection of samples. The last one was connected to a pressure valve, which allowed pressure balance with the ambient air inside the incubator.

An additional 2.5 L abiotic control reactor was operated under identical conditions and duration. The objective of the abiotic control was to evaluate the sorption of CECs onto loess sediments, since any attenuation observed in the absence of microorganisms can only result from sorption processes. This single abiotic control design follows common practice in batch and column experiments, where one abiotic control is used to evaluate abiotic losses (sorption) in comparison to biotic reactors (Gulde *et al.*, 2014; De Wilt *et al.*, 2018; Schübl *et al.*, 2021; Pujades-Garnes *et al.*, 2025; Villa *et al.*, 2025). To set-up the abiotic control, sediments were sterilized by autoclaving at 120°C for 20 minutes to eliminate all microbial activity. After sterilization, synthetic water was added to the reactor along with sodium azide (NaN_3) at a concentration of $100 \text{ mg}\cdot\text{L}^{-1}$ to ensure the inhibition of any remaining microbial activity (Lichstein and Soule, 1944; Cabrol *et al.*, 2017; Suresh *et al.*, 2020). Previous studies have reported that this sterilization method does not significantly interfere with sorption behaviour of organic chemicals on similar soils (Roberts *et al.*, 2014; Süßmuth *et al.*, 2024). This approach ensures that the abiotic control focuses exclusively on sorption mechanism.

The experiment was conducted within a closed incubator maintained at 14°C in the dark to simulate typical surface water temperatures in Belgium, and to prevent light from affecting bacteriological activity (see Figure 21b). Samples were collected daily during the first week and weekly thereafter for a period of one month to monitor the concentrations of DOC (dissolved organic carbon), major ions and CECs. Dissolved oxygen (DO) was also measured regularly throughout the experiment. Sampling volumes were carefully controlled to maintain the solid-liquid ratio within a 5% margin by the end of the experiment. During each sampling time, nitrogen gas was purged through the system to compensate for the extracted volume and to preserve stable experimental conditions. Additional images of the experimental set-up are provided in the Section 2 of Annex C.

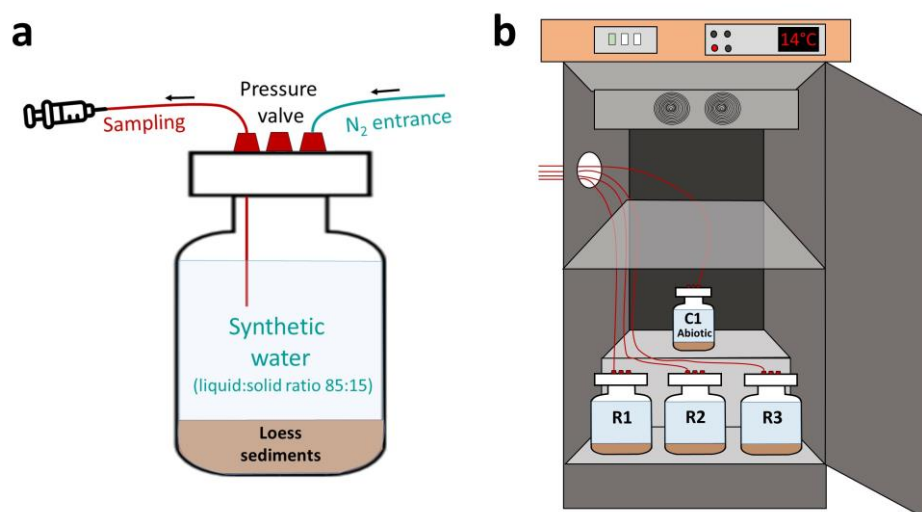


Figure 21. a) Individual batch reactor set-up, and b) arrangement of the batch reactors and the abiotic control in the incubator maintained at 14°C. Note that the nitrogen pipes are not represented in the entire experimental set-up for sake of clarity.

2.2.2. Synthetic runoff water preparation

Synthetic water was prepared by dissolving six different salts ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, KNO_3 , NaHCO_3 , CaCl_2 , $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in Milli-Q water to mimic the major ion composition of runoff water. The resulting ionic composition is detailed in the section 3 of Annex C. Furthermore, the synthetic water was designed to reflect DOC contributions from both loess sediments and runoff water, targeting a concentration of $8 \text{ mg} \cdot \text{L}^{-1}$. DOC measurements were of $3.2 \text{ mg} \cdot \text{L}^{-1}$ from loess sediments and $4.8 \text{ mg} \cdot \text{L}^{-1}$ from runoff. BDOC (biodegradable dissolved organic carbon) was assumed to consist of 60% easily biodegradable carbon (high BDOC) and 40% recalcitrant organic carbon (low BDOC), a reasonable estimate given that soil DOC is largely stabilized as humic substances (Ukalska-Jaruga *et al.*, 2021). To replicate this composition, high BDOC ($4.8 \text{ mg} \cdot \text{L}^{-1}$) was introduced using peptone (mix of amino acids), while low BDOC ($3.2 \text{ mg} \cdot \text{L}^{-1}$) was represented by humic acid salt ($\text{C}_9\text{H}_8\text{Na}_2\text{O}_4$). To assess the evolution of total BDOC over time, samples were collected, acidified and analysed with a total organic carbon analyser (Multi N/C 3100 Analytical Jena) in the CCiTUB laboratory (Spain).

2.2.3. Acclimation phase and CECs spiking

Prior to the introduction of CECs, a 7-day acclimation phase was conducted to allow microbial communities to equilibrate and initiate the degradation of the DOC fraction. During this phase, reactors were bubbled with air twice daily to maintain oxic conditions. It was assumed that the high BDOC fraction (peptone) would be partially biodegraded, while the low BDOC (humic acid) remained largely stable.

At the end of the acclimation period, the same quantity of peptone was re-added to the reactors to restore the initial DOC concentration. Subsequently, target CECs were introduced into the batch reactors and the abiotic control at a final concentration of $0.05 \mu\text{g} \cdot \text{mL}^{-1}$ for each compound. Due to limited availability, PFECHS and NP2EO were added at a lower concentration of $0.0015 \mu\text{g} \cdot \text{mL}^{-1}$. Sodium azide was also added at the end of the acclimation period to the abiotic control at $100 \text{ mg} \cdot \text{L}^{-1}$ to ensure continued inhibition of microbial activity.

Since the results from the batch experiments reflect both sorption and biodegradation processes, their comparison with the abiotic control enables the estimation of the biodegradation contribution to the overall attenuation, assuming that sorption and biodegradation are the primary attenuation mechanisms. Although a biotic control was initially included to isolate the effects of biodegradation, it was excluded from the analysis after no change in DOC concentration was observed, suggesting insufficient microbial activity to support biodegradation.

2.3. Extraction and analysis of CECs

2.3.1. Products acquisition

Standards of benzotriazole and tolyltriazole were purchased from A2S (France). The standard PFECHS, PFOA, PFOS, PFHxA, 6:2 FTS and the internal standards M-PFOA and M-PFOS were purchased from Wellington laboratory (Canada). Finally, nonylphenol diethoxylate (NP2EO) was purchased from Dr. Ehrenstorfer (Augsburg, Germany).

2.3.2. Sample preparation and HPLC-MS/MS analysis

Aqueous samples (20 mL) collected during the batch experiment were transferred into 40 mL polypropylene Falcon tubes and centrifuged at 3500 rpm for 10 minutes to separate fine loess particles. After centrifugation, 1 mL of the supernatant was transferred into 1.5 mL glass vials and stored in the freezer until analysis.

Samples were then thawed, and 500 μL of supernatant was transferred into chromatographic vials. To achieve a final volume of 1 mL with a 50:50 ratio of aqueous to organic solvent, 370 μL of methanol, 50 μL of isotopically labelled internal standard solution (m-PFOA and m-PFOS, 1 $\mu\text{g}\cdot\text{mL}^{-1}$), and 80 μL of ammonium acetate solution (125 mM) were added. The sample was then homogenised using a vortex mixer.

Once all the samples are collected, high performance liquid chromatography coupled to a triple quadrupole mass analyser (HPLC-MS/MS) with an electrospray ion source (Waters, Milford, USA) was used to quantify CECs concentration. A BEH C18 analytical column (100 mm $\times$ 2.1 mm, particle size 1.7 μm) (Acquity, Waters, Milford, USA) was deployed, with a flow rate of 300 $\mu\text{L}\cdot\text{min}^{-1}$ and a sample injection volume of 25 μL . The analysis method was adapted from the method reported for PFAS (Dulsat-Masvidal *et al.*, 2022) to include triazoles and alkylphenols in a single analysis.

The mobile phase consisted of two mixtures: an organic mixture (A) containing methanol and acetonitrile in an 80:20 ratio with 10 mM ammonium acetate, and an aqueous mixture (B) containing water with 10 mM ammonium acetate. The gradient elution began with a 50:50 ratio of A and B, maintained for 3 minutes, and gradually increased to 100% of A over 7 minutes, held this condition for 3 minutes, and finally returned to the initial 50:50 ratio in 5 minutes. Blank samples were regularly included to verify the absence of carry-over and contamination. To eliminate the contribution of background PFAS from the mobile phase and LC tubing, a reused XBridge C18 column (50 $\times$ 4.6 mm, particle size 3.5 μm) was used as a trap column.

Flow injection analysis was conducted to optimize the HPLC-MS/MS parameters (cone collision energy and ionization mode, among others) and ensure the detection of all compounds. The various parameters and experimental conditions are detailed in the section 4 of Annex C. The target compounds were quantified using the internal standard method, with M-PFOA for all perfluorinated

carboxylic acids (PFCA), M-PFOS for perfluorinated sulfonic acids (PFSAs) and both M-PFOA and M-PFOS for compounds other than PFAS. Mass Lynx v.4.1 software was used for instrument setup, data acquisition, and data processing.

2.3.3. Quality control

To accurately quantify the CECs concentration from batch experiment samples, a calibration curve with seven points was built over a concentration range of 0.0005 to 0.1 ng.μL⁻¹ for each studied compound, with internal standards kept at a constant concentration of 0.05 ng.μL⁻¹. The selected concentration range was chosen to match the expected concentration levels of contaminants introduced into the batch reactors, ensuring analytical sensitivity and relevance to the experimental conditions. Calibration standards were prepared in methanol:water (50:50) and buffered with ammonium acetate. Details on samples preparations for the calibration curve are available in the section 5 of Annex C.

Linearity was evaluated by calculating the coefficient of determination (R²), which was above 0.95 for all target analytes, indicating a strong correlation between instrument response and analyte concentration. The relative response factor (RRF) was calculated using the ratio of the analyte peak area to that of its corresponding internal standard. The different calibration curves for each CECs and their associated R² are also available in the section 5 of Annex C.

2.4. Numerical modelling of the hydrochemical processes

Once the batch experiment results were obtained, they were reproduced numerically to gain deeper insights into the behaviour of the target CECs. In addition, the calibration of these models facilitated the determination of key parameters governing CECs attenuation, such as their maximum degradation rate and their sorption coefficient. The hydrochemical processes occurring in the batch reactors were simulated using PHREEQC (Parkhurst and Appelo, 2013), a geochemical modelling software particularly suited for simulating sorption and redox reactions. To refine the model and optimize parameter estimation, automated calibration was conducted using the PEST software (Doherty, 2010).

2.4.1. Sorption modelling

The sorption behaviour was evaluated using a linear reversible sorption model. The rate of adsorption/desorption for an aqueous species *i* is described by Tebes-Steven et al. (1998) by the following equation:

$$r_{sorption} = -k_m \times (C_i - \frac{s_i}{K_d}) \quad (3)$$

where k_m designates the mass transfer coefficient in h⁻¹, C_i the aqueous concentration of species *i* in mol g⁻¹, s_i the adsorbed concentration of species *i* in mol·g⁻¹ and K_d the linear distribution coefficient for linear equilibrium adsorption. This formulation (Eq. 3) accounts for both adsorption and desorption processes driven by concentration gradients between the solid and liquid phases, with molecular diffusion controlling the mass transfer coefficient (Weber et al., 1991) in the absence of advection and dispersion. Desorption was not directly quantified in this study due to the lack of solid-phase concentration measurements.

2.4.2. Reactive modelling

The degradation of high BDOC and CECs was modelled considering the evolving redox conditions in the batch reactors using first-order Monod-type kinetics, accounting for oxygen availability and inhibition effects under nitrate reducing (NR) conditions (Barkow *et al.*, 2021):

$$r_{A,oxic} = -\lambda_{A,oxic} \times C_A \times \frac{C_{O_2}}{K_{O_2} + C_{O_2}} \quad (4)$$

$$r_{A,NR} = -\lambda_{A,NR} \times C_A \times \frac{K_{inh,O_2}}{K_{inh,O_2} + C_{O_2}} \times \frac{C_{NO_3^-}}{K_{NO_3^-} + C_{NO_3^-}} \quad (5)$$

where A represents either high BDOC or a CEC, λ the maximum degradation rate ($\text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$), C_A the concentration of high BDOC or a CEC ($\text{mol}\cdot\text{L}^{-1}$), C_{O_2} the oxygen concentration ($\text{mol}\cdot\text{L}^{-1}$), $C_{NO_3^-}$ the nitrate concentration ($\text{mol}\cdot\text{L}^{-1}$), K_{O_2} and $K_{NO_3^-}$ the half-saturation constants ($\text{mol}\cdot\text{L}^{-1}$) and K_{inh,O_2} the inhibition coefficient of oxygen ($\text{mol}\cdot\text{L}^{-1}$). Additional details on the complete set of stoichiometric reactions and the corresponding ordinary differential equations (ODEs) are provided in Section 6 of Annex C.

2.4.3. Model calibration

The calibration process was carried out to reproduce the redox evolution observed in the triplicates. A linear oxygen source term ($d[\text{O}_2]/dt = \lambda \cdot t$) was included to account for the gradual increase of dissolved oxygen measured in the biotic reactors. In addition, a conditional switch between oxic and nitrate-reducing conditions (see section 2.4.2) was implemented: the oxic rate expression was applied when $[\text{O}_2]$ was superior to $4 \text{ mg}\cdot\text{L}^{-1}$, whereas the nitrate-reducing rate expression was applied when $[\text{O}_2]$ dropped below this threshold. This value was chosen based on experimental observations (see Section 3.2), where nitrate started to decrease right after $[\text{O}_2]$ fell below $4 \text{ mg}\cdot\text{L}^{-1}$. This is consistent with the findings of Green *et al.* (2008), who reported that denitrification can occur even at dissolved-oxygen concentrations greater than $3 \text{ mg}\cdot\text{L}^{-1}$.

Calibration was then performed iteratively. First, oxygen consumption was adjusted by calibrating the maximum degradation rate and half-saturation constant for high BDOC under oxic conditions. Then, using these fixed parameters, nitrate depletion and nitrite production were reproduced by adjusting the corresponding parameters under nitrate-reducing conditions. At each stage, the oxygen source term (λ) was adjusted simultaneously to reproduce both O_2 and DOC dynamics. Finally, a global refinement of all parameters was carried out to ensure accurate reproduction of the overall redox evolution. Following this calibration of redox species, the second step focused on simulating the degradation of CECs under oxic and nitrate-reducing conditions. Similarly to high BDOC reproduction, the degradation rate constants, half-saturation constants, and inhibition coefficients of CECs were adjusted to reproduce their temporal evolution in the triplicates, while sorption parameters (K_m , K_d) were calibrated to fit the data from the abiotic control.

3. Results and discussion

3.1. Occurrence of CECs in runoff water

Table 4 summarizes the detected CECs in the runoff water and their potential source of contamination. Benzotriazole concentrations ranging from 360 to $1400 \text{ ng}\cdot\text{L}^{-1}$ were detected in winter, likely due to the seasonal use of de-icing agents (Olds *et al.*, 2021). Additionally, alkylphenols were detected in

stormwater basins from both the traffic roads and the airport at concentrations from 42 to 126 ng·L⁻¹, attributed to their common use as surfactants in cleaning products (Lamprea *et al.*, 2018). Finally, various per- and polyfluoroalkyl substances (PFAS) were identified at concentrations between 13 and 590 ng·L⁻¹, likely originating from multiple sources (Pramanik *et al.*, 2020). These include their use in Aqueous Film-Forming Foams (AFFF) during fire response training at the airport, as well as their presence as surfactants in cleaning products and corrosion inhibitors in aircraft hydraulic fluids (Wang *et al.*, 2016a; Milley *et al.*, 2018; Liu *et al.*, 2022). Notably, these compounds were detected at higher concentration in winter. This seasonal pattern can be explained by two factors. First, winter season is characterized by greater precipitation and snowmelt events, increasing runoff volumes and subsequently, the mobilization of PFAS and other airport-related contaminants. Secondly, the exclusive use of de-icing and anti-icing fluids in winter accounts for the elevated benzotriazole concentrations observed (Breedveld *et al.*, 2002; Cancilla *et al.*, 2003; Olds *et al.*, 2021).

In addition, Figure 22 illustrates the molecular structures of the target compounds, including NP2EO, benzotriazole, tolyltriazole, and the selected PFAS. This figure provides a visual comparison of functional groups and chain lengths, which are later discussed in relation to sorption and biodegradation processes (see Section 3.4.4).

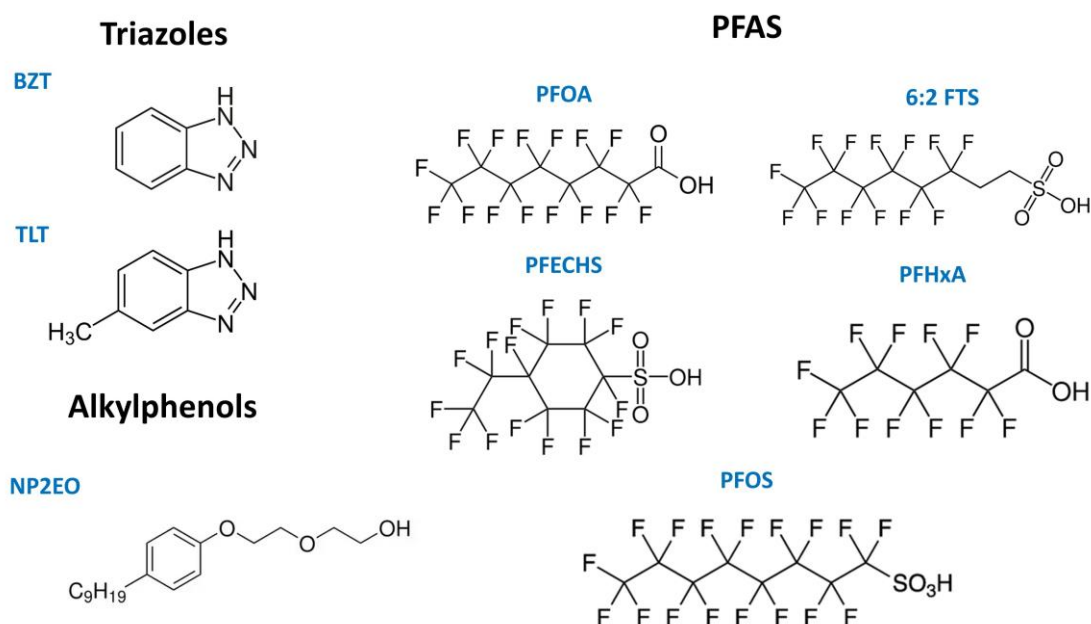


Figure 22. Molecular structures of the target contaminants.

Table 4. Concentration in ng·L⁻¹ of the identified CEC in runoff water collected in four stormwater basins in spring 2022 and winter 2023 (n=8).

Name	Acronym	Family	CAS	Min	Max	Median	Origin
Benzotriazole	Bzt	Triazoles	95-14-7	390	1400	895	Corrosion inhibitors in de-icing fluids
Tolyltriazole	Tlt		136-85-6	360	440	400	
Nonylphenol diethoxylate	NP2EO	Alkylphenols	2315-61-9	42	126	56	Additives in industrial surfactants and cleaning agents
Perfluorooctanoic acid	PFOA	PFAS	335-67-1	19	19	19	Surfactants
Perfluorooctanesulfonic acid	PFOS		1763-23-1	13	310	24	
Perfluorohexanoic acid	PFHxA		307-24-4	25	60	55	Degradation product of 6:2 FTS
Perfluoroethylcyclohexane Sulfonate	PFECHS		335-24-0	190	490	210	Corrosion inhibitor in aircraft hydraulic fluid
1H,1H,2H,2H-Perfluorooctanesulfonic acid	6:2 FTS		27619-97-2	63	590	180	Additive in AFFF

In addition to runoff monitoring, groundwater samples collected from a piezometer located directly beneath the airport were analysed. None of the target compounds (PFAS, benzotriazoles, alkylphenols) were detected in these samples. This observation is consistent with the current infrastructure, since the stormwater basins function as sealed retention basins with concrete bottoms, which discharge to WTPs that release treated wastewater directly to the nearby Meuse River. As such, these basins are not hydraulically connected to the underlying groundwater system, and no contamination is expected under present conditions. In addition, drilling data indicate that the unsaturated zone consists of successively ≈ 10 m of loess, ≈ 10 m of flint conglomerate, and ≈ 10 m of unsaturated chalk before reaching the groundwater table at ≈ 30 m of depth. This stratigraphy provides a significant natural buffer, as infiltration through the loess cover alone delays the recharge by several months, allowing further attenuation processes to occur. Nevertheless, the potential for groundwater impact exists if infiltration pathways are created, such as with SAT operations, which justifies the following physico-chemical behaviour evaluation performed in this study.

3.2. Redox conditions

To assess the evolution of redox conditions in the batch reactors, DO concentration was monitored during the experiment. Redox-related species such as NO_3^- and NO_2^- provide insights into potential denitrification processes occurring when DO becomes unavailable as an electron acceptor for bacteria to degrade organic matter. Figure 23 illustrates the mean concentration evolution of DO, NO_3^- and NO_2^- in the batch experiments.

As shown in Figure 23a, DO depletion occurred rapidly within the first four days, dropping from 8.8 to 4 $\text{mg}\cdot\text{L}^{-1}$. This depletion is expected, as oxygen is the first electron acceptor used by bacteria to degrade high BDOC. Afterward, the DO concentration decreased more slowly before increasing again in a linear way. Although the batch reactors were designed as closed systems, the consistent oxygen increase observed later on during the experiment is most likely explained by unintended entrance through the pressure valves, which were directly connected to the ambient air inside the incubator. Initially, this oxygen influx was not observable due to simultaneous oxygen consumption by bacteria at rates higher than the incoming oxygen. However, once the available BDOC was consumed, oxygen influx overcame consumption, leading to an increase in DO levels across the batch experiments. This results in three distinct phases: (i) oxic conditions ($\text{DO} > 4 \text{ mg L}^{-1}$) during the first four days, (ii) nitrate reducing conditions (NR) ($3 < \text{DO} < 4 \text{ mg L}^{-1}$) from day 4 to day 15, and (iii) a return to oxic conditions ($\text{DO} > 4 \text{ mg L}^{-1}$) lasting until the conclusion of the experiment.

These observations are corroborated by nitrate and nitrite dynamics shown in Figure 23b. As O_2 concentrations decreased sufficiently, bacteria started using NO_3^- as an electron acceptor. Simultaneously, nitrate reduction led to the production of nitrite. Once DO levels exceeded 4 mg L^{-1} , denitrification is inhibited, leading to a cessation of nitrate consumption and thus, no further nitrite production. This observation is supported by Green et al. (2008), who reported that denitrification can persist even when measured DO concentrations exceeding 3.0 $\text{mg}\cdot\text{L}^{-1}$, a process known as aerobic denitrification.

The model calibration closely reproduced the observed O_2 , nitrate, and nitrite concentrations (see Figure 23). The model successfully replicates the O_2 depletion and subsequent increase over time. The only significant deviation occurs at day 15, where the O_2 concentration measured was higher than predicted. Regarding nitrate and nitrite, the model accurately captures their consumption and depletion during the nitrate reducing phase. However, error bars indicate greater uncertainty in nitrite and nitrate measurements than for oxygen.

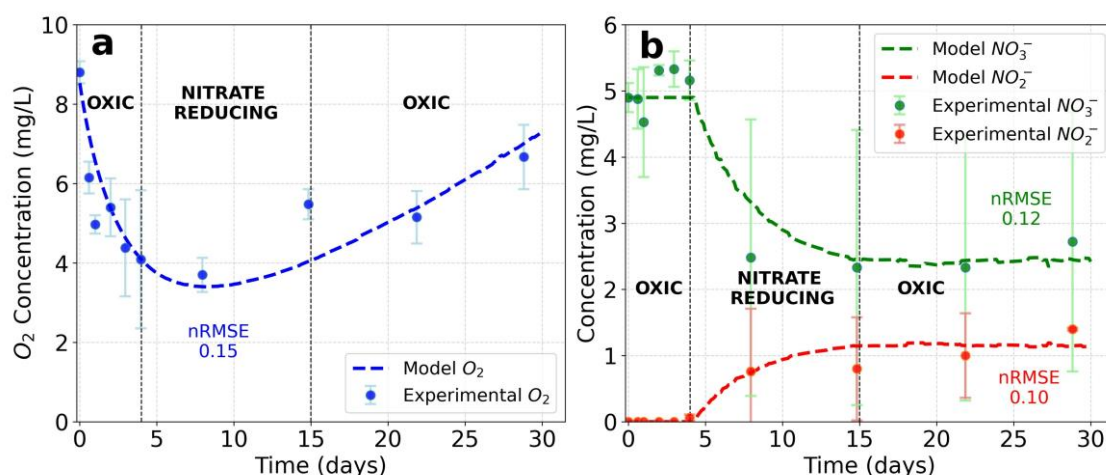


Figure 23. Temporal evolution of the mean concentrations in the batch experiments and corresponding chemical model predictions for a) oxygen and b) nitrate/nitrite.

3.3. BDOC evolution

Total BDOC concentration evolution was monitored in the batch experiments and in the abiotic control to assess bacteriological activity (see Figure 24). High BDOC introduced into the synthetic water was assumed to be biodegradable, while low BDOC remained recalcitrant. Under oxic conditions, bacteria consumed oxygen to degrade high BDOC. Once oxygen is sufficiently low, nitrate serves as an alternative electron acceptor under NR conditions, allowing biodegradation to continue. Figure 24a shows an initial rapid degradation of high BDOC under oxic conditions. In NR conditions, biodegradation continues but at a slower rate. Once oxic conditions are restored, most of the high BDOC (peptone) has already been biodegraded, resulting in a constant BDOC concentration, which represents the total concentration of humic acid.

The model accurately reproduces the initial BDOC concentration the first days (see Figure 24a). However, the subsequent BDOC observations are underestimated. This discrepancy may be due to the model not accounting for the potential release of additional organic matter from the sediments. Despite higher variability at intermediate times (e.g., third and seventh observations), a clear overall decrease is visible across the three replicates, with the mean BDOC concentration declining from 18.3 to $12.9 \text{ mg}\cdot\text{L}^{-1}$ between the start and the end of the experiment. Similarly, total BDOC concentration was also monitored in the abiotic control to assess its reliability (see Figure 24b). In contrast, the abiotic control showed BDOC concentrations fluctuating around a constant mean BDOC value without systematic decrease, confirming that sterilization effectively inhibited microbial activity.

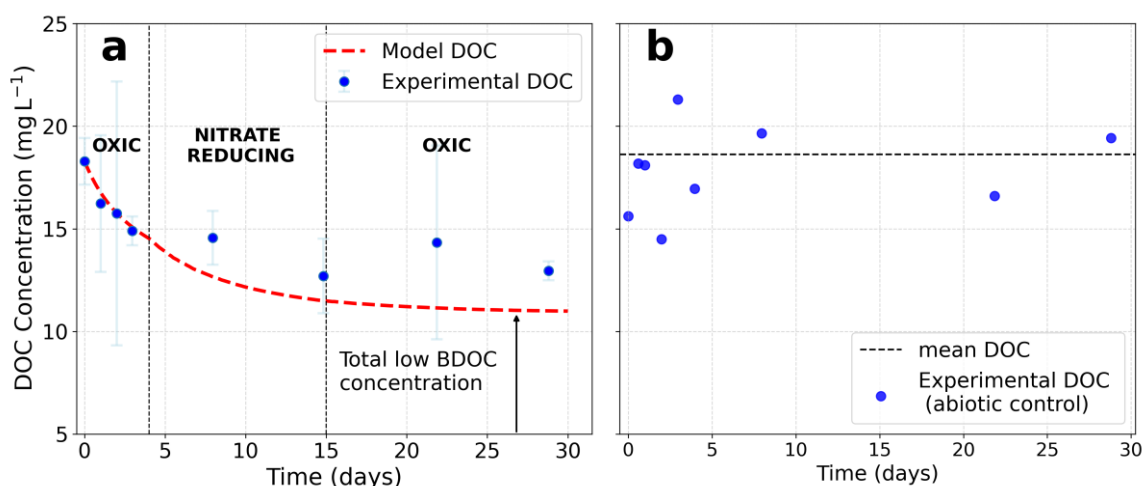


Figure 24. Total BDOC evolution in a) the batch experiments and b) the abiotic control.

3.4. CECs evolution

The following section describes the temporal evolution of each studied CECs in the abiotic control (see Figure 25) and in the batch experiments (see Figure 26). Additionally, the chemical models developed to reproduce the experimental results will also be presented, thereby highlighting the differences in physico-chemical behaviour between each CEC and how redox conditions affect it. A comparison between the fitted sorption parameters and those reported in the literature is included to assess consistency. Finally, total attenuation is quantified for each compound as the ratio between the model-predicted concentration at the end of the experiment (day 21) and the initial concentration. The complete set of calibrated parameters is available in the section 7 in Annex C.

The results will be represented in relative concentration form, i.e. by comparing the concentration of each contaminant to its initial value. Observation points showing concentrations higher than the initial concentration were excluded from the analysis. While such increases could, in principle, result from the transformation of precursor compounds into degradation products, as is the case for PFHxA potentially formed from the degradation of 6:2 FTS (Yang *et al.*, 2014), this process is considered negligible in our system, since 6:2 FTS is predominantly removed through sorption rather than biodegradation. Notably, the observed increases are more likely attributable to analytical variability or measurement uncertainty, given the very low concentrations involved in these experiments.

3.4.1. Abiotic control

Benzotriazoles

Figure 25a-b illustrates the temporal evolution of benzotriazole and tolyltriazole relative concentrations in the abiotic control. Both compounds show a consistent decline over time, suggesting their removal from the aqueous phase through sorption onto the loess sediments. The integrated sorption models accurately closely match the experimental data, with RMSEs values of 0.019 for benzotriazole and 0.017 for tolyltriazole.

By the end of the experiment, approximately 16% of the initial benzotriazole mass and 19% of the tolyltriazole mass had been adsorbed onto the sediments. This higher sorption of tolyltriazole is consistent with its higher log K_{oc} compared to benzotriazole, as also reported by Hart *et al.* (2004) in

different types of soils. This implies stronger interactions with the organic matter content of the loess sediments.

PFAS

PFAS also exhibited sorption onto loess materials, with the extent of sorption varying depending on the specific PFAS compound. Figure 25c-f illustrates the temporal evolution of different PFAS concentrations in the abiotic control. All compounds, except PFECHS, showed a decrease in concentration to varying extents.

Sorption of PFAS is particularly more complex than that of conventional organic compounds, as highlighted by Kookana *et al.* (2022). This complexity arises from the unique properties of PFAS, including the exceptional strong C-F bond and the molecule's amphiphilic nature, with a hydrophobic tail and a hydrophilic head (Itumoh *et al.*, 2024). In this study, the PFAS were predominantly present in their anionic forms, which make them more soluble in water than under cationic or zwitterionic forms (Mejia-Avendaño *et al.*, 2020). In saturated soils, factors influencing PFAS sorption include the physiochemical properties of the specific PFAS compounds, soil organic matter content, mineral composition, pH, and soil solution chemistry (Kookana *et al.*, 2022). Nevertheless, in the abiotic control, these complex interactions are integrated all together, making it challenging to attribute the sorption behaviour of a particular PFAS compound to a single factor. Hypotheses can only be proposed to explain why some PFAS compounds exhibit stronger sorption than others. As such, a detailed comparison of our results with previous PFAS sorption studies is provided in Section 3.4.3.

It should also be noted that sodium azide addition in the abiotic control led to higher sodium and nitrate concentrations than in the biotic reactors (see Table C1 of Annex C). However, previous studies indicate that such moderate changes in ionic strength or nitrate presence as a competing anion have only limited influence on PFAS sorption compared to dominant factors such as chain length, functional group, and sediment properties (Wanzek *et al.*, 2023; Woke *et al.*, 2025). Another possible source of uncertainty is sorption to reactor walls. Yet, glass containers are known to adsorb significantly less PFAS than polymeric materials such as polypropylene or HDPE, and adsorption to glass reaches equilibrium rapidly (Zenobio *et al.*, 2022). Importantly, vessel sorption would affect all reactors equally and thus cannot explain the systematic concentration differences between abiotic and biotic treatments.

Finally, it is important to note that the sorption capacity of loess sediments is not unlimited. Under continuous exposure to contaminated water, the available sorption sites could progressively become saturated, leading to a decline in removal efficiency over time. This is particularly relevant in SAT systems, where the soil acts a reactive medium over extended periods. As this study focused on short-term batch conditions, the potential for sorption site exhaustion and contaminant desorption during repeated infiltration cycles in SAT systems was not addressed here.

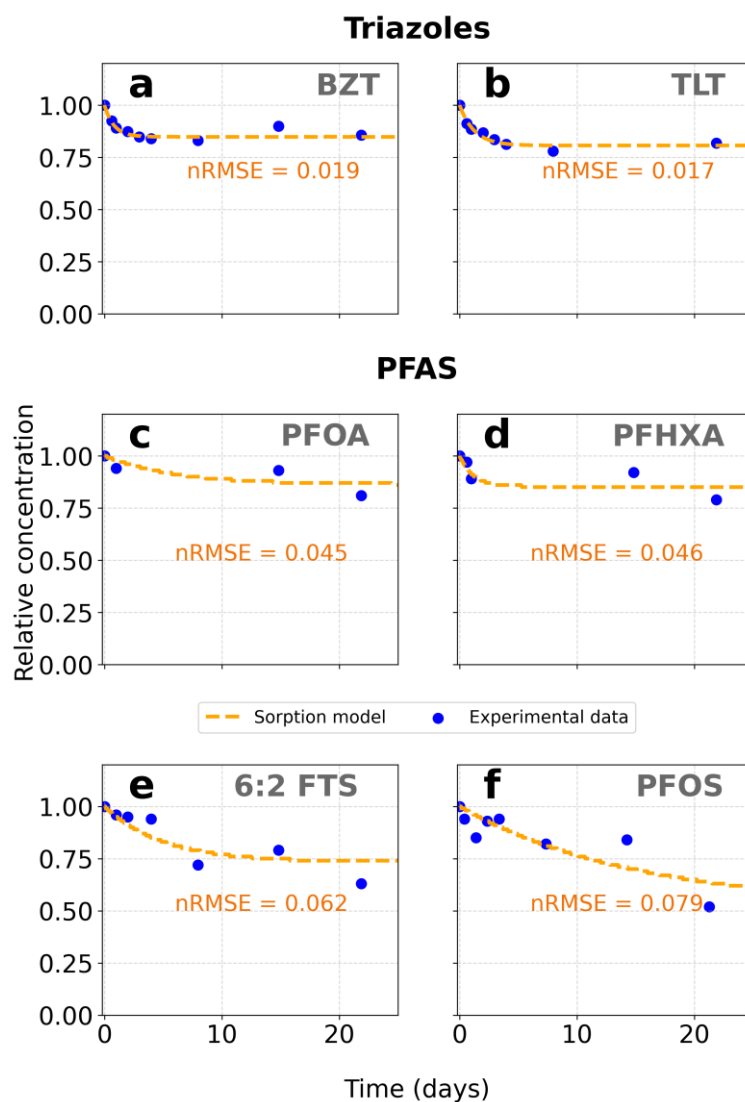


Figure 25. Concentration evolution of a) benzotriazole, b) tolyltriazole, c) PFOA, d) PFHxA, e) 6:2 FTS and f) PFOS in the abiotic control.

3.4.2. Batch experiments

Benzotriazoles

Figure 26a-b illustrates the total attenuation of triazoles across batch experiments. The developed chemical model integrates both sorption and degradation processes. For benzotriazole, a higher biodegradation rate was observed under oxic conditions compared to nitrate reducing conditions. Additionally, more pronounced attenuation was observed during the first four days. This was attributed to the sorption model being included in the overall attenuation model. The model fits the experimental data reasonably well, with a calculated RMSE of 0.078. However, the last experimental data point deviates from the predicted downward trend in concentration, indicating that the combined effects of sorption and biodegradation may diminish over time or be influenced by additional processes not captured by the model. Therefore, the estimated total attenuation for benzotriazole was based solely on the lower limit of the last observation point. A total attenuation of 38% is thus obtained, with sorption accounting for 16% of this total.

For tolyltriazole, a similar redox-dependent trend is observed. Biodegradation proceeds more efficiently under oxic conditions than under nitrate reducing conditions. As with benzotriazole, attenuation is more significant during the initial phase of the experiment, reflecting the influence of rapid sorption onto loess sediments. Note that the final observation point (day 22) was not included in the model calibration due to elevated uncertainty associated with that measurement.

PFAS

Figure 26c-g illustrates the evolution of PFAS concentration in the batch experiments. Both sorption and biodegradation models were applied to reproduce the observed concentration trends, as for the other contaminants. However, given the strong persistence of PFAS, the attenuation fraction theoretically attributed to biodegradation should be interpreted with caution.

Under oxic conditions, PFAS concentrations initially decreased rapidly, reflecting fast sorption processes that occurred during the early-stage contact between the aqueous phase and the loess sediments. This was followed by a period of relative stabilization under nitrate-reducing conditions, when sorption reached near-equilibrium for most PFAS. The only exceptions were PFOS and 6:2 FTS, which showed an additional decrease in concentration attributed to continued sorption. After approximately 15 days, as the system returned to oxic conditions, a gradual decline in dissolved PFAS concentrations was again observed. Given the well-documented persistence of PFAS, this secondary attenuation phase may be explained by the development of new sorptive phases associated with oxic microbial activity. One possibility is that re-oxygenation stimulated the formation or restructuring of soil biofilms, which can act as effective sorbents (Flemming, 1995). Indeed, respiration and electron-acceptor availability are known to govern biofilm formation, with oxygen providing the highest energy yield and supporting pronounced biofilm development (Martín-Rodríguez, 2023). This interpretation is consistent with Muñoz-Vega et al. (2023), who observed increased contaminant sorption in systems (batch and columns) with higher biological activity due to biofilm formation. Such biofilm-induced sorption processes could explain the additional attenuation observed during the second oxic phase and is not captured by the linear sorption isotherm. However, as solid-phase PFAS and biofilm biomass were not quantified in this study, this mechanism remains a working hypothesis requiring further validation.

Consequently, PFAS attenuation in this study is best explained by sorption processes alone. For PFOS and 6:2 FTS, the linear isotherm model reproduces about 80 % of the total attenuation observed experimentally, while for PFOA and PFHxA it accounts for 62 % and 63 %, respectively. The remaining difference is likely associated to additional sorption mechanisms not represented by the simple linear model, particularly those associated with biofilm formation during the second oxic phase, as discussed above.

The only exception is 6:2 FTS, whose molecular structure includes two non-fluorinated carbon atoms (see Figure 22). Previous studies (Yan, Dong, Woodcock, *et al.*, 2024) have demonstrated its potential for partial biotransformation under oxic conditions. Therefore, while sorption fully explains the attenuation of all other PFAS studied, a minor contribution from biotransformation cannot be excluded for 6:2 FTS.

Alkylphenols

Figure 26h illustrates the evolution of NP2EO concentration in the triplicate. Unlike the other studied CECs, the total attenuation of NP2EO was nearly complete after 21 days, reaching 90%. This attenuation is entirely attributed to biodegradation, as no measurable sorption onto loess sediments was observed in the abiotic control (see section 8 of Annex C). In addition, no significant differences were observed between oxic and nitrate-reducing conditions. Despite the higher solubility of NP2EO, it degrades relatively quickly, with 50% of its initial concentration disappearing within just 5 days. Therefore, if water containing NP2EO were to infiltrate through loess sediments, the compound, while not expected to undergo significant sorption, is likely to degrade rapidly. However, it is important to note that in this study, we did not account for the formation of degradation products, some of which may be of concern. For instance, NP2EO can degrade into nonylphenol (NP), a more persistent, hydrophobic, and toxic compound known for its endocrine-disrupting properties (Soares *et al.*, 2008).

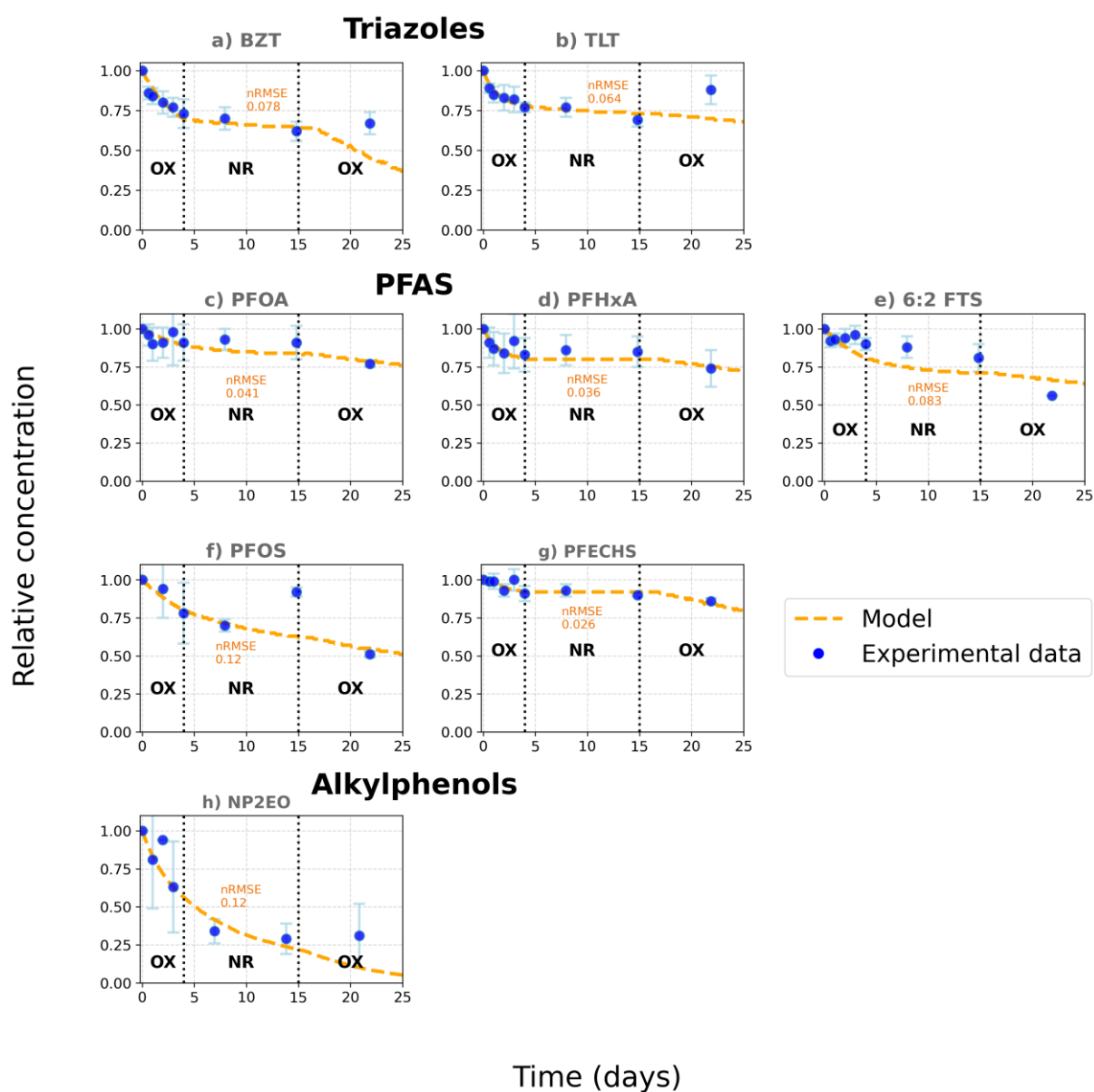


Figure 26. Concentration evolution of a) benzotriazole, b) tolyltriazole, c) PFOA, d) PFHxA, e) 6:2 FTS, f) PFOS, g) PFECHS and h) nonylphenol diethoxylate in the batch reactors.

3.4.3. Comparison of sorption parameters with literature data

For comparison with the scientific literature, the K_d values obtained from the calibration of chemical models were used to calculate K_{oc} values, based on the organic carbon fraction f_{oc} (Eq. 6). In this study, the organic carbon analysis of the loess indicated an organic carbon content of $f_{oc} = 2.23\%$.

$$K_{oc} = \frac{K_d}{f_{oc}} \quad (6)$$

Estimated $\log K_{oc}$ values of 1.34 and 1.47 were calculated for benzotriazole and tolyltriazole respectively, based on K_d values derived from the interpretation of abiotic control results. These values are lower than those documented in the literature for similar soils. Specifically, Hart et al. (2004) and Alotaibi et al. (2015) reported $\log K_{oc}$ of 1.66 for benzotriazole and 1.97 for tolyltriazole in soils with comparable grain size and carbon content. The discrepancy likely arises from differences in experimental conditions, as they used a 1:1 solid-to-liquid ratio and procedures that enhanced contaminant–sediment interaction, leading to higher sorption estimates.

For PFAS compounds, the differences in sorption behaviour per PFAS compound were assessed based on the fluorinated chain length. Table 5 presents a comparison of the K_{oc} values obtained from the abiotic control with those reported in the study of Fabregat-Palau et al (2022). Their study compiles a dataset of K_{oc} values of 13 different PFAS from their own experiments and from a larger dataset reporting K_{oc} values from the literature. In addition, an equation correlating the $\log K_{oc}$ values with the number of CF_2 was developed in their study to predict K_{oc} based on PFAS physicochemical properties.

Table 5. Comparison of partition coefficients derived from the abiotic control with values of the compiled dataset of Fabregat-Palau et al (2022) and their correlation analysis.

Compound name	Number of $-CF_2$	K_d ($L\ kg^{-1}$)	K_{oc} ($L\ kg^{-1}$) $f_{oc} = 2.23\%$	$\log K_{oc}$	$\log K_{oc}$ derived from Fabregat-Palau et al (2022) dataset	$\log K_{oc}$ obtained from correlation analysis
PFHxA	5	0.47	21	1.32	[1.11 – 1.23]	[0.85 – 1.85]
6:2 FTS ⁵	6	0.99	45	1.65	-	-
PFOA	7	0.44	20	1.29	[2.01 – 2.05]	[1.59 – 2.75]
PFOS	8	2	90	1.95	[2.77 – 2.80]	[1.96 – 3.20]

The K_{oc} values derived from our experiments are overall lower than those reported by Fabregat-Palau et al (2022). As with benzotriazoles, this discrepancy may be attributed to the static nature of our batch experiments, in contrast to most of sorption experiments conducted in small falcons that are agitated to enhance contact between sediments and contaminants (Zhang et al., 2015; Askeland et al., 2020; Barth et al., 2021; Dai et al., 2023; Hubert et al., 2023). A similar trend is observed with the K_{oc} values

⁵ For the fluorotelomer 6:2 FTS, it should be noted that its tail made of six $-CF_2$ groups is connected to it is sulfonate head with two $-CH_2$, which make it structurally different from PFHxA, PFOA and PFOS.

derived from correlation analysis, which is expected since this analysis is based on K_{oc} values from the same dataset.

Despite these differences, the sorption hierarchy observed in our study aligns with previous findings in the literature (Milinovic *et al.*, 2015, 2016). As expected, PFOS exhibits the highest sorption due to its longer carbon chain and sulfonate functional group. The 6:2 fluorotelomer FTS ranks second, as its sulfonate group makes it more sorbable than perfluorocarboxylic acids, despite its fluorocarbon chain being one carbon shorter than PFOA. Interestingly, PFOA and PFHxA show surprisingly similar K_d values, despite a difference of two CF_2 groups. The key distinction lies in the sorption kinetics: PFHxA reaches equilibrium within 2–3 days, while PFOA requires approximately 10 days to stabilize. Finally, PFECHS compound shows no noticeable sorption behaviour, which can likely be attributed to its distinct chemical structure. Unlike the other PFAS compounds studied, PFECHS features a cyclohexane ring instead of a linear fluorinated carbon chain.

It is important to remind that the sorption model presented in this study is a simple linear isotherm, which is commonly applied to conventional organic micropollutants present at low concentrations. However, such an approach may not fully capture the complex sorption behaviour of PFAS. As extensively discussed by Kookana *et al.* (2022), PFAS sorption is governed by multiple interacting mechanisms, including hydrophobic interactions, electrostatic forces, fluid–fluid interfacial adsorption (e.g. air–water and NAPL–water interfaces), and physical entrapment within soil micropores. These mechanisms are influenced not only by PFAS properties such as chain length, headgroup functionality, and ionic form, but also by diverse soil characteristics like mineral composition, pH-dependent surface charge, and the presence of polyvalent cations or organic matter. This is consistent with previous studies demonstrating that PFAS sorption correlates strongly with soil organic carbon but is also influenced by soil mineralogy and surface charge (Milinovic *et al.*, 2015, 2016). In addition, as discussed in section 3.4.2, biologically mediated sorption through biofilm development under oxic conditions may contribute to additional retention pathways not accounted for in the linear model. Therefore, while linear sorption models provide a useful first-order approximation, they likely underestimate the complexity of PFAS retention under environmentally relevant conditions.

3.4.4. Total attenuation

Figure 27 compiles the total attenuation of the studied contaminants in the triplicates after 21 days, along with the relative contribution of the different attenuation mechanisms. Here, total attenuation refers to the overall decrease in concentration relative to the initial value. Although both sorption and biodegradation models were implemented for all compounds, the interpretation of these contributions differs depending on the contaminant class, as discussed in section 3.4.2. Note that in a dynamic system such as a column experiment or natural aquifer flow, sorption primarily contributes to contaminant retardation rather than permanent attenuation, unless the sorption is irreversible. Total attenuation values per CECs are detailed in the Section 9 of Annex C.

For alkylphenols (NP₂EO), attenuation was almost complete and entirely due to biodegradation, with total removal close to 90%. Triazoles (benzotriazole and tolyltriazole) showed moderate attenuation (30–40%), resulting from a combination of sorption and biodegradation, the latter being favoured under oxic conditions. In addition, sorption contributed slightly more to the attenuation of tolyltriazole due to its higher hydrophobicity. These results can be partially explained by the chemical structure and functional groups of the studied compounds. NP₂EO, a non-ionic surfactant with a polyethoxylated

chain (Figure 22), is known to be readily biodegradable under oxic conditions (Ekdal *et al.*, 2022), explaining its rapid attenuation. Regarding benzotriazole compounds, benzotriazole and tolyltriazole are structurally similar (Figure 22), consisting of a 1,2,3-triazole ring fused to a benzene ring. However, the presence of a methyl substituent in tolyltriazole (primarily in the 4- or 5-position) increases its hydrophobicity, enhancing its affinity for organic matter and resulting in stronger sorption behaviour (Hart *et al.*, 2004). Both compounds are considered polar and relatively persistent, but benzotriazole tends to be slightly more biodegradable under aerobic conditions than tolyltriazole (Reemtsma *et al.*, 2010). These structural and physicochemical characteristics explain the moderate attenuation observed for tolyltriazole, driven more by sorption than biodegradation.

For PFAS compounds, total attenuation was primarily attributed to sorption. In Figure 27, PFAS attenuation is therefore divided into two components: (i) the fraction of sorption reproduced by the linear isotherm model, and (ii) the additional retention processes not captured by that model. These additional mechanisms may include biologically mediated sorption such as the formation or restructuring of biofilms during oxygen renewal, as discussed previously. This representation better reflects the complex sorption behaviour observed during the whole experiment. Among PFAS, PFOS and 6:2 FTS showed the highest overall attenuation, with roughly 80 % reproduced by the linear isotherm. For PFOA and PFHxA, the linear model accounted for about 60 %, suggesting stronger limitations of the linear isotherm approach for these compounds. PFECHS showed negligible sorption and correspondingly low total attenuation.

Differences in PFAS attenuation are closely related to their chain length and functional groups (Figure 22). PFOS (a sulfonate) and 6:2 FTS (a fluorotelomer sulfonate) showed higher sorption potential compared to PFOA and PFHxA (carboxylates), likely due to the higher hydrophobicity and lower polarity of sulfonates, as well as the presence of more fluorinated carbon atoms (Mejia-Avendaño *et al.*, 2020; Fabregat-Palau *et al.*, 2022; Kookana *et al.*, 2022). PFECHS also displayed low attenuation, which may be attributed to its relatively high chemical stability, due to the presence of a cyclic ether moiety within the perfluorinated carbon chain, and its low sorption affinity in the tested sediment matrix (Wang *et al.*, 2016a).

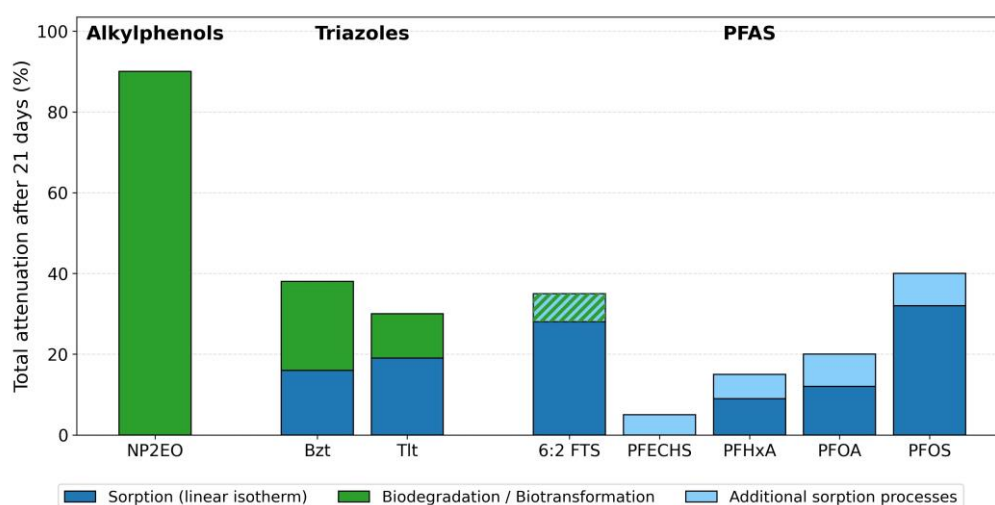


Figure 27. Total attenuation of individual contaminants after 21 days in the batch reactor, with contributions from sorption (linear isotherm + additional processes) and biodegradation/biotransformation. The blue–green diagonal pattern for 6:2 FTS represents a mixed attenuation mechanism.

When extrapolating these laboratory results to field conditions, it is important to consider the protective role of the thick unsaturated zone described in Section 3.1. This layer provides a significant delay and additional opportunities for contaminant attenuation before the recharge water reaches the aquifer (Brouyère et al., 2004). However, in the context of SAT operations, continuous recharge through infiltration basins is expected to establish a saturated reactive zone beneath the basin. The saturated batch experiments presented here therefore capture the main processes expected under such conditions, although dynamic column experiments would be needed for more representative field conditions. Indeed, the hydraulic regime can further influence CECs attenuation, as infiltration dynamics controls solute residence times and the spatial distribution of redox conditions, which in turn govern biodegradation. This has notably been highlighted by Gorski et al. (2019), who established a quantitative relationship between infiltration rate and denitrification. This implies that under SAT operations, degradation rates of organic contaminants may vary with recharge intensity through their control on redox evolution. To address these aspects, complementary studies using HYDRUS reactive transport modelling and the obtained parameters are currently in progress to quantify the influence of the vadose zone and infiltration dynamics on contaminant fate.

4. Conclusion

This study investigated the attenuation capacity of loess sediments overlying the Hesbaye chalk aquifer (Belgium) when exposed to airport runoff water contaminated with alkylphenols, triazoles and PFAS. Our findings reveal different behaviours among the target CECs, with attenuation processes varying by compound class. Sorption emerged as the dominant mechanism for PFAS compounds, while biodegradation played a major role in the attenuation of benzotriazoles and alkylphenols.

Among the studied compounds, NP2EO exhibited the highest total attenuation, reaching nearly 90%, with biodegradation accounting for the entirety of its removal. This suggests that, despite its solubility, NP2EO poses a low risk for aquifer contamination under the studied conditions. However, the potential formation of transformation products, such as nonylphenol, was not evaluated and may present additional risks.

Benzotriazole and tolyltriazole showed moderate attenuation levels of 38% and 30% respectively, with sorption contributing to 16% and 19% respectively. The stronger sorption of tolyltriazole suggests a greater potential for sediment accumulation compared to benzotriazole, which may be less concerning for groundwater quality. However, leaching of tolyltriazole could still occur if clean recharge water percolates through contaminated sediments. Additionally, biodegradation of these compounds was found to be redox-dependent, with higher degradation rates observed in oxic conditions.

As expected for persistent pollutants, PFAS compounds demonstrated limited overall attenuation, which was primarily attributed to sorption onto loess sediments. Among them, PFOS and 6:2 FTS showed the highest retention, while PFOA and PFHxA were less sorbed, and PFECBS displayed little interaction with the solid phase. Given their well-known resistance to microbial degradation, PFAS attenuation in this study is expected to result solely from sorption processes rather than biodegradation. The fraction of attenuation not reproduced by the linear isotherm may reflect additional sorption processes, such as biologically activated sorption occurring under oxic condition through the formation or restructuring of biofilms. The only compound for which biotransformation cannot be excluded is 6:2 FTS, which can undergo partial transformation under oxic conditions. Given that PFAS sorption potential is strongly dependent on soil composition, further research should investigate their behaviour across a range of soil types. Moreover, investigating the formation of PFAS

degradation products might be interesting, as partial breakdown may lead to smaller, more mobile, and potentially more hazardous compounds.

Even though the biotic control in our experiments did not function as intended, the results allow for an indirect estimation of biodegradation by considering total attenuation as the sum of sorption and biodegradation contributions. Furthermore, this study provides key parameters on sorption and biodegradation processes that will be valuable for modelling the transport and fate of CECs if SAT is implemented using airport runoff as a recharge source. Integrating these experimental results into transport models will allow for a more accurate assessment of contaminant mobility, persistence, and potential groundwater impacts, aiding in the development of sustainable SAT strategies. However, in the context of long-term SAT operations, the sorption capacity of loess sediments may progressively decline as sorption sites become saturated, reducing removal efficiency over time. Such long-term effects should be considered together with attenuation processes occurring in the unsaturated zone, which represents an additional natural buffer before recharge water reaches the aquifer. Future work, including unsaturated column studies and reactive transport modelling with HYDRUS, will help to assess the influence of this vadose zone on contaminant transport. Expanding similar experiments to a wider range of soil types and environmental conditions will be essential for improving risk assessments and ensuring the safe use of SAT for groundwater recharge. Improving experimental design to ensure effective biotic controls should also be a priority in future studies, enabling more precise quantification of biodegradation processes.

Finally, some methodological aspects should be improved in future studies to strengthen the robustness of the conclusions. In particular, the absence of solid phase measurements in this work prevents a complete mass balance and limits the ability to fully separate sorption from biodegradation. Minor differences in geochemical conditions between the abiotic control and the batch reactors, as well as potential sorption to glass vessels, represent additional sources of uncertainty. However, these effects are expected to be small and would apply equally to all reactors, meaning they cannot account for the systematic differences observed, but they cannot be fully excluded. In addition, although a single abiotic control was sufficient to support the interpretation of sorption processes, including replicate abiotic controls would reduce statistical uncertainty and allow a more rigorous assessment of differences with biotic reactors.

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Chapter 6

Innovative use of passive and active distributed temperature sensing for estimating infiltration rates in a managed aquifer recharge framework

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Abstract⁶

Managed Aquifer Recharge (MAR) has become an essential strategy for sustainable water management. Effective design of surface recharge systems relies on the accurate estimation of the soil infiltration capacity. In this context, the use of heat as a tracer has recently gained attention to quantify infiltration dynamics. Particularly, methods relying on Distributed Temperature Sensing (DTS) along fiber optic (FO) cables have been developed to account for the spatial variability of the recharge. This study explores an innovative approach that combines two types of temperature sensing techniques, passive and active-DTS measurements, to evaluate infiltration rates in a MAR pilot site. An FO cable, buried in the loess sediments of an infiltration basin, recorded temperature changes during an infiltration test. First, the passive method monitored natural temperature changes as cooler water filled the basin, enabling the estimation of initial infiltration rates. Twenty-four hours later, the active method involved heating part of the cable to further assess infiltration rates during ongoing infiltration. The analysis of DTS data facilitated the mapping of the recharge within the MAR system. Furthermore, results show that the infiltration rate is significantly higher at the start of the infiltration test, demonstrating that combining passive and active-DTS measurements provides a better understanding of the infiltration dynamics. The findings demonstrate the viability of MAR in loess-based systems at the studied site and highlight the potential of DTS methods for long-term monitoring of MAR operations.

Keywords: Managed Aquifer Recharge (MAR); Distributed Temperature Sensing (DTS); Infiltration monitoring; Recharge mapping; Heated Fiber Optic Cable; Heat tracer experiment

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Chapter context

A central question that emerged from this PhD thesis is whether the Hesbaye loess cover, despite its relatively low permeability, can sustain infiltration rates that are compatible with MAR systems. When selecting MAR site locations, loamy or fine-grained soils are often discarded because of their lower hydraulic conductivity, and thus, poorer infiltration performances. However, in regions such as Hesbaye where high-permeability sediments are scarce, MAR implementation must inevitably deal with low to moderate permeability materials that prevail. As such, the design and long-term performance of surface spreading systems depend on accurately quantifying infiltration capacity, its spatial variability across the base of infiltration basins, and its temporal dynamics.

In this context, the present chapter, presented as an article published in *Journal of Hydrology*, investigates the use of heat as a tracer to quantify infiltration rates within a MAR pilot site located above the Hesbaye chalk aquifer. The study relies on Distributed Temperature Sensing (DTS) along a fiber optic (FO) cable buried in the loess sediments forming the base of an existing sedimentation basin hydraulically connected to a production well. By monitoring temperature changes during a controlled infiltration test, we aim to (i) quantify infiltration rates representative of MAR operation in loess soils, (ii) characterize their spatial variability along the FO cable, and (iii) explore how infiltration evolves over time as the basin is filled and subsequently drained.

Overall, the infiltration rates inferred from DTS technology range between roughly 33 and 130 cm day⁻¹ depending on the phase of the test and demonstrate that loess sediments in Hesbaye can sustain recharge rates comparable to those reported in sandy SAT systems. This finding shows that the common practice of systematically excluding fine-grained sediments from MAR feasibility assessments is not always relevant. Instead, it suggests that such materials can support effective recharge while providing additional water quality benefits via filtration and sorption in the unsaturated zone, given appropriate basin design, maintenance and monitoring. The infiltration parameters derived in this chapter form the hydrodynamic input for the reactive transport modelling presented in chapter 7.

1. Introduction

Groundwater availability and sustainability are threatened by climate change and anthropogenic pressure (Green *et al.*, 2011). The Intergovernmental Panel on Climate Change (IPCC) predicts an increase in the global mean temperature, which would directly impact the hydrological cycle by increasing surface water evaporation rates, enhancing vegetation transpiration, and altering precipitation patterns (Calvin *et al.*, 2023). These changes are anticipated to result in a long-term decline in groundwater availability. Concurrently, water demand is expected to increase, particularly during peak periods such as summer months (Boretti and Rosa, 2019; Wu *et al.*, 2020). In this context, Managed Aquifer Recharge (MAR) emerges as an adaptive strategy to address disparities between groundwater supply and water demand. MAR is defined as “the purposeful recharge of water to aquifers for subsequent recovery or environmental benefit” (Dillon, 2009) and is an essential component of sustainable water resource management, as it enhances subsurface water storage (Dillon, 2005; Page *et al.*, 2018). As water is filtered through soil during recharge, MAR also ensures the long-term availability of clean and reliable water sources for various applications (Amy and Drewes, 2007; Sharma and Kennedy, 2017; Sprenger *et al.*, 2017).

Effective design of surface recharge systems relies on the accurate estimation of soil infiltration capacity to assess the permeability of the vadose zone (Bouwer *et al.*, 2008). Soil infiltration capacity is a critical parameter for the deployment of MAR (Maliva, 2015; Prathapar *et al.*, 2015) and is strongly influenced by soil texture, one of the primary factors governing its ability to infiltrate water into the subsurface (Singh *et al.*, 2013; Bonilla Valverde *et al.*, 2016). Coarse soils, such as sands or gravels, typically facilitate drainage of water due to their larger and more interconnected pore spaces, resulting in higher permeability. Conversely, soils with fine pores or high clay content (>10%), such as loamy soils, often have lower permeability and infiltration capacity due to less connected pores, restricting water movement. Consequently, these soils are generally excluded from MAR design due to their reduced capacity to transmit water effectively (Bouwer, 2002; Kallali *et al.*, 2007). Nevertheless, implementing surface spreading MAR systems for aquifers overlaid by low to moderate permeability soils can still be beneficial. The low permeability layer can enhance water purification by acting as a natural filter, removing contaminants, and improving water quality as it percolates through the soil (Nadav *et al.*, 2012; Sharma and Kennedy, 2017). Moreover, in regions where high-permeability soils are limited and low-permeability soils prevail, this approach may be the only viable option. Although infiltration rates are slower than in high-permeability soils, spreading the recharge over a larger surface area can still result in effective aquifer replenishment.

Traditional methods to measure infiltration rates often use cylinder infiltrometers, such as single-ring or double-ring infiltrometers. A double ring infiltrometer consists of two concentric metal cylinders. Water is poured into both cylinders, and the infiltration rate is measured in the inner ring, with the outer ring minimizing lateral flow. This method provides useful local estimates of infiltration rates but may overestimate the infiltration rate due to lateral water flow beneath the infiltrometer (Bouwer, 1986).

Innovative methods, such as using heat as a tracer, overcome this limitation and allow for a more comprehensive estimation of infiltration rates on a larger spatial scale. For instance, Caligaris *et al.* (2022) used heat as a tracer to assess the recharge plume in a MAR system. They monitored temperature data using sensors installed at various depths in wells near the MAR site. This approach

underscored the interest of monitoring temperature variations in groundwater to gain a better understanding of dynamic subsurface water movements. Other studies on heat experiments in the context of MAR (Pidlisecky and Knight, 2011; Racz *et al.*, 2012) have successfully quantified infiltration rates. However, these studies also emphasize that infiltration rates vary over time and space, highlighting the need for methods that can characterize the spatial and temporal variabilities of this critical parameter.

In this context, the use of Distributed Temperature Sensing (DTS) technology, which provides distributed temperature measurements at high resolution along a Fiber Optic (FO) cable, is of particular interest. Racz *et al.* (2012), Becker *et al.* (2013), and Mawer *et al.* (2016) employed DTS to estimate infiltration rates in recharge basins and infiltration ponds. The DTS measurements facilitated the estimation of infiltration rates over both time and space by analysing diurnal temperature fluctuations recorded along buried FO cables, which are induced by the propagation of air temperature changes at depth. It is important to note that the term “passive-DTS” measurements is frequently employed to describe natural temperature fluctuations.

While passive-DTS measurements are useful for characterizing infiltration rate variabilities, they face limitations such as low thermal response sensitivity at very low infiltration rates and dependence on natural temperature fluctuations (Gilmore *et al.*, 2019; Le Lay *et al.*, 2019; Koruk *et al.*, 2020; Simon *et al.*, 2022). Conversely, active-DTS methods introduce an artificial heat source by injecting electricity through the steel armouring of the FO cable. This allows for controlled heating and measurement of the thermal response (Read *et al.*, 2014; Bense *et al.*, 2016). This approach provides high spatial resolution estimates of groundwater flux, independent of natural temperature variations (Simon *et al.*, 2021). Although active-DTS has been successfully applied in streams (Simon *et al.*, 2022, 2024; Sai Louie *et al.*, 2023), its potential for exploring recharge variability in MAR systems remains unexplored.

The implementation of active-DTS within MAR framework has the potential to significantly improve recharge monitoring, as it provides measurements that are independent of natural temperature fluctuations. This makes it a more reliable and flexible option, enhancing the accuracy and applicability for MAR assessment. The objective of this study is to demonstrate the effectiveness of DTS technology. To that end, the study quantifies the spatial and temporal variability of recharge rates. This is accomplished by integrating both active and passive-DTS measurements along a FO cable during an infiltration test. Furthermore, this study investigates the temporal dynamics of infiltration in low-permeability sediments by interpreting DTS data at different stages of the test. This approach aims to evaluate the feasibility and benefits of MAR applications in soils with low to moderate permeability. The infiltration test was conducted in a small infiltration basin located above the Hesbaye chalk aquifer (Belgium). The FO cable was buried in loess sediments at the base of the basin to collect DTS data throughout the experiment.

2. Materials and Methods

2.1. Experimental site

The Geer hydrological basin is located northwest of the city of Liège, in Belgium, and overlays the Hesbaye chalk aquifer, one of the most significant groundwater bodies in Wallonia. The aquifer supplies approximately 15 million cubic meters of water annually to the city of Liège through pumping wells and drainage galleries (Orban *et al.*, 2014b; CILE, 2022). However, this major aquifer is facing

threats to its quantity and quality (Hakoun *et al.*, 2017b). A significant decline in groundwater levels has been documented, with a 6-meter reduction observed between 1990-2020 compared to 1960-1990 (Goderniaux *et al.*, 2023). This trend is largely attributed to climate change, which has altered precipitation patterns and increased evapotranspiration, reducing recharge efficiency and increasing the aquifer's susceptibility to long-term depletion. Specifically, Goderniaux *et al.* (2023) reported a decrease in mean annual recharge from 207 mm·yr⁻¹ in 1960-1990 to 117 mm·yr⁻¹ in 1990-2020, underscoring the importance of MAR strategies in the region. MAR has thus been identified as a promising mitigation approach to enhance subsurface storage and maintain groundwater availability in the region.

The Geer hydrological basin is primarily composed of Quaternary loess (aeolian loamy sediments), which can reach up to 20 m in thickness and cover the chalk aquifer (Batlle Aguilar *et al.*, 2007). This loess layer is characterized by moderate hydraulic conductivity, around 10⁻⁷ m·s⁻¹ (Brouyère, 2001). Due to the low permeability of this layer, the implementation of MAR may be challenging in this area, as the reduced infiltration capacity can limit the rate at which water can be introduced into the aquifer. MAR applications in loess environments are not frequently documented. This underscores the necessity for site-specific assessments to evaluate their feasibility in such geological settings.

In this context, a pre-existing sedimentation basin connected to a production well was selected as a pilot site for investigating recharge processes occurring through the loess. The basin's truncated pyramid shape (see Figure 28) ensures uniform distribution of water over a large surface area, facilitating effective infiltration. The base of the structure consists of a 30-centimeter layer of cobblestone, which overlays loess sediments. The basin's concrete sides offer structural stability and prevent lateral leakage. The basin is connected to a pumping well through a steel pipe that enables the filling of the basin with a flow rate of around 15 m³·h⁻¹. Drilling data in the area revealed a layer of loess ranging from 7.25 to 11.5 meters in thickness beneath the surface, succeeded by an 8-meter layer of silt and flint conglomerate before encountering a chalk layer approximately 35 meters thick.



Figure 28. Infiltration basin during a) the installation of the FO cable and b) its replenishment.

2.2. Experimental configuration

DTS measurements were conducted using a 3.8 mm diameter FO cable (4 multimode 50/125- μm fibres). The cable was arranged in a U-shape in the basin (see Figure 29) and buried within the loess sediments at a depth of approximately 10 centimetres. Within the buried section measuring 17.5 meters, 7.5 meters were electrically connected to a Heat Pulse Control System (see Figure 29). This system was used to inject electricity into the electric cables/FO cable system for active-DTS measurements.

DTS measurements were conducted using an AP Sensing interrogator instrument (DTS N4386B), which provided temperature records every 25 centimetres along the FO cable with a 10-second sampling interval. The data were calibrated using two calibration baths: one cold bath filled with ice and water and one warm bath with heated water using a heating resistor. Approximately 10 meters of FO cable section were immersed in the calibration baths (see Figure 29). Temperature sensors (PT100) with 0.1°C accuracy were also submerged in the calibration baths for data calibration. The interrogator was configured using an enhanced version of the single-end configuration (Hausner *et al.*, 2011), as two sections of the FO cable were placed in the cold calibration bath. This configuration enabled verification that signal attenuation along the FO cable was negligible. The use of calibration baths ensured high-quality measurements along the entire cable.

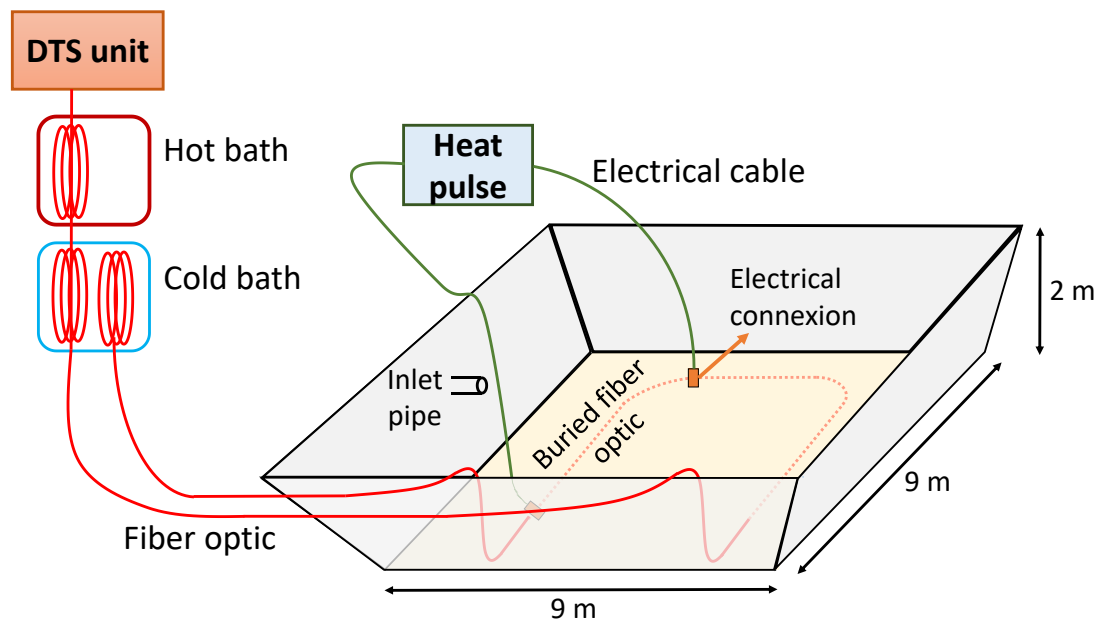


Figure 29. DTS configuration. Please note that this schematic excludes the cobblestone layer. The continuous red line indicates the FO cable, which is not buried, while the dashed red line delineates the buried section of the FO cable. The heated section of the FO cable is comprised between the two electrical connections.

One pressure sensor (CTD diver type) was buried within the cobblestone layer to monitor water pressure evolution during the infiltration test. The data acquisition process was programmed with a five-minute sampling interval. These data were used to obtain a comprehensive estimate of the infiltration rate for the entire basin over time, enabling a comparison and validation of infiltration rate estimates obtained through passive and active-DTS analysis.

2.3. Active and passive-DTS measurements

The infiltration test was conducted at the end of July 2023. The basin was initially empty and subsequently filled with water for a period of seven hours (see Figure 30). Passive-DTS measurements were continuously recorded to monitor natural temperature variations along the entire FO cable throughout the entire experiment. These measurements captured soil temperature before, during, and after the basin replenishment. Since the water used to fill the basin was 14°C, colder than the initial sediment temperature of 16 °C, a decrease in soil temperature was expected as the cooler water reached the FO cable. The resulting temperature changes were used to estimate the infiltration rate at the onset of the infiltration test. This approach is particularly useful for assessing initial infiltration dynamics, offering valuable insights into the early stages of water movement through the subsurface. Furthermore, passive-DTS measurements can be interpreted along the entire length of the FO cable, providing a comprehensive view of the infiltration process beyond the heated section. This enhances the overall understanding of the infiltration dynamics within the basin.

The active-DTS experiment was initiated 24 hours after the start of the basin replenishment (see Figure 30) and involved heating a segment of the FO cable. The section of cable connected to the heat pulse (7.5 meters) was heated for a duration of 9 hours and 30 minutes by injecting a constant electrical current of 17.98 W.m⁻¹. Active-DTS measurements were analysed to estimate the infiltration rate 24 hours after the infiltration test began, as well as the thermal conductivity of the soil surrounding the FO cable. The thermal conductivity values derived from active-DTS measurements served as inputs for the heat transfer finite element numerical model to interpret passive-DTS data. Therefore, this section first presents the methodology for interpreting active-DTS, as it provides essential thermal properties required for the analysis of passive-DTS measurements. Subsequently, the interpretation of passive-DTS data is detailed.

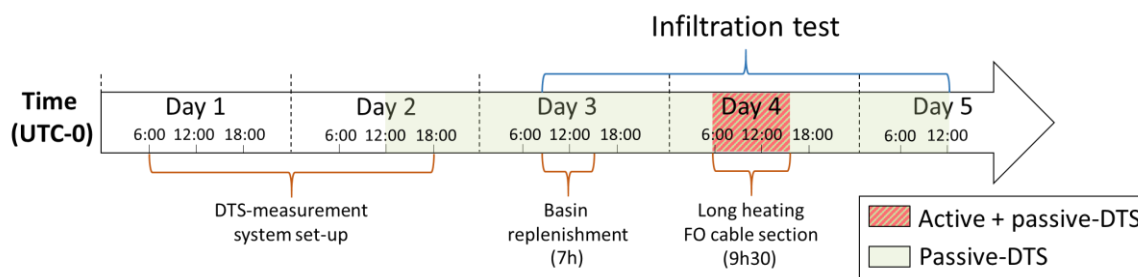


Figure 30. Schedule of the experiment.

2.3.1. Interpretation of Active-DTS measurements

The use of heated FO cables in saturated porous media to estimate water flux has been investigated in several studies (Des Tombe *et al.*, 2019; Del Val *et al.*, 2021; Simon *et al.*, 2021). Active-DTS involves the use of an artificial heat source, caused by electrical current injection, and the subsequent monitoring of the induced temperature increase (ΔT) over time. During the initial heating phase, the temperature increase is primarily driven by heat conduction and storage within the FO cable. Heat storage within the cable leads to a significant temperature increase (ΔT_{FO}) (Del Val *et al.*, 2021; Simon *et al.*, 2021).

Once the heat begins to propagate into the surrounding porous media, conduction and advection are the two primary heat transfer processes that control the temperature evolution. Conduction refers to

the transfer of heat through direct contact between solid grains in the porous media, while advection involves the transfer of heat due to the movement of the water, as defined by Anderson (2005). Initially, the temperature increase is governed by conduction, which depends on the thermal conductivity of the porous media. During this stage, a continuous and gradual temperature increase is observed over time on a semi logarithmic plot. Consequently, the thermal conductivity (λ) can be estimated by analysing the thermal response measured during this phase. Subsequently, the heat is dissipated by advection due to the groundwater flux (q). Advection processes, which depend on flow conditions, are responsible for temperature stabilization at later times of heating. High water fluxes facilitate greater heat dissipation through advection, resulting in lower temperature increases. Conversely, lower water fluxes result in reduced heat dissipation, leading to greater temperature increases (Simon *et al.*, 2021).

Active-DTS measurements were interpreted using the ADTS toolbox proposed by Simon and Bour (2023). The ADTS toolbox employs a mathematical model referred to as the Moving Instantaneously Line Source (MILS) to simulate the temporal variations in temperature resulting from the movement of heat through the porous media (Simon *et al.*, 2021). The MILS model conceptualizes the heat source as an infinite line that instantaneously releases heat, thereby enabling the analysis of the subsequent heat dispersion through the surrounding medium. It facilitates the automatic interpretation of each measurement point along the heated section of the FO cable, providing estimates of both the sediment thermal conductivity and groundwater flux. This approach offers two key advantages. First, it enables the direct and spatially distributed estimation of groundwater flux without relying on hydraulic conductivity values, which are often uncertain, point-based, and not representative of the study scale. Secondly, while thermal conductivity is necessary for accurately interpreting the thermal response along the FO cable, its spatial variability also provides valuable insights into subsurface heterogeneity.

The ADTS Toolbox employs a two-step process to interpret thermal response curves measured during the heating phase. After evaluating the early-stage temperature increase (ΔT_{FO}) within the FO cable, the first step consists in estimating the thermal conductivity (λ) of the porous media by analysing the thermal response along the heated FO cable during the conduction-dominant period. The linear increase in temperature (ΔT) observed on a semi-logarithmic plot during the conduction-dominated phase is governed solely by thermal conduction and is not influenced by advective flow (q). This behaviour is modelled using the MILS analytical solution with a flow velocity $q = 0 \text{ m}\cdot\text{s}^{-1}$, allowing for the determination of λ . In the second step, the temperature stabilization observed during the advection-dominant period is reproduced using the MILS model by adjusting the groundwater flux q , providing a reliable estimate of local infiltration rate.

To interpret active-DTS measurements, it is essential to consider natural temperature variations that may occur during the heating period. In their study, Simon *et al.* (2024) demonstrated that the temperature signal recorded during heating is a combination of the natural temperature variations and the induced temperature variations resulting from artificial heat injection. Natural temperature variations may result from the propagation in depth of diurnal temperature fluctuations in case of downward water fluxes controlling advective heat transport (Constantz, 2008). Given the extended heating period (9.5 hours), it is anticipated that ambient temperature variations may also occur during the heating process. The methodology proposed by Simon *et al.* (2024) to remove ambient temperature variations from the signal was therefore applied. The process entails identifying a “*matching point*” for each measurement along the heated section of the FO cable. The matching point

is a location along the non-heated section where similar temperature fluctuations are expected to be measured as along the heated section. After identifying the matching point, a corrective adjustment is applied to the heated section's data. This adjustment involves subtracting the temperature recorded at the matching point from the temperature recorded at the associated heated section's measurement point. This procedure ensures that the remaining temperature variations exclusively reflect variations induced by the heat injection.

2.3.2. Interpretation of Passive-DTS measurements

The passive-DTS measurements recorded during the infiltration basin's replenishment were interpreted using a finite element heat transfer numerical model with fluid flow (see Figure 31). The model was developed with the "heat transfer in porous media" module of COMSOL Multiphysics® (COMSOL, 2024). It simulates temperature variations in loess caused by the infiltration of cooler water. A 2D vertical model was adopted, assuming that water flow predominantly occurs in the vertical direction with minimal lateral variation. This assumption is supported by the shallow burial depth of the FO cable (Kurylyk *et al.*, 2017) and the predominance of advective over conductive heat transport under these conditions, as further detailed in Section 4.1. Consequently, both heat advection and conduction are expected to occur along the vertical dimension only, as the infiltration basin uniformly distributes water across its surface. The numerical modelling approach was selected over analytical solutions, as it enables the simulation of coupled heat and water flow processes that are too complex to be captured analytically.

The model dimensions are 50 × 20 cm along the vertical and horizontal axes, respectively. The model's finite element grid consists of thin triangular elements with sides of approximately 1.85 cm (see Figure 31). This element size has been selected to ensure numerical stability, with a Courant number calculation ($C = 0.5$) confirming that the time step and mesh resolution used result in a stable solution (see Section 1 of Annex D). The initial temperature values assigned to the entire model correspond to the soil temperature before the infiltration began, ranging from 15.41°C to 16.71°C. A constant temperature is applied at the top of the model, set to the average stabilized water temperature following basin replenishment (ranging from 13.57°C to 14.39°C). This average is computed over a stabilization period to mitigate thermal noise. The constant temperature of the basin water reflects the rapid thermal equilibrium, driven by continuous replenishment, providing the model with stable thermal input. This constant temperature is coupled with a constant prescribed water flux, representing the infiltration rate. The bottom boundary is defined by a convection-dominated outflow, permitting heat loss solely through convection. The lateral boundaries are assigned a zero-heat flux condition ($0 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$).

To estimate the infiltration rate, the prescribed flow in the model is adjusted until the simulated temperature at the FO cable depth (10 cm) closely aligns with passive-DTS observations. The best fit is obtained by minimizing the root mean square error (RMSE) between the observed and simulated thermal responses. Although a stationary flow is assumed, recharge may vary over time, especially at the start of the infiltration. This aspect is further explored through a comparison of constant and transient recharge models in Section 3.2.3. Model-derived infiltration rates were also compared with field measurements from a constant-head well permeameter conducted in loess sediments inside and outside the basin prior to the infiltration test (see Section 2 of Annex D).

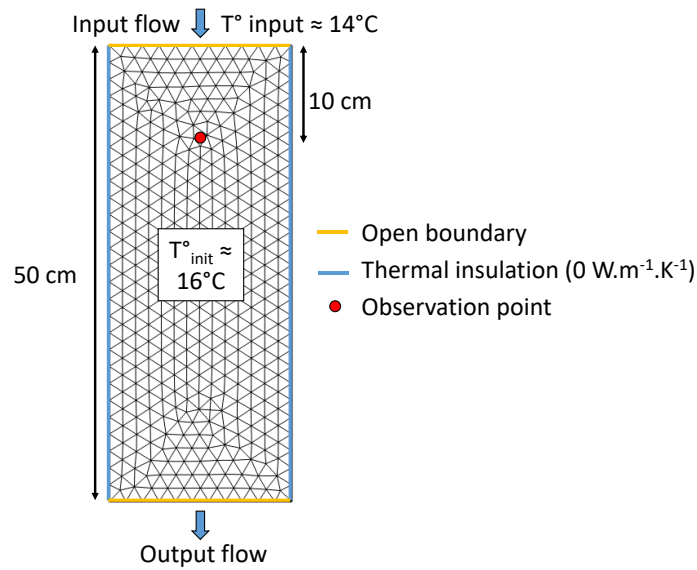


Figure 31. Heat transfer model implemented in COMSOL to interpret passive-DTS measurements.

Table 6 presents the physical and thermal properties of the loess sediments, water and saturated porous medium. Granulometry tests were carried out to estimate the bulk density and the porosity of the loess, using samples collected from the infiltration basin. The volumetric heat capacities of the saturated porous material and of the water were defined based on literature (Bilskie, 1994; Stauffer *et al.*, 2013; Alnefaie and Abu-Hamdeh, 2020). The mean thermal conductivity of the saturated sediments was estimated using active-DTS. Detailed explanations regarding the derivation of all properties listed in Table 6 are provided in the section 3 of Annex D, including the distinction between the thermal properties of the saturated porous medium and those of the solid matrix, which were calculated using COMSOL-based equations.

Table 6. Input parameters for COMSOL software. 1 : measured; 2: from literature.

Property	Unit	Saturated porous media	Liquid	Solid
Thermal conductivity ¹	$\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$	1.78	0.58	2.65
Density ¹	$\text{Kg}\cdot\text{m}^{-3}$	-	1000	2700
Volumetric Heat capacity at constant pressure ²	$\text{MJ}\cdot\text{m}^{-3}\cdot\text{K}^{-1}$	3	4.1	2.2
Total porosity ¹	-	0.42	-	-

2.4. Transient infiltration rate modelling

The interpretation of passive-DTS measurements was conducted under the assumption of stationary flow conditions. However, as demonstrated by Horton (1933, 1939), recharge decreases exponentially over time during infiltration. This decline can be attributed to several factors, including the swelling of colloids, the closing of soil cracks, the movement of fine particles into sediment pores, and soil packing due to increased water pressure. To address this phenomenon, new numerical simulations were conducted considering transient infiltration rates. Horton (1939) demonstrated that the evolution of

the infiltration rate f at the beginning of the infiltration phase can be modelled using the following equation:

$$f = f_f + (f_0 - f_f) \times e^{-kt} \quad (7)$$

with f_0 the initial infiltration rate (capacity), f_f the final infiltration rate, k a constant related to soil properties and t the time from the beginning of the infiltration. The final infiltration rate f_f was estimated from pressure data at the end of the passive-DTS data interpretation period (after 21.92 hours), just prior to the collection of active-DTS data. Subsequently, the infiltration model (Eq. 7) was calibrated by adjusting both the initial infiltration capacity f_0 and the parameter k to reproduce the infiltration rate evolution derived from pressure data. To identify the optimal parameter set, an initial infiltration rate f_0 was prescribed, and the coefficient k was iteratively adjusted to minimize the RMSE between the modelled transient infiltration rate and the rate inferred from pressure data. For each optimal pair of f_0 and k , the transient infiltration model was implemented into COMSOL. The combination yielding the lowest RMSE between simulated and observed thermal responses was selected as the best fit.

2.5. Sensitivity analysis

Both passive and active-DTS analyses rely on assumptions that introduce uncertainties into the results. To assess the impact of critical parameters on these results, a sensitivity analysis was conducted. For active-DTS measurements, the proposed methodology has proven reliable (Simon *et al.*, 2022). The ADTS toolbox quantifies uncertainty related to instrumentation by assessing the impact of data noise on estimates of thermal conductivity and groundwater flux. It computes temperature increases over a range of thermal conductivity and flux values and derives associated uncertainties based on the system's temperature resolution (Des Tombe *et al.*, 2019; Simon and Bour, 2023).

For passive-DTS data interpretation, the sensitivity of the results depends on soil-related parameters introduced into the COMSOL model. In this study, we specifically examined the effects of thermal conductivity, volumetric heat capacity, and porosity on the model's output. Additionally, we investigated the impact of burial depth of the FO cable, as its exact positioning is subject to uncertainty and may influence the thermal response.

To assess how variations in these parameters impact the simulated thermal response, multiple models were tested by varying the values of each parameter. These models were then compared to a reference model, which was established using the parameters listed in Table 6 and the median infiltration rate inferred from passive-DTS analysis. The relative deviation is subsequently calculated using Eq. 8. This calculation indicates the degree to which the infiltration rate q_{model} diverges from the reference model rate q_{ref} . This analysis provides insight into the influence of both soil properties and FO burial depth on infiltration rate estimations.

$$relative\ deviation = \frac{q_{model} - q_{ref}}{q_{ref}} \times 100 \quad (8)$$

3. Results

The results are presented in two subsections. First, active-DTS data are interpreted using the MILS analytical model implemented within the ADTS toolbox. The analysis begins with the interpretation of

the thermal response at a single point along the FO cable and is then extended to the entire heated section. Subsequently, passive-DTS data are analysed using the COMSOL heat transfer numerical model. Similarly, the analysis starts at an individual location and is then generalized to the full extent of the buried FO cable. Note that full temperature profiles, recorded along the entire FO cable, are provided in the section 4 of Annex D. These profiles show distinct thermal zones along the FO cable associated with calibration baths, surface exposure, and the buried section within the infiltration basin.

3.1. Active-DTS measurements

3.1.1. Thermal response interpretation

Figure 32 illustrates the two-step approach used to interpret the temperature increase recorded at a distance of 72.5 m along the FO cable, starting from the DTS unit. The first step entails reproducing the temperature increase that was measured during the conduction-dominant stage (see Figure 32a). Please note that during this stage, the heat propagation is primarily governed by conduction. This means that the temperature increase is exclusively dependent on the thermal conductivity of the porous media. This phase is observed between approximately 2 min 30 s and 5 h 20 min, during which a linear increase in the thermal response is observed. Among all the thermal conductivity values tested, $1.89 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ yielded the most accurate reproduction of the thermal response. The second step expands the interpretation to encompass the thermal response observed during both the conduction- and advection-dominant periods (see Figure 32b). At later times, a stabilization of the thermal response is observed due to heat dissipation by advection. The model shows that the infiltration rate of $4.16 \times 10^{-6} \text{ m}\cdot\text{s}^{-1}$ leads to a temperature stabilization that aligns well with the observed data.

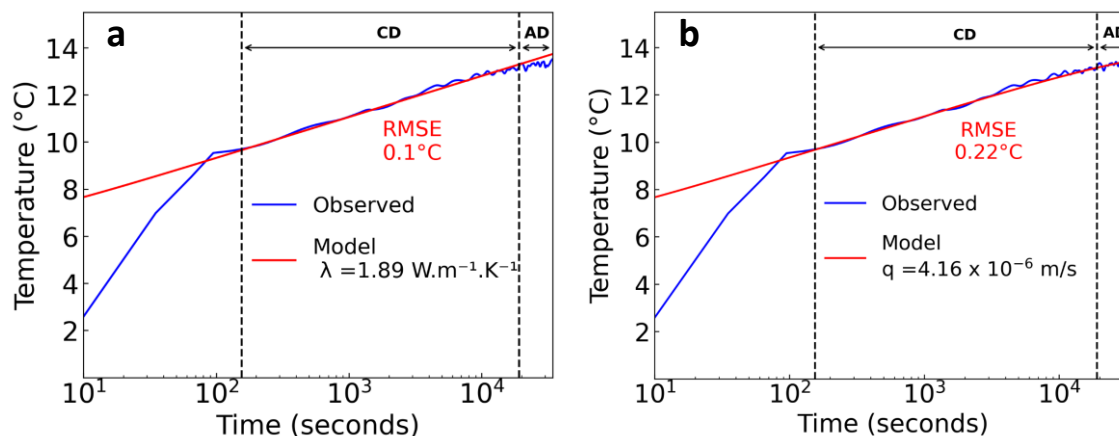


Figure 32. Thermal response recorded at 72.5 m from the DTS unit during the heating phase, along with the best-fit modelled curves obtained using the MILS model considering: a) only the conduction-dominant (CD) period, and b) both the conduction- and advection-dominant period (CD and AD). In both cases, ΔT_{FO} is set to 6.4°C .

3.1.2. Spatial variability of the infiltration rate along the heated FO cable section

The ADTS toolbox automatically implements the two-step interpretation previously introduced for each measurement point located along the heated section of the FO cable. It provides high-resolution estimates of both thermal conductivity and groundwater flux, facilitating the mapping of the thermal conductivities and infiltration rates within the basin sediments (see Figure 33a and b).

The results indicate that thermal conductivity values along the heated section range from 1.59 to 1.89 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, with an average of 1.78 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (see Figure 33a). Given the spatial variability of thermal conductivity and the associated uncertainties in active-DTS interpretation using the ADTS toolbox (0.28 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$), the total estimated range of thermal conductivity values is between 1.31 and 2.17 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. Laboratory measurements conducted on saturated loess samples collected from the infiltration basin yielded a thermal conductivity of 1.55 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, which is in good agreement with the DTS-based estimates. Additional details on the laboratory measurement are provided in Section 5 of Annex D. A gradual increase in thermal conductivity is observed along the active section from the beginning to the end of the active section (point B to point C). Infiltration rates estimated along the heated section range from $2.01 \times 10^{-6} \text{ m}\cdot\text{s}^{-1}$ and $4.69 \times 10^{-6} \text{ m}\cdot\text{s}^{-1}$ (see Figure 33b), with a mean value of $3.79 \times 10^{-6} \text{ m}\cdot\text{s}^{-1}$ ($\approx 33 \text{ cm}\cdot\text{day}^{-1}$). As for the distribution of thermal conductivity values, infiltration rates also increase progressively from point B to point C.

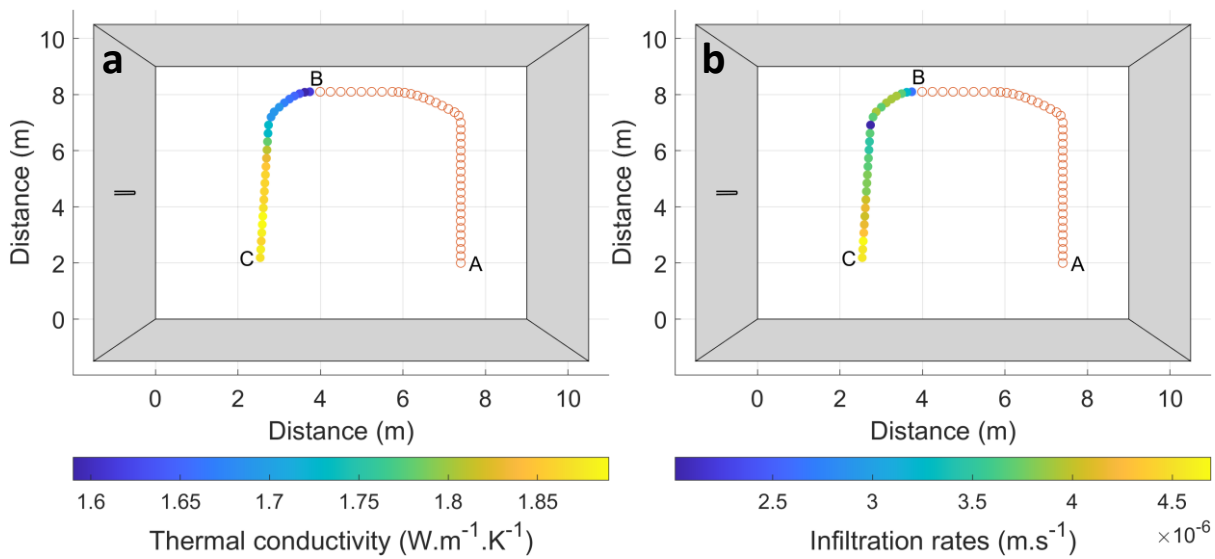


Figure 33. Maps of a) thermal conductivity and b) infiltration rate values derived from the interpretation of active-DTS data.

3.2. Passive-DTS measurements

3.2.1. Thermal decrease reproduction

The interpretation of passive-DTS measurements consists in reproducing the thermal response measured at the start of the basin replenishment with cold groundwater. Figure 34 illustrates an example of data interpretation for a single measurement point, located at a distance of 61 m along the FO cable, starting from the DTS unit. It appears that a recharge rate of $8.00 \times 10^{-6} \text{ m}\cdot\text{s}^{-1}$ results in the best agreement between the model and the temperature measurements ($\text{RMSE} = 0.06^\circ\text{C}$).

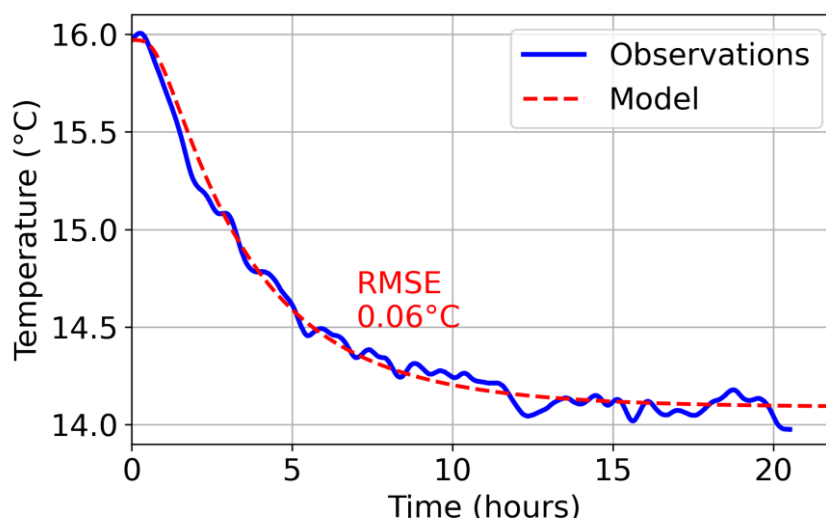


Figure 34. Thermal response model at 61 m along the FO cable from the DTS unit at the onset of the infiltration test.

3.2.2. Spatial variability of the initial infiltration rate along the FO cable

In contrast to the interpretation of active-DTS measurements, which permitted the estimation of infiltration rates exclusively along the heated section, the interpretation of passive-DTS measurements is applicable to any measurement point located along the buried section of the cable. Consequently, estimates of recharge rates can be obtained along the entire buried section (see Figure 35a). In accordance with the results derived from active-DTS analysis, an increase in the recharge rate is observed from B to C (see Figure 35b), with infiltration rates ranging from $1.15 \times 10^{-5} \text{ m}\cdot\text{s}^{-1}$ to $2.90 \times 10^{-5} \text{ m}\cdot\text{s}^{-1}$. Conversely, there is a gradual decrease in the recharge rate from B to A (see Figure 35a and b), with estimated infiltration rates ranging from $1.70 \times 10^{-5} \text{ m}\cdot\text{s}^{-1}$ to $7.5 \times 10^{-6} \text{ m}\cdot\text{s}^{-1}$. The mean infiltration rate along the entire buried section of the FO cable is $1.51 \times 10^{-5} \text{ m}\cdot\text{s}^{-1}$ ($130 \text{ cm}\cdot\text{day}^{-1}$). This value is in good agreement with field measurements obtained using a constant-head well permeameter, which ranged from 1.12 to $1.5 \times 10^{-5} \text{ m}\cdot\text{s}^{-1}$, thereby reinforcing confidence in the modelling results (see section 2 of Annex D). RMSE values calculated between modelling results and field data range between 0.06 and 0.15°C , indicating a good fit of the models. The disparities in infiltration rates derived from the analysis of active- and passive-DTS data are addressed in the section 4.2.

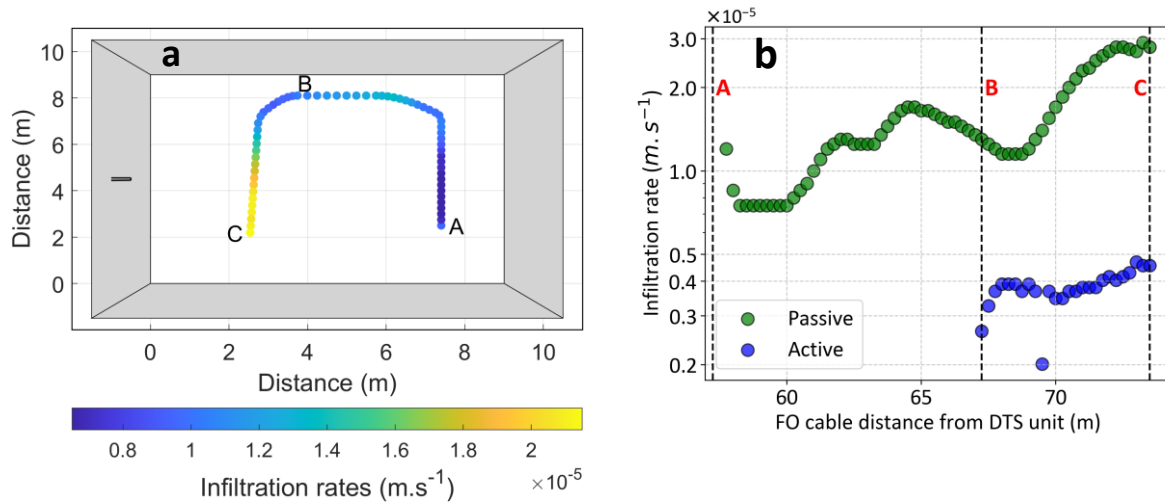


Figure 35. a) map of recharge rates derived from the interpretation of passive-DTS data; b) variation of infiltration rate along the entire buried section of the FO cable, derived from both passive and active-DTS data analysis.

3.2.3. Comparative analysis: stationary and transient infiltration rates

The pressure sensor installed within the cobblestone layer of the basin recorded water level variations during the basin-filling phase for the first seven hours and throughout the basin-emptying phase, which lasted from approximately 7 to 135 hours (Figure 36a). As the basin water level decreased over time, this decline reflected the volume of water infiltrating per unit area. The temporal derivative of the water level signal provides an estimate of the infiltration rate at the basin scale (Figure 36b). Note that the infiltration rate was not calculated during the basin-filling stage as water infiltrates simultaneously with the rising water level.

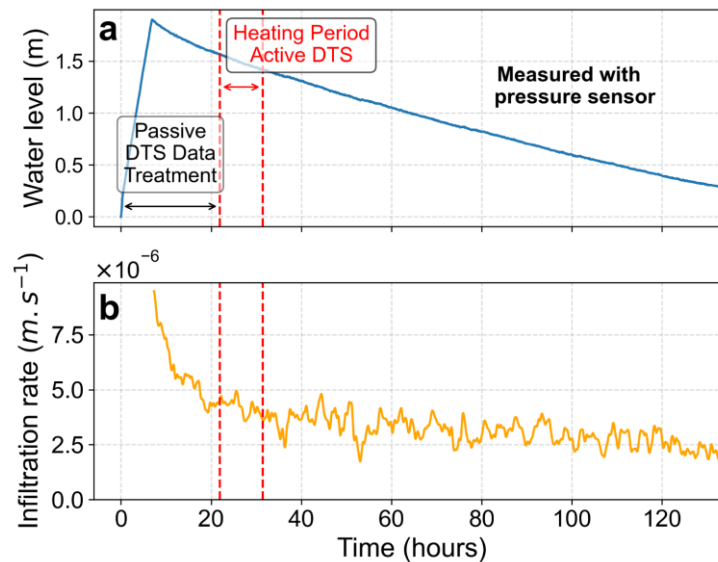


Figure 36. Pressure sensor data showing a) water level evolution during the infiltration test, and b) the corresponding instantaneous infiltration rate derived from the temporal derivative of the water level.

Given the rapid and significant decrease in infiltration rate at the start of the test, the stationary flow conditions assumed in the numerical model for interpreting passive-DTS measurements may be inaccurate. Therefore, new simulations were conducted considering transient infiltration rates to

account for the actual dynamics of the infiltration rates. The analysis focuses on a single point along the FO cable, located 70 meters from the DTS unit.

Figure 37a presents the optimized transient infiltration rate model, while Figure 37b compares the thermal response curves derived from passive-DTS data interpretation under both stationary and transient infiltration conditions. Under the assumption of stationary flow, the optimal infiltration rate was determined to be $1.35 \times 10^{-5} \text{ m.s}^{-1}$. The thermal response model simulated considering transient infiltration dynamics closely aligns with the thermal response obtained under stationary conditions.

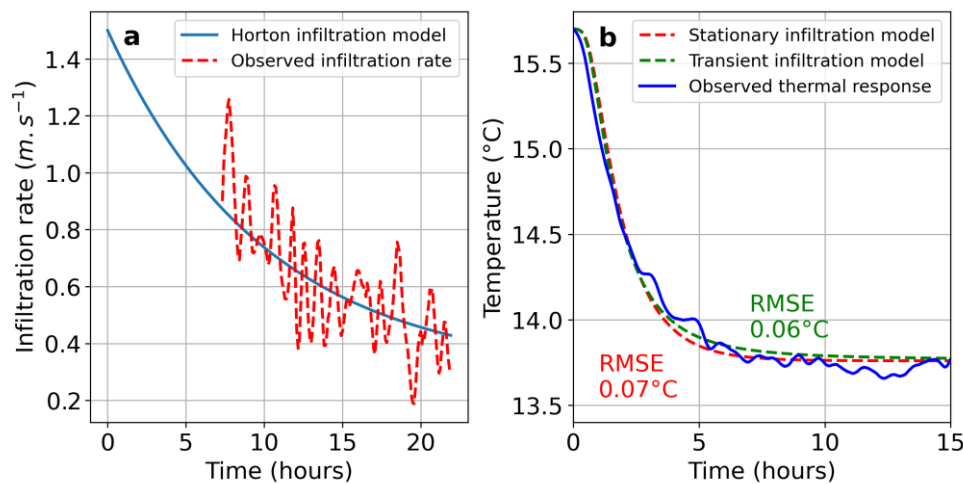


Figure 37. a) Optimized transient infiltration model with an initial infiltration rate of $1.50 \times 10^{-5} \text{ m.s}^{-1}$, and b) corresponding simulated thermal response model (green dotted line) compared to the best-fit thermal model assuming a stationary infiltration rate of $1.35 \times 10^{-5} \text{ m.s}^{-1}$ (red dotted line).

4. Discussion

The discussion provides an in-depth examination of the findings and implications from both passive- and active-DTS data analysis. Firstly, the sensitivity of infiltration rate estimates to changes in model parameters has been evaluated. The discrepancy in results between passive- and active-DTS data interpretation is then explained by describing the differing infiltration dynamics observed during the test. The discussion also explores the spatial variability in the estimated infiltration rates, highlighting potential factors influencing these variations. Finally, the outcomes of this study regarding MAR operations and monitoring strategies are discussed.

4.1. Sensitivity analysis on infiltration rate estimates from DTS data analysis

The interpretation of both passive- and active-DTS data relies on assumptions that may influence the reliability of the estimates. In the analysis of active-DTS data, the ADTS toolbox addresses instrumental uncertainty by assessing the impact of temperature noise on the determination of thermal conductivity and flux values. In this study, a mean temperature noise of 1°C resulted in uncertainties of $0.28 \text{ W.m}^{-1}.\text{K}^{-1}$ for thermal conductivity and $2.98 \times 10^{-6} \text{ m.s}^{-1}$ for the derived infiltration rates.

The accuracy of infiltration rate estimates in passive-DTS analysis depends on the reliability of the parameters incorporated within the heat transfer numerical model. Key parameters influencing heat

transfer dynamics include total porosity, volumetric heat capacity, and thermal conductivity of the saturated porous medium. Additionally, the burial depth of the FO cable introduces further uncertainty. As outlined in Section 2.5, the sensitivity assessment methodology involves computing the relative deviation of infiltration rates necessary to align with the reference model. The resulting deviations, presented in Table 7, provide insights into how variations in these parameters affect the estimated infiltration rates.

During the installation of the FO cable, efforts were made to bury it as close as possible to a depth of 10 cm. However, actual burial depth may vary slightly across different locations. To assess the impact of burial depth on thermal responses, temperature variations were modelled at depths ranging from 5 cm to 15 cm (see Figure 38a). Thermal responses simulated at shallower depths (5 cm and 7.5 cm) require a lower infiltration rate to accurately replicate the reference model, whereas those at greater depths (12.5 cm and 15 cm) require higher infiltration rates. The range of relative deviations from the reference model is from -16 to 19% for a 5-centimeter depth uncertainty and from -30 to 33% for a 10-centimeter depth uncertainty.

Similarly, the impact of the thermal conductivity on thermal response curves was evaluated by simulating temperature variations across different ranges for λ (see Figure 38b). For loess material, a thermal conductivity range of 1.5 to 3.5 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ is expected (Andújar et al., 2016), resulting in relative deviations from -3 to 13%. However, this range of uncertainty can be reduced by considering thermal conductivity values inferred from active-DTS data interpretation. A refined range of 1.31 to 2.17 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ is obtained when accounting spatial variability and the intrinsic error (0.28 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) associated with active-DTS measurements. This refinement leads to relative deviations from -4 to 3%.

Although the utilization of thermal conductivity data derived from active-DTS reduces uncertainty, the error remains relatively small in both cases. This can be attributed to the thermal Peclet number, a dimensionless parameter that quantifies the ratio of heat transfer by advection to conduction (Anderson, 2005). In this study, the thermal Peclet number is greater than one, indicating that heat transfer is dominated by advection rather than conduction during the initial stages of infiltration. For more information on Peclet number calculation, please refer to Section 6 of Annex D. Consequently, the sensitivity associated to thermal conductivity is relatively low. Note that even with low-permeability materials, such as loess, advection dominates heat transfer leading to low sensitivity to thermal conductivity. In more permeable materials (e.g., sand and gravel, among others), advection would play an even more dominant role, further reducing the impact of thermal conductivity uncertainties.

The values of total porosity and volumetric heat capacity exert minimal influence on the simulated thermal response (see Figure 38c and Figure 38d). For loess, total porosity typically ranges between 36% and 55% (Jie Zhang et al., 2023), although Delvoie (2017) refined this range to 40%–46% in their study on Hesbaye loess characterization. Within this refined interval, variations in the inferred infiltration rate remain below 1%. Even when considering more extreme porosity values, the resulting deviation does not exceed 3%. This finding indicates that the uncertainty associated with porosity has a negligible effect on infiltration rate estimates. Conversely, the volumetric heat capacity of saturated loess exerts a slightly greater influence on model outcomes. The expected values for this parameter range between 2.5 and 3.5 $\text{MJ}\cdot\text{m}^{-3}\cdot\text{K}^{-1}$ (Alnefaie and Abu-Hamdeh, 2020), leading to a calculated relative deviation of 9% in infiltration rate estimates.

A worst-case scenario is considered, incorporating a 5-centimeter depth uncertainty in FO cable placement, thermal conductivity values ranging from 1.31 to 2.17 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (inferred from active-DTS analysis), volumetric heat capacities between 2.5 and 3.5 $\text{MJ}\cdot\text{m}^{-3}\cdot\text{K}^{-1}$, and porosity values from 36% to 55%. The maximum deviation in estimated infiltration rates is thus approximately 30%. This level of uncertainty is comparable to that associated with conventional in-situ infiltration measurement techniques, such as lysimeters and double-ring infiltrometers, which also demonstrate uncertainties up to 30% (Amaral *et al.*, 2018; Rönnqvist, 2018; Silva *et al.*, 2020). However, these methods provide only localized measurements, whereas DTS-based approaches offer spatially integrated estimations of infiltration, reducing the impact of site-specific variability. Despite these advantages, the burial depth of the FO cable remains a critical factor in minimizing uncertainty. Improving cable installation procedures could significantly reduce depth-related errors and enhance the accuracy of DTS-based measurements.

While the sensitivity analysis provides valuable insights into how variations in key parameters influence thermal response and infiltration rate estimates, extending this uncertainty quantification along the entire buried fiber optic cable is not feasible. This finding further validates the enhanced reliability of the active-DTS method in comparison to passive-DTS measurements. However, it's important to consider this perspective with nuance. Active-DTS data analysis provides highly accurate infiltration rates at any stage of the infiltration test, whereas passive-DTS data interpretation offers insights into initial infiltration rates but with higher uncertainty. Nevertheless, the passive-DTS method remains more reliable than traditional in-situ techniques because it provides spatially resolved values at the scale of a pilot site.

Table 7. Relative deviation in estimated infiltration rate due to parameter variation in COMSOL.

	depth (cm)	$q_{\text{model}} (\text{m}\cdot\text{s}^{-1})$	Relative deviation (%)
d₁	5	7.35×10^{-6}	-30
d₂	7.5	8.85×10^{-6}	-16
d₃	12.5	1.25×10^{-5}	19
d₄	15	1.40×10^{-5}	33
	thermal conductivity ($\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$)	$q_{\text{model}} (\text{m}\cdot\text{s}^{-1})$	Relative deviation (%)
λ_1	1.31	1.01×10^{-5}	-4
λ_2	1.50	1.02×10^{-5}	-3
λ_3	2.17	1.08×10^{-5}	3
λ_4	3.50	1.19×10^{-5}	13
	Volumetric heat capacity ($\text{MJ}\cdot\text{m}^{-3}\cdot\text{K}^{-1}$)	$q_{\text{model}} (\text{m}\cdot\text{s}^{-1})$	Relative deviation (%)
VHC₁	2.5	9.50×10^{-6}	-9
VHC₂	3.5	1.14×10^{-5}	9
	Porosity (%)	$q_{\text{model}} (\text{m}\cdot\text{s}^{-1})$	Relative deviation (%)

n_1	36	1.06×10^{-5}	1
n_2	40	1.05×10^{-5}	0
n_3	46	1.04×10^{-5}	-1
n_4	55	1.02×10^{-5}	-3

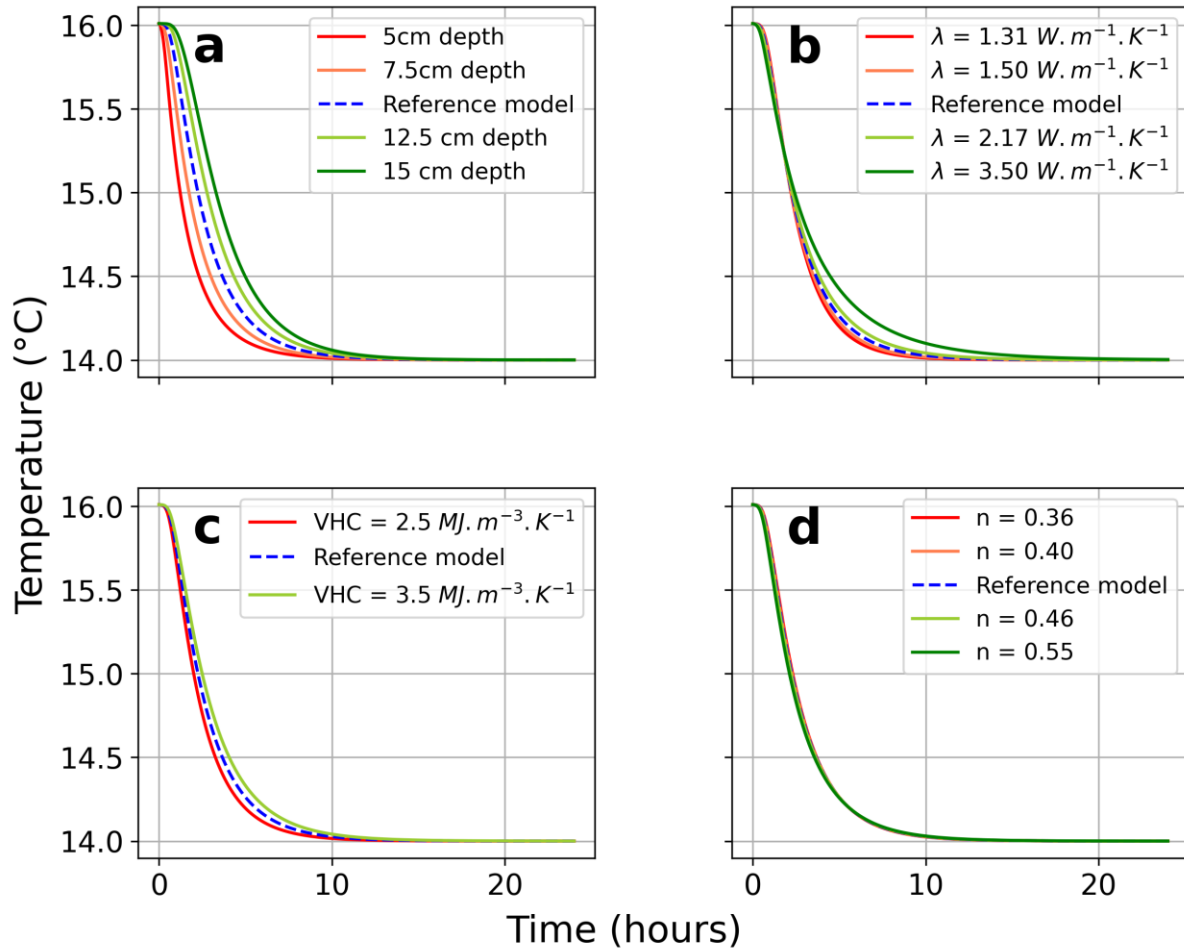


Figure 38. Sensitivity of thermal response models to variations in a) depth, b) thermal conductivity, c) volumetric heat capacity (VHC) and d) total porosity.

4.2. Temporal variations in infiltration rates

Estimates of infiltration rates derived from active- and passive-DTS measurements differ by one order of magnitude. Passive-DTS data interpretation yielded a higher mean recharge rate of $1.51 \times 10^{-5} \text{ m}\cdot\text{s}^{-1}$, compared to $3.79 \times 10^{-6} \text{ m}\cdot\text{s}^{-1}$ from active-DTS data analysis. As outlined in Section 4.1, the impact of parameter uncertainty on these estimates is minimal, with a maximum reasonable deviation of approximately 30%. This finding suggests that the observed discrepancy in magnitude between passive and active-DTS interpretations cannot be attributed to parameter uncertainty, but rather to the temporal dynamics of infiltration (see Figure 36b).

To further validate this interpretation, infiltration rates derived from DTS analysis were compared with those inferred from pressure data. Passive-DTS measurements reflect infiltration rates during the early

stage of the infiltration test, whereas active-DTS measurements were conducted 24 hours later. The higher infiltration rates estimated from passive-DTS represent the initial rapid infiltration before decreasing exponentially over time, as described in Horton's theory (1933, 1939). These findings are consistent with the behaviour observed from pressure data (see Figure 36b). Given that the infiltration rate measured from pressure data is representative of basin-scale infiltration, the mean infiltration rate derived from active-DTS, which integrates variations along the FO cable, provides a suitable basis for comparison. In fact, the mean infiltration rate obtained from pressure data during the heating period was approximately $4 \times 10^{-6} \text{ m}\cdot\text{s}^{-1}$, which aligns well with the $3.79 \times 10^{-6} \text{ m}\cdot\text{s}^{-1}$ derived from active-DTS. These values are consistent with those reported in studies of infiltration basins with loamy sediments (Beganskas and Fisher, 2017), supporting the validity of the applied approach. It is important to note that the actively heated segment of the FO cable traverses only the left portion of the infiltration basin (see Figure 33a). Therefore, the mean infiltration rate obtained from active-DTS analysis may not fully represent the recharge dynamics across the entire basin. This consideration underscores the importance of incorporating the temporal dynamics of infiltration, a component frequently overlooked in conventional methods that prioritize the initial stages of infiltration, such as lysimeters.

On July 25th 2023, groundwater levels were measured in two piezometers located a few meters from the infiltration basin. These measurements indicate that the basin and the aquifer are unlikely to be hydraulically connected. This suggests that the temporal evolution of infiltration is governed by processes within the unsaturated zone, rather than by direct hydraulic interaction with the aquifer. As infiltration progresses, a dynamic water front delineates the saturated and unsaturated zones within the soil (Alastal and Ababou, 2019), with pressure data revealing a gradual decline in the recharge rate, from approximately $4 \times 10^{-6} \text{ m}\cdot\text{s}^{-1}$ to $2 \times 10^{-6} \text{ m}\cdot\text{s}^{-1}$, before the water level reaches the top of the pebblestone layer. According to Darcy's law, the reduction in infiltration rate can be attributed to the diminishing pressure head, which results in decreased groundwater flux and, consequently, a lower recharge rate. This phenomenon has been notably documented by Helles and Mogheir (2022), who observed a linear decrease in infiltration rates in permeable stormwater basins as the pond water depth decreased.

Given that passive-DTS interpretation assumes steady-state flow, we assessed the potential influence of transient conditions through additional simulations. The infiltration rate derived from passive-DTS data at a distance of 70 meters from the DTS unit (see Section 3.2.2), estimated at $1.35 \times 10^{-5} \text{ m}\cdot\text{s}^{-1}$, is slightly lower than the initial rate of $1.50 \times 10^{-5} \text{ m}\cdot\text{s}^{-1}$ used in the transient recharge model (see Section 3.2.3). This slight underestimation suggests that, while passive-DTS interpretation provides valuable insights into early infiltration dynamics, it may not fully capture the rapid changes occurring during the initial phase of infiltration. However, the difference (approximately 10%) is relatively small compared to the inherent variability of infiltration rates. Nevertheless, it is important to acknowledge that this difference ($1.5 \times 10^{-6} \text{ m}\cdot\text{s}^{-1}$) is smaller than the uncertainty associated with the estimates evaluated in the sensitivity analysis. Consequently, this underestimation may also be a result of the inherent uncertainty in the measurements and analysis, rather than indicative of a systematic error in the passive-DTS interpretation approach.

While the transient recharge model offers valuable insights into infiltration dynamics, its application along the entire FO cable presented certain limitations. At points where temperature changes were slower, it was difficult to assign a sufficiently low initial infiltration rate that matched the observed

data. This challenge arises because the infiltration data inferred from water pressure measurements reflect average values across the system and cannot account for localized deviations in soil properties. While the transient recharge model provides a more comprehensive representation of the infiltration process dynamics, the approximation using a constant infiltration rate for passive-DTS data analysis is adequate for estimating the spatial distribution of recharge rates at the onset of the infiltration test. Therefore, the necessity of considering transient recharge at every point along the FO cable for passive-DTS data interpretation may not be necessary for practical applications. The constant infiltration rate approximation offers an efficient and effective approach for assessing initial infiltration rates over space, without significantly altering the overall interpretation. However, it is important to note that this conclusion is specific to the present study site and that differing soil conditions at other sites may yield different results.

In light of these findings, future work should focus on developing methods to integrate transient infiltration models that reproduce thermal responses from passive-DTS data, thereby capturing the temporal dynamics of early recharge rather than assuming constant infiltration rates. Such models would enable a more accurate representation of the evolving infiltration process. While most DTS-based studies rely on longer time series (e.g., days to months) and focus on broader-scale patterns such as diurnal variations (Hatch *et al.*, 2006), few have addressed infiltration dynamics at the short time scales (seconds to minutes) that characterize early recharge. The high temporal resolution of the measurements (10 s) enables a more detailed capture of infiltration rate changes, underscoring the need to develop new methodologies for transient recharge model integration in such contexts.

4.3. Spatial distribution of infiltration rates

As illustrated in Figure 33a and Figure 35a, infiltration rates exhibit spatial variability, with a slight increase observed along the heated section of the FO cable (from B to C). The consistency of this trend across both passive- and active-DTS data interpretations (Figure 35b) reinforces the reliability of the results. Several factors may explain these observed differences. As indicated in the sensitivity analysis, the depth at which the fiber is buried affects the inferred infiltration rates. Therefore, a gradual increase in burial depth from point B to point C could partly explain the rising infiltration estimates along the heated section. Additionally, slight irregularities in the sediment surface, such as a subtle slope, may cause small variations in water depth, contributing to differences in the results. It is likely that a combination of these factors accounts for the observed variability. Nevertheless, the variations remain relatively minor, and the method proves effective for identifying meaningful spatial differences.

Furthermore, the interpretation of passive-DTS data reveals lower fluxes along the B-A section compared to B-C. In addition to the effects of burial depth and sloped sediment surface, a plausible explanation is that the B-C section lies directly beneath the basin's filling pipe. Since passive-DTS data capture conditions at the onset of the infiltration test, turbulence from the incoming water may locally enhance infiltration by temporarily increasing pressure and scouring fine sediments (Maltauro *et al.*, 2024). This process could lead to higher initial infiltration rates on that side of the basin.

These observations raise the question of whether the spatial patterns reflect actual variability or measurement uncertainty. As indicated in the sensitivity analysis, variations in burial depth can cause the estimated infiltration rate at a single point to range from 7.35×10^{-6} to $1.4 \times 10^{-5} \text{ m}\cdot\text{s}^{-1}$. Conversely, the interpretation of passive-DTS data reveals a spatial variability from 7.5×10^{-6} to $1.7 \times 10^{-5} \text{ m}\cdot\text{s}^{-1}$,

falling within the same range. This suggests that the apparent spatial differences may reflect methodological uncertainty rather than actual heterogeneity in soil properties. This represents a significant limitation of the passive-DTS method, as the uncertainty associated with burial depth is of the same order of magnitude as the spatial variability it aims to capture. Nevertheless, the spatial trend in infiltration rates derived from passive-DTS measurements is consistent with that observed in active-DTS measurements (Figure 35b). This agreement reinforces the reliability of the observed increase in groundwater flux from B to C, despite the underlying uncertainties. It also underscores the value of conducting active-DTS measurements in parallel with passive-DTS to accurately capture spatial variability.

4.4. Strengths and Limitations of Passive and Active-DTS Methods

Both active and passive-DTS approaches offer distinct advantages and limitations. Active-DTS provides accurate infiltration rate estimates with high spatial resolution and low associated uncertainty. In contrast to passive-DTS, it does not rely on natural temperature variations, enabling estimation of recharge rates at any time during the infiltration process. Moreover, active-DTS can be applied year-round, regardless of the temperature contrast between the soil and the recharge water. However, this method requires the injection of electric current into the steel armouring of the FO cable to generate heat, making it reliant on an external power supply. As a result, active-DTS may not be optimal for long cable sections (e.g., over several hundred meters), where uniform heating would require substantially higher power.

In contrast, passive-DTS interpretation provides estimates of the initial infiltration rate, primarily capturing the early and more rapid phase of infiltration. Nevertheless, passive-DTS measurements offer the advantage of covering a larger spatial domain, as DTS units are capable of monitoring temperature variations across several hundred meters. However, as discussed in Section 4.1, the numerical model used to interpret passive-DTS data is subject to input-related uncertainties. In particular, uncertainty in the burial depth of the FO cable introduces a 19% to 33% margin of error in recharge estimates, which complicates the detection of small flux variations.

Conversely, active-DTS remains largely unaffected by burial depth. Only two specific conditions regarding burial depth could influence active-DTS measurements. First, as demonstrated by Simon et al. (2024), if the cable is buried less than 3 cm, a portion of the generated heat may dissipate to the surface, thereby reducing the measured temperature increase. Secondly, filtering out natural temperature fluctuations in active-DTS data typically requires support from passive-DTS measurements. Therefore, it is essential to apply an appropriate filtering procedure. In this study, the cable was buried deep enough to avoid interference from surface heat exchange. Passive-DTS data were filtered accordingly before interpreting active-DTS results (see Section 2.3.1). Therefore, active-DTS measurements can be considered effectively independent of the cable's burial depth in this context.

The reliability of passive-DTS data, on the other hand, depends on achieving a sufficient temperature contrast between the infiltrating water and the surrounding soil. This contrast must exceed both the instrument's noise level and any natural temperature fluctuations occurring during basin replenishment. In this study, conducted in July, the temperature difference was approximately 2°C, well above the DTS noise level of 0.05°C. Based on the mean stabilized temperature recorded along the FO cable and its associated noise, we calculated a mean signal-to-noise ratio (SNR) of 49 dB,

indicating a high-quality signal (Young, 2015). Maintaining infiltration rate estimates within a 10% error margin requires a minimum temperature difference of 1 °C when noise is 0.05 °C (i.e., $\Delta T > 20 \times \text{noise}$). Conducting studies in colder seasons or climates may benefit from larger contrasts between soil and infiltrating water. Alternatively, temperature contrast limitations can be addressed through the analysis of natural temperature signal propagation at various depths, as demonstrated by Becker et al. (2013) and Mawer et al. (2016). Their method uses phase shifts in diurnal temperature signals detected by co-located FO cables at various depths to estimate infiltration rates. This approach enables the inference of daily infiltration dynamics and their spatial variability. However, it requires cables to be installed at multiple depths, which presents technical challenges.

Overall, combining both active and passive-DTS data is particularly advantageous. Passive-DTS provides estimates of the initial infiltration rate over a broad spatial extent. Conversely, active-DTS provides accurate estimates during the infiltration period. Furthermore, as emphasized by Simon et al. (2022), estimating the thermal conductivity of sediments with active-DTS data significantly reduces uncertainties in passive-DTS-derived infiltration rates. Without these estimates, the model would rely on a broader range of thermal conductivity values from the literature, thereby increasing the uncertainty of the results.

4.5. Use of DTS technology in MAR schemes

DTS-based methods have proven highly effective for estimating recharge rates and offer significant advantages for MAR operation management. Their ability to provide high-resolution spatial data enhances understanding of hydrological dynamics within infiltration basins. By burying a FO cable in the basin sediments, it becomes possible to monitor the spatial distribution of recharge and detect preferential infiltration pathways, leading to multiple operational benefits.

A key application of this capability is the detection and management of clogging, a common issue in MAR systems that leads to reduced infiltration efficiency due to the formation of low-permeability layers beneath the basin (Van Cuyk, 2001; Pavelic *et al.*, 2011; Barry *et al.*, 2017). As demonstrated by Medina et al. (2020), repeated DTS surveys can effectively identify zones of reduced infiltration caused by clogging. This information enables targeted maintenance, helping to minimize downtime and preserve system performance. Beyond maintenance, DTS also supports real-time optimization of water delivery. By adjusting ponding depth and flow rates in response to spatially resolved temperature data, operators can enhance infiltration efficiency and adapt to changing conditions. This contributes to more sustainable and cost-effective MAR operations.

Integrating DTS data into operational decision-making allows for more precise control over recharge processes, ultimately improving groundwater management. Future research should explore long-term monitoring to assess the effectiveness of various operational strategies, such as maintaining steady water levels or alternating between wetting and drying cycles. Additionally, exploring the integration of DTS with other monitoring technologies could further enhance MAR management by improving diagnostic capabilities and ensuring the long-term reliability and effectiveness of these critical systems.

5. Conclusion

Passive- and active-DTS measurements were conducted during an infiltration test to demonstrate the applicability of the technology to accurately quantify recharge rates within the framework of MAR. The

results demonstrate that DTS methods are particularly well suited for capturing the spatial variability of infiltration rates, an important advantage given the challenges associated with estimating soil hydraulic permeability. In this study, DTS provided direct and reliable estimates of infiltration, offering valuable insight into the soil's infiltration capacity and enhancing the overall understanding of recharge dynamics.

DTS measurements were carried out along a FO cable, buried within the loess sediments forming the base of the infiltration basin. These fine-grained materials, which are typically characterized by low to moderate permeability, are often overlooked in MAR applications. However, the infiltration rates inferred from DTS measurements in this study were found to be relatively high, ranging between 33 and 130 cm·day⁻¹. These findings suggest that loess-based systems can support effective infiltration under the specific environmental conditions observed at the study site. Conducting similar studies in comparable geological contexts would underscore the importance of not systematically excluding loess sediments when assessing the feasibility of MAR. Moreover, the observed infiltration rates are comparable to those reported for sandy materials in Soil Aquifer Treatment (SAT), such as those documented in Negev et al. (2020), where rates ranged from 48 to 120 cm·day⁻¹. This comparison underscores the potential of loess to support recharge capacities similar to those of more permeable materials when managed appropriately. As such, the results indicate that MAR can be successfully implemented in regions where high-permeability soils are limited, contributing to the long-term sustainability of groundwater recharge strategies across diverse environments. By demonstrating the viability of loess for effective infiltration, this study opens new perspectives for MAR implementation in areas traditionally deemed unsuitable.

Beyond the clear advantage of using DTS technology to quantify spatial variations in infiltration rates, the combined application of active- and passive-DTS measurements also offers valuable insights into the temporal dynamics of infiltration. Passive-DTS measurements were analysed during the early phase of the test to capture natural temperature changes in the soil induced by infiltrating water. In contrast, active-DTS measurements are independent of natural temperature fluctuations and can be conducted anytime during the infiltration process. This flexibility offers a significant advantage, as repeated active-DTS surveys enable continuous monitoring of infiltration dynamics over time, enhancing the understanding and managed of MAR system performance.

Future research should prioritize long-term monitoring to evaluate the effectiveness of various operational strategies. In particular, comparative studies between constant water level infiltration and alternating wetting-drying cycles could help determine the most efficient approach for optimizing MAR system performance.

Data availability

The data presented in the paper are available and accessible through the following link in the ULiège dataverse: <https://doi.org/10.58119/ULG/SZTN6A>.

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This experimentation was made possible through collaboration with the regional water distribution company, CILE (Compagnie Intercommunale Liégeoise des Eaux), which granted access to their installation facility and provided clean abstracted groundwater to fill the infiltration basin.

The characterization of loess properties was carried out at the Building Materials Laboratory (LMC) within the Urban and Environmental Engineering (UEE) department at the University of Liège, under the supervision of Pierre Illing. We are sincerely grateful to him for his valuable assistance in conducting the measurements of the physico-thermal properties of the loess sediments.

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Chapter 7

Contaminant transport modelling under MAR conditions

1. Introduction

Throughout this thesis, the feasibility of managed aquifer recharge (MAR) in the Hesbaye has been investigated from both quantitative and qualitative perspectives, within a context of increasing climatic variability and constant anthropogenic pressure on groundwater resources. The previous chapters have progressively addressed the key elements required to assess whether MAR using urban/airport runoff as a potential recharge source could represent a realistic and sustainable water management measure for the region or be a threat for groundwater quality.

From a quantitative point of view, field investigations conducted at a pilot infiltration site in the municipality of Kemexhe allowed the characterization of infiltration rates within Hesbaye loess sediments at the basin scale. Conventional techniques (infiltrimeters, pressure sensors) were combined with innovative approaches based on passive and active distributed temperature sensing with fiber optic (DTS-FO), providing accurate and spatial estimates of infiltration rates under realistic operating conditions. In addition, the groundwater balance of the Hesbaye chalk aquifer was analysed from 2000 to 2020, demonstrating a groundwater deficit of around $100,000 \text{ m}^3 \text{ yr}^{-1}$. This quantitative assessment allows the identification of potential and available recharge volumes required to partially reduce this deficit in the region.

From a qualitative perspective, an extensive characterization of urban runoff, identified as potential recharge waters, has highlighted the presence of contaminants of emerging concerns (CECs) that may represent a risk for groundwater quality if not properly handled. Among these, benzotriazoles, alkylphenols, and per- and polyfluoroalkyl substances (PFAS) were systematically detected with concentration reaching up several hundreds of ng L^{-1} depending on compounds and associated rainfall events. Complementary batch experiments conducted on Hesbaye loess sediments have provided insights into the attenuation mechanisms affecting these contaminants during infiltration. Results have confirmed the expected strong persistence and limited attenuation of PFAS, mainly controlled by sorption processes, whereas benzotriazole and alkylphenols both underwent sorption and biodegradation mechanisms.

Based on this experimental and field investigation framework, the objective of this final chapter is to integrate the entire set of obtained results through numerical modelling to evaluate the impact of runoff-based recharge on groundwater quality during MAR operations in Hesbaye. The modelling approach aims to translate the knowledge derived from field and lab work into a predictive tool capable to assess both recharge efficiency and contaminant transport under realistic operating scenarios. This integrated evaluation is intended to support decision-making by identifying expected recharge volumes, potential risks to groundwater quality, and operational constraints associated with MAR operations.

Accordingly, a two-dimensions numerical model was developed to represent MAR operations through an infiltration basin identical to the pilot site, coupling variably saturated flow model in the unsaturated zone with the transport of selected contaminants. Simplifying assumptions were introduced regarding porous media properties, boundary conditions, and the representation of biogeochemical processes, while ensuring consistency with observations from previous chapters. This chapter first presents the variably saturated flow model set-up and the MAR cycle scenarios. It then develops contaminant transport simulations that integrates sorption and

biodegradation/transformation processes for diverse contrasting scenarios. Finally, simulation outputs are interpreted in terms of groundwater-quality risks.

2. Variably saturated flow model

2.1. Description of the model

2.1.1. Objective of the model

The objective of the variably saturated flow model is to reproduce, as realistically as possible, the physical processes governing water infiltration through the unsaturated zone under MAR conditions. The model is designed to represent an infiltration basin identical to the pilot site previously investigated in chapter 6. It simulates water percolation from the basin through the loess deposits down to the top of underlying chalk formation.

In addition to reproducing individual infiltration events, the model serves as a quantitative tool to evaluate the recharge potential of MAR operations at the site scale. By implementing different scenarios representative of MAR operating conditions (wet and dry cycles), the model estimates the cumulative volume of water that can effectively contribute to groundwater recharge over a typical year of MAR operation. This enables a comparison between the annual recharge volume simulated for MAR operation and the groundwater deficit estimated at the aquifer scale in Chapter 2.

The model further also serves as a prerequisite for the solute transport simulations developed later in this chapter. Because the transient flow field in the vadose controls contaminant migration, a physically consistent representation of infiltration processes is required prior to transport and risk evaluation.

To meet these objectives, a two-dimensional vertical cross-section model was adopted to represent the subsurface domain beneath infiltration basin, while preserving a realistic representation of basin geometry and operating conditions.

2.1.2. Conceptual model

Before building the geometry and finite element (FE) mesh of the numerical model, a conceptual scheme is established to identify the main hydrogeological units and flow processes to be represented. The basin geometry and local stratigraphy are based on technical information provided by the CILE company, including basin dimensions and nearby drilling data from the Kemexhe production site. Borehole data indicate approximately 10 m of loess deposits, underlain by about 5 m of flint conglomerate, before reaching the chalk formation constituting the Hesbaye aquifer. The groundwater table is located at a depth of approximately 30 m below ground surface, implying that a significant thickness of the chalk formation is unsaturated above the groundwater table.

In this study, modelling focuses on water flow and contaminant transport across the unsaturated zone above the chalk aquifer. The model domain is limited to the upper 15 m beneath the infiltration basin, corresponding to the loess and flint conglomerate units. For modelling purposes, the loess and flint conglomerate are represented as a single homogeneous loess layer. This simplification was adopted to limit parameterization complexity and reduce uncertainty associated with the limited documentation of transport parameters for the flint conglomerate unit. The further unsaturated

portion of the chalk is not included in the model, as the objective is to assess contaminant transfer to the top of the aquifer rather than transport within the chalk matrix itself. Once contaminants reach the top of the chalk, the aquifer is considered potentially impacted, as preferential pathways (e.g. fracture network) may facilitate their transfer toward the saturated zone.

Recharge water is applied at the surface of the infiltration basin and infiltrates vertically through the unsaturated loess layer. The model is governed by variably saturated conditions, with hydraulic conductivity and water content evolving as functions of pressure head. The governing equations and numerical formulation are presented in the following section. No lateral inflow is imposed through the lateral boundaries of the model domain. However, lateral spreading of contaminants along the vertical flow field is expected to occur due to dispersive processes.

At the base of the domain, the chalk formation is represented as a highly transmissive drainage boundary, consistent with the presence of a fracture network. This representation assumes efficient vertical drainage of infiltrating water toward the deeper chalk aquifer. Although chalk fractures are heterogeneous and may increase with depth, this behaviour is simplified here to represent recharge transfer toward the aquifer.

The geological cross-section used for the model is illustrated in Figure 39a, while the associated conceptual model for variably saturated flow and contaminant transport is presented in Figure 39b.

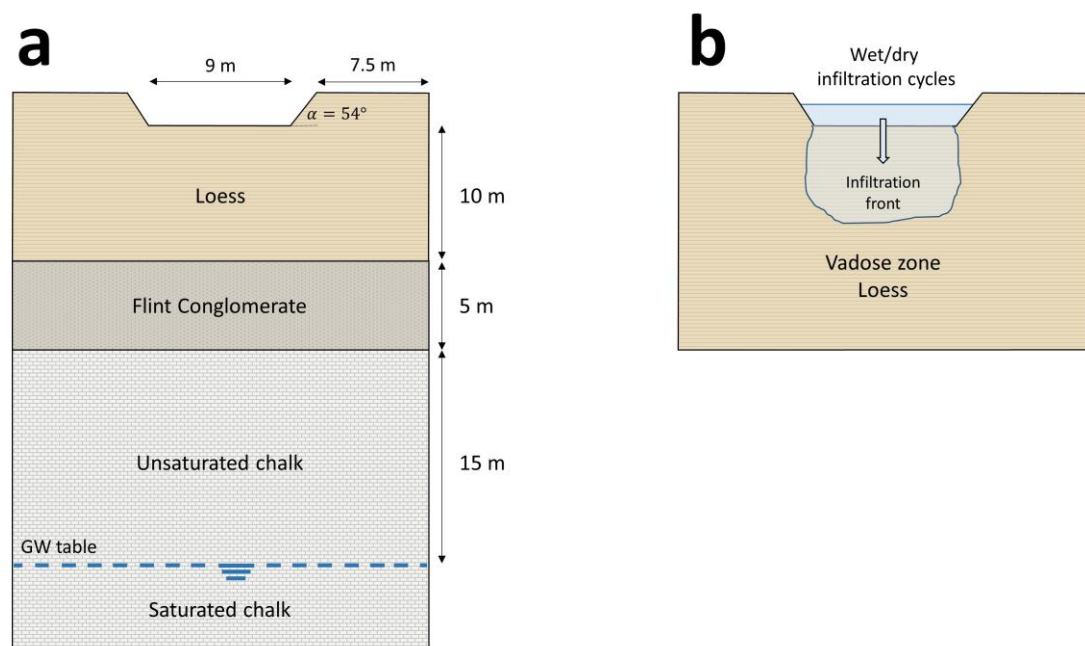


Figure 39. (a) Geological cross-section of the subsurface beneath the Kemexhe infiltration basin. (b) Conceptual model of the numerical domain used for unsaturated flow and contaminant transport simulations.

2.1.3. Model geometry and discretization

The model domain is defined as a two-dimensional vertical cross-section beneath the infiltration basin. Due to the symmetrical basin geometry, only half of the domain is simulated. Laterally, the domain extends 7.5 m outward from the basin edge, so that boundary-condition effects remain negligible

within the zone of interest beneath the basin, while keeping the model size limited to avoid unnecessary computational cost.

The numerical domain is discretized using a finite element mesh composed of regular triangular elements, with a base element size of 0.25 m over most of the domain. To improve numerical accuracy and stability, mesh refinement is applied beneath the infiltration basin where element sizes are reduced to 0.1 m. This refinement allows an accurate representation of steep hydraulic and concentration gradients developing during wet and dry infiltration cycles. More importantly, it ensures numerical stability of the contaminant transport simulations under transient flow conditions. The FE mesh applied on the model is depicted on Figure 40.

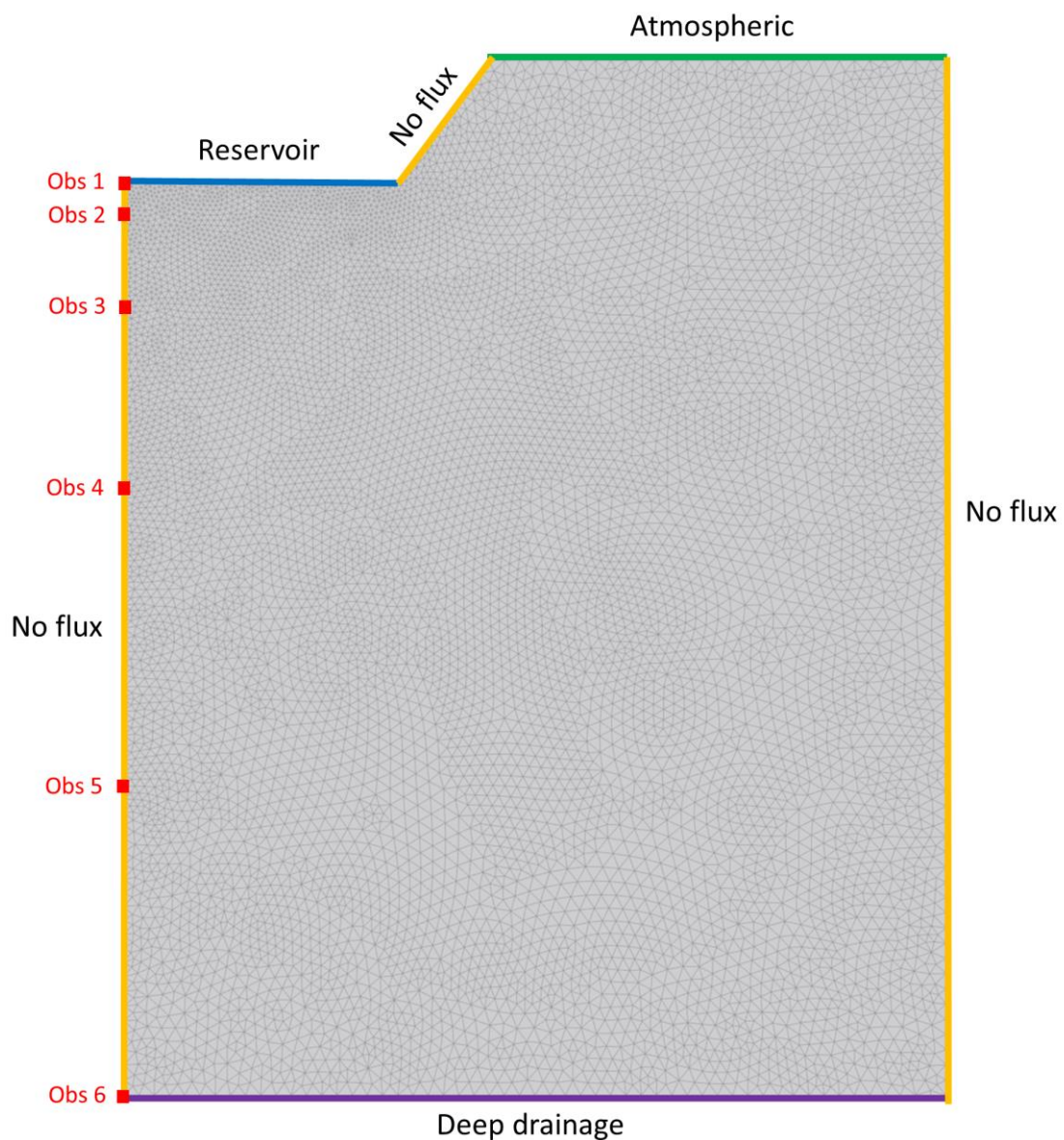


Figure 40. FE grid, boundary conditions, and observation points associated with the variably saturated flow model.

2.1.4. Governing equations and flow conditions

Water flow within the unsaturated zone is simulated under transient conditions using Richards' equation, which describes variably saturated flow in porous media and is well suited to simulate infiltration processes under alternating wet and dry conditions. This is typically described using the Richards equation (Richards, 1931) in its mixed and isotropic form:

$$\frac{\partial \theta}{\partial t} = \nabla[K(\theta)\nabla(h + z)] + S \quad (9)$$

Where θ is the volumetric water content [$L^3 L^{-3}$], h is the pressure head [L], S is a sink/source term [T^{-1}] such as root water uptake or evaporation, z is the elevation head, t is the time [T], and $K(\theta)$ is the unsaturated hydraulic conductivity as a function of water content [$L T^{-1}$]. As mathematically described, Richards's equation is nonlinear because both the conductivity K and the water content θ are strongly dependent on pressure head h , and therefore change as the system wets and drains during the simulated cycles.

The relationship between water content (θ) and pressure head (h) is typically expressed through the soil-water retention curve (SWRC). Physically, the SWRC reflects how water is distributed in pores of different sizes since large pores drain at low suction while higher suction is necessary to drain smaller pores. These relationships allow a continuous representation of flow conditions from dry to saturated states, which is essential for simulating infiltration events and subsequent drainage phases. As an illustration, Figure 41 depicts SWRCs for different soils, where sandy soils drain quickly at low suction while clay-rich soils retain water much longer.

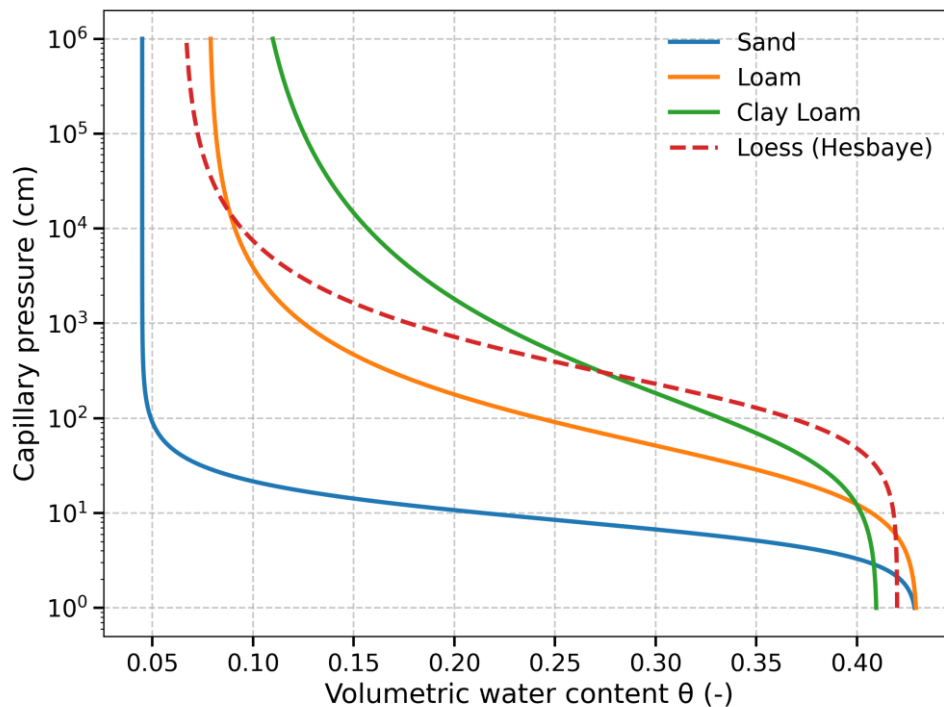


Figure 41. SWRC curves for sand ($\theta_r = 0.045$, $\theta_s = 0.43$, $\alpha = 0.145 \text{ cm}^{-1}$, $n = 2.68$, $K_{sat} = 7.13 \text{ m day}^{-1}$), loam ($\theta_r = 0.078$, $\theta_s = 0.43$, $\alpha = 0.036 \text{ m}^{-1}$, $n = 1.56$, $K_{sat} = 0.25 \text{ m day}^{-1}$) and clay loam ($\theta_r = 0.095$, $\theta_s = 0.41$, $\alpha = 0.019 \text{ m}^{-1}$, $n = 1.31$, $K_{sat} = 0.062 \text{ m day}^{-1}$). The associated Van Genuchten parameters for these soils were extracted from the Rosetta pedotransfer model implemented within HYDRUS (Schaap et al., 2001). The SWRC associated to loess samples from the study area is also represented, with a red dotted line.

To describe this curve mathematically, the Van Genuchten (1980) model is commonly used:

$$\theta(h) = \theta_r + \frac{\theta_s - \theta_r}{(1 + \alpha|h|^n)^m} \quad (10)$$

Where θ_s is the saturated water content, θ_r is the residual water content, α and n are fitting parameters related to the air-entry pressure and pore size distribution respectively, and $m = 1 - \frac{1}{n}$. This equation provides a continuous function for $\theta(h)$, which can then be used in Richards's equation to simulate variably saturated flow. The corresponding unsaturated hydraulic conductivity function used in Richards equation is defined using the Mualem model (Mualem, 1976), defined as:

$$K(\theta) = K_s S_e^{\frac{1}{2}} \left[1 - \left(1 - S_e^{\frac{1}{m}} \right)^m \right]^2 \quad (11)$$

Where K_s is the saturated hydraulic conductivity (LT^{-1}), and $S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r}$ is the effective saturation.

The governing equations are solved numerically using a finite element formulation, consistent with the discretization presented in the previous subsection. From a temporal perspective, the model is solved under transient conditions using an implicit (backwards) finite difference scheme for time discretisation, allowing the simulation of rapid changes in hydraulic conditions induced by infiltration cycles or atmospheric conditions. The time stepping scheme is adaptive, with an initial time step of 0.001 days, a minimum time step of 1×10^{-5} days, and a maximum time step of 1 day. The resulting pressure head and water content provide the hydraulic framework governing contaminant transport simulations.

2.1.5. Soil hydraulic parameters

In the present study, the hydraulic behaviour of the loess material is described using the Van Genuchten formulation to build the SWRC (Eq. 10), and the Mualem model to compute unsaturated hydraulic conductivity for a given water content (Eq. 11). Hysteresis effects between wetting and drying paths are not considered, and a single retention curve is used. This assumption is considered reasonable given the modelling objective and the lack of detailed hysteresis data for the site.

The Van Genuchten parameters ($\theta_r, \theta_s, \alpha, n$) were estimated using pedotransfer functions based on soil texture (sand, silt, clay fractions) and bulk density. These soil properties were determined experimentally and presented in previous chapters. Parameter estimation was performed using the Rosetta pedotransfer model implemented within the HYDRUS framework (Schaap *et al.*, 2001). The resulting parameters for the loess layer are presented in g individual infiltration test.

Table 8, and the associated SWRS is depicted on Figure 41. These values provide the parameterization for the variably saturated flow model. The saturated hydraulic conductivity K_s is expected to exert a strong control on infiltration dynamics and is therefore adjusted during model calibration to reproduce the pressure head evolution measured at the surface of the basin during individual infiltration test.

Table 8. Hydraulic parameters of the loess material.

Parameter	Symbol	Value	Unit
Residual water content	θ_r	0.065	-
Saturated water content	θ_s	0.42	-
Van Genuchten parameter	α	0.68	m^{-1}
Van Genuchten parameter	n	1.59	-
Saturated hydraulic conductivity	K_s	0.09	$m\ day^{-1}$

2.1.6. Boundary conditions

Upper boundary conditions

Reservoir BC

At the surface of the infiltration basin, a reservoir boundary condition is applied (Figure 40). This option implemented in HYDRUS allows explicit representation of a surface water body whose water level evolves dynamically based on all incoming and outgoing fluxes (Figure 42). These fluxes include water that can be added to or removed from the reservoir, atmospheric fluxes (precipitation, evaporation and transpiration), and infiltration. More specifically, the reservoir water level is computed internally by the model based on a mass balance applied to the basin volume. At each time step, the temporal evolution of the water volume stored in the basin $V(t)$ and the associated water level $h_w(t)$ are given by:

$$V(t) = \frac{1}{2}h(t)(a + b) = \frac{1}{2}h_w(t)\left(a + a + \frac{h_w(t)}{\tan \alpha}\right) = h_w a + \frac{h_w^2(t)}{2 \tan \alpha} \quad (12)$$

$$\frac{dV(t)}{dt} = Q_{in}(t) - Q_p(t) + (P(t) - E(t))b \quad (13)$$

$$a \frac{dh_w(t)}{dt} + \frac{h_w(t)}{\tan \alpha} \frac{dh_w(t)}{dt} = \left(a + \frac{h_w(t)}{\tan \alpha}\right) \frac{dh_w(t)}{dt} = Q_{in}(t) - Q_p(t) + (P(t) - E(t))b \quad (14)$$

where a is the half-width of the bottom of the basin [L], b is the half-width of the water level [L], h_w is the water level in the basin [L], Q_{in} the water infiltration rate from the basin to the soil profile [L^2T^{-1}], Q_p is the pumping or injecting rate [L^2T^{-1}], dt is the time step [T], P and E are precipitation and evaporation rates [LT^{-1}], respectively. As a result, the basin water level varies naturally over time in response to both basin filling and drainage processes. This formulation is equivalent to a variable-head boundary condition, with the distinction that the water level is not prescribed externally but rather computed from the coupled surface–subsurface mass balance. This approach is particularly well suited for managed aquifer recharge simulations, as it allows realistic representation of wetting and drying phases during infiltration cycles. A schematic representation of the reservoir mass balance and its coupling with subsurface is illustrated in Figure 42. The lateral sides of the infiltration basin are assumed to be impermeable due to its concrete composition. No-flux conditions are therefore assigned to the edges of the basin, which prevents water losses through these sides.

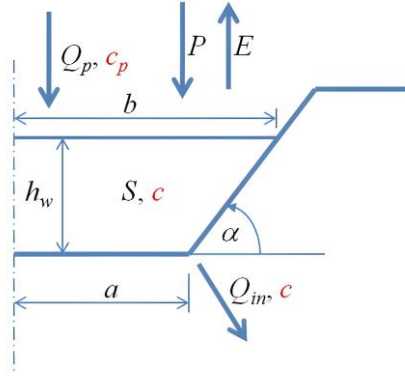


Figure 42. Scheme of reservoir boundary condition in HYDRUS (Šejna et al., 2022).

Atmospheric boundary conditions

Outside the infiltration basin, the ground surface is represented using an atmospheric boundary condition (Figure 40), where precipitation and potential evapotranspiration are prescribed as time-dependent inputs. The actual atmospheric flux is internally computed based on surface pressure head conditions, with evaporation being limited by a critical pressure head h_{crit} . This critical pressure head depends on atmospheric humidity conditions and is calculated based on the following equation:

$$H_r = e^{\left(\frac{hMg}{RT}\right)} \quad (15)$$

where H_r is the relative humidity, g is the gravitational acceleration [LT^{-2}] ($= 9.81 \text{ m s}^{-2}$), M is the molecular weight of water [$M \text{ mol}^{-1}$] ($= 0.018015 \text{ kg mol}^{-1}$), R is the universal gas constant [$J \text{ mol}^{-1}K^{-1}$] ($= 8.314 \text{ J mol}^{-1}K^{-1}$), T is the absolute temperature [K], and h is the pressure head [L].

Atmospheric data were derived from the regional atmospheric model of the Royal Belgian Meteorological Institute (IRM, Belgium), using grid data corresponding to the model cell closest to the Kemexhe site.

Lower boundary conditions

At the base of the model domain, a free drainage boundary condition is prescribed (Figure 40). This boundary condition assumes a unit vertical hydraulic gradient, corresponding to a zero-pressure head gradient at the lower boundary. Under these conditions, water leaves the domain only because of gravity. The free drainage condition is commonly used to represent drainage in the vadose zone when the groundwater table is located far below the lower limit of the modelled domain. In such situations, there is indeed no hydraulic influence of the saturated zone on unsaturated flow, and downward percolation can be approximated by gravity-driven flow. In the present study, the groundwater table is located approximately 30 m below ground surface, while the model domain extends only over the upper 15 m of the vadose zone. The distance between the base of the domain and the groundwater table justifies the use of a free drainage condition, allowing infiltrating water to leave the system without artificial accumulation.

Lateral boundary conditions

A no-flow boundary condition is imposed along the vertical plane located at the centreline of the infiltration basin (Figure 40). This boundary represents the plane of symmetry of the system, where

horizontal flow is zero by definition. A no-flow boundary condition is also applied at the outer lateral boundary of the model domain (Figure 40). At this location, the domain remains completely within the unsaturated zone, where flow is predominantly vertical. Consequently, no lateral inflow is expected. The boundary is placed sufficiently far from the infiltration basin to ensure that it does not influence infiltration processes beneath the basin.

2.1.7. Initial conditions

Before simulating infiltration cycles associated with managed aquifer recharge operations, the model must be initialized with physically consistent hydraulic conditions. In particular, the initial distributions of pressure head and water content within the vadose zone should reflect realistic soil moisture conditions before to set-up infiltration events.

To establish such conditions, the model was first initialized using a hydrostatic pressure head distribution. A long-term transient simulation was then performed using atmospheric boundary conditions with daily climatic data from 1st January 2000 to 23rd July 2023, corresponding to the day preceding the first infiltration test conducted for the DTS measurements. During this preliminary transient simulation, pressure head and water content evolve naturally in response to precipitation and evapotranspiration, allowing the vadose zone to progressively equilibrate with climate conditions.

The overall framework used to derive the initial conditions is illustrated in Figure 43, which shows the initial hydrostatic pressure distribution, the applied atmospheric fluxes over the simulation period, and the resulting water content distribution at the final time step. This final distribution is subsequently used as the initial hydraulic state for all infiltration scenario simulations involving the infiltration basin.

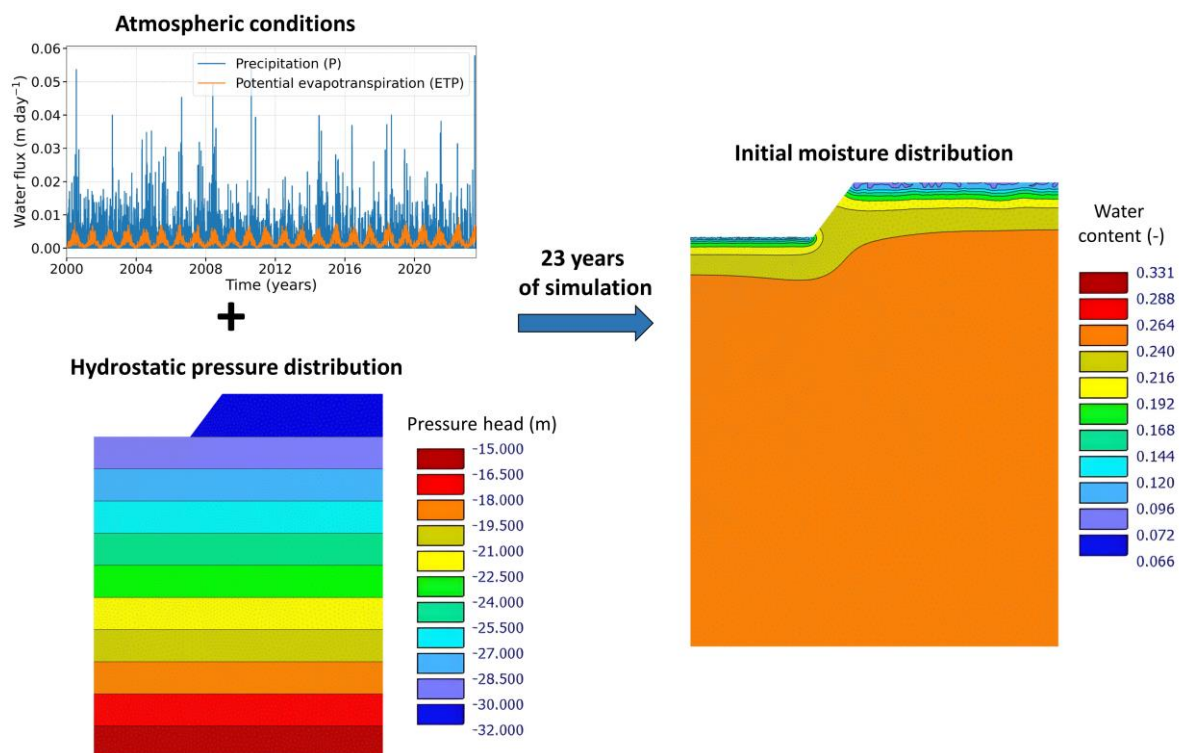


Figure 43. Framework for the definition of initial hydraulic conditions.

In addition, the temporal evolution of pressure and water content at selected depths beneath the infiltration basin during the preliminary transient simulation is presented in Figure 44. The stabilization

of both variables over time indicates that the model has reached a dynamically consistent hydraulic regime. This supports the use of the final pressure head and water content distribution as physically coherent initial conditions for subsequent simulations. Note that oscillations in pressure head and volumetric water content are stronger at observation points closer to the surface, as these zones are more strongly influenced by climatic variations.

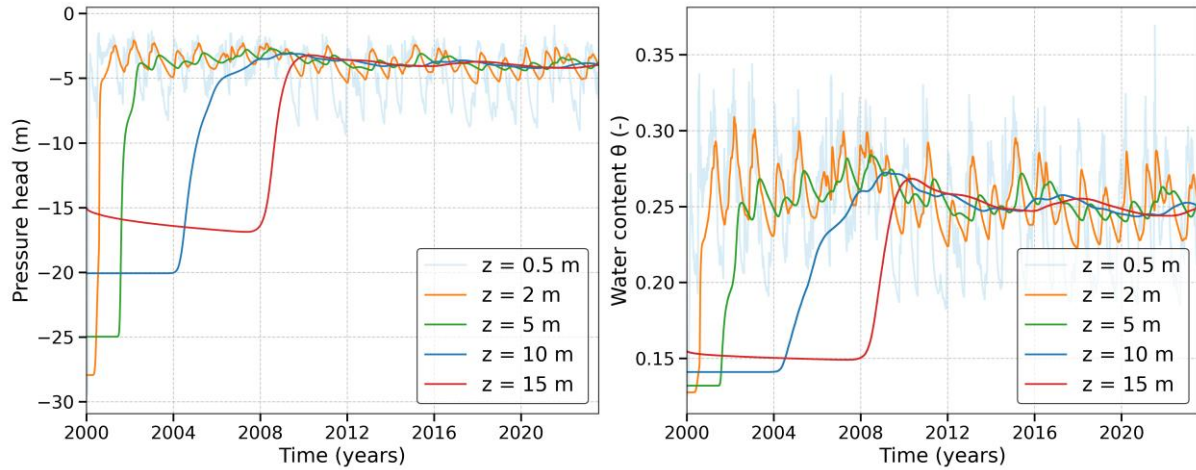


Figure 44. pressure head and water content distribution at selected depth beneath the infiltration basin during the preliminary transient simulation.

2.1.8. Calibration of the variably saturated flow model

The variably saturated flow model was calibrated based on the infiltration experiment conducted at the Kemexhe pilot site and presented in the previous chapter. During this experiment, a pressimetric probe (Diver) was installed at the surface of the infiltration basin to continuously monitor the water level evolution within the basin during this controlled recharge event. The objective of the calibration procedure was to reproduce this infiltration test numerically by applying identical operational conditions in the model and adjusting the saturated hydraulic conductivity value until the simulated pressure head evolution within the basin matched the observations. The calibration therefore relies on a direct comparison between observed and computed water head dynamics at the basin surface.

The infiltration test was conducted by filling the basin with clean groundwater at a constant flow rate of $23.3 \text{ m}^3 \text{ h}^{-1}$, measured using a flowmeter, over a duration of 7 hours. This filling phase is followed by a natural drainage phase without additional replenishment. For implementation in HYDRUS, which uses a two-dimensional vertical cross-section, the measured three-dimensional discharge was converted into an equivalent inflow per unit out-of-plane width⁷. The basin dimension in this third direction is 9 m. In addition, only half of the basin is represented in the model. Therefore, the imposed inflow corresponds to half of the total discharge. Therefore, the resulting injection flux applied at the reservoir boundary condition for a duration of 7 hours is :

$$Q_p = \frac{23.3 \left(\frac{\text{m}^3}{\text{h}}\right)}{9 \text{ (m)} \times 2} \times 24 \text{ (h)} = 31.1 \text{ m}^2 \text{ day}^{-1} \quad (16)$$

⁷ Per meter perpendicular to the model cross-section.

A value of $K_s = 0.18 \text{ m day}^{-1}$ ($2.08 \times 10^{-6} \text{ m s}^{-1}$) resulted in the best agreement between simulated and observed water head dynamics, as illustrated in Figure 45. A slight discrepancy is observed during the late drainage phase. This difference is attributed to the presence, in the real basin, of an approximately 30 cm thick cobblestone layer covering the basin bottom overlaying the loess layer which is not explicitly represented in the numerical model.

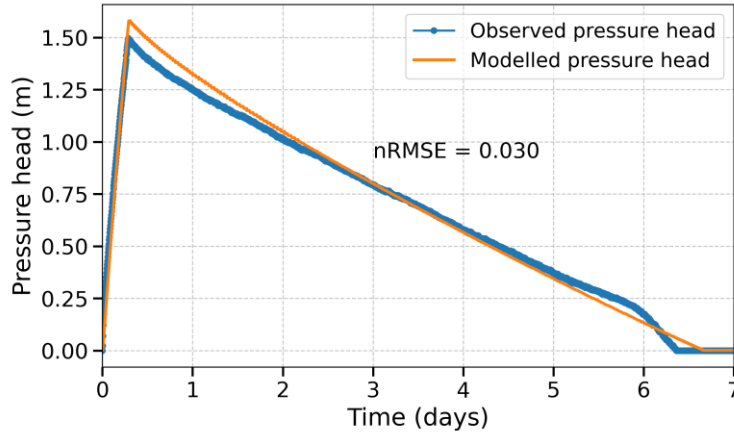


Figure 45. Observed and modelled pressure head evolution at the infiltration basin surface during the infiltration test used for model calibration.

2.1.9. Definition of MAR operating scenarios

Once the saturated hydraulic conductivity has been correctly defined, the variably saturated flow model can be used to investigate different MAR operating scenarios. In Soil Aquifer Treatment (SAT) systems, infiltration operations are typically implemented through successive wetting and drying cycles, as continuous flooding leads to a rapid decrease in infiltration capacity due to surface clogging processes such as algal growth suspended solid deposition and bacterial growth (Kopchynski *et al.*, 1996; Quanrud *et al.*, 1996). Drying phases allow partial recovery of infiltration capacity by re-aerating the upper soil layer to limit the persistence of reducing conditions, and by allowing the soil surface to dry and crack apart (Quanrud *et al.*, 1996).

According to Sharma & Kennedy (2017), wetting-drying (W/D) cycles applied in infiltration basins range from 8h-16h to several weeks, with W/D ratios generally lower than 1. Reported values from real SAT schemes depend on both the quality of the infiltrating water and the targeted treatment objectives. For primary effluents, W/D ratios are typically below 0.2. For secondary effluents, ratios are around 0.1 when the objective is to maximize hydraulic performance and nitrification, while higher ratios (0.5-1) are commonly adopted when nitrogen removal is the main objective.

As discussed in the sampling campaign chapter, Urban runoff is relatively “clean” in terms of biodegradable organic matter and suspended solids (low BDO₅, COD, TSS and TOC). Its chemical quality can therefore be considered closer to that of secondary effluent than to a primary effluent. Based on this assessment, intermediate W/D ratios of 0.33, 0.50 and 0.75 were selected to represent realistic MAR operating conditions, ranging from relatively long drying periods to more intensive recharge operations. The wetting-drying ratio is defined as:

$$W/D = \frac{T_{wet}}{T_{dry}} \quad (17)$$

where T_{wet} is the duration of the wet period and T_{dry} is the duration of the dry period. In this study, the wet period was fixed to 10 days for all scenarios. This wet period includes both basin flooding and the subsequent drainage phase, such as there is water remaining present within the basin. The dry period corresponds to the time during which the basin is empty and the soil surface is exposed only to atmospheric conditions. The duration of the dry period for each MAR operating scenario is adjusted according to the selected W/D ratio. The characteristics of the chosen scenarios are summarized in Table 9.

Table 9. Definition of MAR operating scenarios considered in this study.

Scenario	W/D ratio (-)	Wet periods T_{wet} (days)	Dry periods T_{dry} (days)	Cycle duration (days)	Number of cycles per year?
S₁	0.33	10	30.3	40.3	10
S₂	0.5	10	20	30	13
S₃	0.75	10	13.3	23.3	16

To evaluate the impact of MAR operations on groundwater recharge, simulations were conducted over a total duration of 10 years. The first year consists of repeated W/D infiltration cycles according to the selected scenario, whereas the following 9 years simulate natural conditions without MAR to track post-operation drainage and to assess how long the MAR-induced signal persists after basin operation stops. Throughout the entire simulation period, atmospheric conditions were applied using daily climatic data. To isolate the effect of MAR operation from inter annual climate variability, climatic conditions from the year 2024 were repeated identically for each simulated year.

During each wet period, reservoir boundary conditions were applied to the basin surface. The basin was first filled using the same inflow rate than during the field infiltration test employed for model calibration. Then, a lower inflow was imposed to maintain an approximately constant water level within the basin for several days. Finally, the inflow was stopped, allowing the basin to drain naturally. These operational conditions ensure that the total duration of the wet period remains equal to 10 days. The different steps defining the basin operation during a wet period are summarized in Table 10.

Table 10. Reservoir operating conditions.

Description	Duration (days)	Reservoir inflow ($\text{m}^2 \text{ day}^{-1}$)
1. Basin filing	0.3	31.1
2. Maintenance of a constant water level	4.1	1.5
3. Natural drainage	5.6	0

2.2. Variably saturated flow modelling results

Using the calibrated model, simulations were carried out under the different MAR operating conditions defined in the previous section. The objective is to evaluate over a 10-year simulation period, the impact of one year of MAR operation with different W/D ratios on groundwater recharge beneath the infiltration basin.

Results are first presented in terms of pressure head and water content evolution at selected depths within the vadose zone, to characterize the hydraulic response of the system to MAR operations. Then, effective recharge volumes, defined as the cumulative water flux crossing the bottom boundary of the model domain, are quantified to provide an order of magnitude estimate of groundwater recharge to the chalk aquifer under the different MAR scenarios.

2.2.1. Pressure head and water content dynamics

The hydraulic response of the vadose zone to MAR operations was analysed through the temporal evolution of pressure head and water content at selected depths under the infiltration basin. Results are presented for the entire simulation period (10 years) in Figure 46, and for the first 500 days in Figure 47 to provide a zoomed view of individual wetting-drying cycles during the MAR operating phase.

As expected, the number of wetting-drying cycles observed during the first year of simulation differs between scenarios, reflecting the different W/D ratios imposed to the model (Figure 47). These cycles are identifiable with the sharp increase in pressure head and water content beneath the basin during the flooding period, followed by a gradual decrease during drainage phase. During this initial phase, higher W/D ratios imply shorter drainage periods, limiting soil drying and leading to a faster recovery toward fully saturated conditions beneath the basin during the next cycle wetting cycle. In addition, the hydraulic response is stronger at observation points closer to the ground surface, where infiltration events and atmospheric conditions exert greater influence on soil moisture conditions. With increasing depth, the magnitude of pressure head and water content variations progressively decreases, and the response to infiltration events becomes slightly delayed in time. This buffering effect of the vadose zone reflects the downward propagation of the infiltration front, which is further discussed in the following section. After the end of MAR operations, water content stabilizes around values of approximately 0.28, translating the establishment of a balanced moisture state in the vadose zone under constant meteorological conditions of the year 2024 that are repeated throughout the simulation.

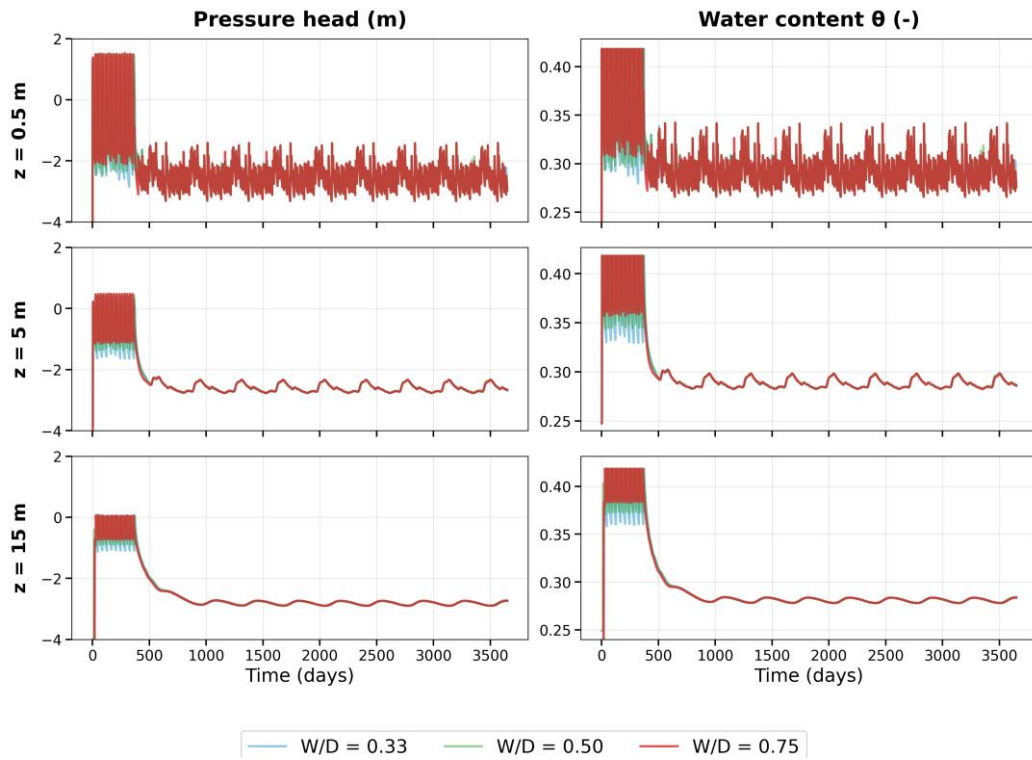


Figure 46. Pressure head and water content evolution at different depths beneath the infiltration basin during the 10 years simulations, for different wetting/drying (W/D) scenarios.

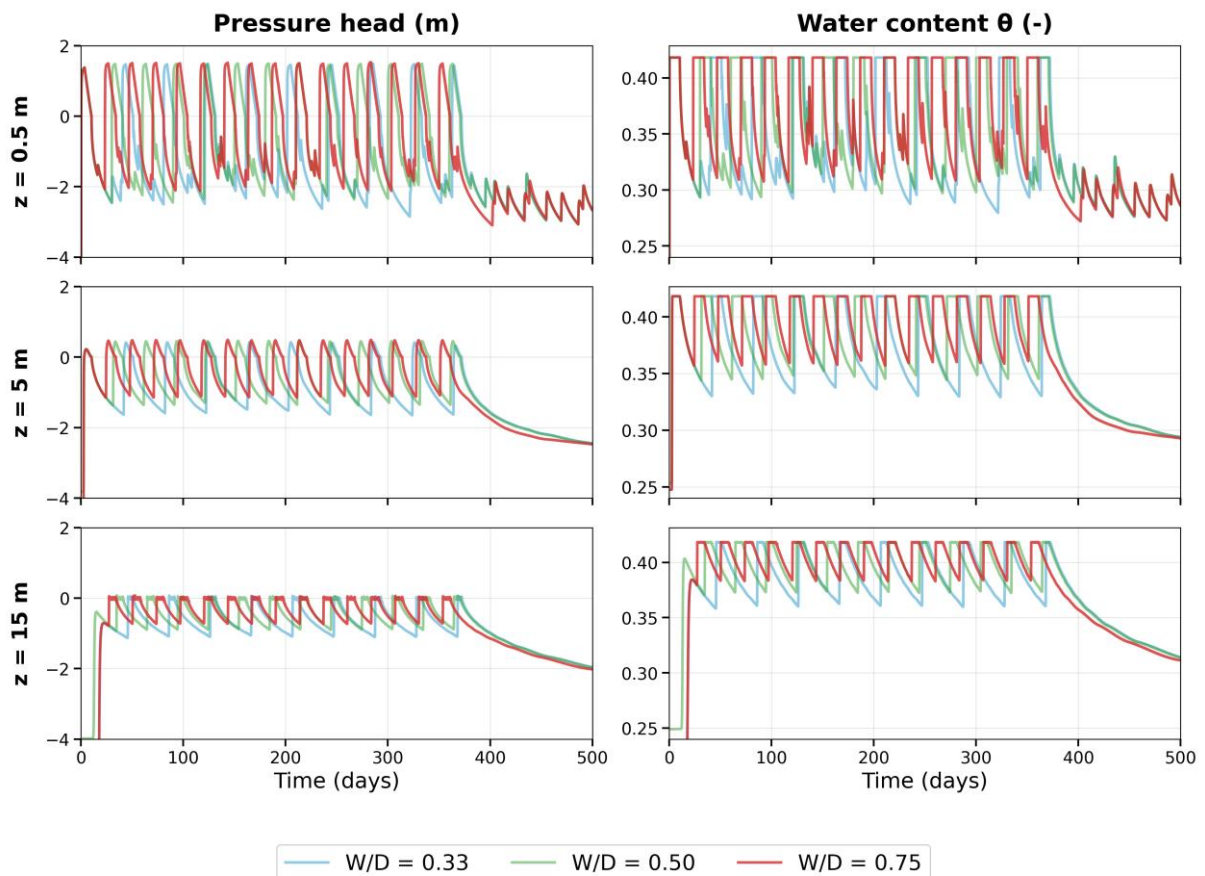


Figure 47. Pressure head and water content evolution at different depths beneath the infiltration basin during the 500 first days of simulation, for different wetting/drying (W/D) scenarios.

2.2.2. Effective recharge to the aquifer

To quantify the effective contribution of MAR operations to groundwater replenishment, cumulative water volumes were computed for each operating scenario. More specifically, two indicators were evaluated:

- 1) *The infiltration volume*, defined as the cumulative downward water flux crossing the upper boundary of the model beneath the infiltration basin.
- 2) *The effective recharge volume*, defined as the cumulative downward flux crossing the bottom boundary of the model domain.

These two quantities differ as part of the infiltrated water may return to the atmosphere through evaporation, while another fraction is temporarily stored within the vadose zone. Consequently, only a part of the water infiltrating at the surface effectively contributes to downward percolation toward the Hesbaye chalk aquifer. Although the simulations were performed in two dimensions, volumetric estimates were obtained by multiplying cumulative fluxes (expressed in $\text{m}^2 \text{ day}^{-1}$) by 9 m, corresponding to the basin length in the transverse (y) direction, and by a factor of 2 to account for the use of symmetry. This approach assumes that water percolating toward the bottom boundary of the model does not spread along the transverse direction and provides a reasonable estimate of recharge volumes at the basin scale.

Figure 48 presents the temporal evolution of both infiltration and effective recharge volumes for each W/D scenario. Outside MAR operating year, natural infiltration leads to a cumulative effective recharge of approximately 1200 m^3 over 9 years, which corresponds to an average natural recharge of about $133 \text{ m}^3 \text{ year}^{-1}$ beneath the basin. This natural recharge contribution is identical for all scenarios, as atmospheric conditions remain the same. In contrast, MAR operations during a single year result in significantly higher effective recharge volumes, which increases with W/D ratio. After one year of MAR operation, effective recharge volumes of 1927 m^3 , 2838 m^3 , and 3612 m^3 were obtained for W/D ratios of 0.33, 0.50, and 0.75 respectively. These values largely exceed the annual recharge associated with natural infiltration alone, highlighting the strong potential of MAR to enhance groundwater replenishment. This comparison is notably depicted in Table 11.

Table 11. Comparison between MAR-induced and natural groundwater recharge beneath the infiltration basin.

Scenario	W/D ratio	Effective MAR recharge ($\text{m}^3 \text{ year}^{-1}$)	Natural recharge ($\text{m}^3 \text{ year}^{-1}$)	MAR/natural ratio
S ₁	0.33	1927	133	14.5
S ₂	0.50	2838	133	21.3
S ₃	0.75	3612	133	27.2

As indicated in chapter 2, the cumulative groundwater deficit estimated for the Hesbaye chalk aquifer over the 2000–2020 period ranges roughly between 50 and 60 million m^3 , corresponding to an average annual deficit of approximately $2.5\text{--}3 \text{ million m}^3 \text{ year}^{-1}$. To assess the potential contribution of MAR at the regional scale, a simple scaling exercise was performed with the assumption that MAR could compensate 50% of this annual deficit, corresponding to a target recharge volume of $R_{\text{target}} = 1.5 \text{ million m}^3 \text{ year}^{-1}$.

Upscaling was based on the effective recharge volume simulated for a single infiltration basin operated under different W/D scenarios (Table 11). The required MAR effort was quantified as an equivalent total infiltration area A_{req} needed to reach R_{target} , assuming that recharge scales linearly with basin area and that hydraulic performance remains constant. Using the Kemexhe pilot basin area $A_0 = 9 \times 9 = 81 \text{ m}^2$ and the corresponding simulated annual recharge $R_0 \text{ (m}^3 \text{ year}^{-1}\text{)}$, the required area is:

$$A_{req} = A_0 \frac{R_{target}}{R_0} \quad (18)$$

And the side length of an equivalent single square basin is:

$$L_{eq} = \sqrt{A_{req}} \quad (19)$$

The results are summarized in Table 12. Depending on the operating scenario, the required total infiltration area ranges from approximately 6.3 ha (S_1 , W/D = 0.33) to 3.4 ha (S_3 , W/D = 0.75), corresponding to an equivalent single square basin of about $251 \times 251 \text{ m}$ and $183 \times 183 \text{ m}$, respectively. From a quantitative perspective, the W/D = 0.75 scenario is therefore the most favourable, as it minimizes the infiltration area footprint required to reach the target recharge volume.

This exercise assumes constant hydraulic performance over time and does not account for potential reductions in infiltration capacity due to clogging processes or operational constraints. Nevertheless, it provides a first-order estimate of the potential role of MAR in reducing the groundwater deficit at the scale of the Hesbaye chalk aquifer.

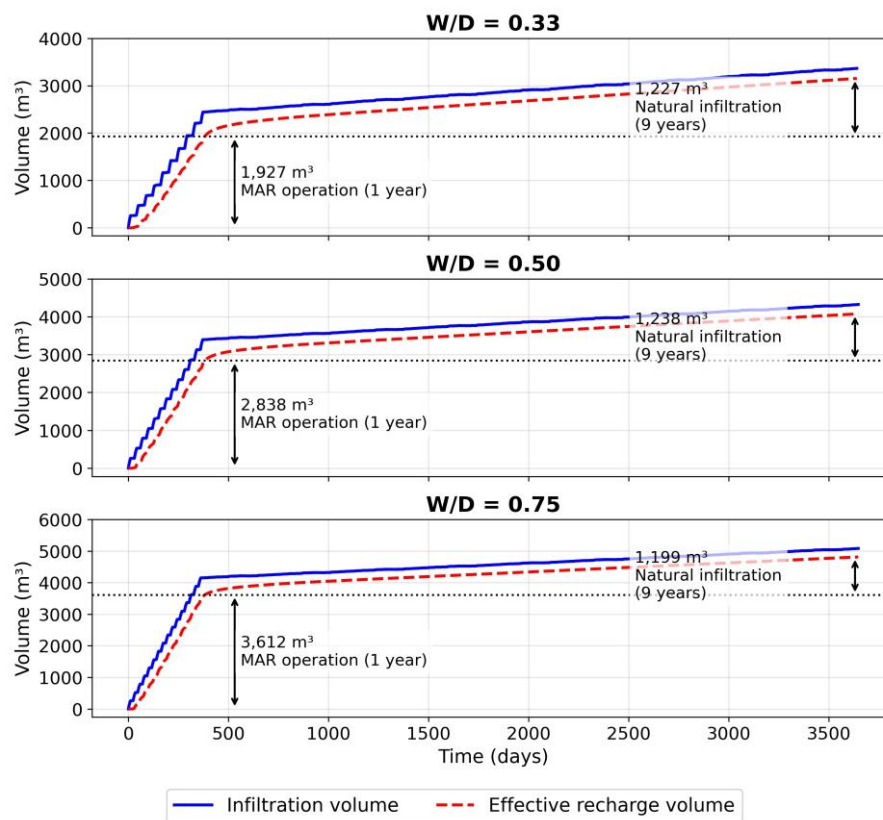


Figure 48. Temporal evolution of cumulative infiltration volume at the basin surface and effective recharge volume crossing the bottom boundary for the different MAR operating scenarios.

Table 12. Infiltration area required to achieve a recharge target of $1.5 \times 10^6 \text{ m}^3 \text{ year}^{-1}$ under different W/D scenarios.

Scenario	Effective MAR recharge ($\text{m}^3 \text{ year}^{-1}$)	Total required infiltration area (ha)	Equivalent single square basin ($\text{m} \times \text{m}$)
S₁ (W/D = 0.33)	1927	6.31	251 × 251
S₂ (W/D = 0.50)	2838	4.28	207 × 207
S₃ (W/D = 0.75)	3612	3.36	183 × 183

3. Description of the transport model

3.1. Objectives of transport modelling

Following the variably saturated flow simulations presented in the previous section, which describe MAR operating conditions at a single pilot infiltration basin using a physically coherent flow model, this section focuses on the transport modelling of the contaminants identified in runoff waters. Transport simulations are directly built upon the calibrated variably saturated flow model and incorporate biogeochemical processes that control contaminant behaviour introduced into the system via MAR operations.

The main objective of this transport model is to evaluate the potential risk associated with the use of untreated recharge water in MAR schemes, with a focus on the migration of CECs toward the Hesbaye chalk aquifer. The model is designed as a scenario-based and risk-oriented tool, rather than a fully predictive instrument that forecasts contaminant concentrations in the subsurface. Its purpose is to identify the key transport mechanisms governing the subsurface behaviour of the selected CECs and to compare the risks associated with different contaminant families under a range of modelling assumptions. More specifically, transport simulations aim to assess the evolution of the selected micropollutants under MAR operating conditions by addressing the following objectives:

1. Evaluate the vertical and temporal evolution of CECs originating from recharge water during MAR operations, from their leaching through the unsaturated zone to their arrival into the chalk aquifer interface.
2. Identify and quantify the role of the different attenuation mechanisms such as sorption and biodegradation, by progressively increasing model complexity depending on the studied contaminant family.
3. Assess the uncertainties and limitations associated with the developed transport model.

The outcomes of this section provide a better understanding of contaminant transport under MAR operating conditions and form the basis for the subsequent risk evaluation.

3.2. Transport conceptual model

3.2.1. General modelling framework and governing transport equation

Transport modelling was performed with HYDRUS by coupling the calibrated variably saturated flow model developed in section 2 with a solute transport formulation describing contaminant migration

under MAR operating conditions. The objective is to capture the main physical transport processes controlling the vertical migration (advection, dispersion and diffusion) of targeted contaminants, while accounting for the attenuation processes quantified in the experimental work (sorption and biodegradation/transformation) and, for PFAS, additional retention at the air–water interface.

Solute transport is solved numerically with a Galerkin finite element method for spatial discretization combined with a Crank-Nicolson time-weighting scheme. The Galerkin finite element approach ensures mass conservation at the element scale, while the Crank-Nicolson scheme is a time-centered implicit method (i.e. it averages transport terms between current and next time-step) that offers a good compromise between numerical stability and accuracy. This choice ensures stable numerical solutions, with both Courant and Peclet numbers remaining overall below unity, which limits numerical oscillations and artificial dispersion.

Under the present configuration, solute transport is simulated in the same two-dimensional (vertical cross-section) domain as the variably saturated flow model. Dissolved contaminant migration is described using the reactive advection–dispersion equation under variably saturated conditions, including advection, hydrodynamic dispersion, retardation associated with sorption mechanisms, and biodegradation/transformation. In compact form, the governing equation for a generic compound can be written as:

$$R_f \frac{\partial \theta C}{\partial t} = \nabla \cdot (\theta \mathbf{D}^* \nabla C) - \nabla \cdot (\theta \mathbf{v} C) + R(C) \quad (20)$$

Where C is the aqueous solute concentration (ML^{-3}) and θ is the water content (-). R_f represents the retardation factor (-) associated with sorption processes, including AWI retention. The term $\nabla \cdot (\theta \mathbf{D}^* \nabla C)$ represents hydrodynamic dispersion, $\mathbf{D}^*$ being the hydrodynamic dispersion tensor ($\text{L}^2 \text{T}^{-1}$) accounting for mechanical dispersion and molecular diffusion. The term $-\nabla \cdot (\theta \mathbf{v} C)$ represents advective transport with $\mathbf{v}$ being the pore-water velocity vector (L T^{-1}). Finally, $R(C)$ represents the net reaction term associated with biodegradation/transformation processes.

This formulation provides a compact way to represent the coupling between (i) physical transport in the mobile water phase and (ii) attenuation processes represented as effective reactions and/or retardation. In the following, each transport and attenuation process included in this equation is described in more detail.

3.2.1.1. Advection

Advection represents the transport of solutes induced by the movement of mobile pore water. In the governing equation (Eq. 20), it corresponds to the advective flux term $\frac{\partial}{\partial z} (\theta v C)$. The pore-water velocity v is determined from the transient flow field simulated under MAR operation, i.e. from the time-varying water content θ and groundwater flux computed by the flow model.

From a transport perspective, advection controls the mean travel time toward depth, whereas dispersion influences plume spreading and the shape of breakthrough curves. Attenuation processes then act by delaying the solute front (retardation) and/or decreasing mass during travel (degradation/transformation).

3.2.1.2. Mechanical dispersion and molecular diffusion

Solute plumes do not migrate as sharp fronts. Even for purely advective flow, heterogeneity in pore-scale velocities causes spreading. In the model, spreading is represented by the hydrodynamic dispersion coefficient D^* , which groups both mechanical dispersion and molecular diffusion:

$$D^* = D_w \tau + \alpha_L v \quad (21)$$

Where D_w is the molecular diffusion coefficient in water [L^2T^{-1}], α_L is the longitudinal dispersivity [L], and τ is the tortuosity factor (-) to account for the reduction of diffusion transport due to pore-scale complexity. The tortuosity factor is set to a default value of 0.5, which is a common choice for porous media when detailed pore-scale information is not available. In this modelling framework, diffusion is assumed to occur only in the mobile water phase. This means that immobile-water domains and mass transfer between mobile/immobile water regions are not explicitly represented.

The advection–dispersion equation (ADE) provides the baseline description of solute transport in the vadose zone. Conservative solutes are expected to follow this framework and produce approximately symmetric breakthrough curves. In the context of PFAS transport, only ultra-short PFAS such as trifluoroacetic acid (TFA) or perfluoropropanoic acid (PFPrA) may reasonably approach tracer behaviour, as they are highly soluble and exhibit negligible retardation in many soils (Sadia *et al.*, 2023). Short-chain carboxylates, such as perfluorobutanoic acid (PFBA) or perfluorohexanoic acid (PFHxA), may approach this behaviour at shallow depths or early stages of infiltrations. However, experimental studies reveal increased retardation with depth compared to bromide used as a conservative tracer (Kolade *et al.*, 2026). In contrast, long-chain PFAS such as perfluorooctanoic acid (PFOA) or perfluorooctane sulfonate (PFOS) deviate strongly from the conservative transport model. This is notably explained by their retention on solids and at air-water interfaces, which leads to delayed breakthrough curves that cannot be captured by ADE alone (Brusseau *et al.*, 2019b).

Finally, in MAR settings, infiltration is inherently transient. Natural (rainfall) or artificial infiltration events (irrigation, MAR) induce wetting and drying conditions that affect soil water content and pore-water velocity. These changes directly affect hydrodynamic dispersion and solute mobilization, since the previously sorbed compounds (PFAS notably) may be released during rewetting pulses (Wallis *et al.*, 2022). Therefore, while the ADE provides the baseline theory for describing CECs migration, additional terms reflecting sorption kinetics and potential biodegradation are necessary to reproduce the complex CECs behaviour observed in unsaturated soils.

3.2.1.3. Biodegradation and transformation (first-order kinetics)

Biodegradation and transformation are represented using first-order kinetics, introduced in the reactive transport equation through a reaction term $R(C)$. The first-order assumption is a common compromise for vadose-zone modelling when detailed microbial dynamics are not explicitly represented. The reaction term $R(C)$ handles both direct degradation of precursor compounds and potential production of associated daughter compounds i . It is written as:

$$R(C) = \begin{cases} -k_{deg} C_p & (\text{precursor transformation}) \\ +Y_i k_{deg} C_p & (\text{formation of daughter product } i) \end{cases} \quad (22)$$

Where C_p is the aqueous concentration of the precursor [ML^{-3}], k_{deg} is the first-order transformation rate constant [T^{-1}], and Y_i is the molar yield of daughter i (mol of daughter produced per mol of precursor transformed). This formulation allows precursor decay and daughter production to be included consistently in the transport equation without introducing an explicit multi-step reaction

network. When multiple daughter products are considered, yields are chosen to be consistent with mass-balance conservation within the limits of the tracked species. In practice, apparent yields may deviate from strict closure due to uncharacterized intermediates.

In the context of PFAS transport, PFAS are characterized by an extreme resistance to degradation associated from the strength of the carbon-fluoride bond, which has one of the highest bond dissociation energies in organic chemistry (Buck *et al.*, 2011; Cousins *et al.*, 2020). As a result, abiotic and biotic degradation of most PFAS is minor in the vadose zone, and thus not explicitly represented in transport models.

However, a large group of PFAS precursors that include fluorotelomer alcohols (FTOHs), fluorotelomer sulfonates (FTSs), and polyfluorinated sulfonamides can undergo biotic and/or abiotic transformation in soils (Wang *et al.*, 2005; Liu *et al.*, 2010; Liu and Mejia Avendaño, 2013; Yang *et al.*, 2014; Mejia Avendaño and Liu, 2015). These reactions yield shorter-chain PFAS that are comparatively more mobile. Laboratory studies have demonstrated such pathways. Typically, Liu and Mejia Avendaño (2013) reported that FTOHs and related precursors can undergo relatively rapid transformation under aerobic conditions, producing a range of intermediate products before yielding persistent per- and polyfluoroalkyl acids (PFAAs) such as PFOA, PFBA, PFPeA and PFHxA. More recently, Dong *et al.* (2024) showed that precursors contained in AFFF formulations can also transform in soil microcosms, generating perfluoroalkane sulfonamides and PFAAs over long incubation periods. These studies demonstrate that precursor degradation is an important indirect source of mobile and persistent PFAS in the vadose zone, that may continue to leach degradation products even after direct discharge of precursors have stopped.

3.2.1.4. Sorption to the solid phase and retardation

Sorption to the solid matrix is one of the main attenuation processes that can delay contaminant migration in the vadose zone. In transport modelling, this process is commonly represented by relating the sorbed concentration C_s to the aqueous concentration C_{aq} through a solid-liquid distribution coefficient K_d :

$$K_d = \frac{C_s}{C_{aq}} \quad (23)$$

For conventional hydrophobic organic contaminants, sorption is largely controlled by partitioning into soil organic matter (Chiou *et al.*, 1979). In that context, it is common to normalize sorption to the fraction of organic carbon in the soil (f_{oc}) using the organic-carbon normalized partition coefficient K_{oc} ($L\ kg^{-1}$). The two are related by:

$$K_d = f_{oc} K_{oc} \quad (24)$$

This relationship facilitates comparison between soils with different organic carbon contents and supports transfer of sorption estimates across sites when f_{oc} is known. In practice, K_d should nevertheless be interpreted as an integrative parameter that reflects the combined effect of several retention mechanisms (e.g., partitioning to organic matter, mineral surface interactions) under the considered geochemical conditions. This implicitly assumes that geochemical conditions remain stable over the simulated period (e.g., pH, ionic strength, and the composition of dissolved organic matter and competing ions), so that the sorption relationship does not vary in time or space.

In reactive transport modelling, sorption is mathematically incorporated through a retardation factor R_f , which accounts for the additional mass stored on the solid phase relative to the aqueous phase. Under the assumption of linear and instantaneous equilibrium sorption, the retardation factor is expressed as:

$$R_f = 1 + \frac{\rho_b}{\theta} K_d \quad (25)$$

Where ρ_b is the soil bulk density [ML^{-3}] and θ the water content [-]. Introducing R_f in the transport equation delays the migration of the solute front compared to a simple ADE model, without explicitly removing mass from the system. Sorption therefore acts primarily as a reversible retention process that increases the apparent travel time through the vadose zone.

More elaborate sorption representations are available, such as Freundlich (non-linear equilibrium) and Langmuir (finite sorption capacity) isotherms, as well as kinetic (rate-limited) sorption models. These approaches can better describe concentration-dependent or site-saturation effects, but they require additional parameters to be robustly constrained. In the present study, the linear approach was retained to limit parameter uncertainty and because most published sorption data for the targeted CECs are reported as K_d and/or K_{oc} coefficient, enabling consistent parameterization and transfer to other soils via f_{oc} .

3.2.1.5. Specific case: PFAS retention processes

Multiple retention processes

Sorption behaviour of PFAS is considerably more complex than that of conventional organic micropollutants. In contrast to classical organic contaminants, PFAS cannot be described only by hydrophobic interactions with soil organic matter. Their retention results instead from a combination of mechanisms operating simultaneously within the vadose zone. Typically, their amphiphilic structure and functional heads enable multiple concurrent mechanisms that cannot be explained by a single partitioning coefficient (Li *et al.*, 2018; Hubert *et al.*, 2023).

A comprehensive study by Kookana *et al.* (2022) highlights that PFAS sorption in soils and sediment can be broadly grouped into four categories: hydrophobic interactions, electrostatic interactions, interfacial accumulation and physical entrapment. These different processes occur in parallel and often interact with each other, explaining the wide variability of reported K_d values across soil types and PFAS compounds (Fabregat-Palau *et al.*, 2022). These four mechanisms are described here above and represented in Figure 49.

- **Hydrophobic interactions:** These arise from the amphiphilic nature of PFAS compounds. Each molecule consists of a perfluorinated “tail,” which is both hydrophobic and lipophobic, and a polar functional “head”, which is hydrophilic. The hydrophobic tail has a strong tendency to avoid aqueous environment and associate instead with nonpolar phases, such as soil organic matter. This partitioning effect becomes stronger as the chain length increases, which explains the systematic rise in sorption magnitude with the number of CF_2 moieties. In addition, functional groups also matter as perfluoroalkyl sulfonate show stronger sorption than carboxylates of the same length, due to their larger and more polarizable head group (Higgins and Luthy, 2006).

Soil organic matter therefore plays a dominant role in PFAS sorption. Typically, peat soils and organic-rich surface horizons show significantly higher sorption than coarse sandy soils with

little organic matter that promote rapid leaching (Hubert *et al.*, 2023). The quality of organic matter also affects hydrophobic interactions as humic/fulvic fractions and humin (non-extractable) fraction provide different retention environments (Kookana *et al.*, 2022).

- **Electrostatic interactions:** These interactions also play an important role in sorption mechanism of PFAS because of the diversity of functional heads and the variable charge characteristics of soils. While most of PFAS include PFAAs that are anionic at environmental pH due to their carboxylate or sulfonate groups, other PFAS classes include cationic species, such as perfluoroalkyl sulfonamido amines, and zwitterionic species such as perfluoroalkyl betaines. As a result, electrostatic interactions may either enhance or reduce sorption depending on PFAS charge state and the charge at soil solid surfaces.

Soils contain a broad variety of charged sorbents. For instance, aluminosilicate and phyllosilicate clays exhibit permanent negative charges that provide sorption sites for cationic or zwitterionic PFAS. On the other hand, organic matter, Fe and Al oxides and clay minerals such as kaolinite have pH-dependent charges. Typically, below their point of zero charge (pH $\approx$ 8 for Fe and Al oxides), these minerals can carry positive charges and therefore sorb anionic PFAS through electrostatic interaction. In contrast, anionic PFAS are generally repelled by negatively charged mineral surfaces at typical environmental pH values ($6 < \text{pH} < 8$), which explains their relatively low sorption in comparison with cationic and zwitterionic PFAS.

However, this repulsion is mitigated through several mechanisms: (i) **cation bridging**, where multivalent cations such as Ca^{2+} or Mg^{2+} can form complexes with mineral surfaces that lead to net positively charged sites that enhance the sorption of anionic PFAS; (ii) **surface complexation**, either through outer-sphere electrostatic attraction to positively charged sites or inner-sphere ligand exchange with surface hydroxyls; and (iii) **salting-out effect**, where dissolved cations screen negative charges on PFAS functional heads and partially neutralize surface charges, promoting molecular reorientation and stronger tail-surface hydrophobic interactions (Cai *et al.*, 2022).

- **Interfacial accumulation:** Since PFAS are chemically designed as active surfactants, they readily adsorb at fluid-fluid interfaces, such as air-water or NAPL-water. This mechanism is central in the vadose zone, where the presence of an air phase creates an additional interfacial area. Interfacial sorption is highly dependent on soil moisture as it increases as water content decreases (greater AWI), and decreases as soils are saturated.
- **Physical entrapment:** At high concentrations, PFAS can form micelles and hemi-micelles that are physically entrapped in inner pores of the solid matrix. Soil texture therefore influences this mechanism, with fine-grained soils with large surface areas and complex pore networks that provide more opportunities for entrapment, whereas coarse soils promote rapid transport. In the context of this study, dissolved PFAS concentrations are far below reported critical micelle concentrations, so micelle or hemi-micelle formation in the aqueous phase is not expected under the investigated conditions (Brusseau and Van Glubt, 2021; H. Li *et al.*, 2023).

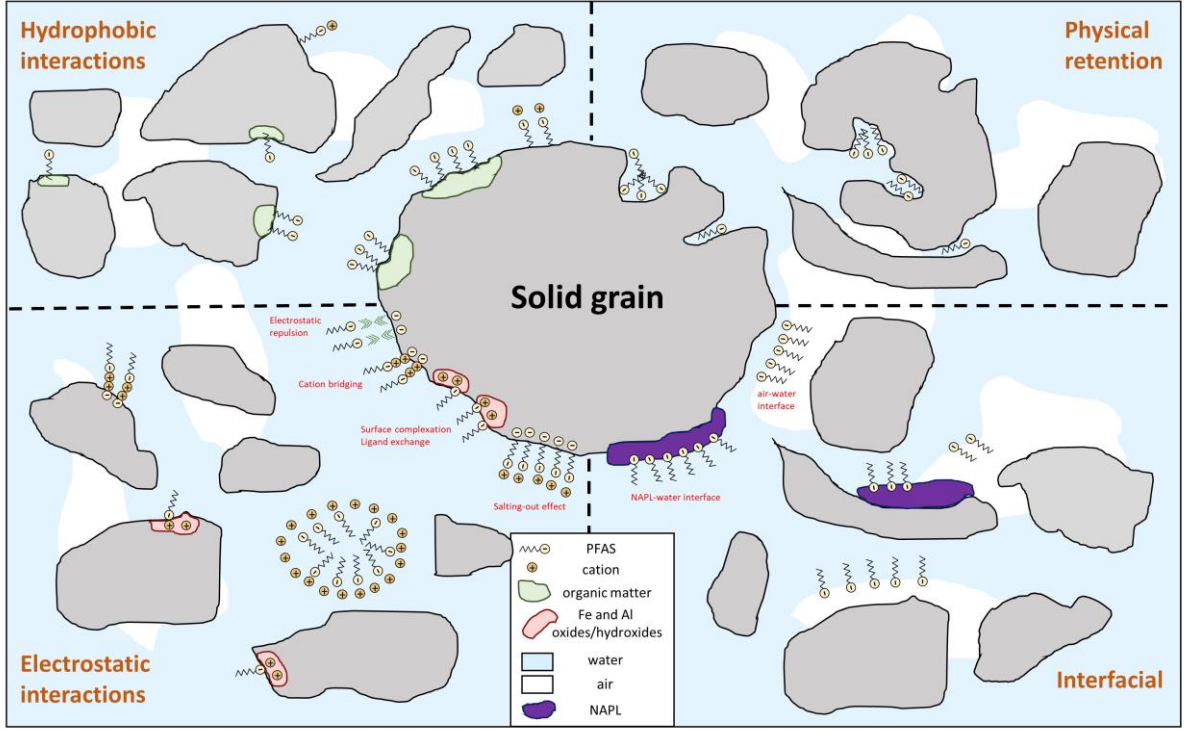


Figure 49. Scheme of the different sorption mechanisms PFAS undergo in the vadose zone: hydrophobic interactions, physical retention, interfacial, electrostatic interactions. Note that in reality, these mechanisms are not mutually exclusive: they interplay with each other within the unsaturated soil matrix. Adapted from Kookana et al (2022).

Air-water interfacial adsorption (AWI)

It is difficult in practice to integrate mathematically each of the sorption mechanisms described in Figure 49 into the reactive transport model. However, one process that is both significant and that can be explicitly represented is sorption at air-water interface (AWI). Since most PFAS act as surfactants, they accumulate at fluid-fluid interface in the vadose zone, which is predominantly air-water interface in the absence of Non-Aqueous Phase Liquid (NAPL). Therefore, similarly to sorption onto solid surfaces, interfacial sorption can be represented with an interface partitioning coefficient K_{awi} (L) such as:

$$C_{awi} = A_{awi} K_{awi} C_{aq} \quad (26)$$

Where C_{awi} the solute concentration at air-water interface (ML^{-3}), C_{aq} the aqueous solute concentration (ML^{-3}) and A_{awi} the air-water interfacial area per bulk volume of porous medium (L^2L^{-3}). As such, the new retardation factor depicted in Eq. 25 becomes:

$$R_f = 1 + \frac{\rho_b}{\theta} K_d + \frac{K_{awi} A_{awi}}{\theta} \quad (27)$$

And can directly be introduced into Eq. 20 to obtain the complete reactive transport equation for modelling PFAS behaviour in the vadose zone.

To date, estimating AWI parameters is a very recent area of research since most of the relevant studies have appeared after 2020 (Brusseau et al., 2019b; Brusseau et Guo, 2022b; Silva et al., 2022; Stults et al., 2022, 2023, 2025; Brusseau, 2023). Notably, Silva et al. (2022) and Brusseau (2023) reviewed three main approaches for estimating the air-water interfacial area (A_{awi}):

- **Leverett Thermodynamic Model (LTM):**

This theoretical method derives the A_{awi} from the thermodynamic work of capillary pressure as soils drain (Silva *et al.*, 2022). Using the soil-water retention curve already introduced in Eq. 10, A_{awi} is calculated by integrating the capillary pressure over the range of water contents:

$$A_{awi}(\theta) = \frac{1}{\sigma} \int_{\theta}^{\theta_s} P_c(\theta) d\theta \quad (28)$$

where θ is the volumetric water content, θ_s the saturated water content, σ the water surface tension, and P_c the capillary pressure (associated to h via $P_c = \rho_w g h$). In practice, the Van Genuchten formulation of the SWRC (Eq. 10) provides the required $\theta(h)$ relationship, which is then used to compute A_{awi} . As soils drain, θ decreases and the air-water interfacial area increases, approaching a maximal value at the residual water content θ_r . At this stage, only thin water films remain and A_{awi} approximates the specific geometric surface area of the porous medium. However, because the LTM assumes smooth particle surfaces, it tends to underestimate A_{awi} in real soils where surface roughness adds extra interface.

- **X-ray microtomography (XMT):**

A direct imaging technique that rebuilds pore geometries in 3D and calculates interfacial areas (Brusseau *et al.*, 2007). XMT can capture capillary interfaces and adsorbed films, but its resolution is limited. As a result, the measured A_{awi} reflects mainly the smooth geometric surface of soil grains and underestimates the true interfacial area, since part of the specific surface is missed.

- **Aqueous tracer-based methods:**

These experimental techniques rely on introducing surface-active tracers into unsaturated column or batch systems and then quantifying the loss of tracer mass due to adsorption at the air–water interface (Araujo *et al.*, 2015). Because the tracers are themselves surface-active, they interact with the same types of interfaces as PFAS. As a result, tracer-based methods are widely considered the most representative for PFAS transport studies, since they directly capture the fraction of the interface that is actually accessible to aqueous solutes, including contributions from thin water films and roughness features that theoretical models or imaging methods may miss.

In practice, when modelling PFAS transport in unsaturated soils, the LTM is most often used to estimate A_{awi} because it is naturally connected to numerical hydrological model via the SWRC. Nevertheless, its values need to be scaled up with an empirical factor so that predicted A_{awi} matches tracer-based measurements (Silva *et al.* 2022). This empirical scaling procedure has been developed by Brusseau (2023) by systematically comparing thermodynamic estimates of A_{awi} to tracer-test measurements for sands and soils. The outcome was a correlation between the scaling factor (SF), median grain diameter (d_{50}), and water saturation (S_w):

$$SF = (-0.65S_w + 1.33)(-0.45d_{50} + 5) \quad (29)$$

Where d_{50} is expressed in mm. Average values for sands and soils typically fall around 4–5, meaning that thermodynamic predictions of A_{awi} should be multiplied by this factor to reproduce tracer-based measurements. This approach allows to account for soil texture, degree of saturation and surface roughness effects when correcting LTM-derived values.

Regarding air-water interface partitioning coefficient, very limited experimental data exist. To address this gap, Stults *et al.* (2023, 2025) developed quantitative structure-property relationships (QPSR) equations that predict K_{awi} from molecular descriptors such as perfluorinated chain length, total chain length, molar volume, and aqueous concentration. These QPSRs provide a first methodology to

estimate K_{awi} across a range of PFAS structures. In this work, the QPSR formulation developed by Stults et al. (2023) was identified as the most robust (Eq. 30).

$$\log_{10}(K_{awi}[m]) = [0.078 \times \text{longest } F \text{ chain}] + [0.80 \times C18_{RT}] + \left[-0.35 \times \log_{10} \left(C_{aq} \left(\frac{ng}{L} \right) \right) \right] + [-8.5] \quad (30)$$

This formulation relies on the following predictors: (i) the longest perfluorinated chain length, (ii) chromatographic retention time ($C18_{RT}$), and (iii) the logarithm of the aqueous concentration (expressed in $ng\ L^{-1}$). Importantly, this QPSR was developed for environmental relevant concentration ranges (approximately 10^1 to $10^6\ ng\ L^{-1}$) and implies that K_{awi} depends on aqueous concentration, decreasing as C_{aq} increases. Using a higher reference aqueous concentrations therefore yields lower K_{awi} values and thus provides therefore a conservative assumption in terms of PFAS mobility (i.e., weaker predicted AWI retention). The compound-specific descriptors and resulting K_{awi} values used in the simulations are provided in Section 3.3.3.2. However, these relationships were derived primarily from sandy soils under controlled conditions. This raises uncertainties regarding their applicability to finer-textured soils such as loess.

3.2.2. Soil parameters

Bulk density and granulometric data of the porous medium were derived from loess samples collected on site. In particular, a mean bulk density of $1.56\ kg\ dm^{-3}$ was determined from loess samples analysed in the laboratory. This value was assigned to the entire model domain and is used in the retardation factor formulation associated with sorption processes.

Mechanical dispersion was characterized through the assignment of longitudinal and transverse dispersivity values. Longitudinal dispersivity is known to be scale-dependent and to increase with the characteristic length over which transport occurs. Neuman (1990) proposed an empirical relationship, applicable for distances shorter than 3500 m, that connects longitudinal dispersivity (α_L) with the characteristic length (L) according to:

$$\alpha_L = 0.0175 \times L^{1.46} \quad (31)$$

In the present model, the characteristic transport length corresponds to the distance between the infiltration basin and the bottom boundary of the domain of interest ($L = 15\ m$), which yields a longitudinal dispersivity of $\alpha_L = 0.91\ m$. Transverse dispersivity was set to 10% of the longitudinal value, resulting in a $\alpha_T = 0.091\ m$. This choice is commonly adopted in modelling practices.

Note that the empirical relationship proposed by Neumann was originally developed for saturated porous media. However, in the absence of site-specific dispersivity data for partially saturated conditions, this formulation provides a reasonable approximation of mechanical dispersion. This is especially justified by the limited distances considered and the dominant role of advection during MAR events.

3.2.3. Initial, boundary and operational conditions

For each simulated contaminant, initial concentrations within the model domain were set to zero. This assumption allows to evaluate contaminant migration induced by MAR operations assuming there is no interference with any pre-existing background contamination. Their presence within loess

sediments is indeed not expected as the studied runoff water has never been in contact with the soil of the study area.

Contaminant input was introduced at the infiltration basin surface using third-type (Cauchy) boundary conditions. During basin filling periods, the concentration of the infiltrating water was set to 1 mg L^{-1} for each contaminant at the upper boundary (basin–loess interface), so that solute mass enters the domain with the imposed infiltration flux. A unit concentration was intentionally selected for all contaminants to enable direct comparison of transport behaviour and attenuation processes across contaminant families. Differences in simulated concentrations are therefore representative of differences in biogeochemical behaviours rather than in initial concentration contrasts.

Transport simulations were performed using the variably saturated flow model associated with a scenario corresponding to a W/D ratio of 0.75. This choice was motivated by the fact this configuration provides the largest recharge volumes and therefore represents the worst-case scenario in terms of contaminant mass input. The simulated period consists of one year of MAR operation followed by nine years of natural climatic conditions, allowing the evaluation of both short-term migration and longer-term persistence or attenuation of the studied contaminants. A schematic overview of the transport modelling framework is provided in Figure 50

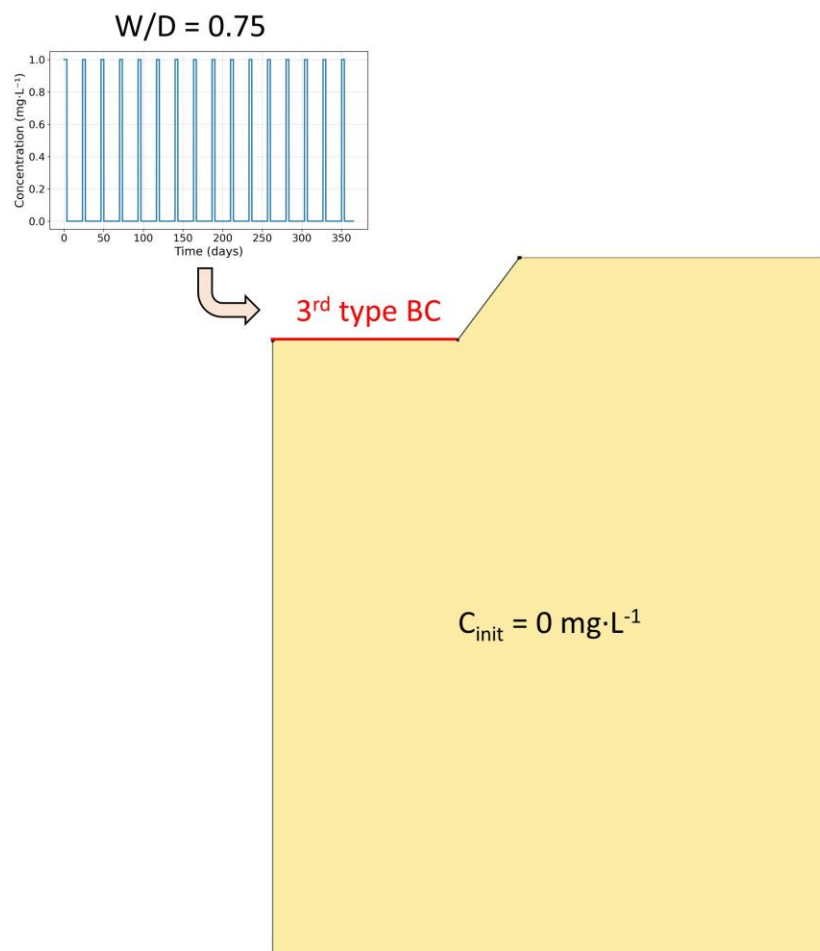


Figure 50. Transport conceptual model.

3.3.2. Molecular diffusion coefficients

As indicated in the transport equation (Eq. 20), the hydrodynamic dispersion term D^* controls the spreading of solutes during their transport in the liquid phase. This parameter combines both (i) mechanical dispersion, which is governed by flow velocity and dispersivity, and (ii) molecular diffusion, which depends on the intrinsic biogeochemical properties of each target compound. Mechanical dispersion is independent of the studied compounds, assuming that they do not affect flow velocity (e.g. through viscosity changes), and has already been addressed and parameterized previously in section 3.2.2. The present subsection therefore focuses on the molecular diffusion coefficient in mobile water (D_0) for each contaminant.

When available, molecular diffusion coefficients were preferentially taken from the literature, although such data remain scarce, especially for contaminants of emerging concern. In particular, no aqueous molecular diffusion coefficients were found for NP2EO or for benzotriazole and tolyltriazole. In contrast, for several PFAAs, experimentally derived aqueous diffusion coefficients have been reported by Schaefer et al. (2019). The values retained for the PFAS considered in this study are presented in Table 13. Note that aqueous molecular diffusion coefficient increases with decreasing perfluorinated carbon chain length, which is consistent with the higher mobility generally observed for short-chain PFAS in aquatic environments.

Table 13. Molecular diffusion coefficients for several PFAAs, derived from Schaefer et al. (2019)

Compound	Aqueous molecular diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
PFOS	5.4×10^{-10}
PFOA	4.9×10^{-10}
PFHxA	7.8×10^{-10}
PFPeA	1.2×10^{-9}
PFBA	2.5×10^{-9}

For compounds for which diffusion data are not available in the literature, plausible diffusion coefficients must be estimated. A commonly used approach is the application of the Stokes-Einstein equation (Evans *et al.*, 2018). However, such a formulation relies on strong assumptions: (i) solute behaves as a rigid spherical particle, (ii) is much larger than solvent molecules, and (iii) does not account for solute-solvent interactions (Evans *et al.*, 2018). These assumptions are generally not valid for CECs which are typically small, flexible, and non-spherical organic molecules.

Instead, the diffusion coefficients were estimated using the Wilke-Chang correlation (Wilke and Chang, 1955) and is expressed as:

$$D_w = 7.4 \times 10^{-8} \frac{(\varphi M_w)^{1/2} T}{\mu V_b^{0.6}} \quad (32)$$

Where T is the temperature ($^{\circ}\text{K}$), μ is the dynamic viscosity of water (cP), M_w is the molecular weight of water ($18.015 \text{ g mol}^{-1}$), φ is the solvent association factor (2.6 for water), and V_b is the solute molar volume at its normal boiling point ($\text{cm}^3 \text{mol}^{-1}$). In practice, because boiling molar volumes were not

available, V_b was approximated based on molar mass (MW) and density (ρ) such as $V_b \approx MW/\rho$. All diffusion were computed at 14°C ($T = 287.15$ °K), using a dynamic viscosity of water of $\mu \approx 1.17$ cP.

Using the Wilke-Chang equation together with the molar volume proxy, aqueous molecular diffusion coefficients were computed for the remaining contaminants and are reported in Table 14. The consistency of magnitude was verified by applying the same approach to the compounds listed in Table 13 and comparing the resulting diffusion coefficients with experimentally derived values available in the literature.

Table 14. Aqueous molecular diffusion coefficients estimated from Wilke-Chang equation.

Compound	ρ (g cm ⁻³)	MW (g mol ⁻¹)	V_b (cm ³ mol ⁻¹)	D_w (m ² s ⁻¹)
Bzt	1.369	119.127	87.02	8.53×10^{-10}
Tlt	1.273	133.151	104.60	7.63×10^{-10}
6:2 FTS	1.680	428.170	254.86	4.47×10^{-10}
PFECHS	1.930	462.130	239.45	4.64×10^{-10}
NP2EO	0.9987	308.460	308.86	3.99×10^{-10}

3.3.3. Solute sorption

3.3.3.1. Sorption of non-PFAS contaminants

Transport parameterization for sorption relied on a combination of (i) values derived from batch experiments performed on Hesbaye loess (Chapter 5) and (ii) literature values, either when experimental data were unavailable or to represent broader conditions. Within this modelling framework, simulations enabled to evaluate the sensitivity of transport predictions to this parameter choice.

Triazoles

For benzotriazole and tolyltriazole, K_d values were derived from literature K_{oc} data reported by Alotaibi et al. (2015), who investigated the sorption behaviour of benzotriazoles compounds in a range of soils with contrasting granulometry and organic carbon content. From this dataset, K_{oc} values corresponding to soil properties closest to the loess material investigated in this study were selected. As a result, reported $\log K_{oc}$ values of 1.66 and 1.97 were retained for benzotriazole and tolyltriazole respectively. Using the measured organic carbon fraction of the loess samples ($f_{oc} = 2.23\%$), applying Eq. 24 resulted in K_d values of 1.0×10^{-3} L·g⁻¹ for benzotriazole and 2.1×10^{-3} L·g⁻¹ for tolyltriazole.

These literature-based values were compared with distribution coefficients independently obtained from batch sorption experiments conducted on the same loess material (Chapter 3). Batch experiments yielded lower K_d values of 4.89×10^{-4} L·g⁻¹ for benzotriazole and 6.54×10^{-4} L·g⁻¹ for tolyltriazole, corresponding to $\log K_{oc}$ values of 1.34 and 1.47 respectively.

Nonylphenol diethoxylate

For NP₂EO, literature data were extracted from the RIVM environmental quality assessment for alkylphenols (Van Vlaardingen et al., 2003), which reports an estimated $\log K_{oc}$ value of 2.97. Similarly than for benzotriazole and tolyltriazole, using Eq. 24 leads to a K_d value of 2.08×10^{-2} L·g⁻¹, indicating

weaker sorption than for the other compounds. In contrast, batch experiments detailed in chapter 3 did not show measurable sorption of NP2EO onto loess material. However, this result is to be interpreted with caution as there is higher uncertainty in the interpretation of the abiotic control results for this compound in particular.

Comparison of sorption parameters

A comparison between sorption parameters derived from literature data and experimentally derived is provided in Table 15. This comparison highlights the relatively weak sorption of these compounds in loess soils and supports their classification as mobile organic micropollutants. Transport simulations were therefore carried out using both literature-based and experimentally derived sorption coefficients, allowing the model sensitivity evaluation to sorption parameterization.

Table 15. Comparison of distribution coefficient for non-PFAS contaminants.

Compound	$\log K_{oc}$ (literature)	K_d (L·kg ⁻¹ , literature)	$\log K_{oc}$ (batch)	K_d (L·kg ⁻¹ , batch)
Bzt	1.66	1.0	1.34	0.489
Tlt	1.97	2.1	1.47	0.654
NP ₂ EO	2.97	20.8	-	0

3.3.3.2. Sorption of PFAS compounds

As indicated in section 3.2.1.5, PFAS sorption cannot be reduced to hydrophobic partitioning onto organic matter alone as PFAS retention in the vadose zone involves multiple concurrent mechanisms. This subsection aims thus to introduce progressive complexity in the parameterization of PFAS sorption. Sorption is first represented through conventional interactions with soil organic matter and electrostatic interactions with mineral surfaces. Then, the retention of PFAS at the air-water interface (AWI) is added to sorption processes, as it has been shown to play a key role in PFAS retardation in variably saturated conditions. This approach allows to represent PFAS sorption as realistically as possible within the context of MAR operations.

PFAS sorption to organic matter and mineral surfaces

Sorption of PFAS compounds was parameterized by accounting for both hydrophobic interactions with soil organic matter and electrostatic interactions with mineral surfaces. In this study, organic carbon sorption coefficients (K_{oc}) and mineral sorption coefficients (K_{min}) were taken from the literature review carried out by Fabregat-Palau et al. (2021), which compiles average sorption parameters derived from 435 individual experimental studies conducted on a wide range of soils and under variable geochemical conditions. In the present simulations, mean PFAS-specific values were retained, while the associated standard error were not explicitly considered at this stage.

Based on these parameters, PFAS sorption in the transport model was represented using a combined formulation accounting for organic matter and mineral surface contributions, with the solid-water distribution coefficient being calculated as:

$$K_d = K_{oc} \cdot f_{oc} + K_{min} \quad (33)$$

Where f_{oc} is the measured organic carbon fraction of the loess material (2.23%), as already described in Chapter 5. The resulting K_d values calculated for PFOA, PFOS, PFHxA, PFPeA, and PFBA are reported in Table 16, together with the corresponding K_{oc} and K_{min} values from Fabregat-Palau et al. (2021).

Table 16. Solid-water distribution coefficient calculated based on K_{oc} and K_{min} values reported by Fabregat-Palau et al. (2021).

Compound	K_{oc} (L kg ⁻¹)	K_{min} (L kg ⁻¹)	K_d (L kg ⁻¹)
PFOS	609	9.4	22.98
PFOA	107	3.3	5.69
PFHxA	15	0.46	0.79
PFPeA	15	0.46	0.79
PFBA	2.9	0.43	0.49

For 6:2 FTS, mineral sorption coefficients were not available in the literature and K_{min} was therefore set to zero. Nevertheless, literature data from Barzen-Hanson et al. (2017) report a K_d value of 8.5 L kg⁻¹ for soils with properties most similar to the loess material. This value was therefore retained in the present transport simulations.

For PFECHS, no experimental K_d , K_{oc} or K_{min} values were reported from experimental studies. However, QSAR (Quantitative Structure-Activity Relationship) based estimates reported by Xiao et al. (2017) indicate a $\log K_{oc}$ value of 3.37. Using the measured organic carbon fraction of 2.23% leads to a K_d estimate of 52.3 L kg⁻¹, derived only from organic matter partitioning in the absence of mineral sorption data. By analogy with PFOS that is also a sulfonated PFAS with a comparable fluorinated carbon number, K_{min} of PFECHS might be expected to be the same order of magnitude than of PFOS, but this remains uncertain and was not constrained here.

The sorption coefficient obtained from literature were then compared with distribution coefficients derived from the batch experiments conducted with loess material and detailed in chapter 5. This comparison is summarized in

Overall, good agreement in order of magnitude is observed for PFOS and PFHxA. For PFOA, batch-derived results are approximately one order of magnitude lower than those based on literature. A similar discrepancy is observed for 6:2 FTS. The largest discrepancy concerns PFECHS, for which no measurable sorption was observed in batch experiments, whereas literature-based estimates suggest strong sorption potential. As discussed in Chapter 3, the lower sorption coefficients obtained from our batch experiments may be explained by the static nature of the experimental setup, in contrast to agitated systems commonly used in classical sorption studies. Given these differences, literature-based K_d values were considered for the transport simulations in the present study, as they reflect overall sorption tendencies from multiple independent experimental studies.

Table 17. Comparison between solid-water distribution coefficients obtained from literature and derived from batch experiments.

Compound	K_d literature (L kg ⁻¹)	K_d batch (L kg ⁻¹)
PFOS	22.98	46.3
PFOA	5.69	0.436
PFHxA	0.79	0.470
PFPeA	0.79	-
PFBA	0.49	-
6:2 FTS	8.5	0.994
PFECHS	52.3	≈ 0

PFAS sorption at the air-water interface

While the solid-phase sorption coefficients described above provide a first-order representation of PFAS retention in soils, they are not sufficient to fully explain PFAS retardation in variably saturated systems. As discussed in detail in section 3.2.1.5, PFAS sorption in the vadose zone is also controlled by retention at the AWI. This mechanism becomes increasingly important under unsaturated conditions.

Based on the QSPR equation (Eq. 30) of Stults et al. (2023) and an aqueous concentration of 1 mg L⁻¹, consistent with the input concentration, K_{awi} values were calculated for every PFAS. This relatively high reference concentration leads to a conservative (lower) estimate of K_{awi} . The resulting K_{awi} values are reported in Table 18, together with the corresponding molecular descriptors used as QSPR inputs. These values are consistent with those reported by Brusseau & Guo (2022) and were therefore retained for the transport simulations carried out in this study. An exception is observed for PFOS which is one order of magnitude lower than that reported in the literature. Given the well-documented strong sorption behaviour of PFOS, the $K_{awi} = 5 \times 10^{-4}$ m reported by Brusseau & Guo (2022) was retained for the transport simulations. For PFECHS, K_{awi} could not be estimated due to its non-linear structure and the absence of reported values in the literature. Air–water interfacial sorption was therefore not considered for this compound.

Within the HYDRUS PFAS module, air-water interfacial sorption is implemented by prescribing K_{awi} for each studied solute, while the air-water interfacial area is dynamically computed as a function of water content using the Leverett thermodynamic formulation (LTM). This approach ensures a consistent coupling between hydrological conditions and PFAS retention processes during MAR operations.

Table 18. Air-water interfacial distribution coefficients obtained from QSPR developed by Stults et al. (2023)

Compound	Longest F chain	C18 _{RT} (min)	Log ₁₀ C [ng L ⁻¹]	K_{awi} (m)
PFOS	8	7.36	6	8.17×10^{-5}
PFOA	7	7.14	6	4.55×10^{-5}
6:2 FTS	6	7.13	6	3.73×10^{-5}
PFHxA	5	6.31	6	6.89×10^{-6}
PFPeA	4	5.8	6	2.25×10^{-6}
PFBA	3	5.18	6	6.00×10^{-7}

The scaling factor was computed from Eq. 29 to correct the thermodynamic estimates of A_{awi} to account for the effects of soil texture and solid surface heterogeneity. For the loess material considered in this study ($d_{50} = 0.00249$ cm), and under moisture conditions observed after MAR operations which stabilize at a water content around 0.28 (corresponding to $S_w = 0.67$), the resulting scaling factor is $SF = 4.47$.

3.3.4. Solute biodegradation

Biodegradation was also included in the transport model for the non-fluorinated organic contaminants for which evidence of microbial degradation has been reported (Ying *et al.*, 2002; Liu *et al.*, 2013). Batch experiments in this thesis (chapter 5) primarily provided qualitative evidence of degradation behaviour and redox dependence (oxygen and nitrate availability as electron acceptors), rather than quantitative kinetic parameters that can be directly implemented in HYDRUS. Because the present transport model does not explicitly couple biodegradation kinetics to evolving redox conditions (e.g., via PHREEQC), biodegradation was represented using first-order rate constants taken from the literature. First-order biodegradation rate constant k_{deg} can be calculated from the reported half-life time ($t_{1/2}$) as:

$$k_{deg} = \frac{\ln 2}{t_{1/2}} \quad (34)$$

For benzotriazole and tolyltriazole, biodegradation half-lives reported by Liu *et al.* (2013) were retained. In this study, they observed aerobic degradation of triazoles with reported half-lives of 43 days for BZT and 31 days for TLT. This leads to first-order biodegradation rates of 0.016 days^{-1} and 0.022 days^{-1} . Overall, triazoles are widely reported as contaminants whose attenuation is commonly explained by aqueous concentration decay, even though biodegradation is governed by sediment-associated microbial communities (Giger *et al.*, 2006a; Reemtsma *et al.*, 2010; Liu *et al.*, 2013; Trček *et al.*, 2018).

For nonylphenol diethoxylate, biodegradation has also been reported in aquatic and soil environments by the San Francisco Estuary Institute (Ying *et al.* 2002; Klosterhaus *et al.*, 2012). Their synthesis reported half-lives of 58 days, corresponding to a first-order degradation rate 0.012 days^{-1} . In the absence of kinetic data describing sorbed-phase biodegradation, the first-order degradation rate of NP₂EO was applied to the dissolved concentration only.

Finally, PFAS are widely recognized as environmentally persistent, with no evidence of significant biodegradation under natural subsurface conditions. Consequently, biodegradation was not considered for any PFAS included in the transport model, and degradation rate constants were set to 0 days^{-1} for all PFAS compounds.

Biodegradation in the present model was represented using first-order decay coefficients applied to the aqueous concentration only. Nevertheless, to evaluate the sensitivity of the non-PFAS contaminant transport to this assumption, additional simulations will be performed considering a hypothetical sorbed-phase degradation rate defined as:

$$k_{deg,sorbed} = \alpha \times k_{deg,aqueous} \quad (35)$$

with $\alpha = 0$ (reference scenario), 0.5 and 1.

3.3.5. Solute biotransformation

Among the studied contaminants, 6:2 FTS was treated as a precursor compound since its partially fluorinated chain allows aerobic biotransformation in soils. This leads to the formation of shorter chain PFCA. In the present study, biotransformation parameters were derived from the recent experimental work of Yan et al. (2024) who investigated the aerobic biotransformation of 6:2 FTS in soils collected from two sites impacted by aqueous firefighting films. The soil microcosm with the most similar granulometric distribution and organic carbon content (Loring soil) was retained as the reference system from which biotransformation parameters were extracted for this study. In particular, Yan et al. (2024) reported a half-life of 43.3 days for 6:2 FTS. Based on Eq. 34, this half-life leads to a first-order biotransformation rate of $k_{deg, 6:2 FTS} = 0.016 \text{ days}^{-1}$ such as:

$$\frac{\partial C_{6:2 FTS}}{\partial t} = -k_{deg, 6:2 FTS} \cdot C_{6:2 FTS} \quad (36)$$

Yan et al. (2024) also quantified the formation of stable terminal PFCA after the complete disappearance of 6:2 FTS in the soil microcosm. In particular, the reported molar yields expressed as the fraction of the initial 6:2 FTS molar mass were 1.3% for PFBA, 7% for PFPeA and 5.3% for PFHxA. As a result, the formation of PFBA, PFPeA, and PFHxA was implemented as first-order production process (Eq. 22), proportional to the degradation rate of 6:2 FTS and scaled by the corresponding molar yield such as:

$$\begin{aligned} \frac{\partial C_i}{\partial t} &= Y_i \cdot k_{deg, 6:2 FTS} \cdot C_{6:2 FTS} \\ &= k_{prod, i} \cdot C_{6:2 FTS} \end{aligned} \quad (37)$$

Based on the reported molar yields and the obtained degradation rate constant, the resulting first-order production rates were calculated as:

$$k_{prod, i} = Y_i \cdot k_{deg, 6:2 FTS} \quad (38)$$

Table 19 summarizes the degradation and production parameters used to represent 6:2 FTS biotransformation.

Table 19. Summary of biotransformation parameters associated to 6:2 FTS.

Compound	Process	Half-life (days)	Molar yield (%)	Rate constant (day ⁻¹)
6:2 FTS	Biotransformation	43.3	-	0.016
PFBA	Production	-	1.3	2.05×10^{-4}
PFPeA	Production	-	7	1.12×10^{-3}
PFHxA	Production	-	5.3	8.48×10^{-4}

Biotransformation of 6:2 fluorotelomer sulfonate was represented using a first-order biotransformation rate applied only to the dissolved concentration as no kinetic data were available for the sorbed phase. Therefore, the same sensitivity analysis methodology as described for the biodegradation of non-PFAS contaminants (Section 3.3.4) was applied, by testing hypothetical sorbed-phase biotransformation rates.

3.4. Transport modelling scenarios

As demonstrated in the previous sections, uncertainty in this transport model is mostly associated with the parameterization of contaminant transport and attenuation processes in the vadose zone. This uncertainty depends both on the types of contaminants considered (non-PFAS versus PFAS) and on the processes included in the transport model, such as sorption, biodegradation, biotransformation, and air-water interface retention. In this study, rather than relying on a single parameter set, transport modelling was conducted using a scenario-based approach designed to explore a range of contaminant behaviours by integrating parameter uncertainty in the interpretation of model outcomes. Accordingly, the transport scenarios implemented in the model are described below.

3.4.1. Scenarios for non-PFAS contaminants

For benzotriazole, tolyltriazole and nonylphenol diethoxylate, uncertainty in transport modelling is mainly associated with two aspects:

- Sorption processes, for which both literature-based distribution coefficient and batch-derived parameters were considered.
- Biodegradation of the sorbed phase, for which the extent of degradation is uncertain. As discussed in the section 3.3.4, biodegradation was primarily applied to the dissolved phase as a reference scenario, but additional simulations were tested assuming partial degradation of the sorbed fraction.

The transport scenarios for non-PFAS contaminants were defined by combining the uncertainty associated with sorption parameterization and the biodegradation of the sorbed phase, characterized by α coefficient from Eq. 35. These resulting combinations are summarized in Table 20, leading to a total of six transport scenarios for non-PFAS contaminants.

Table 20. Transport scenarios for non-PFAS contaminants combining sorption parameterization and biodegradation of the sorbed phase.

Biodegradation of sorbed phase	Sorption (literature)	Sorption (batch-derived)
$\alpha = 0$	S_{1a}	S_{2a}
$\alpha = 0.5$	S_{1b}	S_{2b}
$\alpha = 1$	S_{1c}	S_{2c}

3.4.2. Scenarios for PFAS contaminants

For PFAS contaminants, uncertainty in transport modelling is mainly associated with the representation of air–water interface (AWI) sorption and precursor biotransformation. In particular, three levels of complexity were considered for PFAS sorption:

- No integration of AWI sorption, accounting only for solid-phase sorption.
- Integration of AWI sorption, using air–water interfacial partitioning coefficients.
- Integration of AWI sorption with scaling factor, correcting interfacial areas to account for soil surface roughness.

In parallel, uncertainty related to the biotransformation of 6:2 FTS was addressed using the same sensitivity methodology as for biodegradation of non-PFAS contaminants (Section 3.3.4), by varying

the biotransformation rate of the sorbed phase through the coefficient α . This leads to a total number of nine scenarios for PFAS contaminants, as depicted in Table 21.

A modelling limitation must however be noted: when the PFAS module is activated in HYDRUS, parent-daughter decay chains are not implemented, so sequential biotransformation reactions cannot be simulated⁸. As a result, 6:2 FTS can still be simulated as a compound undergoing biodegradation, but its transformation into daughter products (PFBA, PFPeA, PFHxA) cannot be represented in scenarios where the PFAS module is used (i.e., AWI and AWI + scaling). Under these scenarios, the model therefore captures the attenuation of 6:2 FTS but not the consecutive formation and transport of its transformation products. PFHxA is only represented because it is included directly among the solute inputs.

Table 21. Transport scenarios for PFAS compounds, combining AWI retention complexity and uncertainty associated with sorbed-phase biotransformation of 6:2 FTS

Sorbed-phase biotransformation of 6:2 FTS	No-AWI sorption	AWI sorption	AWI sorption + scaling factor
$\alpha = 0$	P _{1a}	P _{2a}	P _{3a}
$\alpha = 0.5$	P _{1b}	-	-
$\alpha = 1$	P _{1c}	-	-

4. Transport modelling results

This section presents the transport modelling results, focusing first on non-PFAS contaminants and subsequently on PFAS contaminants. For each modelling scenario, results are presented using two different approaches. First, the temporal evolution of contaminant concentrations is evaluated at different depths beneath the infiltration basin, allowing the assessment of breakthrough dynamics and attenuation through the vadose zone. Second, a cumulative mass balance based on solute fluxes inputs and outputs is established to make a distinction between the fraction of contaminant retained within the model domain, the fraction leaving through the deep drainage lower boundary, and the fraction removed by biodegradation. This combined analysis provides an integrated view of both the kinetics and the fate of contaminants under the different transport scenarios.

4.1. Transport of non-PFAS contaminants

4.1.1. Triazoles compounds

As described in Section 3, contaminant transport was simulated over a 10-year period, with MAR operations occurring during the first year of simulation, resulting in contaminant input into the vadose zone. Among the compounds included in the simulations, benzotriazole and tolyltriazole were investigated. Six different modelling scenarios were performed according to the combinations described in Table 20.

⁸ A plausible reason is that the module was primarily developed to represent PFAS retention processes (notably air–water interfacial adsorption) for compounds generally regarded as highly persistent, and therefore does not include a decay-chain framework by default.

Figure 52 shows the temporal evolution of benzotriazole concentrations at the surface and at depths of 0.5 m, 2 m, 5 m, 10 m, and 15 m for each modelling scenario. To compare scenarios between each other, three metrics were defined: (i) first arrival time, (ii) peak concentration, and (iii) residence time, defined as the duration following the end of the last MAR injection cycle during which aqueous concentrations remain above 1% of the peak concentration. These metrics are consistent with the APSÛ process-based framework developed at ULiège for intrinsic groundwater vulnerability, which relates vulnerability to travel time, concentration levels and the duration of contamination at the groundwater target (Thomas *et al.*, 2018; Popescu *et al.*, 2019; Collignon *et al.*, 2024). The metrics calculated for benzotriazole at a depth of 15 m are reported in Table 22. The time of peak concentration is not included as a comparison metric, as it is identical for all solutes and scenarios. This timing is indeed controlled by the duration of MAR input rather than by differences in transport behaviour. Once the last MAR cycle ends, concentrations immediately begin to decrease, resulting in a consistent peak timing across depths and compounds.

As a reminder, sorption distribution coefficients derived from the literature are higher than those inferred from batch experiments. This is notably reflected when comparing results from scenarios S_1 and S_2 . As shown in Table 22, the residence time in scenario S_{1a} (1996 days) is longer than in scenario S_{2a} (1093 days). This stronger retardation delays downward transport and contributes to the lower peak concentration in scenario S_{1a} ($0.304 \text{ mg}\cdot\text{L}^{-1}$) compared to scenario S_{2a} ($0.351 \text{ mg}\cdot\text{L}^{-1}$). This effect is also apparent in the first arrival time, which is delayed in S_{1a} (119 days) relative to S_{2a} (62 days).

The inclusion of biodegradation on the sorbed phase alters the transport behaviour significantly. Under scenarios S_{1b} – S_{2b} and S_{1c} – S_{2c} , the fraction of contaminant retained by sorption is progressively biodegraded, which limits long-term persistence of benzotriazole within the vadose zone. Under these conditions, the choice of sorption parameters primarily influences the first arrival time and peak concentration, while the total residence time becomes less sensitive to sorption strength. In this configuration, stronger sorption can further enhance attenuation because a larger fraction of contaminant mass is temporarily sorbed onto the solid phase where biodegradation is assumed to occur ($\alpha > 0$), effectively increasing the contact time with reactive surfaces and promoting mass-integrated degradation. This effect is clearly illustrated in Figure 52 with the noticeable reduction in peak concentrations for scenarios S_{1b} – S_{2b} and S_{1c} – S_{2c} compared to scenarios S_{1a} – S_{2a} .

Table 22. Metrics associated with benzotriazole transport in the vadose zone beneath the infiltration basin.

Scenario	Sorption	Biodegradation sorbed phase: α	Depth	First arrival (days)	Peak concentration (mg L^{-1})	Residence time (days)
S_{1a}	Literature	0	15 m	119	0.304	1996
S_{2a}	Batch	0	15 m	62	0.351	1093
S_{1b}	Literature	0.5	15 m	103	0.067	526
S_{2b}	Batch	0.5	15 m	58	0.159	476
S_{1c}	Literature	1	15 m	99	0.017	311
S_{2c}	Batch	1	15 m	56	0.076	311

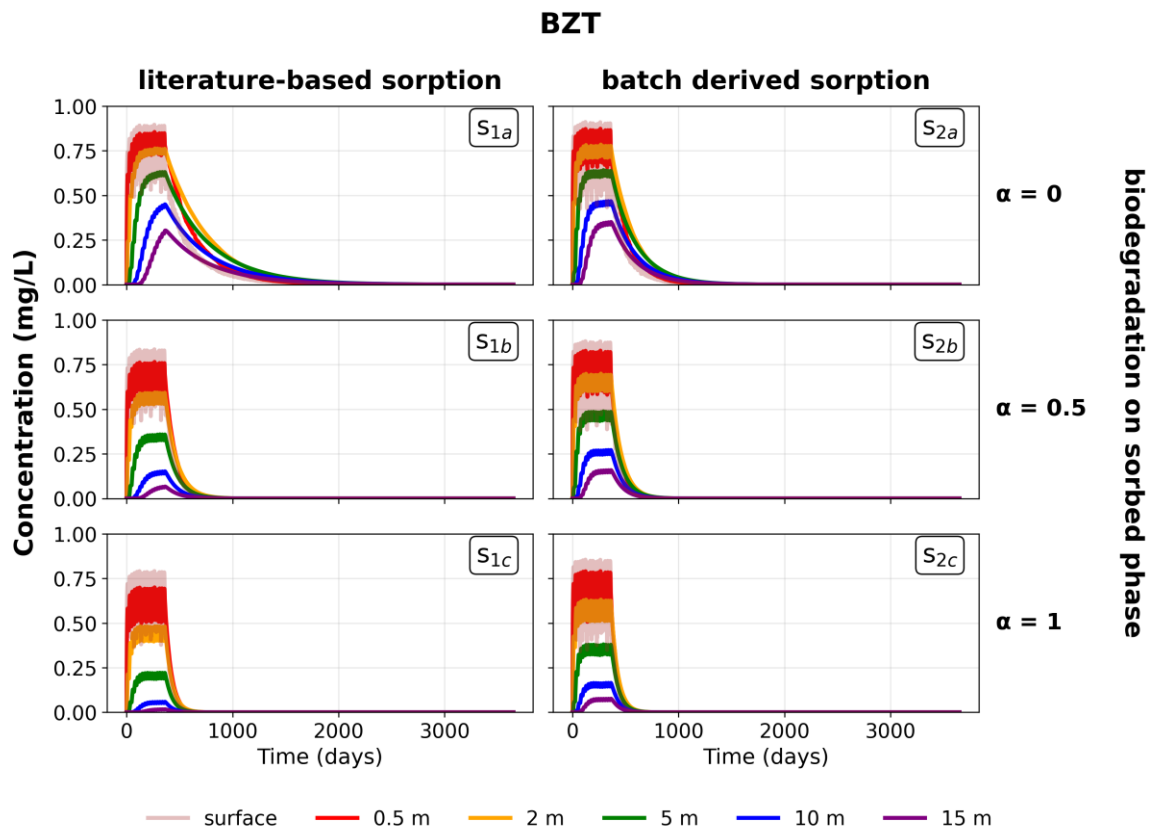


Figure 52. Benzotriazole concentration evolution at different depths, for each scenario defined in section 3.4.1.

Figure 52 suggests that contaminant concentrations at a depth of 15 m decrease to values close to zero for all modelling scenarios, which could be interpreted as complete attenuation within the vadose zone. However, concentration profiles alone do not provide information on the ultimate fate of the contaminant mass. To address this, cumulative solute fluxes were analysed to establish a mass balance over the simulation period. Specifically, cumulative solute fluxes at the upper boundary of the model (solute input), at the deep drainage lower boundary (leaving mass), and associated with biodegradation were calculated. These cumulative input and output fluxes are presented in Figure 53 and allow the distinction between contaminant mass retained within the model domain (blue), exported beyond the vadose zone (green), or removed through biodegradation (red).

Figure 53 shows that, depending on the modelling scenario, a non-negligible fraction of the injected contaminant mass is exported into the chalk aquifer. To facilitate comparison between scenarios, Figure 54 summarizes the relative proportions of contaminant mass retained within the model domain, removed by biodegradation, and leaving the model through deep drainage. These proportions are expressed as fractions of the total injected mass.

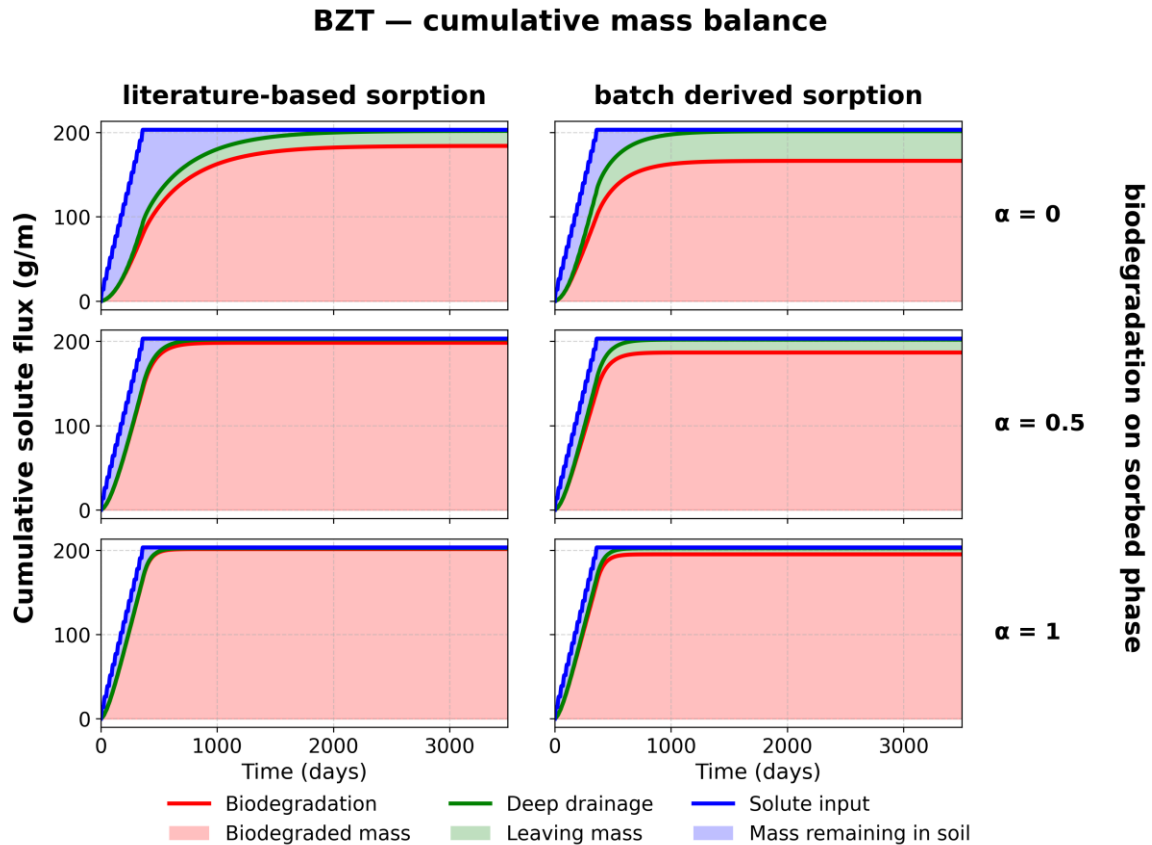


Figure 53. Cumulative mass balance for benzotriazole transport derived from cumulative solute fluxes.

In the absence of biodegradation of the sorbed phase, differences in sorption strength strongly influence the mass balance. When weaker sorption is considered (S_{2a}), a larger fraction of the contaminant mass reaches the aquifer (17%) compared to the scenario with stronger sorption (S_{1a}), for which 9% is leaving the model domain through deep drainage.

On the other hand, including biodegradation of the sorbed phase also influences significantly mass balance results. This inclusion increases, for both sorption scenarios (S_1 and S_2), the fraction of contaminant removed by biodegradation, leading thus to a noticeable reduction of the mass exported beyond the vadose zone. For literature-based sorption scenarios, the exported fraction decreases from 17% in S_{1a} to 8% in S_{1b} and 4% in S_{1c} , while for batch-derived sorption scenarios it decreases from 9% in S_{2a} to 2% in S_{2b} and 1% in S_{2c} .

Finally, Figure 54 also indicates that only a negligible fraction of the contaminant mass remains stored within the model domain at the end of the simulation period. This reflects the dominant role of biodegradation in removing benzotriazole mass from the vadose zone, although a fraction is still transferred to the aquifer through deep drainage.

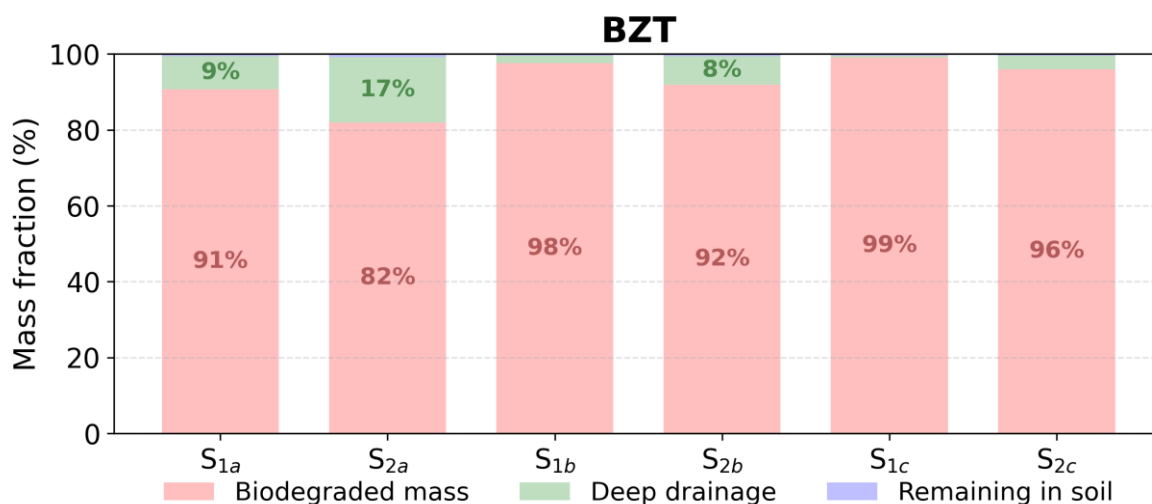


Figure 54. Mass balance fractions of benzotriazole derived from cumulative solute fluxes at the end of the simulation. Fractions correspond to the proportions of injected mass that were biodegraded, transported out of the system via deep drainage, or remained in the soil domain.

Tolyltriazole exhibits transport behaviour very similar to that of benzotriazoles across all modelling scenarios, which is consistent with their comparable biogeochemical properties. Consequently, tolyltriazoles results are not discussed in detail here, and the corresponding figures and metrics are provided in the section 1 of Annex E.

4.1.2. Alkylphenols – Nonylphenol diethoxylate (NP₂EO)

Nonylphenol diethoxylate shows a considerably different behaviour compared to triazoles, with strong discrepancies between literature-based and batch-derived sorption parameterizations. In particular, batch experiments did not show measurable sorption for NP₂EO ($K_d \approx 0 \text{ L}\cdot\text{kg}^{-1}$), in contrast to literature values, which are relatively high ($K_d \approx 20.8 \text{ L}\cdot\text{kg}^{-1}$) and exceed those of triazole compounds by one to two orders of magnitude.

Figure 55 presents the temporal evolution of NP₂EO concentrations at the surface and at depths of 0.5 m, 2 m, 5 m, 10 m, and 15 m for the different modelling scenarios. Under literature-based sorption scenarios (S_{1a} – S_{1c}), sorption is sufficiently strong to retain NP₂EO at shallow depths. Concentration increases are indeed visible down to 2 m, but no breakthrough is observed at depths > 5 m over the simulation period. This indicates that NP₂EO cannot reach the deeper part of the vadose zone under these conditions, indicating a very high attenuation capacity governed by sorption. In addition, when biodegradation of the sorbed phase is included, NP₂EO does not remain indefinitely retained within the soil matrix. Instead, concentrations decrease rapidly, leading to near complete removal within approximately 1000 days of simulation (scenario S_{1b}).

In contrast, under batch-derived sorption scenarios (S_{2a} – S_{2c}), NP₂EO exhibits no sorption, resulting in identical transport behaviour across all scenarios since the biodegradation of the sorbed phase is ineffective in the absence of sorption. Under these conditions, concentration breakthrough curves decrease steeply after the end of MAR operations, reflecting rapid biodegradation of NP₂EO in the aqueous phase in the absence of retardation induced by sorption.

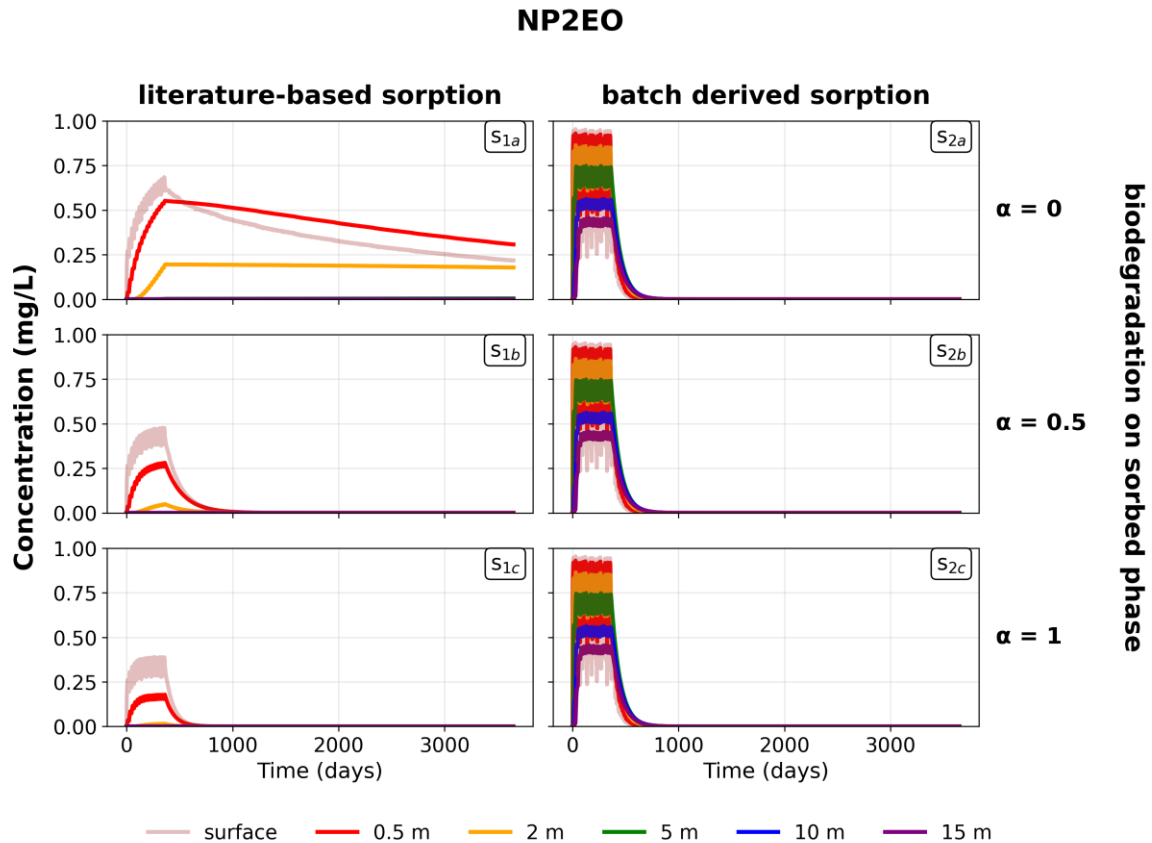


Figure 55. Nonylphenol diethoxylate concentration evolution at different depths, for each scenario defined in section 3.4.1.

In terms of mass balance, Figure 56 shows the cumulative solute fluxes and associated partitioning of NP₂EO between retention within model domain, export through deep drainage and biodegradation. In addition, the bar chart depicted in Figure 57 summarizes these fractions related to the total recharged mass of NP₂EO. For literature-based sorption scenarios, there is no exported fraction through deep drainage as NP₂EO remained sorbed within the soil matrix, and biodegraded depending on the scenario. On the other hand, under batch-derived sorption conditions ($K_d \approx 0 \text{ L}\cdot\text{kg}^{-1}$), a non-negligible fraction (34%) of the total injected mass is transferred beyond the vadose zone, reflecting the absence of retardation and the dominance of advective and dispersive transport in the aqueous phase.

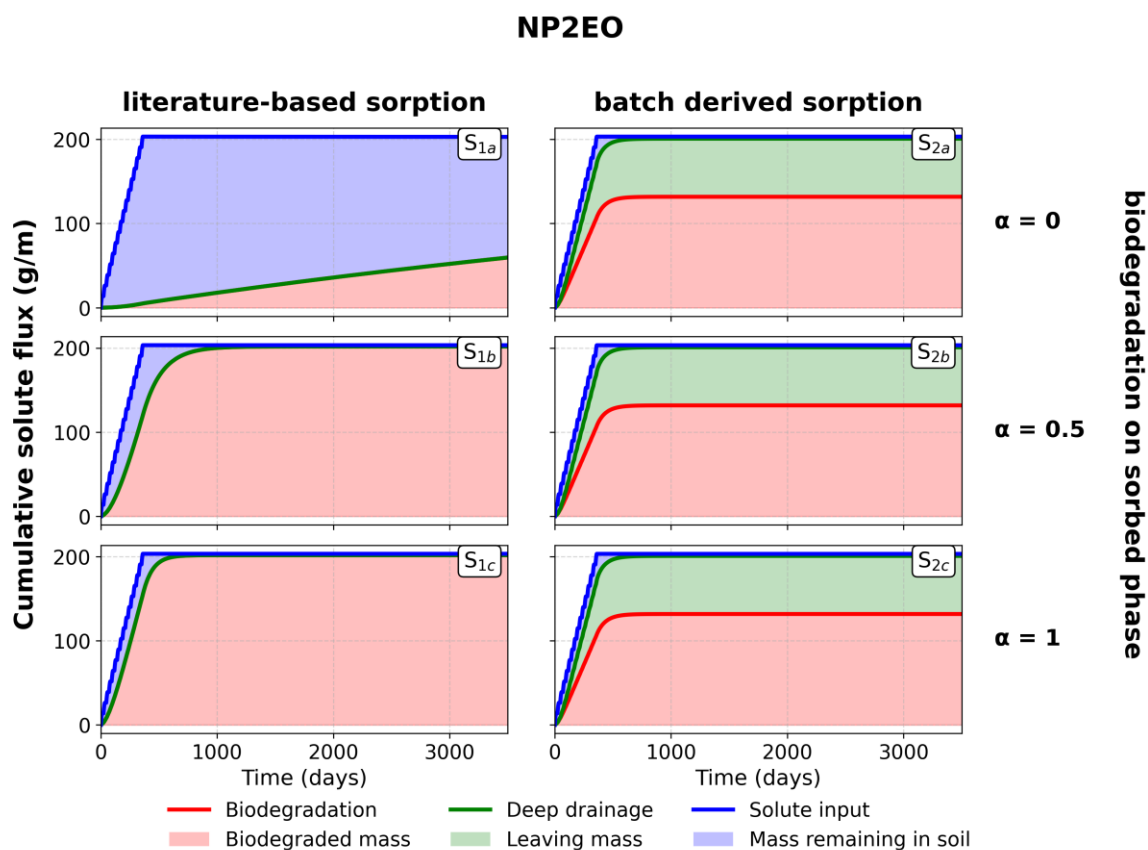


Figure 56. Cumulative mass balance for benzotriazole transport derived from cumulative solute fluxes.

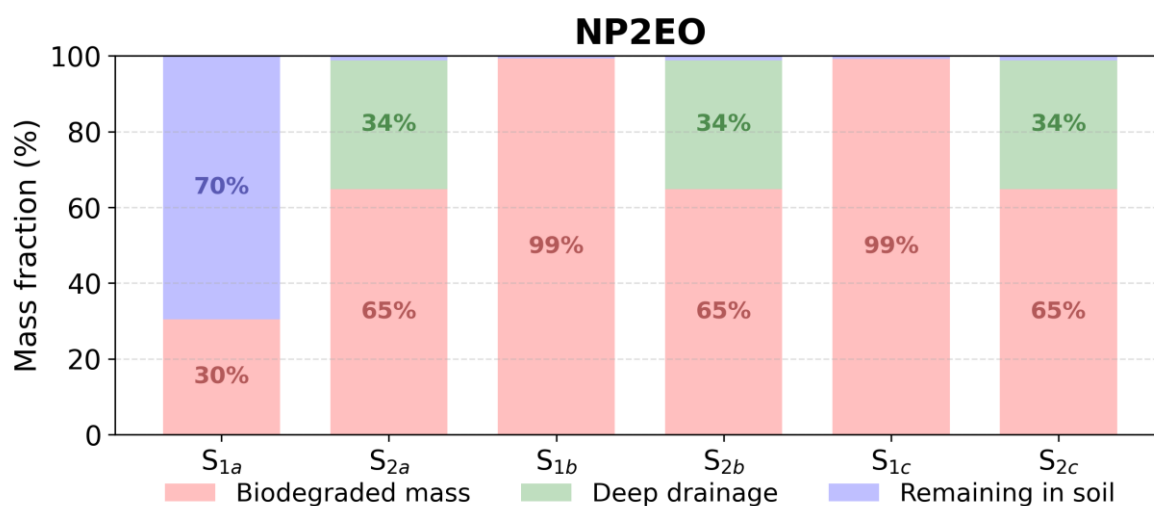


Figure 57. Mass balance fractions of nonylphenol diethoxylate derived from cumulative solute fluxes at the end of the simulation. Fractions correspond to the proportions of injected mass that were biodegraded, transported out of the system via deep drainage, or remained in the soil domain.

4.2. Transport of PFAS compounds

4.2.1. Persistent PFAS

Transport of PFAS within the vadose zone exhibits specific behaviour compared to the non-PFAS compounds described previously. Unlike conventional organic contaminants, PFAS sorption is not only governed by hydrophobic interactions with organic matter or electrostatic interactions with charged mineral surfaces, but also by retention at the air-water interface (AWI) due to their surfactant properties. The present section therefore focuses on assessing the influence of AWI processes on PFAS transport by comparing three modelling configurations. There are the scenarios P_{1a} , P_{2a} , and P_{3a} , which respectively neglect AWI sorption, include AWI sorption, and include AWI sorption with scaling to account for surface roughness effects. Transport results are presented for persistent PFAS compound that are not associated with the biotransformation of 6:2 FTS within the model framework. PFHxA is included as an exception, as it is already present in the recharge water as a solute input.

Figure 58 presents the transport modelling results for PFOA, PFOS, PFHxA, and PFECHS under the different AWI-related scenarios. Before discussing the behaviour of individual PFAS compounds, a clear distinction can be observed between the scenarios with no AWI, with AWI, and with AWI combined with scaling, particularly regarding the magnitude of concentration oscillations. In the absence of AWI (scenario P_{1a}), slight oscillations in concentration are observed only at the surface and at a depth of 0.5 m, reflecting the influence of atmospheric boundary conditions. When AWI sorption is included (scenario P_{2a}), oscillations amplitudes increase significantly and propagate to greater depths, where concentration fluctuations also become apparent. This enhanced oscillatory behaviour arises from the strong sensitivity of the retardation factor to the air-water interfacial area (A_{awi}), as expressed in Eq. 27. The interfacial area itself is highly sensitive to variations in water content as it is derived from the SWRC following the Leverett thermodynamic model. As illustrated in **Erreur ! Source du renvoi introuvable.**, the SWRC shows steep variations near saturation, which is a condition frequently encountered at shallow depths during MAR operations or after rainfall events. Small changes in water content under these conditions therefore induce large variations in A_{awi} , resulting in greater oscillations in solute concentrations. This effect is further amplified when the scaling factor is applied (scenario P_{3a}), as the scaled interfacial area directly increases the sensitivity of the retardation factor (Eq. 27), leading to larger oscillations.

For each PFAS compound, terminal concentrations at depths of 2 m, 5 m, 10 m, and 15 m were extracted at the end of the simulation for different AWI-related scenarios in order to compare attenuation effects associated with AWI processes. These values are reported in Table 23. For PFOA notably, for PFOA, as indicated in Figure 58, final concentrations decrease progressively with the inclusion of AWI sorption and further with application of the scaling factor. At a depth of 2 m, concentrations decrease from $0.66 \text{ mg}\cdot\text{L}^{-1}$ in scenario P_{1a} to $0.60 \text{ mg}\cdot\text{L}^{-1}$ in P_{2a} and $0.46 \text{ mg}\cdot\text{L}^{-1}$ in P_{3a} , while at 5 m depth they decrease from $0.42 \text{ mg}\cdot\text{L}^{-1}$ to $0.37 \text{ mg}\cdot\text{L}^{-1}$ and $0.26 \text{ mg}\cdot\text{L}^{-1}$, respectively. These results indicate that the inclusion of AWI sorption alone leads to a moderate reduction in PFOA concentration, whereas the additional application of the scaling factor produces a much stronger attenuation effect. Results at depths of 10 m and 15 m are not discussed here, as concentrations are very low at the end of the simulation period, reflecting the retention of PFOA within the upper part of the vadose zone.

For PFOS, a similar decrease in terminal concentration is observed at depth of 2 m, with values decreasing from $0.22 \text{ mg}\cdot\text{L}^{-1}$ in scenario P_{1a} , to $0.16 \text{ mg}\cdot\text{L}^{-1}$ in P_{2a} and further $0.08 \text{ mg}\cdot\text{L}^{-1}$ in P_{3a} . This again highlights the stronger attenuation effect introduced by the scaling factor applied to AWI sorption. However, in contrast to PFOA, PFOS remains strongly retained at very shallow depths and

does not reach 5 m depth even after 10 years of simulation. This behaviour reflects the stronger sorption affinity of PFAS holding a sulfonate functional group compared to carboxylates, which promotes retention within the soil and limits downwards transport toward the aquifer.

PFECHS exhibits transport behaviour similar to that of PFOS, despite the presence of cyclohexane ring, as both compounds share comparable chemical formula and biogeochemical properties. Sorption of PFECHS is nevertheless twice stronger than that of PFOS, resulting in concentration that barely reach a depth of 2 m. In addition, as no AWI-related parameters were available for this compound, no differences are observed between scenarios P_{1a} , P_{2a} , and P_{3a} .

Finally, PFHxA is characterized by significantly weaker sorption than the other PFAS discussed above. As a result, this compound penetrates much deeper into the vadose zone, with concentration increases observed at depths of 10 m and 15 m. In contrast to PFOA and PFOS, the influence of AWI processes on PFHxA transport becomes more pronounced at greater depths. At 10 m depth, terminal concentrations decrease from $0.85 \text{ mg}\cdot\text{L}^{-1}$ in scenario P_{1a} to $0.78 \text{ mg}\cdot\text{L}^{-1}$ in P_{2a} and further $0.59 \text{ mg}\cdot\text{L}^{-1}$ in P_{3a} . A similar trend is observed at 15 m depth. At shallower depths however, PFHxA concentration are only weakly affected by AWI processes, with terminal concentrations remaining relatively similar across scenarios. This suggests that, near the surface, PFHxA transport is strongly influenced by atmospheric boundary conditions and rapid water content fluctuation may partially mask the effect of AWI-related overall retardation. At greater depths, where hydraulic conditions are more stable, retardation associated with AWI sorption becomes apparent and exerts a stronger influence on solute transport.

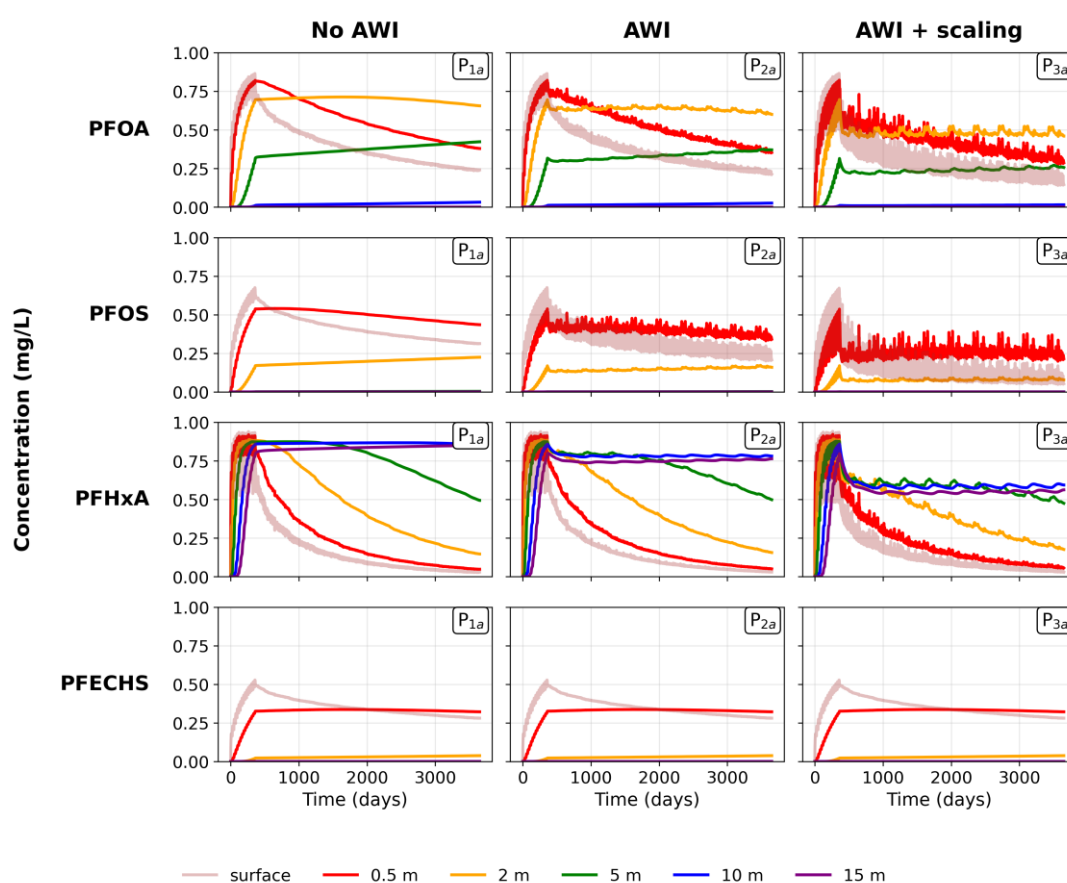


Figure 58. PFAS concentration evolution at different depths and for the different AWI scenarios.

Table 23. Final concentrations of each individual PFAS at different depths under different AWI-related scenarios.

		depth = 2 m			depth = 5 m		
		no AWI	AWI	AWI + scaling	no AWI	AWI	AWI + scaling
Concentration (mg L ⁻¹)	PFOA	0.66	0.60	0.46	0.42	0.37	0.26
	PFOS	0.22	0.16	0.08	0.00	0.00	0.00
	PFHxA	0.15	0.16	0.18	0.49	0.50	0.48
	PFECHS	0.04	0.04	0.04	0.00	0.00	0.00

		depth = 10 m			depth = 15 m		
		no AWI	AWI	AWI + scaling	no AWI	AWI	AWI + scaling
Concentration (mg L ⁻¹)	PFOA	0.03	0.03	0.02	0.00	0.00	0.00
	PFOS	0.00	0.00	0.00	0.00	0.00	0.00
	PFHxA	0.85	0.78	0.59	0.85	0.76	0.56
	PFECHS	0.00	0.00	0.00	0.00	0.00	0.00

In addition to concentration evolution graphics, cumulative mass balances were computed for PFAS compounds following the same approach as for non-PFAS contaminants, with associated graphics depicted in the section 2 of Annex E. These results confirm that for PFOA, PFOS, and PFECHS, the injected mass remains retained within the loess sediments even after 10 years of simulation, no matter which AWI-related scenario was considered. PFHxA is the only compound for which mass export through deep drainage toward the chalk aquifer is observed, consistent with its weaker sorption behaviour. However, the total cumulative mass of PFHxA leaching to the aquifer remains overall unchanged between AWI scenarios, indicating that AWI processes primarily affect concentration dynamics and vertical distribution rather than the overall mass transfer to the aquifer.

Overall, the strong sensitivity of PFAS transport modelling results to the representation of AWI processes, and particularly to the application of the scaling factor, highlights the need for improved characterization of AWI parameters and surface roughness effects in loess sediments. Such parameters could be better constrained through future work dedicated to laboratory experiments or field estimation.

4.2.2. Biotransformation of 6:2 FTS and daughter products production

Although most PFAS are widely recognized as extremely persistent in the environment and therefore not subject to active biodegradation, some PFAS can nevertheless undergo biotransformation into smaller by-products. This is notably the case of 6:2 FTS, whose carbon chain is not fully fluorinated (see Figure 51). The presence of non-fluorinated moieties introduces structural weaknesses that allows microbial transformation of the compound, leading to the formation of smaller perfluorinated carboxylic acids. The main terminal transformation products of 6:2 FTS considered in this study are PFBA, PFPeA and PFHxA (Figure 51).

As described in section 3.4.2, when the PFAS module is activated within HYDRUS to simulate AWI processes, decay chain reactions are not supported. This limitation is likely attributed to the assumption that PFAS are fully persistent and therefore do not require representation of transformation pathways. However, as discussed above, this assumption does not hold for 6:2 FTS which is known to undergo biotransformation processes in the environment. This section therefore focuses on the biotransformation of 6:2 FTS under scenarios P_{1a} , P_{1b} , and P_{1c} , which respectively assume that biotransformation of 6:2 FTS in the sorbed phase represent 0%, 50%, and 100% of the biotransformation rate in the aqueous phase. The resulting concentration profiles of 6:2 FTS and its transformation products PFBA, PFPeA, and PFHxA under these scenarios are presented in Figure 59.

In contrast to PFOA which exhibits a weaker but comparable sorption behaviour ($K_d = 5.7 \text{ L}\cdot\text{kg}^{-1}$) relative to 6:2 FTS ($K_d = 8.5 \text{ L}\cdot\text{kg}^{-1}$), concentrations of 6:2 FTS under scenario P_{1a} decrease more sharply. This behaviour reflects the combined effects of downward advective transport and active biotransformation, which accelerates mass removal compared to purely persistent PFAS. Under this scenario, 6:2 FTS migrates down to depths of approximately 5 m and beyond, but does not reach depths greater than 10 m, as no significant concentration increase is observed at that depth. The retention of 6:2 FTS within shallower parts of the vadose zone compared to PFOA is associated with its stronger sorption potential.

When biotransformation of the sorbed phase is included (scenarios P_{1b} and P_{1c}), the fate of 6:2 FTS is particularly modified. Under these conditions, most of the 6:2 FTS mass is rapidly transformed such as breakthrough curves decrease rapidly to near-zero concentrations after the end of MAR operations. As a result, 6:2 FTS does not reach depths greater than 5 m in these scenarios. This behaviour is further illustrated in Figure 60, which presents the cumulative solute fluxes for all PFAS compounds, following the same approach as applied for non-PFAS contaminants. As observed, no 6:2 FTS mass is exported through the deep drainage boundary under any scenario. Instead, mass is either retained within the model domain or biotransformed under scenario P_{1a} , and almost entirely biotransformed under scenarios P_{1b} and P_{1c} .

The breakthrough curves observed for the biotransformation products PFBA and PFPeA differ significantly from those of the parent PFAS compounds. Unlike 6:2 FTS or PFHxA, the input of PFBA and PFPeA does not originate directly from the infiltration basin, but exclusively from the biotransformation of 6:2 FTS occurring throughout the entire model domain. Consequently, the effective source term of PFBA and PFPeA is distributed over depth and time, rather than being limited to the surface boundary. As a result, peak concentrations of PFBA and PFPeA do not occur simultaneously at all depths but are progressively delayed with increasing depths.

Under scenario P_{1a} , maximum peak concentrations of both PFBA and PFPeA increase with depth. This behaviour reflects the accumulation of by-products formation. As 6:2 FTS is transported downward, an increasing fraction undergoes biotransformation, leading to an increasing mass arrival of PFBA and PFPeA at deeper locations. In contrast, under scenarios P_{1b} and P_{1c} where biotransformation of 6:2 FTS also occurs in the sorbed phase, peak concentration diminishes with depth. In these scenarios, an important fraction of 6:2 FTS is biotransformed close to the surface while sorbed, resulting in a larger production of by-products at shallow depths, and a reduced contribution from deeper layer. This effect is more pronounced in scenario P_{1c} , where full sorbed-phase biotransformation leads to earlier and greater transformation of 6:2 FTS, further limiting the mass available for transformation at depth, and resulting in lower and more attenuated peak concentrations compared to scenario P_{1b} .

PFBA peak concentrations occur earlier than those of PFPeA, reflecting its higher mobility associated with a shorter perfluorinated carbon chain and lower sorption affinity. Overall, PFBA concentrations remain relatively low compared to the parent PFAS input, reaching maximum values of approximately $0.04 \text{ mg}\cdot\text{L}^{-1}$ at the surface. This is consistent with the low molar yield of PFBA associated with 6:2 FTS biotransformation (1.7%). In contrast, PFPeA, which as a higher molar yield (7%), reaches higher peak concentrations, up to approximately $0.18 \text{ mg}\cdot\text{L}^{-1}$.

Although 6:2 FTS does not reach the Hesbaye chalk aquifer, as depicted in Figure 60, due to its strong sorption capacity and biotransformation potential, a different behaviour is observed for its biotransformation products PFBA and PFPeA. Due to their much higher mobility associated to lower solid-liquid distribution coefficients, these compounds can migrate downward after their production and reach the aquifer. This is notably illustrated in Figure 60 by a non-negligible fraction of PFBA and PFPeA exported from the model domain through the deep drainage boundary.

Finally, PFHxA represents a particular case, as its input originates from both direct infiltration through the basin and from the biotransformation of 6:2 FTS within the vadose zone. In contrast to the PFHxA results presented in Figure 58 under scenario P_{1a} , where no contribution from 6:2 FTS biotransformation was considered, the additional production of PFHxA has a negligible impact on overall transport results. Given the continuous PFHxA input at a concentration of $1 \text{ mg} \cdot \text{L}^{-1}$ during one year of MAR operations, the contribution arising from 6:2 FTS biotransformation associated with a molar yield of 5.3% remains minor in comparison. A slight increase in peak concentrations can be observed when biotransformation of 6:2 FTS in the sorbed phase is activated. However, this effect remains limited and does not significantly alter PFHxA transport dynamics. Overall, PFHxA behaviour continues to be dominated by its direct input and transport properties rather than by secondary formation from 6:2 FTS. This is also reflected in Figure 60, where approximately the same cumulative mass of PFHxA is exported through the deep drainage boundary regardless of the scenario considered. This also remains comparable to the case where no contribution from 6:2 FTS biotransformation is included (see Annex B).

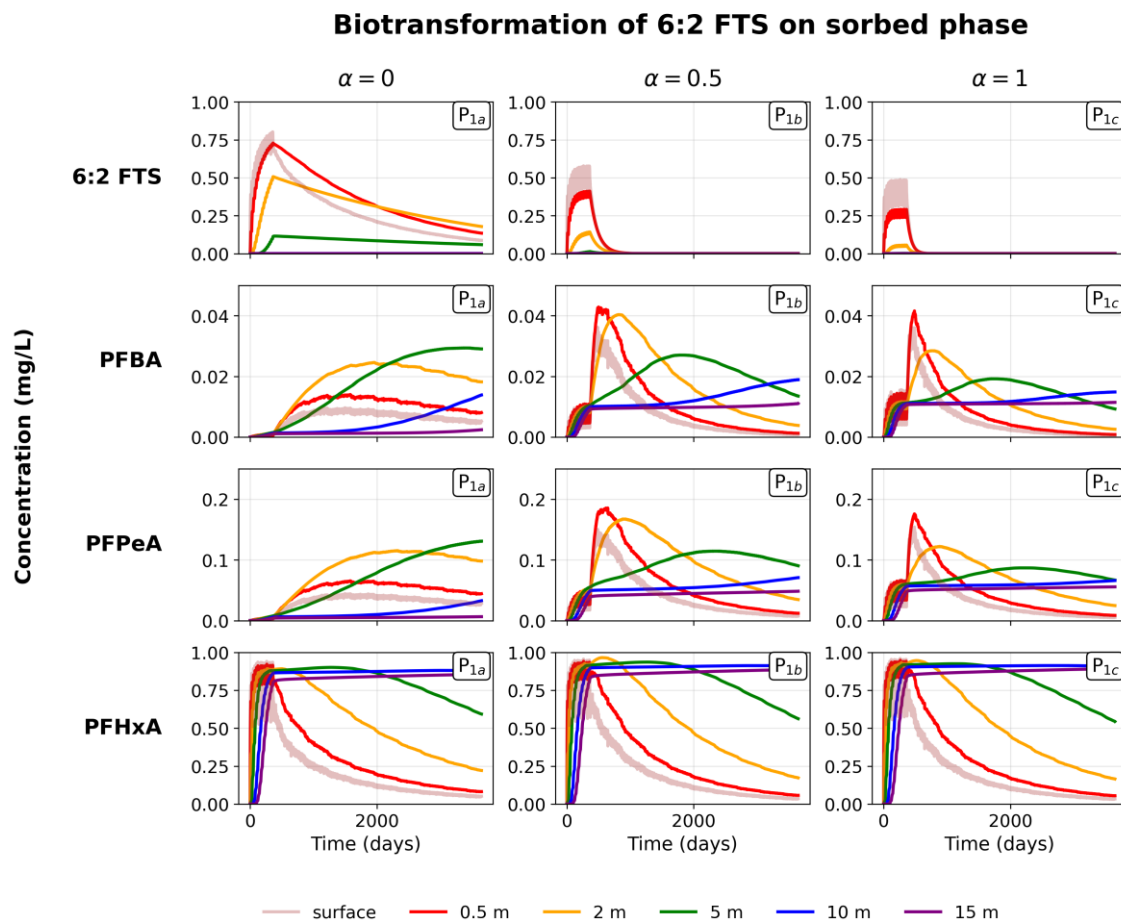


Figure 59. Concentration evolution of 6:2 FTS and its biotransformation products at different depths under different scenarios accounting for the biotransformation or not of 6:2 FTS in sorbed phase.

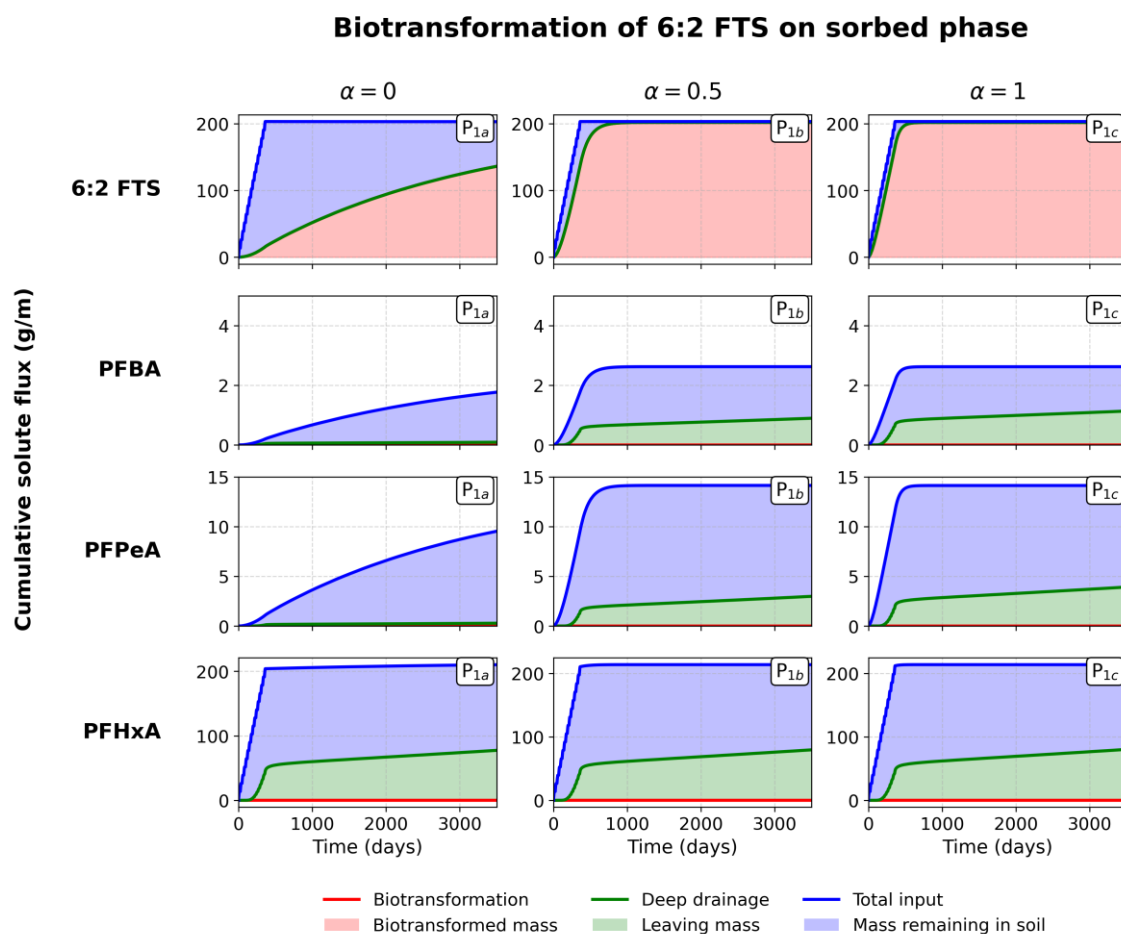


Figure 60. Cumulative mass balance for the transport of 6:2 FTS and its by-products derived from cumulative solute fluxes.

4.3. Comparative transport behaviour across contaminants

When comparing the transport behaviour of all investigated contaminants, there is a clear contrast that arises between non-PFAS and PFAS compounds, as well as within each contaminant family. Non-PFAS compounds generally exhibit transport behaviour that is primarily governed by the classical advection-dispersion framework, with solid phase sorption acting as a retardation mechanism and biodegradation representing a permanent mass removal process. As a result, their mobility within the model is highly sensitive to the magnitude of the sorption coefficient and to the extent of biodegradation occurring in the sorbed phase. In contrast, PFAS transport is dominated by strong retention mechanisms, including sorption on the solid phase and at air-water interface, leading to a limited downward migration for most of these compounds despite their sustained input during MAR operations.

For non-PFAS compounds, breakthrough dynamics and vadose-zone residence times are highly sensitive to the sorption coefficients used, with noticeable differences between simulations parameterized from literature values and those based on batch-derived values. Higher sorption coefficients lead to delayed concentration increase over depth and prolonged residence times, which in turn enhance the potential for biodegradation. The inclusion of biodegradation in the sorbed phase further amplifies this effect, leading to a significant reduction in the fraction of contaminant mass exported through deep drainage. This behaviour is well illustrated by triazole compounds, for which

literature-based and batch-derived sorption coefficients are of comparable magnitude, resulting in relatively similar transport patterns. Differences between these sets of sorption parameters mainly affect mobility, with batch-derived coefficients leading to slightly earlier breakthrough curves and a larger fraction of mass reaching the aquifer. However, because sorption retains a fraction of triazoles within the solid phase in both cases, the subsequent inclusion of biodegradation in the sorbed phase becomes the dominant control on contaminant fate as it controls the extent of mass removal during transport. This leads to a significant reduction in the fraction of contaminant mass exported through deep drainage.

For nonylphenol diethoxylate, a pronounced discrepancy is observed between sorption coefficients derived from the literature and those inferred from batch experiments. In the batch tests performed on Hesbaye loess, no measurable sorption was detected, whereas published studies report strong sorption of alkylphenol ethoxylates onto soils and sediments. In this context, the literature-based parameterization is considered more representative of field conditions, where NP₂EO is expected to be largely retained in the vadose zone and/or degraded. In contrast, not considering sorption at all based on batch results produces unrealistically high mobility and leads to partial export through deep drainage, due to the absence of sorption-related retardation and the exclusion of any potential sorbed-phase biodegradation. This behaviour is unlikely to reflect in situ conditions and may instead result from methodological limitations of the batch approach for this compound. Finally, contaminant removal is represented here only through biodegradation of NP₂EO, whereas other possible transformation pathways (e.g., formation of nonylphenol) were not considered.

As introduced several times within this study, PFAS transport differs from that of non-PFAS compounds primarily because PFAS are assumed to be persistent in the model framework (i.e., no biodegradation is considered for most PFAS), and because their retention is not limited to solid-liquid sorption. In addition to sorption onto the solid phase, PFAS can also be retained at the air-water interface due to their surfactant properties. Including AWI retention in transport modelling framework modifies concentration dynamics, vertical distribution, and breakthrough curves behaviour of the studied PFAS. In addition, the magnitude of these effects is sensitive to the representation of air-water interfacial area and to the application of scaling factors accounting for surface roughness.

Cumulative mass balance results further indicate that over the simulated period, including AWI mainly affects the spatial and temporal distribution of PFAS within the vadose zone, while having a limited impact on the total mass exported to the aquifer. Most PFAS mass remains retained within loess sediments at the end of the simulation, where PFHxA shows measurable export through deep drainage boundary, consistent with its weaker sorption behaviour and thus higher mobility.

Finally, the case of 6:2 FTS highlights the role of transformation pathways for some precursors compounds. Although the parent compound does not reach the aquifer due to retention and biotransformation during transport, its transformation products PFBA and PFPeA are more mobile and can contaminate the chalk aquifer through the deep drainage boundary. This illustrates that biotransformation can increase leaching potential even when the parent is largely retained.

Table 24 provides scenario-independent synthesis of the overall transport behaviour of all investigated contaminants. The comparison highlights strong differences in mobility, retention mechanisms, depth penetration, and aquifer transfer potential between non-PFAS compounds, PFAS, and PFAS transformation products (TP). Together, these characteristics determine their potential to migrate through the vadose zone and possibly reach the aquifer.

Table 24. Overview on transport behaviour of investigated contaminants in the vadose zone.

Compound	Family	Mobility	Main Retention mechanism	Biodegradation / Transformation	Deepest penetration observed	Aquifer transfer potential
Benzotriazole (Bzt)	Triazole	Moderate	Solid sorption	Active biodegradation	> 15 m	Yes, but limited
Tolyltriazole (Tlt)	Triazole	Moderate	Solid sorption	Active biodegradation	> 15 m	Yes, but limited
NP₂EO	Alkylphenol ethoxylate	Low	Solid sorption	Active biodegradation	≤ 2-5 m	Unlikely
PFOA	PFAS (carboxylate)	Low	Solid sorption + AWI retention	Persistent	≤ 5 m	No
PFOS	PFAS (sulfonate)	Very low	Solid sorption + AWI retention	Persistent	≤ 2 m	No
PFECHS	PFAS (sulfonate)	Very low	Solid sorption + AWI retention	Persistent	≤ 2 m	No
6:2 FTS	PFAS precursor	Low - moderate	Solid sorption	Biotransformed	≤ 5 m	No
PFHxA	PFAS (TP)	high	Solid sorption + AWI retention	Persistent and TP	> 15 m	Yes
PFBA	PFAS (TP)	Very high	Solid sorption	Stable TP	> 15 m	Yes
PFPeA	PFAS (TP)	high	Solid sorption	Stable TP	> 15 m	Yes

5. Risk and vulnerability assessment

This section evaluates the specific vulnerability of the Hesbaye subsurface system to contaminants potentially introduced by MAR operations, based on the HYDRUS-2D transport model presented in the previous sections. The analysis uses recharge-water concentrations representative of the contaminants identified in runoff water to assess whether transfer through the loess vadose zone may lead to contaminant fluxes and concentrations of concern at the interface with the underlying chalk aquifer. As the numerical model is restricted to the vadose zone and does not explicitly simulate transport within the saturated chalk aquifer, the interpretation remains focused on transfer to the aquifer boundary and on a first-order discussion of possible implications at aquifer scale.

5.1. Specific vulnerability and hazard indicators

Within the groundwater-protection framework developed in the literature and in the Hydrogeology and Environmental Geology research unit at ULiège (Thomas *et al.*, 2018; Popescu *et al.*, 2019; Micella, 2020; Brouyère *et al.*, 2023; Collignon, 2024), vulnerability, hazard and risk are related but distinct concepts. The APSÛ methodology and its later developments for aquifers in Wallonia and Brussels are based on a process-oriented view of groundwater contamination, in which the transfer of pollutants from the land surface to groundwater is analysed through the hazard–pathway–target concept (Thomas *et al.*, 2018; Popescu *et al.*, 2019; Micella, 2020; Brouyère *et al.*, 2023; Collignon, 2024). In this framework, intrinsic vulnerability refers to the natural sensitivity of the subsurface independently of pollutant-specific behaviour, typically considering a conservative dissolved contaminant. It is classically described using physically based indicators such as the transfer time to groundwater, the maximum concentration reached at the target, and the pollution duration. Specific vulnerability extends this approach by accounting for pollutant-dependent attenuation processes such as sorption and biodegradation. Hazard refers to the contaminant input at the land surface, whereas risk is obtained only when vulnerability is combined with hazard and with the consequences associated with groundwater contamination.

In that context, the present study does not address intrinsic vulnerability, since the simulations explicitly account for contaminant-specific behaviour in the loess vadose zone. At the same time, the approach does not constitute a complete risk assessment in the strict sense, because transport and consequences within the saturated chalk aquifer are not explicitly simulated. Rather, the chapter focuses primarily on the specific vulnerability of the subsurface system beneath the infiltration basin under defined MAR contamination scenarios, while using hazard-related information to support a first-order discussion of potential groundwater-quality implications.

Accordingly, the hazard considered in this chapter is represented by the quality of the recharge water. More specifically, contaminant concentrations measured in untreated urban runoff are used as input concentrations at the infiltration boundary, and two contrasted scenarios are defined: a worst-case scenario based on high runoff concentrations and weak attenuation assumptions, and a realistic-case scenario based on median runoff concentrations and the most defensible parameterisation of attenuation processes. These scenarios will be further detailed in the next section.

The specific vulnerability of the Hesbaye subsurface system is then evaluated using two complementary indicators derived from the HYDRUS-2D simulations. In line with the philosophy of the APSÛ framework (Thomas *et al.*, 2018; Popescu *et al.*, 2019; Micella, 2020; Brouyère *et al.*, 2023;

Collignon, 2024), the first indicator is the fraction of contaminant mass transferred through the lower boundary of the simulated loess profile, expressed as:

$$f = \frac{M_{out}}{M_{in}} \quad (39)$$

Where M_{out} is the cumulative mass leaving the domain through the deep drainage boundary over the 10-year simulation period, and M_{in} is the total mass introduced at the infiltration boundary over the same period. Because HYDRUS simulations are formulated in a two-dimensional vertical plane, these cumulative masses are reported per unit width in the third dimension [ML^{-1}]. This indicator provides an integrated measure of vadose-zone protective capacity as low values of f indicate strong degradation and/or long residence times relative to the simulation period, whereas high values indicate significant transfer to depth. To facilitate interpretation and comparison across contaminants, the following vulnerability classes are defined based on the value of f at the end of the simulation period:

- Not vulnerable: $f < 0.1\%$
- Low vulnerability: $0.1\% \leq f < 1\%$
- Moderate vulnerability: $1\% \leq f < 10\%$
- High vulnerability: $f \geq 10\%$

The second indicator is based on the predicted concentration at the loess–chalk interface after 10 years (C_{15m}). This concentration-based metric complements the mass fraction (f) by providing a more direct basis for comparison with drinking-water guideline values or environmental quality standards (C_{ref}). To facilitate comparison between contaminants with different benchmark values, the results are further interpreted through an exceedance ratio (ER):

$$ER = \frac{C_{15m}}{C_{ref}} \quad (40)$$

Values of $ER < 1$ indicate that the predicted concentration remains below the selected benchmark, whereas $ER \geq 1$ indicates a potential exceedance. This concentration-based interpretation is applied primarily when the system is at least moderately vulnerable, i.e. when $f \geq 1\%$, to focus the discussion on transfers that are both significant in terms of transfer magnitude and potentially relevant for groundwater quality. Together, these indicators allow the identification of contaminants that are most likely to bypass the protective function of the unsaturated zone and to represent a potential concern for the underlying chalk aquifer.

Building on this vulnerability assessment, a first-order evaluation of potential groundwater contamination risk is then proposed through the estimation of aquifer-scale concentrations. These concentrations are derived by converting the simulated contaminant mass transferred across the loess–chalk interface into an equivalent groundwater concentration after dilution by groundwater flow, and are used to discuss the possible implications for groundwater quality.

5.2. Modelling framework and scenario definition

5.2.1. Modelling assumptions

In the present simulations, the recharge water quality is characterized by contaminant concentrations representative of the untreated urban runoff sampled and analysed in chapter 4. To ensure

consistency with the transport modelling framework developed earlier, the following assumptions were retained:

- Initial concentrations of all targeted contaminants in the model domain are set to zero, so that simulated concentrations reflect only the contribution from recharge operations.
- Contaminants are introduced at the infiltration basin surface using third-type (Cauchy) boundary conditions. The prescribed concentrations correspond to median or maximal values measured in untreated urban runoff, depending on the targeted scenario described here after, differing from the unit concentration previously used to compare attenuation mechanisms across the tested conditions.
- Transport simulations were conducted over a 10-year period. A first temporal scheme, consisting of one year of MAR operation followed by nine years under natural conditions, was used to assess the specific vulnerability of the Hesbaye chalk aquifer to introduced contaminants, to assess both short-term transfer and delayed release at the loess–chalk interface from the vadose zone. In addition, a second, more realistic temporal scheme with MAR operations repeated annually over the 10-year period was used to evaluate the potential impact on groundwater quality at the aquifer scale.
- Recharge operations are still represented through wetting-drying cycles ($W/D = 0.75$), where these imposed infiltration events control percolation pulses within the vadose zone.
- Results are primarily interpreted at the loess-chalk interface as an indicator of potential transfer to the Hesbaye chalk aquifer.

5.2.2. Environmental quality standards and/or drinking water quality guidelines

To support the interpretation of the simulated concentrations, model outputs are compared to reference concentration values sourced from regulatory standards or authoritative guideline documents. These values are not all the same nature, as some refer to drinking-water concentration guidelines while others relate to environmental quality standards. In the present framework, they also provide a first-order basis for discussing the potential consequences associated with contaminant transfer, by indicating whether the simulated concentrations may reach levels of concern for groundwater use or environmental protection. These guideline values are defined for the main target contaminant families as follows:

- I. **PFAS:** For drinking water, the EU revised Drinking Water Directive introduced parametric values that Member States must apply from 12 January 2026 (European Parliament and Council of the European Union, 2020). These include (i) 100 ng L⁻¹ for the “sum of PFAS”, defined as the sum of a specified list of 20 PFAS compounds⁹, and (ii) 500 ng L⁻¹ for “PFAS Total”, defined as total PFAS measured by an appropriate analytical approach. These values are used here as the primary drinking-water reference points for interpreting predicted PFAS concentrations. In parallel, a tighter reference is considered based on the Scientific Committee on Health, Environmental and Emerging Risks (SCHEER), which proposed a health-based quality standard of 4.4 ng L⁻¹ expressed as PFOA-equivalents, and recommended this value also for protecting groundwater (SCHEER, 2022). This SCHEER parametric value is not officially

⁹ PFBA, PFPA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTTrDA, PFBS, PFPS, PFHxS, PFHpS, PFOS, PFNS, PFDS, Perfluoroundecane sulfonic acid, Perfluorododecane sulfonic acid, and Perfluorotridecane sulfonic acid.

included in Drinking Water Directive but it provides a conservative benchmark for risk interpretation.

- II. Benzotriazoles:** Regulatory benchmark values for benzotriazole and associated triazoles are limited compared with PFAS. In this thesis, reference values are therefore taken from established health-based guidance documents. The Minnesota Department of Health (MDH) suggests a guidance value of $20 \mu\text{g L}^{-1}$ for benzotriazole in water, with similar risk assessment advice for closely related tolyltriazoles (Minnesota Department of Health and Health Risk Assessment Unit, 2019). Similarly, a Danish Environmental Protection Agency assessment report on benzotriazole and tolyltriazole provides a health-based drinking-water quality criterion based on the same guideline value of $20 \mu\text{g L}^{-1}$ (Beltoft *et al.*, 2013). Given the limited availability of harmonised standards for benzotriazoles, these values are used as practical indicators of groundwater contamination.
- III. Alkylphenols:** For alkylphenols, drinking-water standards are not defined in a harmonised manner neither, but environmental guideline values exist for aquatic-life protection. The Canadian Council of Ministers of the Environment (CCME) established a Canadian Water Quality Guideline for the protection of freshwater aquatic life of $1.0 \mu\text{g/L}$ for nonylphenol and its ethoxylates (Canadian Council of Ministers of the Environment, 2002). This concentration is considered here as a reference value to interpret simulated concentrations for nonylphenol diethoxylate in a conservative environmental-protection perspective.

Overall, these benchmarks are used to (i) identify which compounds remain potentially of concern after vadose-zone transfer and attenuation, and (ii) provide an objective basis for discussing the concentrations at the aquifer scale.

5.2.3. Definition of “worst-case” and “realistic-case” simulations

Transport modelling developed earlier in section 4 relied on a scenario-based approach to represent uncertainty in transport and attenuation processes: sorption, biodegradation/transformation, and air–water interfacial retention for PFAS. To evaluate the aquifer vulnerability to contamination under MAR conditions, this larger set of scenarios is condensed into two parameter sets representing worst-case and realistic-case contaminant transport during recharge operations with untreated runoff.

- **Worst-case simulation.** This configuration is designed to maximise the potential transfer of contaminants across the loess–chalk interface. It combines (i) a hazard set-up based on recharge water concentrations corresponding to the highest levels reported in untreated urban runoff and (ii) parameter choices leading to minimal attenuation and/or maximal mobility in the vadose zone. Sorption parameters are taken from batch experiments, except for PFOS, PFBA and PFPeA for which values are derived from literature. In addition, air–water interfacial retention is not considered for PFAS. These selections provide weaker retention in the sorbed phase. Finally, biodegradation/transformation is applied only in the aqueous phase to limit mass removal, consistent with the worst-case assumption.
- **Realistic-case simulation.** This configuration intends to represent the most plausible contaminant transport behaviour, based on the experimental evidence obtained in chapter 5 and modelling choices developed in this chapter. It combines (i) a realistic hazard set-up with recharge water concentrations imposed at the median levels reported in untreated urban runoff, and (ii) attenuation parameters selected using the most defensible parameterisation for each contaminant family. Sorption coefficients are taken from batch experiments when the

resulting estimates are consistent with literature ranges. Otherwise (or when experimental data are insufficient), literature-based values are applied. For PFAS, sorption explicitly accounts for AWI retention, including the scaling factor, to capture the overall complexity of PFAS behaviour in partially saturated conditions. Biodegradation and biotransformation are applied in both the aqueous and sorbed phases. Since the extent to which sorbed-phase biodegradation/transformation is not well known per contaminant, the sorbed-phase biodegradation/transformation rate is set to 50% of the aqueous-phase rate, representing an intermediate assumption between 0% (no sorbed-phase removal) and 100% (same efficiency as in the aqueous phase).

The detailed parameter values retained for each simulation, including recharge-water concentrations, sorption coefficients and biodegradation/transformation rates, and PFAS-specific retention assumptions, are summarised in Table 25 and Table 26. These parameter sets constitute the reference framework used for subsequent vulnerability and first-order risk interpretation.

In the worst-case simulation, the sum PFAS and total PFAS concentrations imposed in recharge water exceed the reference values of 100 and 500 ng L⁻¹ respectively, indicating a high hazard level and justifying a specific evaluation of the potential transfer of PFAS compounds toward the underlying chalk aquifer. By contrast, recharge-water concentrations of benzotriazole, tolyltriazole and NP2EO remain well below their corresponding guideline values. These compounds are nevertheless retained in the assessment to evaluate their transfer behaviour through the vadose zone, even though the concentration levels reported here do not suggest a significant hazard. Similar conclusions apply to the realistic-case simulation, although in that case the sum PFAS concentration in recharge water remains just below the 100 ng L⁻¹ reference value (98 ng L⁻¹).

Table 25. Parameters and assumptions associated to each simulated contaminant under the worst-case simulation scenario. Contaminant concentrations indicated in red indicate those that exceed reference guideline values.

Worst-case						
Compound	Input concentration (ng L ⁻¹)	Sorption	K _d (L kg ⁻¹)	Inclusion of AWI + scaling factor?	Biodegradation rate in aqueous phase (days ⁻¹)	Sorbed phase biodegradation/biotransformation?
Bzt	1400	Batch derived	0.49	not relevant	0.016	no
tlt	440		0.64		0.022	
NP ₂ EO	126		0		0.012	
PFOA	19	Literature-based	0.44	no	0	not relevant
PFOS	310		23		0	
PFHxA	60	Batch-derived	0.47		0	no
6:2 FTS	590		0.99		0.016	
PFECHS	490	Literature-based	0		0	not relevant
PFPeA	0		0.79		0	
PFBA	0		0.49		0	
Sum PFAS	389					
Total PFAS	1469					

Table 26. Parameters and assumptions associated to each simulated contaminant under the realistic case simulation scenario. Contaminant concentrations indicated in red indicate those that exceed reference guideline values.

Realistic-case						
Compound	Input concentration (ng L ⁻¹)	Sorption	K _d (L kg ⁻¹)	Inclusion of AWI + scaling factor?	Biodegradation rate in aqueous phase (days ⁻¹)	Sorbed phase biodegradation/biotransformation?
Bzt	895	batch-derived	0.49	Not relevant	0.016	Yes, with $\alpha = 0.50$
tlt	400		0.65		0.022	
NP ₂ EO	56	literature-based	21		0.012	
PFOA	19		5.7	yes	0	not relevant
PFOS	24	batch-derived	46		0	
PFHxA	55		0.47		0	
6:2 FTS	180	literature-based	8.5		0.016	Yes, with $\alpha = 0.50$
PFECHS	210		52	not possible	0	not relevant
PFPeA	0		0.79		0	
PFBA	0		0.49		0	
Sum PFAS	98					
Total PFAS	488					

5.3. Hesbaye chalk aquifer vulnerability

5.3.1. Vulnerability to benzotriazoles and nonylphenol diethoxylate

As shown in Figure 61, the Hesbaye chalk aquifer is classified as moderately vulnerable to benzotriazole under the realistic-case configuration ($f = 7.5\%$) and highly vulnerable under the worst-case configuration ($f = 17\%$). Despite these non-negligible exported mass fractions, the computed ER are equal to zero in both scenarios ($\ll 1$), indicating that the estimated concentrations remain far below the selected reference values and therefore do not suggest a significant groundwater-quality concern under the adopted assumptions. This behaviour is explained by the inclusion of biodegradation, which under the adopted kinetic parameterisation, rapidly attenuates benzotriazole concentration during downward migration. This suggests that even under prolonged MAR operation the likelihood of benzotriazole accumulation at the loess–chalk interface would remain limited. A similar pattern is obtained for the tolyltriazoles, with $f = 2.6\%$ (realistic-case) and $f = 10.4\%$ (worst-case), corresponding to moderate to high vulnerability. Nevertheless, ER values also remain again equal to zero, consistently indicating efficient attenuation in the vadose zone and a very limited potential for groundwater-quality concern under the simulated conditions.

In contrast, NP₂EO shows strong divergence between the realistic-case and worst-case configurations (Figure 62), reflecting the uncertainty associated with its retention behaviour. Under the worst-case configuration, the sorption parameterisation is derived from batch experiments in which no sorption was observed. NP₂EO is therefore simulated as highly mobile, leading to $f = 34\%$ and classifying the aquifer as highly vulnerable with respect to NP₂EO transfer. Under the realistic-case configuration, NP₂EO is assumed to sorb relatively strongly, resulting in negligible downward migration ($f = 0\%$). Nevertheless, despite the high transfer potential simulated in the worst-case configuration, the computed ER is equal to zero in both scenarios, indicating that the estimated concentrations remain negligible relative to the selected reference value. Within the assumptions of the present model, this indicates that infiltration of untreated runoff water is unlikely to pose concerns to groundwater quality in terms of NP₂EO.

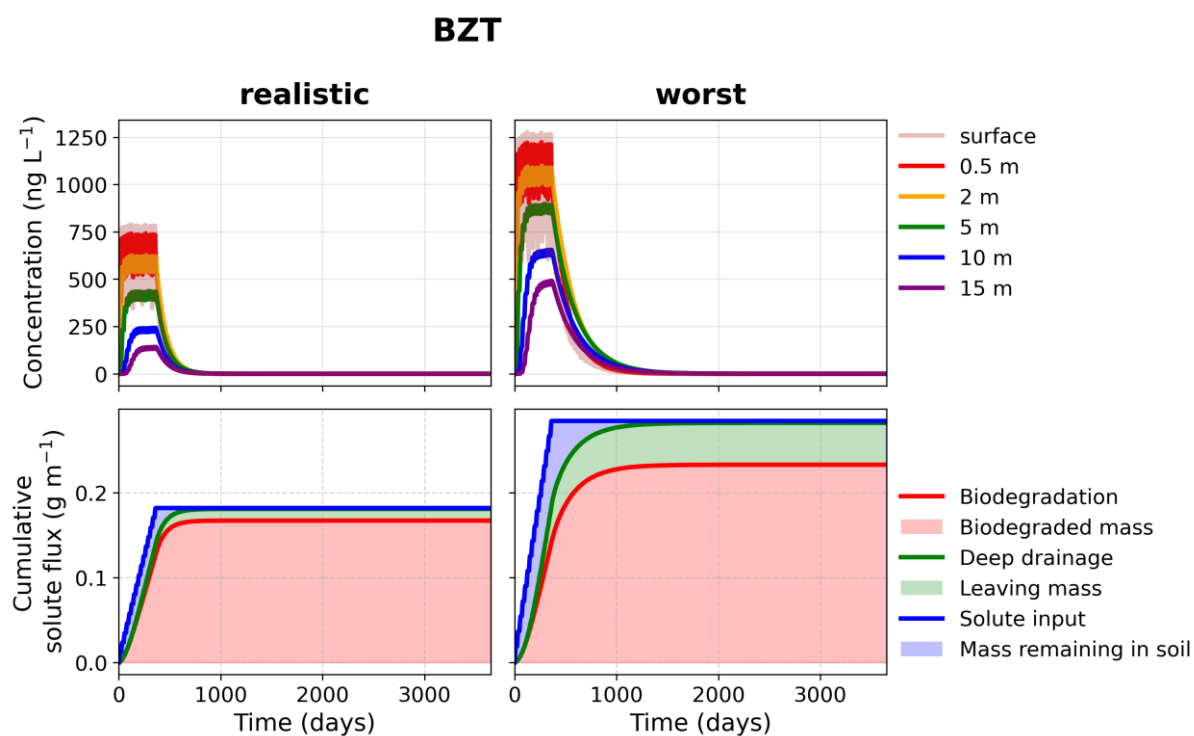


Figure 61. Benzotriazole evolution over depth and cumulative mass balance for both realistic and worst-case simulations.

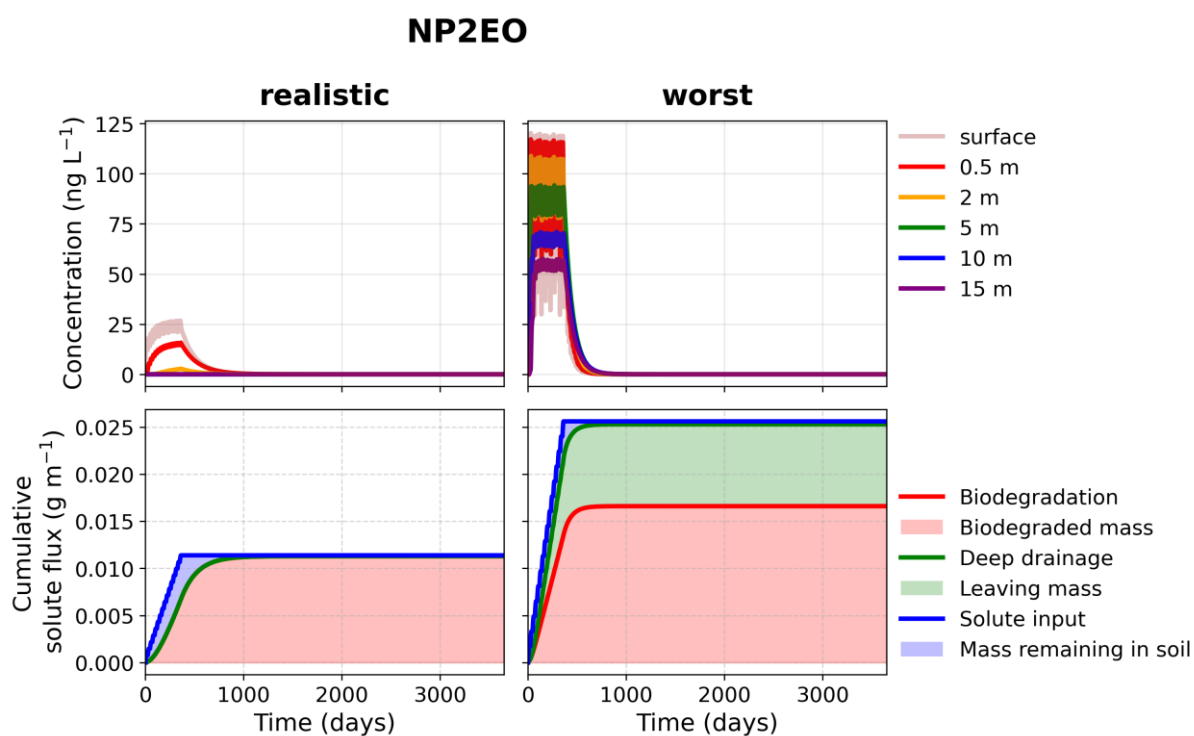


Figure 62. Nonylphenol diethoxylate evolution over depth and cumulative mass balance for both realistic and worst-case simulations.

5.3.2. Vulnerability to PFAS

PFAS represent the most critical contaminant family in the present assessment because of their persistence and their limited retention in the vadose zone for some of them. The vulnerability

indicators derived from the HYDRUS-2D simulations show that PFAS behaviour is highly compound-specific and dependent on the retention parameterisation adopted for the realistic-case and worst-case configurations. Table 27 summarises, for each PFAS, the exported fraction f , the predicted concentration C_{15m} at the loess–chalk interface, and the corresponding ER after 10 years for both realistic-case and worst-case simulations. In addition, the section 3 of Annex E illustrates graphically PFAS concentration evolution at different depths as well as associated cumulative mass balance for both realistic and worst-case configurations.

Table 27. Vulnerability indicators of the Hesbaye chalk aquifer associated with PFAS compounds. ER values greater than 1 are highlighted in red to indicate an exceedance of the selected reference value.

Compound	Transferred mass fraction f (%)		Predicted concentration at 15 m depth C_{15m} (ng L ⁻¹)		ER	
	realistic	worst	realistic	worst	realistic	worst
PFOA	0	60	0	16	-	-
PFOS	0	0	0	0	-	-
PFECHS	0	93	0	49	-	-
6:2 FTS (precursor)	0	9.1	0	0.078	-	-
PFBA (TP)	35	37	2.0	9.1	-	-
PFPeA (TP)	21	27	8.7	38	-	-
PFHxA (input + TP)	36	35	53	80	-	-
Sum PFAS	-	-	64	143	0.64	1.43
Total PFAS	-	-	64	192	0.13	0.38

PFOS is predicted to be effectively immobilised, with no export across the loess–chalk interface in either configuration ($f = 0\%$, $C_{15m} = 0$ ng L⁻¹), which is consistent with its very strong sorption behaviour. In contrast, PFOA shows pronounced scenario dependency: transfer is negligible in the realistic-case ($f = 0\%$, $C_{15m} = 0$ ng L⁻¹), whereas the worst-case configuration results in significant export ($f = 60\%$) and a non-negligible interface concentration ($C_{15m} = 16$ ng L⁻¹). This contrast is consistent with the weak retention assumed in the worst-case parameter set where batch-derived sorption is comparable to short-chain PFAS, combined with the absence of degradation. An even stronger discrepancy is observed for PFECHS, with no transfer in the realistic-case ($f = 0\%$, $C_{15m} = 0$ ng L⁻¹) but extremely high export in the worst-case ($f = 93\%$, $C_{15m} = 48.91$ ng L⁻¹), reflecting the absence of sorption observed in the batch experiments.

A key outcome from this thesis is that vulnerability is not controlled only by the parent PFAS introduced with recharge water, but also by transformation products when relevant. This is notably illustrated by 6:2 FTS, the only PFAS precursor considered in this study, for which biotransformation is explicitly represented. The parent compound shows limited transfer even under the worst-case configuration ($f = 9.1\%$, $C_{15m} = 0.08$ ng L⁻¹), indicating retention and/or transformation in shallow soils. In contrast, its short-chain transformation products show significant export fractions in both configurations. PFBA reaches $f = 35\%$ and $C_{15m} = 2$ ng L⁻¹ in the realistic-case, and $f = 37\%$ and $C_{15m} = 9.12$ ng L⁻¹ in the worst-case. On the other hand, PFPeA reaches $f = 21\%$ and $C_{15m} = 8.7$ ng L⁻¹ in the realistic-case configuration,

and $f = 27\%$ and $C_{15m} = 37 \text{ ng L}^{-1}$ in the worst-case. The most critical compound is PFHxA, because it is present in the recharge water and is also produced as a transformation product. PFHxA displays high export fractions under both configurations ($f_{\text{realistic}} = 36\%$, $f_{\text{worst}} = 35\%$) and the highest predicted interface concentrations among the PFAS considered ($C_{15m,\text{realistic}} = 53 \text{ ng L}^{-1}$, $C_{15m,\text{worst}} = 80 \text{ ng L}^{-1}$). PFHxA is therefore identified as the main driver of PFAS-related vulnerability in this modelling framework.

To relate these results to drinking-water reference guidelines, interface concentrations were combined into (i) *Sum PFAS*, computed here as the sum of PFAS included in the EU list (European Parliament and Council of the European Union, 2020) that are explicitly simulated (PFOA, PFOS, PFBA, PFPeA, PFHxA), and (ii) a study-specific *PFAS total*, computed as the sum of all modelled PFAS (including PFECHS and 6:2 FTS). Under the realistic-case configuration, *Sum PFAS* corresponds to an *ER* of 0.64, indicating that the predicted concentration remains below the 100 ng L^{-1} guideline. Under the worst-case configuration, *Sum PFAS* reaches an *ER* of 1.43, indicating exceedance of the recommended guideline. By contrast, *PFAS total* corresponds to *ER* values of 0.13 and 0.38 under the realistic-case and worst-case configurations, respectively, and therefore remains below the 500 ng L^{-1} guideline in both cases. These values are obtained after only one year of MAR operations followed by natural conditions. Repeated MAR operations over multiple consecutive years would be expected to increase mass transfer and interface concentrations for persistent mobile PFAS, likely leading to exceedance of the relevant quality guidelines. Using the more restrictive SCHEER reference value, the situation becomes highly concerning, as the corresponding *ER* of 6:2 FTS transformation products (PFBA, PFPeA and especially PFHxA) would be well above 1 even under realistic-case conditions. By contrast, long-chain PFAS (PFOS, PFOA and PFECHS) are mainly retained in shallow soil layers and do not contribute to concentrations at the loess–chalk interface within the simulated period.

5.3.3. Overall vulnerability

Overall, the HYDRUS-2D simulations indicate a clear contrast between contaminant families. For benzotriazoles, the exported mass fractions f may reach moderate to high vulnerability classes under both simulation configurations, but predicted concentrations at the loess–chalk interface remain close to zero due to rapid biodegradation. A similar conclusion applies to NP2EO: despite the very high mobility obtained under the worst-case scenario, biodegradation prevents breakthrough at the loess–chalk interface. These results suggest that recharge with untreated runoff is unlikely to generate relevant concentrations of benzotriazoles or alkylphenols at the loess–chalk interface.

In contrast, PFAS represent the most concerning group. Several PFAS are strongly retained, such as PFOS, PFECHS, and PFOA, but the simulations highlight significant vulnerability for mobile and persistent PFAS. This is particularly the case for short-chain species associated with the 6:2 FTS precursor. Under the worst-case configuration, the combined *Sum PFAS* at the loess–chalk interface already exceeds the 100 ng L^{-1} drinking-water guideline after one year of MAR operation. Even under realistic-case conditions, PFAS predicted concentrations remain high, and repeated MAR operation over multiple years would be expected to increase cumulative mass transfer and interface concentrations, potentially leading to exceedances well above guideline levels.

The interface concentrations reported here are local values extracted at the loess–chalk boundary and therefore represent a potential input to the chalk formation rather than a groundwater concentration within the saturated aquifer. Aquifer concentrations will depend on dilution and spreading processes in the saturated zone, including advection, hydrodynamic dispersion and mixing under groundwater flow. Nevertheless, the vulnerability indicators provide a basis for identifying the compounds most likely to drive groundwater quality concerns in a MAR context. In the present case, results identify 6:2

FTS and its transformation products (PFHxA, PFPeA, and PFBA) as priority substances for further assessment of their aquifer-scale concentrations after dilution.

5.4. Risk assessment of contamination at aquifer-scale

The vulnerability indicators discussed in section 5.3 quantify the potential for contaminants to cross the loess-chalk interface, but they do not represent concentrations within the saturated chalk aquifer. The present section therefore provides first-order estimation of contaminant concentration at aquifer-scale by converting the simulated transferred mass into an equivalent groundwater concentration after dilution by groundwater flow. The purpose is to obtain an order-of-magnitude estimate of the concentration range that may occur in the aquifer under MAR operations with untreated runoff water, and to support comparison with the reference guideline values introduced in section 5.2.2. This scaling exercise is applied only to PFAS, since benzotriazole, tolyltriazole, and nonylphenol diethoxylate were shown to yield negligible concentrations at the loess–chalk interface within the present modelling framework.

The analysis is carried out at two levels. First, a theoretical scaling exercise is performed at the scale of the Kemexhe pilot basin, using the simulated transferred masses to estimate equivalent aquifer concentrations beneath the experimental site. This first step is primarily intended to provide a consistent link between the vadose-zone simulations and a simplified aquifer-scale concentration estimate. Second, a more realistic full-scale MAR configuration is considered, based on a basin dimensioned for operational recharge volumes, to discuss how the results may evolve under conditions more representative of actual MAR implementation.

5.4.1. Conceptual mixing model

For each contaminant and scenario, the cumulative solute mass exported through the lower boundary of the HYDRUS domain is taken as the mass potentially transferred to the chalk formation over the considered period. This mass integrates the combined effect of the imposed recharge-water concentrations, the hydraulic forcing during MAR operation and subsequent drainage, and vadose-zone attenuation processes (sorption and biotransformation). Since a symmetry assumption is used in the HYDRUS-2D domain, cumulative exported masses are multiplied by two to upscale results according to the full basin extension.

A simplified mixing approach is then adopted to relate the transferred mass to an equivalent aquifer concentration. This approach is notably described in the SPW reference guide for risk studies (SPW, 2018) and is largely inspired by the work of Connor et al. (1997). Figure 63 depicts a schematic representation of the conceptual mixing model applied in this study.

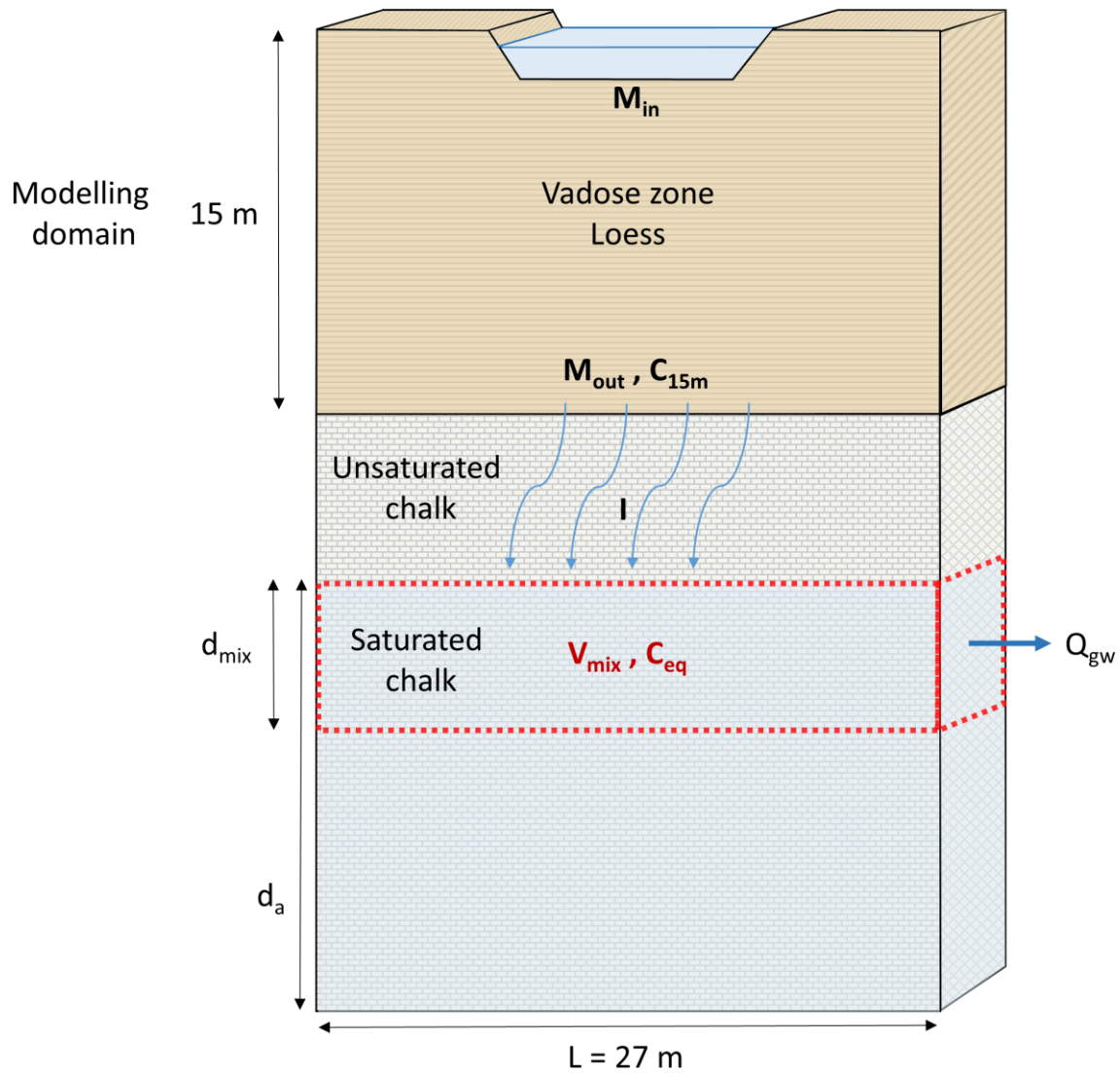


Figure 63. Conceptual mixing model applied to the Hesbaye chalk aquifer.

The mixing approach can be described as follows. First, the average concentration within a conceptual groundwater control volume is approximated as:

$$C_{eq} = \frac{M_{out}}{V_{mix}} \quad (41)$$

Where $M_{out} [ML^{-1}]$ is the cumulative mass transferred to the chalk formation and $V_{mix} [L^3 L^{-1}]$ is an effective mixing volume representing the volume of groundwater per unit width over which the mass is diluted. This mixing volume is expressed as:

$$V_{mix} = Q_{gw} \cdot T \quad (42)$$

Where Q_{gw} is the groundwater flow per unit width through the control volume [$L^2 T^{-1}$] and T is the time over which mixing and renewal are considered [T]. Groundwater flow can be estimated using Darcy's law:

$$Q_{gw} = K \cdot i \cdot d_{mix} \quad (43)$$

where K is the hydraulic conductivity of the chalk [$L T^{-1}$], i the hydraulic gradient [-], and d_{mix} an effective mixing thickness of the saturated chalk contributing to dilution beneath and downgradient of the infiltration basin. Mixing thickness d_{mix} is approximated following the mixing-zone depth concept used in the U.S. EPA Soil Screening framework (EPA, 1996), where mixing results from (i) vertical spreading by dispersivity along the travel distance (d_{α_v}) and (ii) downward penetration of infiltrating water (d_{I_v}), limited by aquifer thickness. It is expressed as:

$$d_{mix} = d_{\alpha_v} + d_{I_v} \quad (44)$$

With:

$$\begin{cases} d_{\alpha_v} = (2\alpha_v L)^{\frac{1}{2}} \\ d_{I_v} = d_a \left\{ 1 - \exp \left[\frac{-LI}{K d_a} \right] \right\} \end{cases} \quad (45)$$

Where L is the source length parallel to groundwater flow [L], I is the infiltration rate [$L T^{-1}$], d_a is the saturated aquifer thickness [L], and α_v is the vertical dispersivity [L]. Vertical dispersivity is expressed as a fraction of longitudinal dispersivity, $\alpha_v = 0.056 \alpha_L$ (Gelhar and Axness, 1983). These equations indicate that the estimated mixing depth increases with source length in the direction of groundwater flow. As a result, infiltration basins elongated parallel to the flow direction would promote a larger mixing depth than basins oriented transversely, meaning that basin geometry may influence the dilution factor applied to transferred contaminants.

In the south-eastern part of the Hesbaye chalk aquifer, which corresponds to the area considered for MAR implementation, α_L was estimated to be approximately 3 m (Orban, 2008), yielding $\alpha_v \approx 0.17$ m. The source length L is defined as the length of the lower boundary of the model, which is of 27 m when considering the entire basin. The regional hydraulic gradient i is set to 0.01 (Brouyère *et al.*, 2004). The hydraulic conductivity K of the saturated chalk aquifer was taken from the statistical database ($n=60$) developed within the SERAN project (Briers *et al.*, 2017), using a mean reference value of $3 \times 10^{-4} \text{ m s}^{-1}$ for the Hesbaye chalk aquifers. Based on drilling data at the study site, the saturated thickness of the Hesbaye chalk aquifer is set to $d_a = 22$ m. Finally, the infiltration rate is defined as the mean infiltration rate simulated at the lower boundary during the year of MAR operation, yielding $I = 1.19 \times 10^{-6} \text{ m s}^{-1}$. Using these parameters in Eq. 36 and 37 results in a mixing depth of $d_{mix} = 11.5$ m.

5.4.2. First-order C_{eq} estimates for the study site

The conceptual mixing model (Eq. 41) is first applied to the Kemexhe pilot basin to derive a theoretical first-order estimate of PFAS concentrations at aquifer scale after MAR operations. In the present approach, V_{mix} is compound-specific because the time window T is taken as the residence time associated with transfer through the vadose zone, defined here as the time lag between (i) the first arrival of a solute signal at the loess-chalk interface and (ii) the time at which the maximum cumulative exported mass is reached at the same interface. This choice allows the dilution calculation to remain consistent with the timing of contaminant delivery to the chalk formation derived from the HYDRUS-2D simulations.

For this pilot-scale exercise, results are presented for two operational assumptions. First, the calculation is performed for the simulated configuration corresponding to one year of MAR operation,

followed by natural conditions. Second a more conservative and operationally relevant case is considered in which MAR is implemented over ten consecutive years. In this simplified extension, the total transferred mass is assumed to scale linearly with the number of operational years. This assumption does not explicitly represent the progressive establishment of a continuous contaminant signal under repeated recharge, but rather provides a conservative upper-bound estimate of cumulative mass transfer based on the one-year simulation. Assuming that dilution occurs within the same conceptual mixing volume, the resulting equivalent aquifer concentrations are therefore multiplied by ten relative to the one-year case.

Table 28 summarises for each PPFAS and for both realistic-case and worst-case parameter sets, the equivalent aquifer concentration C_{eq} obtained for one year and ten years of MAR operations. Under the adopted mixing assumptions, equivalent concentrations remain below the EU Sum PFAS benchmark (100 ng L^{-1}) for both operational durations, whereas Total PFAS in the worst-case reaches 222 ng L^{-1} after ten years, largely driven by PFECHS and, to a lesser extent, by PFHxA and the 6:2 FTS precursor. This concentration remains below the guideline value of 500 ng L^{-1} for Total PFAS.

Table 28. Equivalent aquifer concentrations C_{eq} (ng L^{-1}) for the pilot site under one-year and ten-year of MAR operations. PFAS that are not included in Sum PFAS are outlined in yellow.

Compound	Realistic: 1 year	Realistic: 10 years	Worst-case: 1 year	Worst-case: 10 years
PFOA	0	0	0.44	4.4
PFOS	0	0	0	0
PFECHS	0	0	17.2	172
6:2 FTS	0	0	2.9	29
PFBA	0.031	0.314	0.1	1
PFPeA	0.106	1.06	0.39	3.9
PFHxA	0.91	9.1	1.2	12
Sum PFAS	1.04	10.4	2.13	21.3
Total PFAS	1.04	10.4	22.2	222

5.4.3. Application to a realistic full-scale MAR basin

While the pilot-scale results suggest limited likelihood of guideline exceedance under the adopted assumptions, they are obtained for a small experimental basin and cannot be directly extrapolated to operational MAR volumes without scaling. The conceptual mixing model was therefore applied to a full-scale configuration representative of a realistic MAR system, consisting of a single basin designed to recharge $1.5 \times 10^6 \text{ m}^3 \text{ year}^{-1}$. As described in section 2.2.2, the corresponding footprint is $33,615 \text{ m}^2$, approximated here as a square basin of $183 \text{ m} \times 183 \text{ m}$. Upscaling from the pilot basin (81 m^2 , $9 \text{ m} \times 9 \text{ m}$) is performed consistently with the 2D formulation adopted in the model, i.e. per unit width in the third dimension. Under the assumption of spatially uniform recharge-water concentrations and infiltration fluxes, the injected mass per unit width scales with the source length parallel to groundwater flow. Consequently, for a square basin, the mass input per unit width is increased by a factor:

$$\frac{M_{in,full}}{M_{in,pilot}} \approx \frac{L_{full}}{L_{pilot}} = \frac{183}{9} = 20.33 \quad (46)$$

And the transferred mass M_{out} used in Eq. 41 is scaled accordingly while maintaining the same export fraction f depending on scenario. In parallel, the mixing volume per unit width also increases because the larger basin implies a larger source length L in Eq. 44 and 45, which increases the mixing thickness d_{mix} . For $L=183$ m, the mixing depth computed from the EPA-based formulation exceeds the saturated aquifer thickness. Accordingly, d_{mix} is limited to the aquifer thickness so that $d_{mix} \approx d_a$. As a result, scaling from pilot to full-scale basin increases both the exported mass M_{out} and mixing volume V_{mix} , and equivalent aquifer-scale concentrations C_{eq} therefore do not increase linearly with basin footprint.

Similarly than for the pilot site, equivalent aquifer concentrations are reported for one year of MAR operation and for ten consecutive years, assuming a linear increase of exported mass with the number of operational years and unchanged mixing conditions. Table 29 summarises the resulting C_{eq} values for each PFAS under realistic-case and worst-case parameter sets.

Table 29. Equivalent aquifer concentrations C_{eq} (ng L⁻¹) for full-scale configuration under one-year and ten-year of MAR operations. PFAS that are not included in Sum PFAS are outlined in yellow. Sum and Total PFAS concentration exceeding guidelines are highlighted in red.

Compound	Realistic: 1 year	Realistic: 10 years	Worst-case: 1 year	Worst-case: 10 years
PFOA	0	0	4.7	47
PFOS	0	0	0	0
PFECHS	0	0	183	1831
6:2 FTS	0	0	30.5	305
PFBA	0.33	3.3	1.06	10.6
PFPeA	1.13	11.3	4.2	42
PFHxA	9.6	96	12.7	127
Sum PFAS	11.1	111	22.6	226
Total PFAS	11.1	111	236	2360

Under this full-scale configuration, equivalent concentrations increase relative to the pilot basin, reflecting the higher mass loading associated with a much larger recharge system. However, this increase remains partly moderated by the larger mixing volume. In terms of quality guidelines, Sum PFAS remains below the 100 ng L⁻¹ threshold after one year in both scenarios, but slightly exceeds it after ten years in the realistic-case configuration (111 ng L⁻¹) and more markedly in the worst-case configuration (226 ng L⁻¹). In the realistic-case, this exceedance is driven primarily by PFHxA, with a smaller contribution from PFPeA. In contrast, Total PFAS already exceeds 100 ng L⁻¹ in the worst-case configuration after one year (236 ng L⁻¹) and reaches 2360 ng L⁻¹ after ten years, well above the 500 ng L⁻¹ guideline. This result is largely driven by PFECHS, and to a lesser extent by PFHxA and the 6:2 FTS precursor. This worst-case *Total PFAS* estimate should nevertheless be interpreted with caution, since it is strongly controlled by PFECHS, which is considered to display limited mobility under more realistic conditions and is therefore unlikely to contribute to such aquifer-scale concentration levels.

5.4.4. Limitations of the mixing model

The aquifer-scale concentrations derived from the conceptual mixing approach are intended as first-order estimates and should be interpreted acknowledging several important limitations:

- First, the definition of the mixing volume V_{mix} is inherently uncertain because it depends on parameters that are themselves poorly constrained at site scale. In particular, the mixing thickness d_{mix} is sensitive to the selected values of hydraulic conductivity K , hydraulic gradient i , infiltration I , and dispersivity parameters (notably α_L and the assumed relation used to derive α_V). Among these, hydraulic conductivity is especially important because it directly controls groundwater flow and therefore the effective dilution capacity of the aquifer. As a result, a difference of one order of magnitude in K may lead to a similar order-of-magnitude change in V_{mix} , and consequently in the estimated concentration C_{eq} . Since these parameters are scale-dependent and may vary spatially, the computed mixing depth and resulting aquifer-scale concentrations may differ substantially for equally plausible parameter sets.
- Second, the upscaling from the pilot basin to a full-scale basin is based on simplified geometric scaling assumptions. It implies notably uniform recharge fluxes and concentrations, linear scaling of transferred mass with source length, and unchanged vadose-zone behaviour. However, as shown by the formulation of the mixing depth, the source length parallel to groundwater flow directly influences d_{mix} . Basin geometry and orientation with respect to groundwater flow may therefore affect the effective mixing volume and the resulting dilution factor. In practice, a larger infiltration basin may also exhibit different hydraulic functioning, which could modify both the magnitude and timing of mass transfer to depth compared with the pilot configuration.
- Third, the mixing model does not represent additional attenuation or delay processes that could occur after contaminants reach the chalk formation. Transport through the unsaturated chalk is not simulated, as well as any potential retention, degradation, or delayed release occurring within this time window. This simplification may overestimate the rapidness and magnitude of mass delivery to the saturated zone for compounds that experience additional retention in chalk.
- Fourth, the conceptual control-volume approach assumes that the transferred mass remains within the mixing volume over the time window T , and that dilution can be represented by complete mixing within V_{mix} . This implies that advective transport out of the control volume is neglected, i.e. no mass is assumed to leave the mixing zone during T . In reality, groundwater flow would progressively transport part of the transferred mass downgradient, so only a fraction of the mass would be available within V_{mix} .

Overall, the HYDRUS-2D modelling framework provides robust insights into relative vulnerability of the Hesbaye chalk aquifer with regards to the studied contaminants, by quantifying the tendency of these to migrate through the vadose zone and reach the chalk formation under contrasted scenarios. However, the aquifer-scale concentration estimates derived from the mixing model remain subject to significant uncertainties. Reducing this uncertainty would require coupling a saturated-zone groundwater flow and transport model for the Hesbaye chalk aquifer to represent explicitly biogeochemical processes within the saturated zone and enabling prediction of concentrations at aquifer scale.

6. Conclusion

This chapter has transferred the experimental knowledge gained on CEC behaviour in loess sediments into a reactive transport modelling framework designed to support the risk/vulnerability assessment of MAR operations in the Hesbaye chalk aquifer context. Using 2D variably saturated flow simulations in HYDRUS, the model has reproduced the main hydraulic dynamics expected beneath an infiltration basin and then explored how different contaminant families could migrate through the loess vadose zone toward the chalk aquifer when MAR is operated in repeated wetting–drying cycles. By combining flow and transport, the modelling provides a coherent way to compare compounds with contrasted properties (sorption and biodegradation/transformation) and to move from laboratory-derived parameters to an assessment of potential groundwater exposure.

The results show a clear differentiation between contaminant groups and overall support a favourable perspective with regards to groundwater protection. For the non-PFAS compounds investigated, the simulations consistently indicate that overall attenuation of contaminant loads is primarily driven by biodegradation, while retention mainly acts as a secondary factor on the fraction that remains temporarily stored within the vadose zone. Under the investigated conditions, this leads to limited transfer of benzotriazoles and NP2EO toward depth, supporting the conclusion that these compounds are unlikely to represent a major groundwater-quality concern in the tested MAR scenarios.

In contrast, PFAS remain the most sensitive group for vulnerability because their persistence and the limited retention of short-chain compounds favour their transport to depth. The simulations have further shown that PFAS behaviour in MAR settings cannot be assessed reliably without accounting for specific processes within the vadose zone. Indeed, incorporating air–water interfacial retention modifies retardation under wetting–drying cycles and affect the timing and magnitude of PFAS export at depth, although short-chain PFAS remain comparatively mobile and can still be transported at depth. Another key outcome is that vulnerability cannot be evaluated solely from parent substances (6:2 FTS), since transformation products can be more mobile and therefore more relevant for aquifer exposure. When the vadose-zone outputs are interpreted at the aquifer scale using the conceptual mixing approach, the resulting equivalent aquifer-scale concentrations are lower than the concentrations predicted at the loess–chalk interface, reflecting dilution by mixing with ambient groundwater. The only configuration indicating a potentially concerning signal corresponds to a full-scale basin operated continuously over a decade. However, this tendency is essentially confined to a worst-case scenario driven by PFECHS, for which batch results indicate negligible sorption. This combination is considered unlikely and therefore not representative of the most plausible outcome. Nevertheless, even if PFAS concentrations in groundwater remain low, repeated infiltration with contaminated urban runoff would still contribute to PFAS accumulation in shallow sediments. This indicates that source-water management remains essential and that runoff water should be treated prior to infiltration.

Several limitations frame the interpretation of these results:

- Sorption was represented by a simplified linear equilibrium model, which does not capture non-linear behaviour, kinetic sorption/desorption, competitive effects, geochemical dependencies (e.g., ionic strength and organic matter), or the possible progressive exhaustion of sorption sites over time, potentially leading to an overestimation of retention capacity during sustained MAR operations.

- The PFAS spectrum did not include very mobile and ultra-short compounds such as trifluoroacetic acid (TFA), which would likely behave closer to conservative tracers.
- The translation from vadose-zone outputs to aquifer-scale concentrations relies on a conceptual mixing model whose parameters remain uncertain and may not fully reflect real mixing in the Hesbaye chalk aquifer.
- The operational representation of MAR remains idealized with prescribed cycles and boundary conditions, while real basins are affected by variability in inflow quality and hydraulics efficiency, operational interruptions, and long-term changes such as clogging and maintenance.
- The reactive parameters obtained from batch experiments must be transferred to field conditions, which introduces uncertainty due to scale effects.
- Although air–water interfacial (AWI) adsorption was included to better represent PFAS behaviour in variably saturated media, the associated parameters remain uncertain and can significantly influence predicted retardation.
- Biodegradation for benzotriazoles and NP2EO was represented through simplified kinetics, without explicit coupling to the spatial and temporal distribution of electron acceptors (notably oxygen and nitrate) that can evolve during wetting–drying operations.
- The interpretation of modelled concentrations in terms of “risk” and “vulnerability” is sensitive to regulatory benchmarks, and EU guideline values for PFAS are still evolving, meaning that being below a given guideline at present time should not be interpreted as a guarantee of long-term “no risk”.

Overall, this chapter provides a structured modelling approach that integrates (i) the water-quality information gained from the sampling campaigns, (ii) the biogeochemical behaviour derived from laboratory experiments, and (iii) field-based infiltration rates representative of MAR basins in the Hesbaye context. By explicitly simulating variably saturated flow and reactive transport through the loess vadose zone, it therefore provides a process-based link between measured concentrations and experimentally derived parameters into predicted transfers through the loess vadose zone, as well as equivalent aquifer-scale concentrations through the conceptual mixing approach. The main contribution of this chapter is to identify and quantify the mechanisms driving the pronounced differences in fate and transport among contaminant families, thereby providing a basis to rank the relative vulnerability of the Hesbaye chalk aquifer to the investigated contaminants. The chapter thus supports a structured discussion of groundwater-quality protection during MAR, and highlights the need for a cautious interpretation of PFAS behaviour and for upstream treatment of urban runoff prior to infiltration. The final chapter provides the overall synthesis and conclusion of this thesis.

Chapter 8

Conclusion

1. Research question and thesis contribution

This PhD thesis has addressed a central question for groundwater management in regions facing persistent groundwater deficits: to what extent can urban runoff be mobilised as a recharge resource for MAR operations while preserving quality, particularly when recharge occurs through a thick vadose zone and groundwater is ultimately exploited for drinking water production. To investigate this question, the thesis has focused on the Hesbaye chalk aquifer as a relevant case study to examine MAR configurations that remain comparatively under-documented in practice, notably the use of urban runoff as a recharge source combined with infiltration through loamy/loess deposits, which are often considered unfavourable for MAR because of their low permeability and the associated constraints on sustaining infiltration.

To answer the research question, the thesis has followed a progressive framework combining quantitative and qualitative assessments before integrating these aspects into a risk-oriented evaluation. First, runoff has been characterised as a potential recharge water source through monitoring across contrasted stormwater basins and seasons, to document variability in hydrochemistry and contaminant occurrence. Second, laboratory experiments have been conducted to investigate key attenuation processes in loess sediments under controlled conditions, with a focus on sorption and biodegradation, while chemical modelling has been used to reproduce experimental observations and estimate governing parameters. Third, infiltration behaviour has been investigated at field scale through infiltration tests monitored with conventional instrumentation and distributed temperature sensing with fiber optics technology, allowing spatial and temporal variations in infiltration rates to be quantified under realistic operating conditions. Finally, the quantitative and qualitative results have been integrated within a HYDRUS-based variably saturated flow and solute transport framework to reproduce recharge operations numerically and to translate source-water quality, vadose-zone processes, and parameter uncertainties into a quantitative assessment of contaminant transfer potential to the underlying aquifer.

2. Main findings

This thesis has shown that urban runoff can represent a non-negligible recharge resource, particularly where stormwater infrastructures already collect significant volumes. However, the work has also demonstrated that recharge volumes alone are not a sufficient basis to assess MAR in a drinking-water context. MAR acceptability is ultimately governed by groundwater protection requirements, meaning that recharge performance and groundwater-quality response must be addressed jointly.

Urban runoff monitoring across contrasted basins and seasons has shown that candidate source waters are highly variable. Marked differences have been observed in mineralisation (EC), pH, redox conditions (O_2 /ORP), and ionic composition. Seasonal effects have been especially clear in winter, with a shift towards Na–K–Cl dominance consistent with de-icing inputs, while basins influenced by wastewater inflows have displayed persistently higher mineralisation and more reducing conditions. These contrasts imply that recharge water could induce hydrochemical perturbations during percolation and may increase operational sensitivity to redox disturbance and clogging.

Sampling campaigns have also confirmed the occurrence of pollutant families classically associated with urban runoff generated from traffic-related and airport infrastructures, such as metals and PAHs.

In addition, targeted screening has revealed the presence of PFAS, benzotriazoles, and alkylphenols. These substances are of concern because their persistence and mobility imply that repeated recharge of untreated water may lead to long-term groundwater-quality pressure, even at low concentrations. These results have guided the selection of representative contaminants for the experimental and modelling work.

Batch experiments in loess have shown that attenuation occurs but is strongly compound-dependent. NP₂EO has exhibited strong attenuation mainly driven by biodegradation. Benzotriazole and tolyltriazole have shown moderate attenuation through combined sorption and biodegradation, with biodegradation being more efficient under oxic than under nitrate-reducing conditions. In contrast, PFAS have shown the lowest attenuation, indicating limited removal under the tested conditions. Sorption potential has been more apparent for PFOS and 6:2 FTS, whereas short-chain PFAS have shown weaker retention.

Field infiltration experiments have shown that loess is not necessarily an operational barrier to surface-based MAR systems when infiltration is properly managed. Distributed temperature sensing (DTS) has highlighted spatial heterogeneity and temporal evolution of infiltration, and has provided operationally representative infiltration fluxes on the order of 25–30 cm day⁻¹ during drainage phases. Such rates are compatible with operational MAR requirements and demonstrate that loess/loamy deposits, despite being commonly considered unfavourable for surface-based MAR operations, should not be excluded a priori when appropriate operational strategies are implemented.

Numerical integration of flow and transport has indicated that benzotriazoles and NP₂EO are unlikely to reach the loess–chalk interface at relevant concentrations under the tested scenarios, primarily because biodegradation limits breakthrough during percolation. In contrast, PFAS have emerged as the dominant constraint for MAR with untreated runoff. The simulations have identified PFHxA as the most critical compound, due to both its presence in recharge water and its production as a transformation product from 6:2 FTS, resulting in high export fractions and the highest predicted concentrations at the loess–chalk interface among the simulated PFAS. In the pilot-scale configuration representative of the investigated basin, the simulations indicate PFAS concentrations below the selected drinking-water guideline values under the tested operating scenarios. However, when considering a full-scale basin dimensioned for operational recharge volumes and converting exported contaminant masses into equivalent aquifer-scale concentrations using the conceptual mixing approach, the results suggest that PFAS may become a concern. This conclusion remains associated with significant uncertainty due to the sensitivity of the mixing model to poorly constrained aquifer parameters and geometric scaling assumptions.

Overall, this thesis has supported a clear conclusion: runoff-based MAR can be operated at meaningful infiltration rates in loess-covered settings, with loess acting as a natural protective layer against several organic contaminants. However, in a drinking-water aquifer context, MAR acceptability is ultimately controlled by the management of recharge-water chemistry and by the control of persistent and mobile contaminants, with PFAS emerging as the primary driver of long-term groundwater-quality concern.

3. Limitations

Despite the integrated design of this PhD thesis, several limitations should be acknowledged as they affect the representativeness of the derived data and the level of confidence that can be assigned to the broader interpretation of results.

A first limitation concerns runoff characterisation. While the three campaigns have captured seasonal contrasts, the number of sampled events has remained limited and has not always reflected “pure” runoff conditions. Some basins have shown mixed signals related to stagnant storage and/or continuous wastewater inflows, which has complicated the attribution of measured concentrations to runoff-driven inputs. In addition, only a small number of basins has been investigated and the typologies have remained limited (mainly airport- and traffic-related infrastructures). As a result, the derived chemical signatures cannot be considered representative of the full diversity of stormwater basins, land uses, and event conditions that control contaminant wash-off and occurrence.

The laboratory batch experiments have also included methodological limitations. Transformation products have not been analysed, which is particularly relevant for PFAS precursors (e.g., 6:2 FTS) for which apparent attenuation may reflect biotransformation into more mobile products. The biotic control has not performed as initially planned, which has limited the ability to quantify biodegradation independently from sorption. Finally, solid-phase concentrations have not been measured at the end of the experiments, preventing closure of mass balances and confirmation of sorption as a removal pathway for the “missing” mass.

At field scale, the DTS monitoring has demonstrated that infiltration is spatially heterogeneous and temporally dynamic, but the experimental design has limited direct comparison between approaches. Passive-DTS has primarily captured early filling conditions, whereas active-DTS has been applied during drainage, corresponding to different hydraulic phases. In addition, infiltration tests have essentially been performed as single-event experiments. Seasonal repetitions would be required to quantify how initial moisture conditions and seasonal variability influence infiltration capacity.

Finally, the modelling framework has necessarily relied on simplifying assumptions. The geometry and geology have been simplified and homogenised, and transport through the unsaturated chalk has not been represented explicitly. Uncertainty has been explored through scenario testing, but not within a fully probabilistic/stochastic framework. Biodegradation has been represented in a simplified manner and has not explicitly coupled redox evolution to microbial kinetics. Moreover, the modelling has focused on the vadose zone beneath the basin. Therefore, aquifer-scale concentrations are attached with uncertainty because dilution and transport within the saturated chalk have not been simulated. The modelling results should therefore be interpreted primarily as a vulnerability-oriented assessment rather than as a purely predictive tool.

Overall, these limitations have not invalidated the main conclusions, but they have delimited their applicability and have directly defined priorities for future work: (i) expanding runoff monitoring to a broader set of basin typologies and rainfall conditions, (ii) including transformation product and solid-phase analyses in laboratory experiments, (iii) repeating DTS infiltration tests across seasons and hydraulic phases, and (iv) developing a modelling framework that better represents geological complexity, aquifer-scale dilution, and redox-coupled biodegradation.

4. Perspectives and research directions

The results of this thesis have supported the conclusion that runoff-based MAR can be technically achievable, including in loess-covered settings where surface infiltration systems are often discarded out a priori. The next step is therefore to move from a vulnerability-oriented assessment and numerical reproduction of recharge operations to field-scale demonstration with urban runoff. Operating a pilot site with controlled recharge, dedicated monitoring, and targeted sampling would make it possible to directly observe hydrochemical responses and operational constraints under realistic conditions. Such datasets would also provide the basis to better constrain model parameters and reduce uncertainty when translating vadose-zone transfers into aquifer-scale concentrations. Building on this perspective, several research directions emerge naturally from this thesis and would help refine process understanding and strengthen the predictive capacity of the proposed framework.

At laboratory scale, future experiments should explicitly include transformation products, especially for compounds for which biotransformation is suspected (e.g., 6:2 FTS). In this context, collaboration with analytical chemistry research unit would be particularly valuable to expand the analytical scope toward mobile biotransformation products. In parallel, improving the design of the biotic control is essential to better separate sorption-driven attenuation from biodegradation. Batch experiments could also be complemented by column tests, which would introduce realistic flow conditions and allow the role of residence time, desorption, and transient hydrodynamics to be evaluated more directly. Column setups would also be an appropriate basis to derive air–water interfacial (AWI) adsorption parameters for PFAS, which remain a major uncertainty but can strongly influence vadose-zone transport.

On the modelling side, a key step would be to strengthen the representation of PFAS fate under variably saturated conditions by combining AWI processes with transformation products in a consistent multi-species framework. This would require further developments of existing tools (notably HYDRUS) to make such coupling practically workable. In addition, the current vadose-zone approach should ultimately be coupled with a groundwater flow and transport model to better constrain aquifer-scale concentrations. Finally, coupling HYDRUS with PHREEQC (or an equivalent geochemical solver) would be a logical perspective to represent biodegradation in a more realistic way, linked to dissolved oxygen and nitrate availability. Such an approach would benefit from dedicated monitoring at a pilot site to support calibration and validation.

Beyond the processes addressed in this thesis, future work should also focus on long-term operability of infiltration systems. In particular, clogging mechanisms should be investigated in loess-covered basins together with the identification of early-warning indicators based on hydraulic responses and hydrochemical parameters, to support sustain infiltration performance over time. In parallel, complementary nature-based approaches could be evaluated from a water-quality perspective, for example by testing whether selected aquatic plant species or vegetated treatment zones can enhance the retention and/or transformation of organic micropollutants at basin scale.

5. Key-home message

To close this PhD thesis, this work demonstrates that assessing urban runoff infiltration as a managed aquifer recharge option cannot be reduced to a question of infiltration capacity alone, but requires a clear understanding of how contaminant inputs, subsurface transport and attenuation processes, and

operational constraints jointly impact groundwater vulnerability. By combining runoff monitoring, laboratory experiments with loess sediments, field-scale infiltration rates monitoring using DTS technology, and a 2D variably saturated flow modelling framework, the thesis has highlighted both the benefits and the limits of urban runoff infiltration in the Hesbaye chalk context. In particular, the results have shown that loess-covered settings, although often excluded in MAR feasibility studies, can sustain operationally relevant infiltration rates. An additional benefit is that they can also provide an additional protective buffering capacity through delayed transfer, which can enhance attenuation for contaminants sensitive to sorption and biodegradation compared to coarse-grained settings. Beyond the results presented here, the PhD thesis underlines the need for more consistent approaches that better capture the key processes: tracking transformation products alongside parent compounds, constraining key parameters such as sorption at the air–water interface, and representing biodegradation consistently with redox conditions. This would ensure that modelling outputs become more robust and comparable across sites. In addition, the absence of groundwater breakthrough should not be interpreted as the absence of impact. If persistent compounds are preferentially retained in the vadose zone, repeated recharge may lead to their accumulation in soils, thereby shifting the contamination issue from groundwater to the subsurface. Ultimately, this research supports a pragmatic and protective pathway for MAR implementation with the deployment of a pilot site operated with dense monitoring and early detection of hydraulic performance losses (e.g., clogging). In parallel, recharge operations should rely on clear operating rules and on source-water control, including runoff selection and when required, additional pre-treatment to limit inputs of persistent and mobile contaminants. In a future where climate change is expected to intensify both drought pressure and rainfall extremes, such an approach offers a realistic route to address simultaneously the need to enhance recharge without compromising groundwater quality, and to develop infiltration systems that are not only technically feasible, but reliable, resilient, and safe over the long term.

Annex A

Methodology to infer runoff
exploitable volumes (chapter 2)

This annex presents the methodology used in Chapter 2 to estimate annual exploitable runoff volumes from stormwater basins in Wallonia in cases where detailed design information is incomplete or unavailable (e.g., contributing catchment area, land cover distribution, and associated runoff coefficients). This method consists in 4 steps:

1. Estimation of weighted runoff surface

The first step consists in determining the weighted runoff surface S_w , i.e. the effective surface area contributing to runoff into the basin. Since the actual contributing catchment areas and their land covers are not always documented for stormwater basins, S_w cannot be determined directly from known surfaces and runoff coefficients. Instead, it is estimated indirectly from the basin design assumptions. In Wallonia, stormwater basins are often designed to buffer rainfall events of 3 hours with a 25-year return period, while restricting the outflow discharge to $5 \text{ L s}^{-1} \text{ ha}^{-1}$ (SPW, 2023). The “Groupe Transversal Inondations (GTI)” typically provides the official guidelines and tools for stormwater basin design in Wallonia (Teller *et al.*, 2023).

For each municipality, the Royal Meteorological Institute (IRM) provides the rainfall depth of this extreme reference event (IRM, 2025), as depicted on Table A1 for the city of Liège. The effective S_w can then be back-calculated from the basin storage requirements using the following relation:

$$V_{storage} = (I - q_{out}) \times S_w \times t \quad (A1)$$

And thus:

$$S_w = \frac{V_{storage}}{(I - Q_{out}) \times t} \quad (A2)$$

where $V_{storage}$ is the design storage volume [L^3], I is the rainfall intensity of 3-hour rainfall event with a 25-year return period [$\text{m}^3 \text{ s}^{-1} \text{ ha}^{-1}$], q_{out} is the regulated outflow rate [$\text{m}^3 \text{ s}^{-1} \text{ ha}^{-1}$], S_w is the weighted runoff surface [ha], and t is the duration of the design rainfall [s].

Table A1. Extreme precipitation events for Liège city (IRM, 2025)

Duration	Return period (years)											
	2	5	10	15	20	25	30	40	50	75	100	200
10 min	7.7	11	13.5	15	16.1	17	17.8	19	20	21.8	23.2	26.7
20 min	11.1	15.9	19.6	21.8	23.4	24.7	25.8	27.5	29	31.6	33.6	38.6
30 min	13.1	19	23.5	26.2	28.1	29.7	31	33.2	34.9	38.1	40.5	46.6
1 h	16.3	22.8	27.7	30.7	32.8	34.6	36	38.4	40.2	43.7	46.4	53
2 h	19.5	26.9	32.4	35.7	38.2	40.1	41.7	44.4	46.5	50.4	53.3	60.8
3 h	21.6	29.7	35.8	39.4	42.1	44.2	46	48.8	51.1	55.4	58.6	66.7
6 h	26.1	34.4	40.6	44.3	47	49.2	51	53.9	56.2	60.6	63.8	71.9
12 h	31.9	41.9	49.2	53.6	56.8	59.4	61.5	65	67.7	72.9	76.7	86.3
1 day	39.2	50.6	58.9	63.8	67.3	70.1	72.4	76.1	79.1	84.6	88.6	98.6
2 days	49.8	63.6	73.3	79	83.1	86.3	88.9	93.1	96.4	102.5	106.9	117.8
3 days	53.2	67.9	78.1	84	88.2	91.5	94.2	98.5	101.9	108.1	112.5	123.5
4 days	57.8	73.6	84.4	90.6	95	98.4	101.2	105.7	109.2	115.6	120.2	131.4
5 days	65.7	82.7	94.3	101	105.7	109.4	112.4	117.1	120.8	127.5	132.4	144.1
7 days	75.7	94.2	106.7	113.8	118.8	122.6	125.8	130.7	134.6	141.6	146.6	158.8
10 days	90.2	111.2	125.2	133.1	138.6	142.9	146.3	151.8	156	163.7	169.1	182.1
15 days	109.4	133.8	149.9	158.8	165.1	169.9	173.8	179.9	184.6	193.1	199.1	213.4
20 days	127.4	156	174.5	184.8	192	197.4	201.9	208.8	214.2	223.7	230.5	246.5
25 days	136	166.4	185.9	196.7	204.2	209.9	214.6	221.8	227.3	237.3	244.2	260.7
30 days	158.8	191.3	212	223.5	231.4	237.5	242.3	249.9	255.7	266.2	273.4	290.6

2. Calculation of storage volume

Once the weighted runoff surface has been determined, the runoff volume generated at the outlet of the stormwater basin can be computed. On an annual basis, the available runoff volume is estimated

from the average annual precipitation of the corresponding municipality, applied to the effective contributing surface. The relation is expressed as:

$$V_{runoff} = S_w \times P \quad (A3)$$

Where S_w is the weighted runoff surface [m^2] and P is the average annual precipitation of the associated municipality [m].

3. Storage volume correction

Runoff volume derived from rainfall and runoff surface calculations must be corrected to account for different loss mechanisms that reduce the quantity of water actually exploitable. Three main effects are considered. Firstly, evapotranspiration removes a proportion of the rainfall before it can contribute to runoff. In highly urbanized settings ($\approx 75\text{--}100\%$ impervious cover), vegetation-driven transpiration is low and was therefore neglected in this study (Kazemi, 2014). Evaporation remains difficult to quantify because it depends strongly on meteorological conditions (notably air temperature and humidity), but it is reasonably approximated here as around 30% of total precipitation (Kazemi, 2014; Durieux *et al.*, 2024). Secondly, losses at the basin level may occur because some stormwater basins are designed to be infiltrating, while others may present leakage due to deteriorating infrastructures. Even though these losses cannot be reliably quantified, they must be considered as contributing to the overall uncertainty. Thirdly, small rainfall events ($< 1 \text{ mm day}^{-1}$) do not contribute to runoff volumes but are accounted in annual precipitation statistics. To account for this, only daily rainfalls greater than 1 mm were considered as contributing to runoff. For instance, in Liège, an average of 138.8 days per year experience rainfall of at least 1 mm. Assuming with a safety approach that 1 mm of rain falls on the remaining days of the year, the effective annual precipitation generating runoff was adjusted from 853.7 mm (average total) to 627.5 mm.

$$V_{exp} = V_{runoff} - V_{loss} \quad (A4)$$

4. Precipitation-storage relationship for exploitable runoff estimation

By applying this methodology to five theoretical stormwater basins, each located in municipalities with different annual precipitation regimes, it was possible to establish a relationship between basin storage volume, the annual exploitable runoff volume for MAR operations, and the corresponding mean annual precipitation. This relationship is illustrated in the Figure A1.

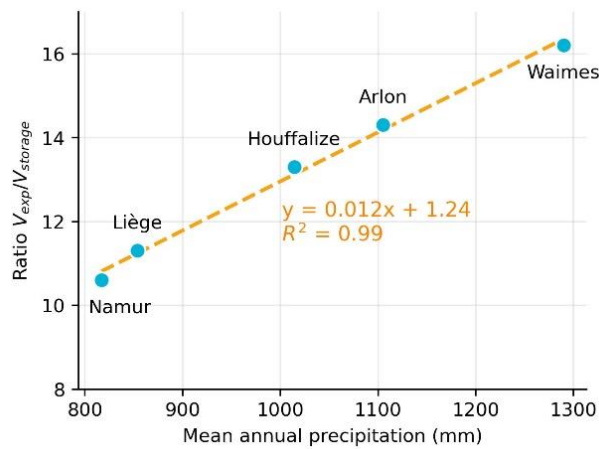


Figure A1. Relationship between storage volume ($V_{storage}$), annual exploitable runoff volume (V_{exp}), and mean annual precipitation (during 1990-2020 period), for five theoretical basins located in different municipalities.

Annex B

Supplementary chapter associated
to Chapter 4

1. Location of groundwater samples used for comparison with urban runoff

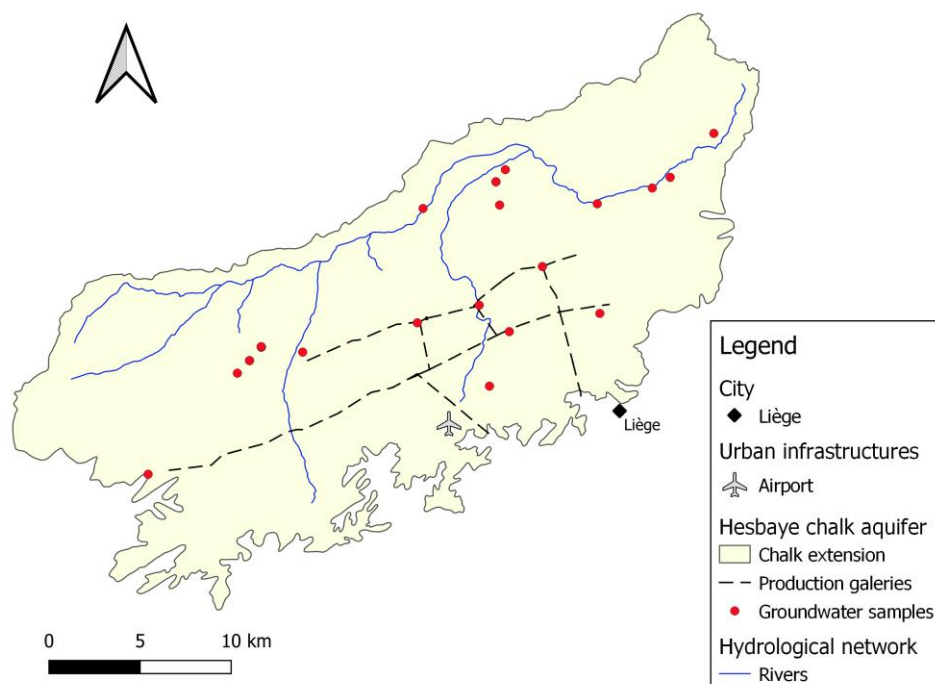


Figure B1. Location of groundwater samples in the Hesbaye chalk aquifer for hydrochemical comparison with urban runoff samples (Chapter 4).

2. Ionic composition of stormwater basins samples

Parameter	unit	T1		T2		A1			A2		
		spring 2022	winter 2023	spring 2022	winter 2023	spring 2022	winter 2023	fall 2023	spring 2022	winter 2023	fall 2023
K+	mg/L	15	10	22	23	27	383	15	31	126	4
Li+	mg/L	0.03	0.02	0.03	0.05	0.03	0.05	0.03	0.02	0.05	0.02
Mg2+	mg/L	8.3	5.0	11.0	9.7	1.4	4.5	2.1	1.2	3.9	1.2
Na+	mg/L	96	58	137	201	8	173	19	22	332	8
NH4+	mg/L	27	13	65	56	1	0	0	2	0	2
Sr2+	mg/L	0.44	0.41	0.47	0.72	0.00	0.75	0.41	0.00	0.70	0.33
Br-	mg/L	0.00	0.00	0.00	0.08	0.00	0.00	0.00	0.00	0.08	0.00
Cl-	mg/L	144	89	215	316	9	92	29	31	442	14
F-	mg/L	0.14	0.07	0.16	0.08	0.22	0.18	0.16	0.17	0.17	0.13
NO2-	mg/L	0.12	3.35	0.00	0.00	0.46	0.00	0.10	0.17	0.00	0.00
NO3-	mg/L	0.64	5.99	0.00	0.00	7.64	0.00	65.00	2.93	0.00	0.34
PO43-	mg/L	7.89	5.42	11.23	11.76	0.27	0.68	4.64	2.18	0.00	0.23
SO42-	mg/L	38	26	42	46	15	36	31	11	39	9
Ca2+	mg/L	80	57	95	93	20	69	38	17	52	26
OH-	mg/L	0.01	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00
CO32-	mg/L	0.66	0.31	0.97	0.65	0.07	0.86	0.07	0.07	0.36	0.02
HCO3-	mg/L	346	202	521	468	80	375	61	99	295	83
free_CO2	mg/L	7.0	5.0	10.8	13.1	3.6	6.3	2.2	5.4	9.4	12.1

Table B1. Ionic composition of stormwater basin samples.

Annex C

Supplementary materials
associated to Chapter 5

1. Granulometry analysis

To characterize the soil used in our experiments, a granulometry analysis was conducted (See Figure C1). Given the presence of very fine particles, sieve analysis was performed for the coarser fraction of the sediments and sedimentometry for the smallest particles, to ensure a comprehensive particle size distribution analysis. These analyses were performed at the Building Materials Laboratory (LMC) within the Urban and Environmental Engineering (UEE) department at the University of Liège.

The analysis revealed that the soil consists of 14.5% clay ($< 2 \mu\text{m}$), 85% silt/loam ($0.002 \text{ mm} - 0.08 \text{ mm}$), and 0.5% sand ($0.08 \text{ mm} - 2 \text{ mm}$). Based on this particle size distribution, the soil is classified as a "loam."

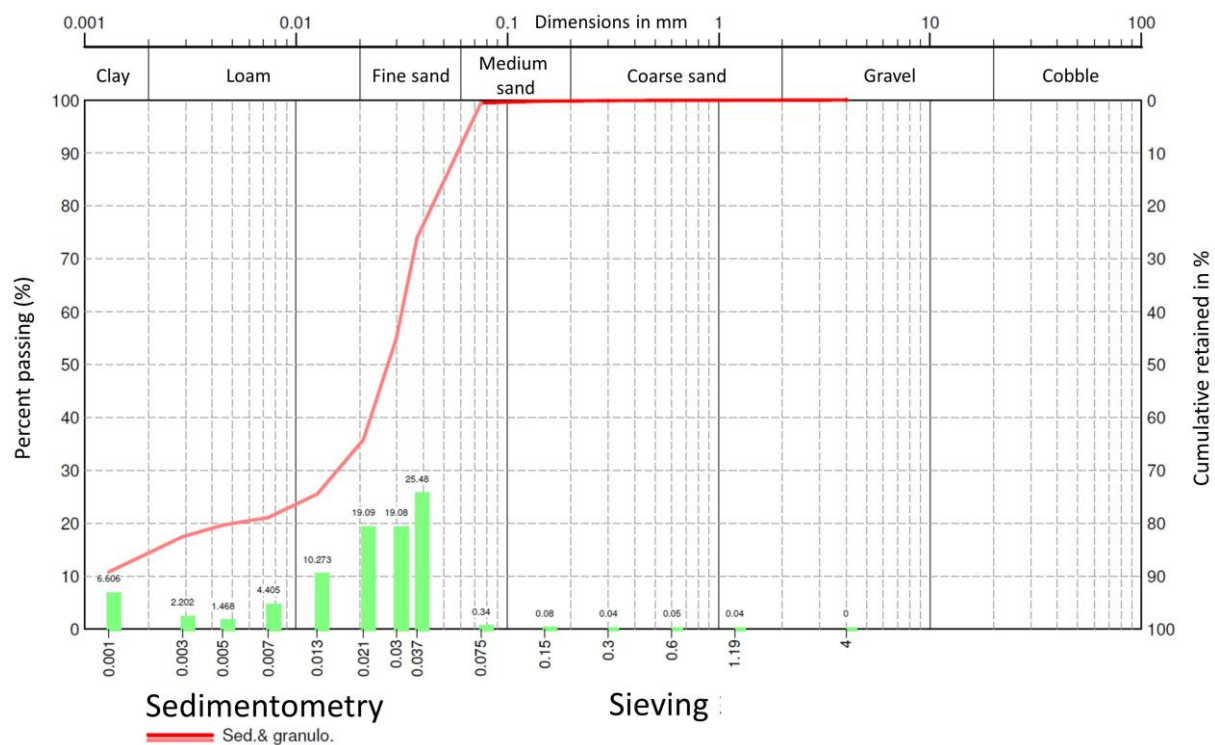


Figure C1. Granulometric analysis for one loess sample.

2. Additional pictures of the experimental set-up

To support the section 2.2.1 of Chapter 5, additional pictures are displayed in this section to better visualize the whole experimental set-up. Figure C2 shows the stock solutions used to prepare the batch reactors, the triplicates after the addition of humic acid and soil, and the placement of the reactors in the incubator.

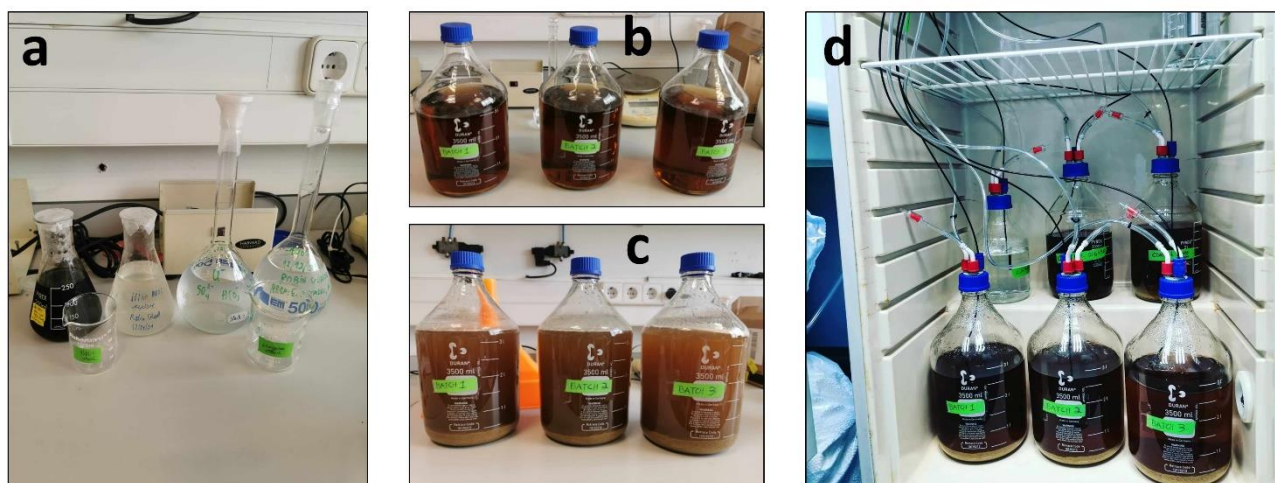


Figure C2. Additional pictures of the batch experimental set-up. a) Stock solutions for low and high BDOC (humic acid and peptone respectively) on the left and major ions on the right. b) Batch reactors after the addition of humic acid. c) Batch reactors after the addition of the soil. d) Triplicates (below) and control reactors (above) in the incubator. In this case, there is also the biotic reactor but as mentioned in Chapter 5, this control proves to be not functioning.

3. Synthetic water: resulting major ions

To achieve the target composition of major ions (Table C1), 6 different salts were dissolved in milliQ water: CaCl_2 , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, KCl , NaHCO_3 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and NaNO_3 . Table C1 provides a comparison of the major ion concentrations in the original runoff water, the theoretical concentrations expected from salt dissolution, and the measured concentrations in the three batch reactors and the abiotic control at the beginning of the experiment.

The overall concentrations in the batch reactors generally aligned with the expected values, except for potassium and sulfate, which were lower than anticipated. Calcium and bicarbonate concentrations were not quantified. Elevated concentrations of sodium and nitrate were detected in the abiotic control, likely due to the addition of sodium azide (NaN_3).

Table C1. Major ion composition in $\text{mg} \cdot \text{L}^{-1}$ in the studied runoff water (observed), in the synthetic water after salt dissolution (theoretical), and in each reactor at the start of the experiment (measured in R1, R2, R3 and C1).

	Observed	Theoretical	R1	R2	R3	C1 (abiotic)
Ca^{2+}	30	30	-	-	-	-
Mg^{2+}	2	2	1.56	1.88	2.04	2.26
Na^+	15	24	19.58	22.03	22.74	66.03
K^+	10	10	3.13	3.22	3.41	4.13
Cl^-	30	40	37.05	41.1	42.42	51.97
HCO_3^-	60	60	-	-	-	-
SO_4^{2-}	30	38	10.31	13.59	14.89	17.7
NO_3^-	5	5	4.66	4.95	5.09	59.92

4. Flow injection analysis conditions

As described in the section 2.3 of Chapter 5, flow injection analysis (FIA) was employed to optimise the parameters for HPLC-MS/MS detection of various CECs used in batch experiments. For FIA, individual standard solutions of each compound were prepared at a concentration of 1 ppm. Each vial contained a total volume of 1000 μL , composed of a 50:50 methanol:water mixture. The methanol portion consisted of 400 μL of methanol and 100 μL of a 10 ppm native stock solution of the target compound. The aqueous portion comprised 420 μL of ultrapure water and 80 μL of a 125 mM ammonium acetate buffer solution. A volume of 10 μL was injected for each FIA run.

The initial step in method development involved optimising the cone voltage. Cone energies ranging from 10 to 80 V were tested to identify the setting that produced the maximum signal intensity for each analyte. Both positive and negative electrospray ionisation (ESI) modes were evaluated. The optimised cone voltages and ionisation modes selected for each compound are summarised in Table C2.

Table C2. Cone voltage optimisation during FIA.

Compound name	molecular mass (g mol^{-1})	ESI	Parent ion (m/z)	Cone (V)
Benzotriazole	119.12	+	120	10
Tolyltriazole	133.15	+	134	10
nonylphenol diethoxylate	308.5	+	326	20
6:2 FTS	428.17	-	427/407	20
PFECHS	462.13	-	461	80

The second step involved optimisation of the collision energy for each compound, based on the previously determined optimal cone voltage. Collision energies were tested over a range of 10 to 50 eV to identify the value that yielded the highest intensity for the selected product ions. The final optimised collision energies and corresponding retention times for each target compound are reported in Table C3.

Table C3. Collision energy optimisation during FIA.

Compound name	Selected daughter 1	Col. Energy (eV)	Selected daughter 2	Col. Energy (eV)	t_R (min)
Benzotriazole	120 > 65	20	120 > 92	10	1.23
Tolyltriazole	134 > 79	10	134 > 106	20	1.62
nonylphenol diethoxylate	326 > 183	10	326 > 121	20	12.63
6:2 FTS	-	-	-	-	9.05
PFECHS	461 > 381	20	461 > 99	20	9.32

5. Calibration curves for HPLC-MS/MS

As indicated in the section 2.3 of Chapter 5, calibration samples were prepared to construct a calibration curve spanning a concentration range of 0.0005 to 0.1 ng/μL. Each calibration point was prepared at a total volume of 1000 μL, using a solvent system consisting of a 50:50 (v/v) mixture of methanol and water.

The organic phase (500 μL) consisted of 50 μL of an internal standard solution at 1 ppm and an appropriate volume of native compound stock solution at 0.5 ppm, adjusted to the required target concentration, with methanol added to complete the total 500 μL of the organic phase. The aqueous phase (500 μL) consisted of 80 μL of 125 mM ammonium acetate buffer solution and 420 μL of HPLC-grade water. The detailed volumes used for each calibration level are provided in Table C4.

Table C4. Volumetric details for calibration samples preparation.

Calibration curve parameters		RC1	RC2	RC3	RC4	RC5	RC6	RC7
Calibration curve parameters	Concentration (ng/μL)	0.0005	0.001	0.01	0.03	0.05	0.07	0.1
	Absolute nanograms (Considering 1000μL final volume)	0.5	1	10	30	50	70	100
Preparation (μL to take from each solution, considering a final volume of 1000μL in vial and 50:50 Methanol Water)								
Organic Solvent	IS uL (From Mix 1ppm)	50	50	50	50	50	50	50
	Native (From solution Mix 0.5 ppm)	1	2	20	60	100	140	200
	Methanol	449	448	430	390	350	310	250
H2O	Tampon amonium acetate from solution 125 mM	80	80	80	80	80	80	80
	H2O (Chromatographic)	420	420	420	420	420	420	420
	Vial Total Volume	1000	1000	1000	1000	1000	1000	1000

The calibration curves associated to each studied CECs and their linearity are depicted in Figure C3.

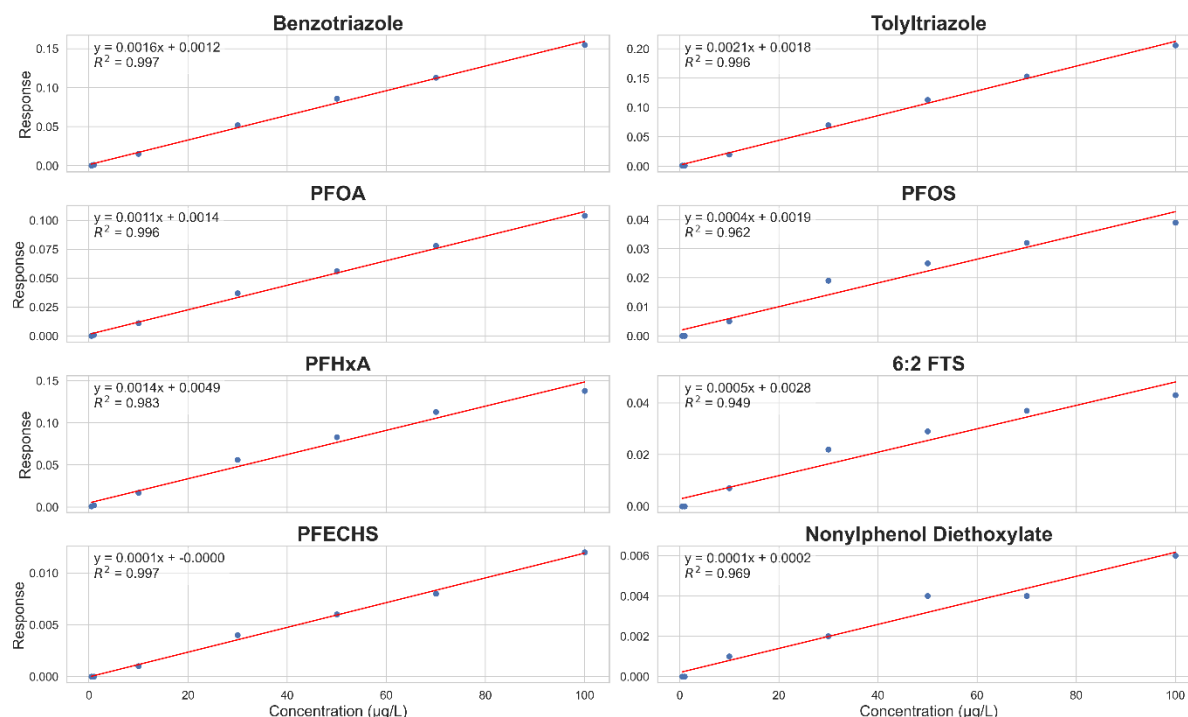


Figure C3. Calibration curves of the studied CECs.

6. Modelled redox reaction and generic mass balance equations

This section presents the stoichiometric chemical reactions and the corresponding mass balance equations, expressed as ordinary differential equations (ODEs), used to represent the degradation of the target compounds under oxic and nitrate reducing conditions in the batch reactors. As mentioned in the section 3.3 of the paper, among all sources of organic matter, only peptone (high BDOC) was assumed to be biodegradable and its average formula stoichiometric formula is $C_5H_{10}NO_2$ (derived from its amino acid composition). In addition, analogous stoichiometric reactions were also defined for the target CECs and are presented in the Table C5.

Table C5. Stoichiometric reactions considered in the reactive batch modelling.

Compound	Oxic conditions	Nitrate reducing conditions
Bzt	$4 C_6H_5N_3 + 35 O_2 \rightarrow 24 CO_2 + 10 H_2O + 12 NO$	$C_6H_5N_3 + 4 NO_3^- + 6 H_2O \rightarrow 2 N_2 + 3 NH_3 + 2 H^+ + 6 HCO_3^-$
Tlt	$4 C_7H_7N_3 + 41 O_2 \rightarrow 28 CO_2 + 14 H_2O + 12 NO$	$5 C_7H_7N_3 + 26 NO_3^- + 27 H_2O \rightarrow 13 N_2 + 15 NH_3 + 9 H^+ + 35 HCO_3^-$
NP2EO	$2 C_{19}H_{32}O_3 + 51 O_2 \rightarrow 38 CO_2 + 32 H_2O$	$5 C_{19}H_{32}O_3 + 102 NO_3^- + 7 H^+ \rightarrow 51 N_2 + 36 H_2O + 95 HCO_3^-$
PFOA	$2 C_8HF_{15}O_2 + 7 O_2 + 14 H_2O \rightarrow 16 CO_2 + 30 HF$	$5 C_8HF_{15}O_2 + 14 NO_3^- + 28 H_2O \rightarrow 61 H^+ + 40 CO_2 + 75 F^- + 7 N_2$
PFHxA	$2 C_6HF_{11}O_2 + 5 O_2 + 10 H_2O \rightarrow 12 CO_2 + 22 HF$	$C_6HF_{11}O_2 + 2 NO_3^- + 4 H_2O \rightarrow 9 H^+ + 6 CO_2 + 11 F^- + N_2$
PFOS	$2 C_8HF_{17}O_3S + 7 O_2 + 16 H_2O \rightarrow 16 CO_2 + 34 HF + 2 SO_2$	$5 C_8HF_{17}O_3S + 14 NO_3^- + 33 H_2O \rightarrow 71 H^+ + 40 CO_2 + 85 F^- + 7 N_2 + 5 SO_2$
PFECHS	$C_8HF_{15}O_3S + 4 O_2 + 7 H_2O \rightarrow 8 CO_2 + 15 HF + SO_2$	$5 C_8HF_{15}O_3S + 16 NO_3^- + 27 H_2O \rightarrow 59 H^+ + 40 CO_2 + 75 F^- + 8 N_2 + 5 SO_2$
6:2 FTS	$C_8H_5F_{13}O_3S + 11 O_2 + 8 H_2O \rightarrow 16 CO_2 + 26 HF + 2 SO_2$	$5 C_8H_5F_{13}O_3S + 22 NO_3^- + 9 H_2O \rightarrow 43 H^+ + 40 CO_2 + 65 F^- + 11 N_2 + 5 SO_2$
Peptone ($C_5H_{10}NO_2$)	$4 C_5H_{10}NO_2 + 23 O_2 \rightarrow 20 CO_2 + 14 H_2O + 4 NH_3$	$10 C_5H_{10}NO_2 + 46 NO_3^- \rightarrow 23 N_2 + 10 NH_3 + 8 H_2O + 50 HCO_3^- + 4 H^+$

In a closed batch system, the temporal change in the concentration of species *A* is by the equation hereafter.

$$\frac{dC_A}{dt} = \sum_r v_{A,r} \times R_r \quad (C1)$$

Where C_A is the concentration of species *i* ($mol \cdot L^{-1}$), $v_{A,r}$ is the stoichiometric coefficient of species *A* in reaction *r* (positive for products, negative for reactants) and R_r the rate of the reaction *r* ($mol \cdot L^{-1} \cdot time^{-1}$). Reaction rates R_r were expressed in Monod-type form (Eq. C2 and C3), limited by the availability of the electron acceptor.

$$r_{A,oxic} = -\lambda_{A,oxic} \times C_A \times \frac{C_{O_2}}{K_{O_2} + C_{O_2}} \quad (C2)$$

$$r_{A,NR} = -\lambda_{A,NR} \times C_A \times \frac{K_{inh,O_2}}{K_{inh,O_2} + C_{O_2}} \times \frac{C_{NO_3^-}}{K_{NO_3^-} + C_{NO_3^-}} \quad (C3)$$

In PHREEQC, the software internally integrates the ordinary differential equations derived from the defined stoichiometric reactions and kinetic rate laws. The explicit formulation provided here (Eq. C1–C3) is intended to illustrate the general structure of the balances. In practice, PHREEQC calculates the coupled system of ODEs implicitly during the simulation.

7. Calibrated parameters for the biodegradation and sorption chemical models

This section presents the full set of parameter values resulting from the calibration of the sorption and degradation models in PHREEQC, which were adjusted to reproduce batch experiments and abiotic control results. Table C6 presents the sorption parameters used to reproduce CECs observation in the abiotic control. Similarly, Table C7 depicts the biodegradation parameters used to reproduce CECs evolution in the batch experiments.

Table C6. Calibrated parameters for the sorption models of each CEC.

Parameter name	Symbol	units	Bzt	Tlt	PFOA	PFHxA	PFOS	6:2 FTS
mass transfert coefficient	k_m	hours ⁻¹	2.17E-06	1.79E-06	2.67E-07	1.48E-06	2.77E-07	6.20E-07
distribution coefficient	K_d	L g ⁻¹	4.89E-04	6.56E-04	4.36E-04	4.70E-04	4.63E-02	9.94E-04

Table C7. Calibrated parameters for the biodegradation models of each CEC.

Parameter name	Symbol	units	Bzt	Tlt	PFECHS	PFHxA	PFOA	PFOS	6:2 FTS	NP2EO
maximal degradation rate under oxic condition	$k_{max-oxic}$	mol L ⁻¹ s ⁻¹	1.05E-04	1.59E-05	1.40E-05	1.72E-04	3.52E-07	5.23E-05	1.75E-04	2.86E-04
half-saturation constant for O ₂	K_{O_2}	mol L ⁻¹ s ⁻¹	8.00E-02	8.09E-02	9.99E-03	3.00E-01	7.20E-04	8.86E-02	2.00E-01	5.00E-02
maximal degradation rate under suboxic condition	$k_{max-suboxic}$	mol L ⁻¹ s ⁻¹	1.40E-06	5.58E-06	6.04E-07	-	-	-	-	5.91E-06
inhibition coefficient of O ₂	k_{inh-O_2}	mol L ⁻¹	1.52E-05	3.00E-06	2.04E-09	-	-	-	-	1.77E-05
half-saturation constant for NO ₃	K_{nit}	mol L ⁻¹	3.75E-04	4.62E-04	5.00E-10	-	-	-	-	1.49E-04

8. Abiotic control results of nonylphenol diethoxylate

As mentioned in the section 3.4.1 of Chapter 5, nonylphenol diethoxylate did not show any evidence of sorption onto loamy sediments, as depicted with its standardized concentration evolution in the abiotic control (Figure C4).

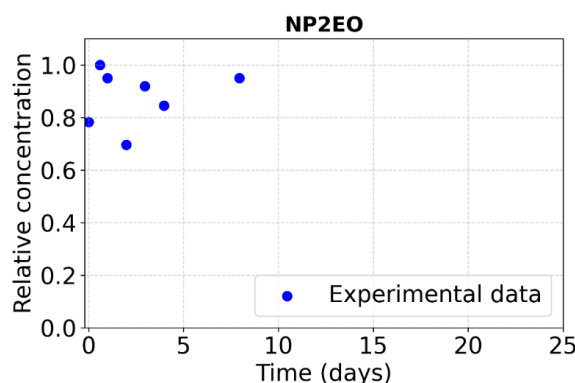


Figure C4. Abiotic control results of nonylphenol diethoxylate.

9. Total attenuation per contaminant

The following section relates to section 3.4.4 of Chapter 5, describing the total attenuation of the contaminants studied at the end of the batch experiments. Therefore, Table C8 describes the attenuation values for each of the contaminants described by the chemical model developed to reproduce the experimental results, as well as the contribution from sorption and biodegradation/biotransformation to total attenuation.

Table C8. Total attenuation per CEC, with contributions from sorption (linear isotherm + additional processes) and biodegradation/biotransformation.

CEC	Total attenuation (%)	Sorption – Linear isotherm (%)	Sorption – additional processes (%)	Biodegradation / biotransformation (%)
BZT	38	16	0	22
TLT	30	19	0	11
PFOA	21	13	8	0
PFOS	45	36	9	0
6:2 FTS	33	26	7	
PFECHS	14	0	14	0
PFHxA	24	15	9	0
NP2EO	90	0	0	90

Annex D

Supplementary materials
associated to Chapter 6

1. Numerical stability of COMSOL model

The Courant number is a dimensionless parameter that indicates the number of mesh cells an information traversed during a specific timestep. As a results, if the Courant number is superior to one, the simulated information might skip a neighbour cell (SIMSCALE, 2020). Therefore, to ensure the stability of the solution, it is recommended to keep this parameter inferior to one. The courant number is defined by:

$$C = \frac{q \times \Delta t}{\Delta x} \quad (D1)$$

With q the groundwater flux, Δt the computational time step and Δx the size of the mesh cell. In this study, $\Delta t = 300$ s, $\Delta x = 0.0185$ m and the maximal flux q estimated from passive-DTS data interpretation is 3.10×10^{-5} m.s⁻¹. As a result, the Courant number is equal to:

$$C = \frac{3.10 \times 10^{-5} \times 300}{0.0185} = 0.5 \quad (D2)$$

which is inferior to 1, ensuring the numerical stability of the solution.

2. Punctual in-situ measurement of infiltration rates

This section describes point-scale infiltration measurements conducted in shallow wells within the loess sediments of the study site using the Porchet method (Colombani *et al.*, 1973), a widely used borehole infiltration test for estimating infiltration rates. This method determines infiltration by monitoring the rate at which water infiltrates from a borehole under a constant head, considering both lateral seepage through the borehole walls and vertical infiltration through the bottom. The test consists of maintaining a steady water level in a pre-drilled borehole while recording the infiltrated volume over time. Figure D1 illustrates the setup for one of the boreholes.

The infiltration rate is computed using the following equation (Colombani *et al.*, 1973) and accounts for lateral seepage.

$$\text{Infiltration rate} = \frac{V}{dt \times \left(2\pi \times r \times \frac{h_1 + h_2}{2} + S \right)} \quad (D3)$$

Where V is the infiltrated volume, dt is the time interval between two successive measurements, S is the cross-sectional area of the well, r is the borehole radius and h_1 and h_2 are the water heights at the beginning and end of the time interval, respectively.

The infiltration rates obtained using this method represent initial infiltration rates and are therefore comparable to those inferred from passive-DTS analysis. Measurements were conducted in three wells: one inside the infiltration basin and two outside, all located within the loess sediments. Initially, a 5-minute refilling period was used, but this was later extended to 15 minutes to minimize errors associated with water height readings.

Results for the three measurement boreholes are depicted in Figure D2. The obtained infiltration rates of 1.12×10^{-5} , 1.25×10^{-5} and 1.50×10^{-5} m.s⁻¹ are of the same order of magnitude as the mean infiltration rate of 1.51×10^{-5} m.s⁻¹ derived from passive-DTS analysis.



Figure D1. Porchet method illustrated in a shallow well within loess sediments.

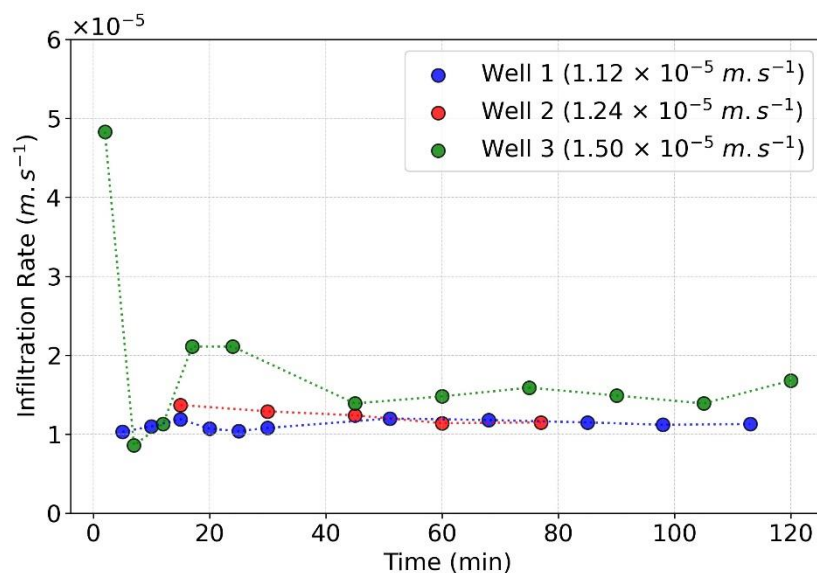


Figure D2. Results from the Porchet method for three shallow boreholes in loess sediments. The written values represent the mean infiltration rate. Note that for well 3, the average value was calculated after the fifth measurement to allow for the stabilization of the rate.

3. Input parameters for the heat transfer model in COMSOL

The purpose of this section is to clarify the origin and calculation of all parameters presented in Table 6 of Chapter 6. COMSOL requires the thermal properties of the solid grains within the sediments, rather than those of the saturated medium. Therefore, the following calculations utilize equations from the COMSOL 'Heat Transfer' module user manual (COMSOL, 2018) to derive the thermal properties of the solid grains from the properties of the saturated medium and the fluid flowing through it. For clarity, we have modified the indices used in the manual: the indices 'eff,' 's,' and 'w' refer to the saturated medium, solid, and water, respectively.

Density and porosity

In parallel with the granulometric analysis, the bulk density of the solid grains was measured and determined to be $\rho_s = 2700 \text{ kg m}^{-3}$. Similarly, the density of water is universally recognized as $\rho_w = 1000 \text{ kg m}^{-3}$.

The total porosity of loess materials was determined through granulometry analysis, yielding a value of $\Theta = 0.42$. Consequently, the solid fraction is calculated as $\Theta_s = 1 - \Theta = 0.58$.

Thermal conductivity

The thermal conductivity of water, denoted as λ_w is sourced from Stauffer et al. (2013) and has a value of $0.58 \text{ W.m}^{-1}.\text{K}^{-1}$. The mean thermal conductivity of the saturated porous media, also named effective thermal conductivity, was determined from active-DTS data analysis, yielding a value of $\lambda_{eff} = 1.78 \text{ W m}^{-1} \text{ K}^{-1}$. Using the equation provided in the COMSOL 'Heat Transfer' module user manual (COMSOL, 2018), we derived the thermal conductivity of the solid materials λ_s .

$$\lambda_{eff} = \theta_s \lambda_s + (1 - \theta_s) \lambda_w \quad (D4)$$

$$\lambda_s = \frac{\lambda_{eff} - (1 - \theta_s) \lambda_w}{\theta_s} \quad (D5)$$

$$\lambda_s = \frac{1.78 - (1 - 0.58)0.58}{0.58} = 2.65 \text{ W m}^{-1} \text{ s}^{-1} \quad (D6)$$

Heat capacity

The volumetric heat capacity of water is sourced from Stauffer et al. (2013) and has a value of $\rho_w C_w = 4.1 \times 10^6 \text{ J m}^{-3} \text{ K}^{-1}$. Similarly, the volumetric heat capacity of saturated porous loess can be approximated to that of saturated loam, yielding a value of $(\rho C)_{eff} = 3 \times 10^6 \text{ J m}^{-3} \text{ K}^{-1}$ (Bilskie, 1994; Alnefaie and Abu-Hamdeh, 2020). Using the relationships and equations provided in the COMSOL 'Heat Transfer' module user manual (COMSOL, 2018), we derived the heat capacity of the solid materials.

$$(\rho C)_{eff} = \theta_s \rho_s C_s + (1 - \theta_s) \rho_w C_w \quad (D7)$$

$$C_s = \frac{(\rho C)_{eff} - (1 - \theta_s) \rho_w C_w}{\theta_s \rho_s} = \frac{3 \times 10^6 - (1 - 0.58) \times 4.1 \times 10^6}{0.58 \times 2700} = 816 \text{ J kg}^{-1} \text{ K}^{-1} \quad (D8)$$

And the volumetric heat capacity of the solid matrix is given by :

$$\rho_s C_s = 816 \times 2700 = 2.2 \text{ MJ m}^{-3} \text{ K}^{-1} \quad (D9)$$

4. Temperature evolution over space

In line with the specified methodology outlined in the section 2, temperature data were systemically collected along the entire length of the FO cable throughout the experimental period. Figure D3 illustrates distinct temperature profiles observed along the FO cable at different stages of the study. Starting from the DTS unit, the cable transits a hot calibration bath (Hot CB) spanning 8.5 and 16.5 m, attaining temperatures of up to 38°C . Subsequently, upon exiting the hot CB for a brief distance, the FO cable encounters the cold calibration bath (Cold CB) within the range of 27.5 to 38 m, resulting in temperatures approximately at 1°C . Following traversal through both calibration baths, the FO cable proceeds towards the infiltration basin, initiating its underground trajectory within loess sediments spanning 57.75 to 75.25 m, with temperatures around 16°C before the replenishment of the basin (Figure D3A), corresponding to the ambient temperature of the superficial loess at that juncture. However, once the basin is filled with water, temperatures recorded along the buried section of the

FO cable are maintained around 14°C, corresponding to the temperature of the recharge water (Figure D3B and Figure D3C). On day 4, within this buried segment, the section between 67.25 and 74.25 m of the cable is subject to electrical heating, resulting in an increase of temperature up to 27-28°C (Figure D3C). On the same day, immediately after emerging from the loess sediments, the FO cable revisits the aforementioned cold calibration bath, recording a return to cold temperatures approximating 0 to 1°C. Out of the sections of the FO cable previously mentioned, temperatures recorded along the FO cable reflect ambient atmospheric conditions prevalent on the experimental day, ranging between 18-20°C. Instances of lower temperatures, such as 14°C before and after the underground traverse through the loess sediments, are attributed to the shading effects induced by the infiltration basin sides, thereby protecting those cable sections from direct solar radiation exposure.

The section of interest in which thermal responses will be studied more accurately corresponds to the buried section within the infiltration basin since it is this particular segment that will be subjected to groundwater flow during the infiltration test. The thermal responses across the entire length of this section will be examined for passive DTS data analysis. In the context of active DTS data analysis, focus will be exclusively on the thermal responses from the electrically heated segment.

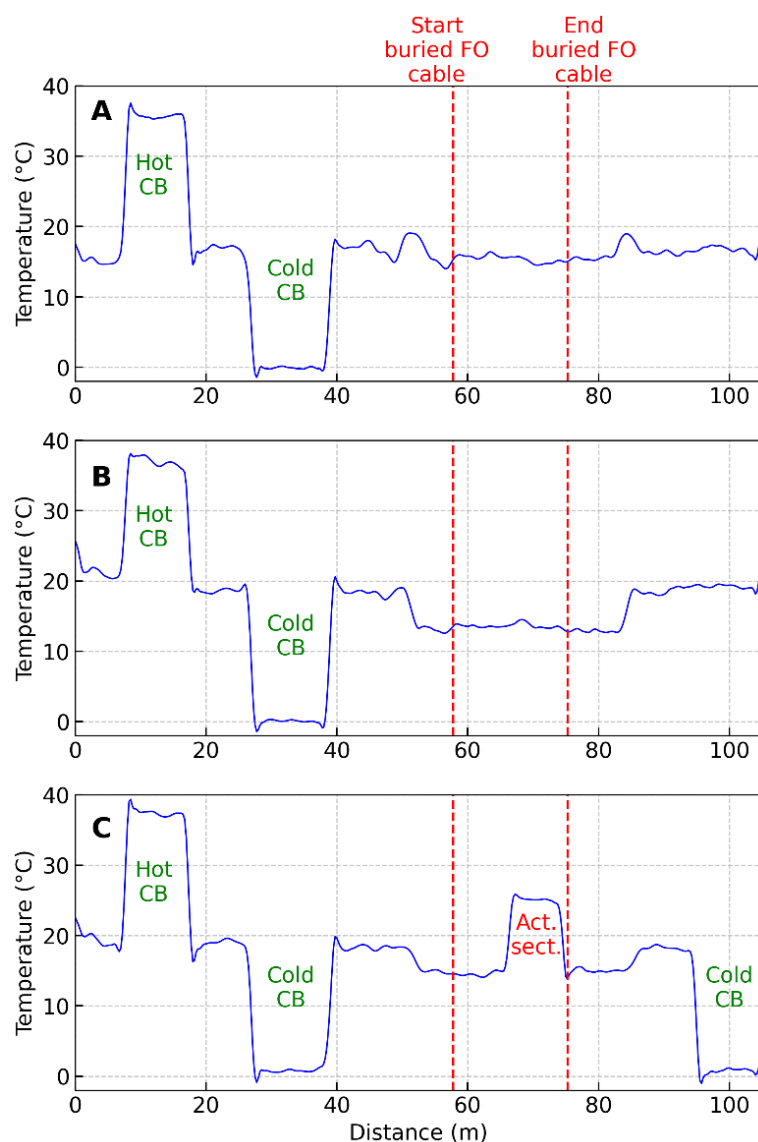


Figure D3. Calibrated temperature evolution along the FO cable before the basin replenishment (A), after the basin replenishment (B) and during the heating of a FO cable section (C).

5. Thermal conductivity measurement in laboratory

To compare the estimated thermal conductivity values from active-DTS data analysis, a needle probe method was applied in laboratory. The thermal conductivity of the loess was measured using a needle probe method. This method involves inserting a needle into a soil sample placed in a cylindrical container. The needle acts as a known heat source at the centre of the container, and the thermal conductivity transmitted by the sample is measured using a thermocouple in the probe.

Loess samples were collected from the bottom of the infiltration basin and saturated by mixing with water to replicate conditions similar to those during the infiltration test. The saturated sample was then placed in a cylindrical container, and a needle probe was inserted into the sample, as illustrated in Figure D4.



Figure D4. Needle probe measurement method of thermal conductivity on saturated loess sample.

The thermal response over time was recorded and is presented in Figure D5 and the thermal conductivity (λ) was determined using the following equation (Fourteau *et al.*, 2022) during the conduction dominant stage:

$$\lambda = \frac{q}{4\pi \times \Delta T} \Delta \ln(t) \quad (D10)$$

With λ is the thermal conductivity, T is the temperature and t the time. The heat input q is defined as $q = \frac{I^2 R}{L}$ where R and L represent the resistance and length of the probe, respectively, and I is the current supplied to the heating resistor. A thermal conductivity of $1.55 \text{ W.m}^{-1}.\text{K}^{-1}$ was measured from the saturated loess sample. This value is slightly lower than the field measurements; however, these results should be interpreted with caution, as laboratory conditions differ from those in the field. In particular, the degree of compaction within the cylindrical container influences the measurement, and it is challenging to determine the level of compaction that best represents in situ conditions.

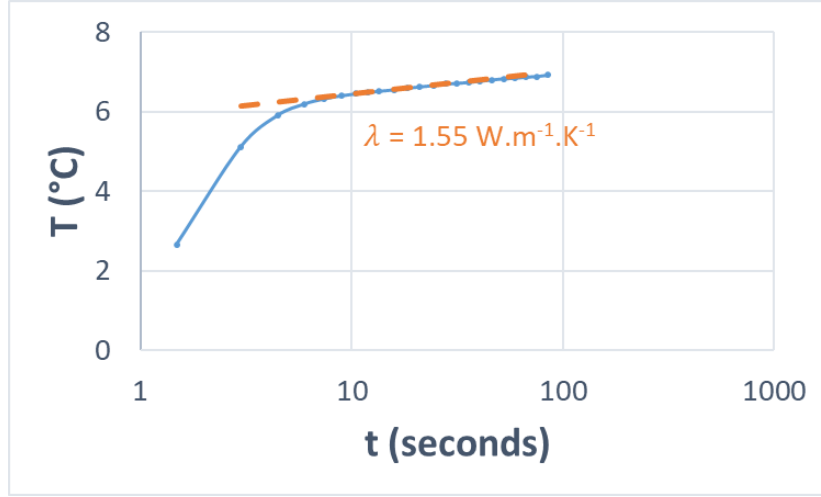


Figure D5. Thermal response obtained using the thermal needle probe (blue) and associated analytical thermal conductivity model (dashed orange).

6. Thermal Peclet number calculation

This section provides a detailed calculation of the thermal Peclet number, which is crucial for understanding the sensitivity of the heat transfer model used for interpreting passive-DTS data. A thermal Peclet number greater than one indicates that heat transfer is dominated by advection rather than conduction. As discussed in the main text, the thermal Peclet number helps explain why thermal conductivity has a relatively low impact on the interpretation of passive-DTS measurements, particularly during the initial stages of infiltration where advection dominates over conduction.

As mentioned by Anderson (2005), the Peclet number is a dimensionless number that represents the ratio of advection to dispersion, used in solute transport and heat transfer studies. As such, the thermal Peclet number has been calculated in the case of the sensitivity analysis for passive-DTS data interpretation to understand the low sensitivity of thermal conductivity in the heat transfer model developed in COMSOL. The thermal Peclet number is given by:

$$Pe = \frac{\rho_w c_w q L}{\lambda_e} = \frac{4.2 \times 10^6 \times 1.05 \times 10^{-5} \times 0.1}{1.78} = 2.48 \quad (D11)$$

With $\rho_w c_w = 4.2 \times 10^6 \text{ J.m}^{-3}.\text{K}^{-1}$ the volumetric heat capacity of the water, $\lambda_e = 1.78 \text{ W.m}^{-1}.\text{K}^{-1}$ the effective thermal conductivity, $q = 1.05 \times 10^{-5} \text{ m.s}^{-1}$ the seepage velocity and $L = 0.1 \text{ m}$ the characteristic length.

Annex E

Supplementary figures
associated with Chapter 7

1. Tolyltriazole transport results

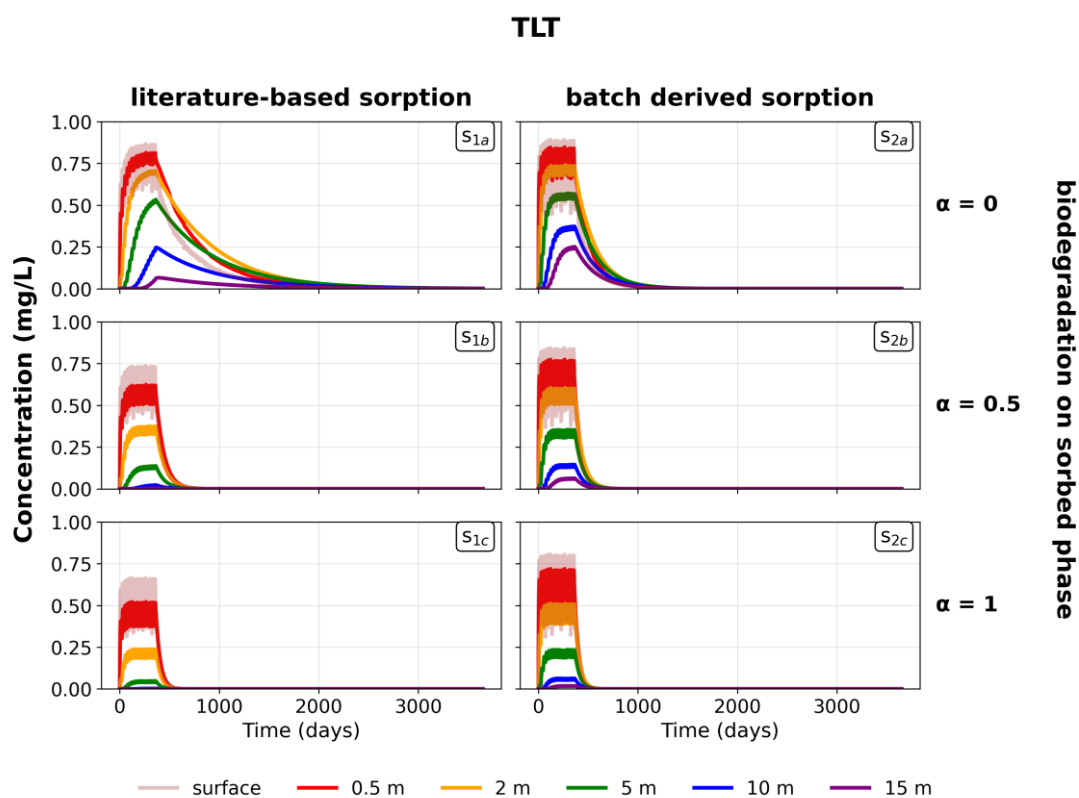
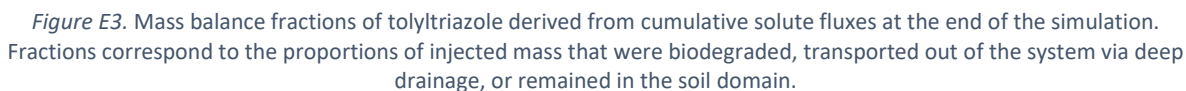


Figure E1. Tolyltriazole concentration evolution at different depths, for each scenario defined in section 3.4.1.

Table E1. Metrics associated with tolyltriazole transport in the vadose zone beneath the infiltration basin.

Scenario	Sorption	Biodegradation sorbed phase: α	Depth	First arrival (days)	Peak concentration (mg L ⁻¹)	Residence time (days)
S _{1a}	Literature	0	15 m	192	0.066	2974
S _{2a}	Batch	0	15 m	79	0.252	990
S _{1b}	Literature	0.5	15 m	169	0.003	418
S _{2b}	Batch	0.5	15 m	75	0.064	364
S _{1c}	Literature	1	15 m	148	0.000	231
S _{2c}	Batch	1	15 m	65	0.019	231



2. PFAS cumulative mass fluxes

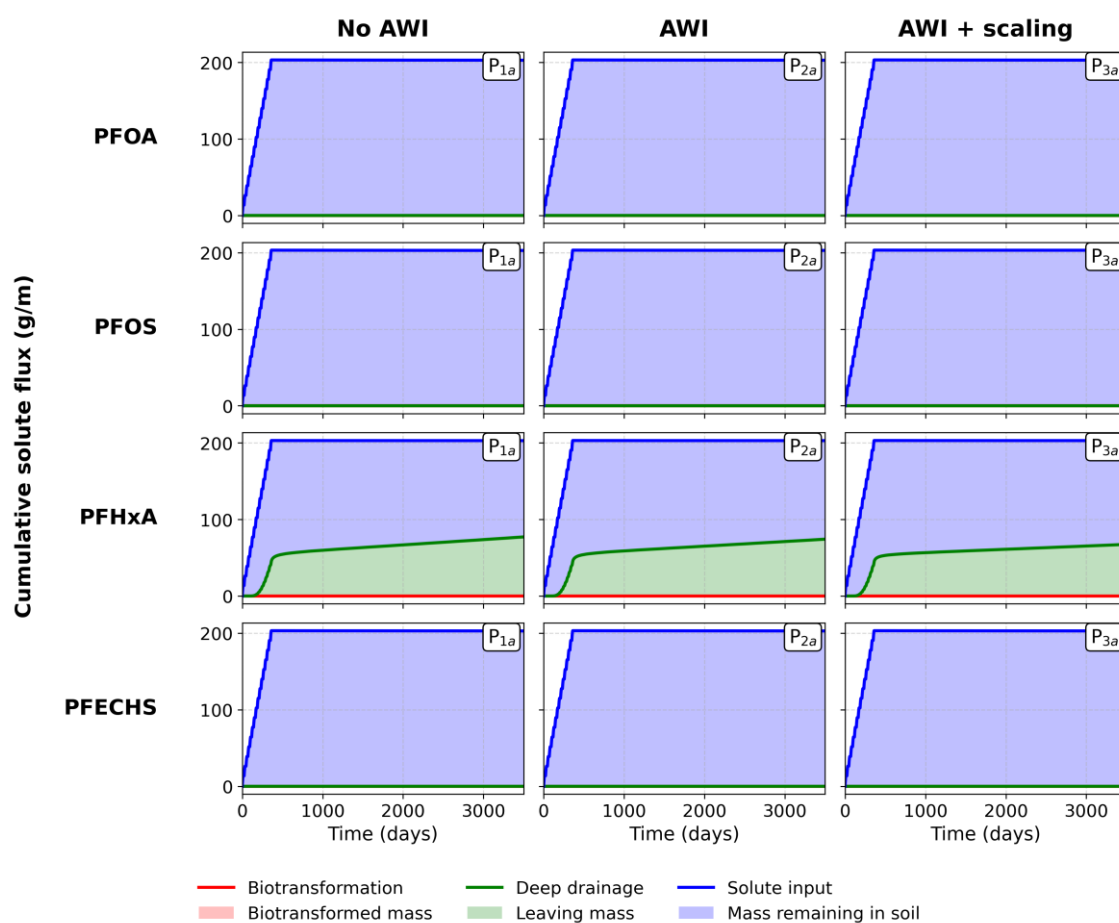


Figure E4. Cumulative mass balance for the transport of PFOA, PFOS, PFHxA, and PFECHS derived from cumulative solute fluxes.

3. PFAS concentration evolution and cumulative mass balance in vulnerability assessment simulations

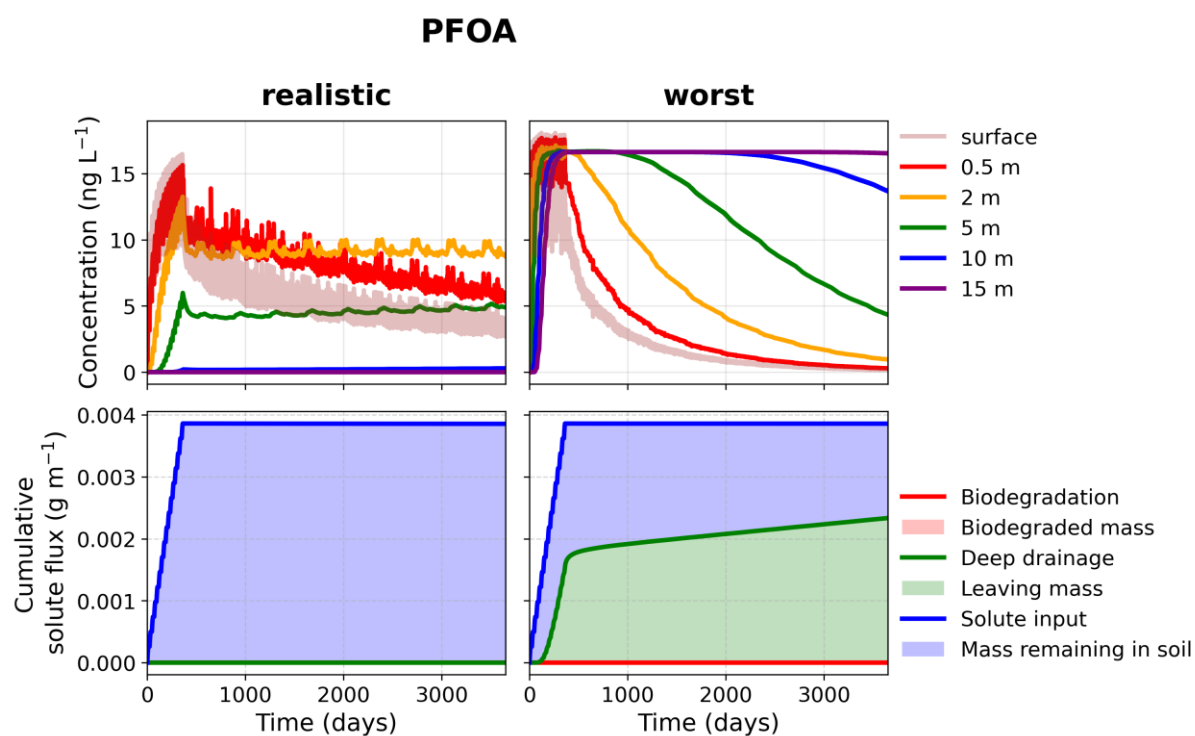


Figure E5. PFOA concentration evolution over depth and cumulative mass balance for both realistic and worst-case simulations.

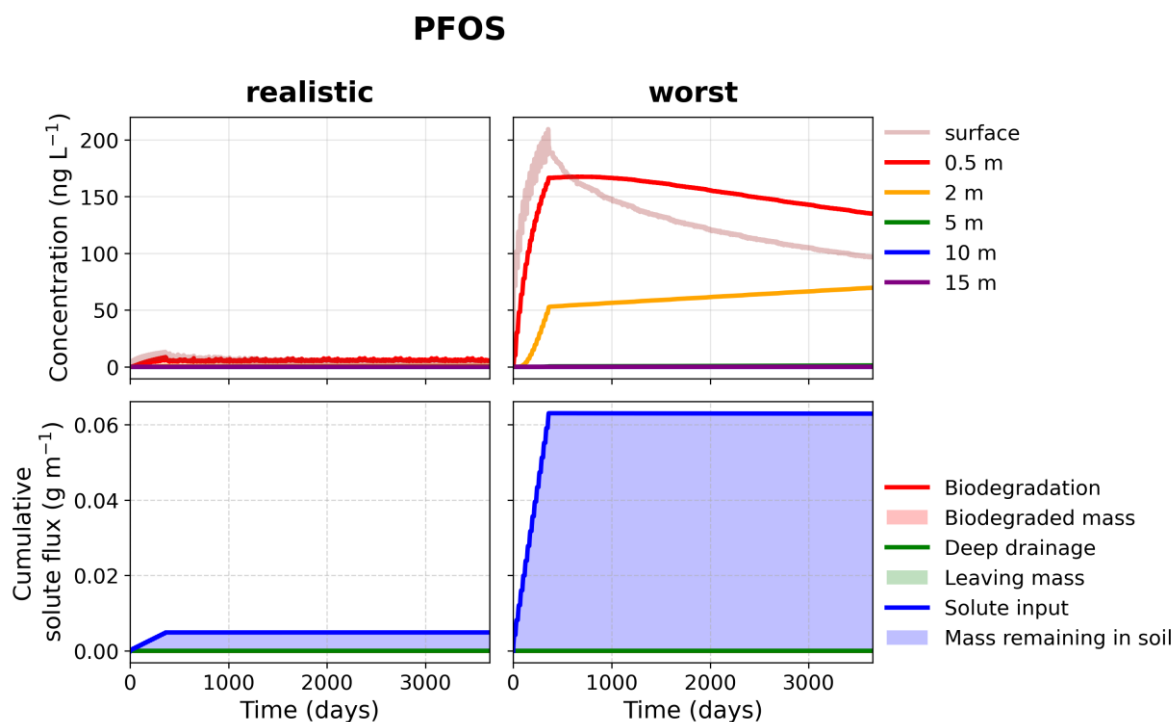


Figure E6. PFOS concentration evolution over depth and cumulative mass balance for both realistic and worst-case simulations.

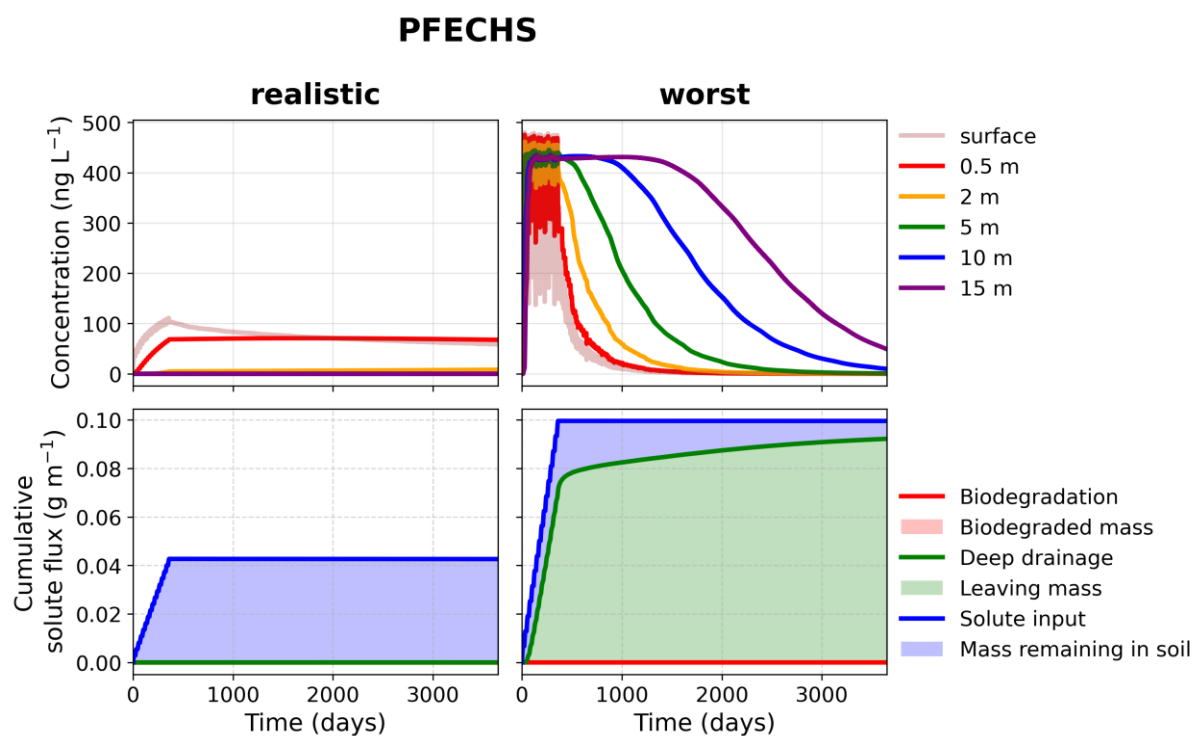


Figure E7. PFECHS concentration evolution over depth and cumulative mass balance for both realistic and worst-case simulations.

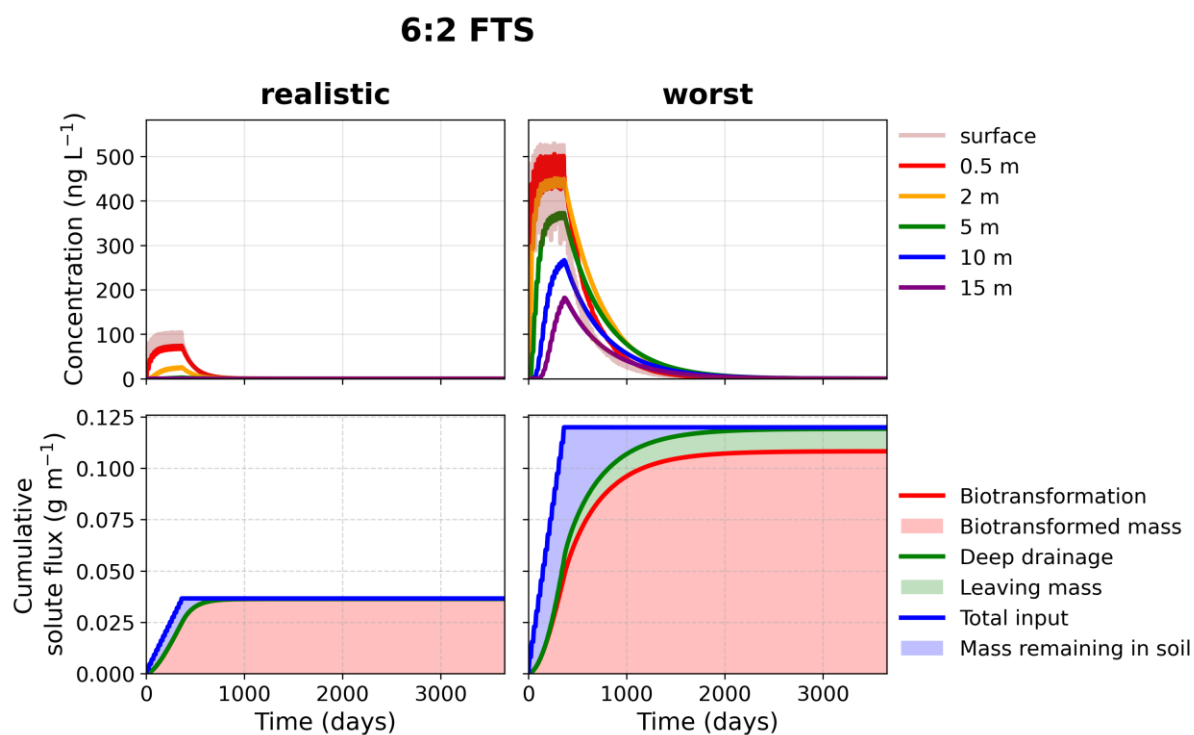


Figure E8. 6:2 FTS concentration evolution over depth and cumulative mass balance for both realistic and worst-case simulations.

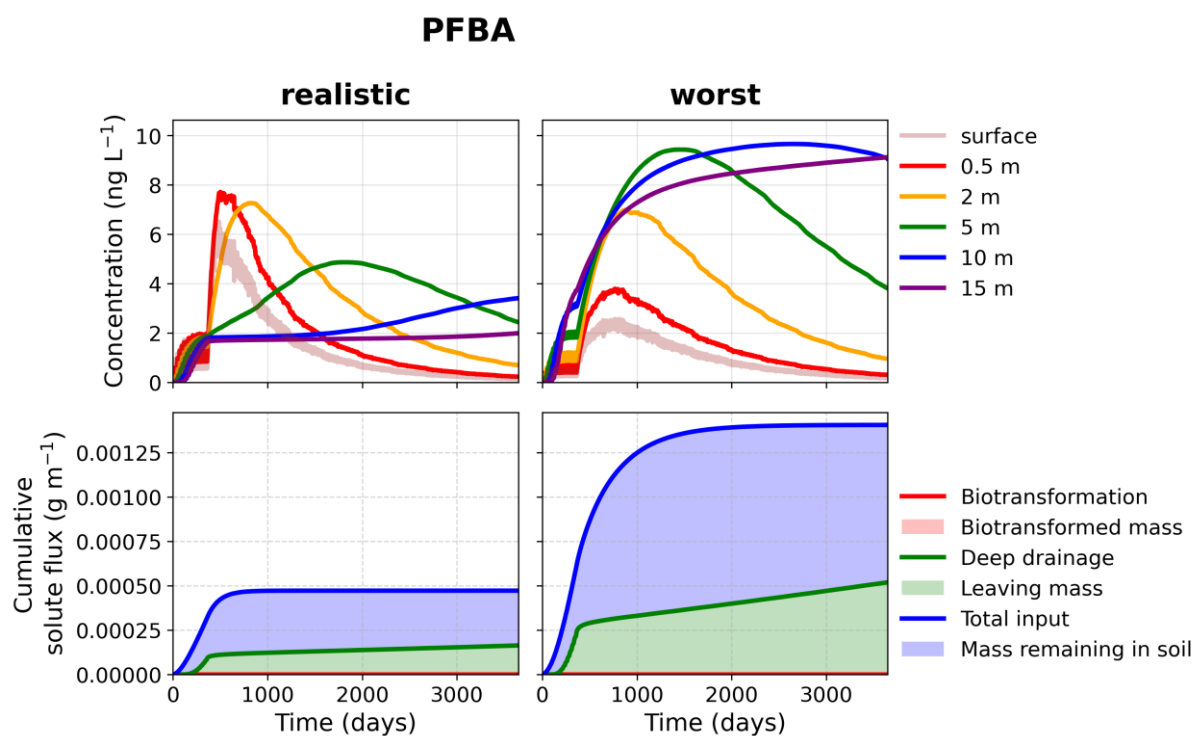


Figure E9. PFBA concentration evolution over depth and cumulative mass balance for both realistic and worst-case simulations.

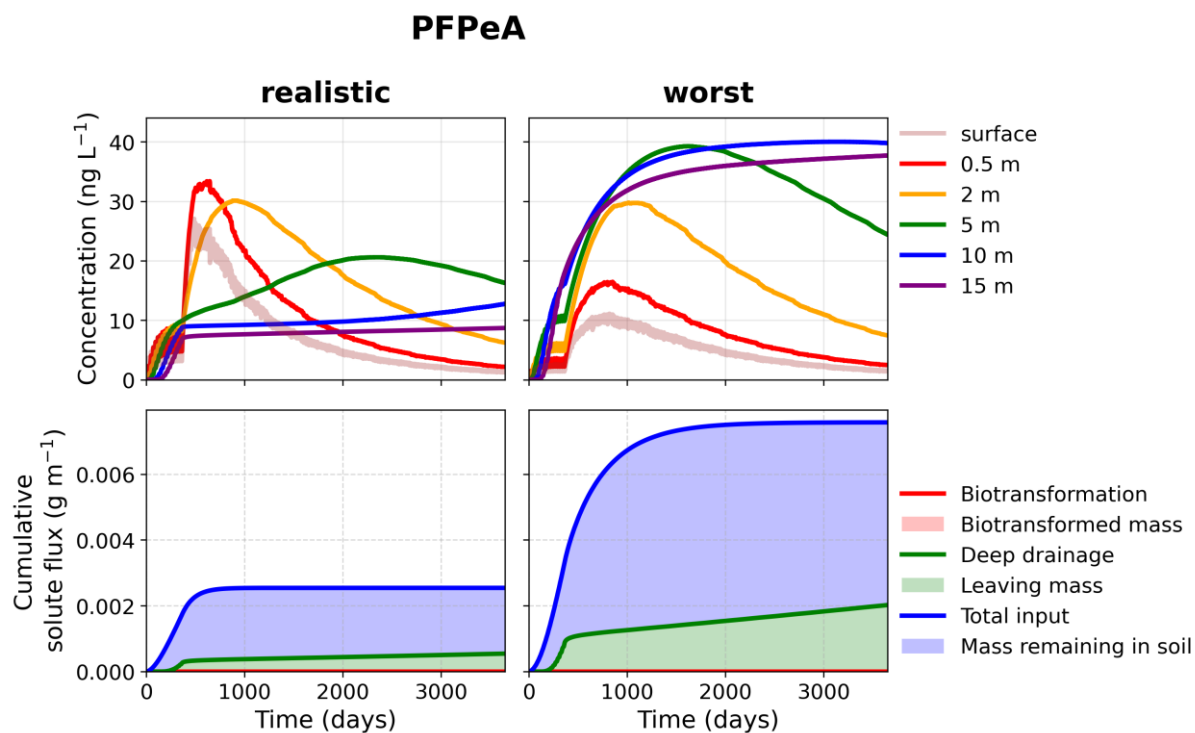


Figure E10. PFPeA concentration evolution over depth and cumulative mass balance for both realistic and worst-case simulations.

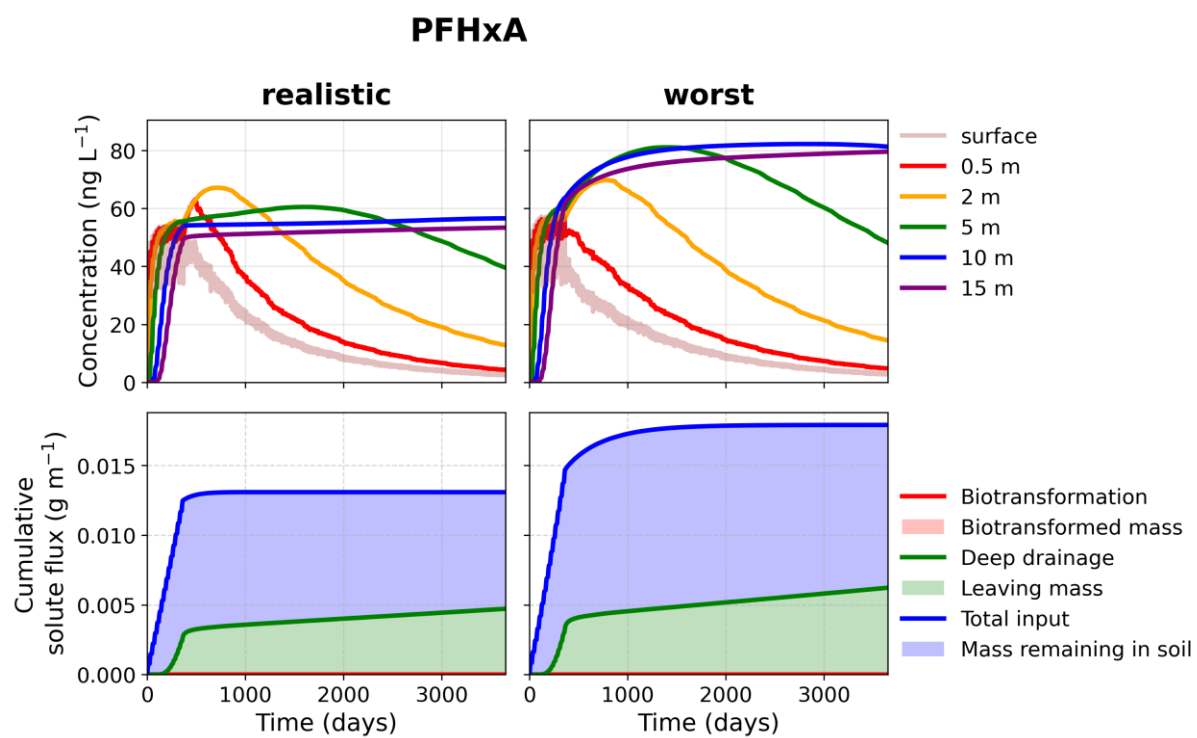


Figure E11. PFBA concentration evolution over depth and cumulative mass balance for both realistic and worst-case simulations.

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