Groundwater Contamination, Recharge, and Flow Dynamics in the Anthropogenic Environment

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Summary

Understanding the dynamics of groundwater resources subject to the pressures of human activity has become a central topic in 21st century hydrogeology. Groundwater availability is defined both in terms of quantity – how much water is stored an aquifer – and in terms of quality – how much groundwater of sufficient quality is available for consumption. Changes in land use have directly impacted both of these facets. Due to its hidden nature, accurately determining the amount of available groundwater is notoriously difficult, and the added complexity of human stressors only augment these difficulties. In addition, the human landscape itself is undergoing rapid change, with a consistent increase in the human population, most of who now live in cities. This population increase has led to increasing land surface dedicated to anthropogenic use, and requires ever greater amounts of water resources for drinking water, agricultural applications, and industrial processes. Hence why a rising number of efforts have emerged in scientific literature on the topic of groundwater in the human environment.

With these facts in mind, this thesis has dealt with identifying the impacts of various anthropogenic land-use patterns on groundwater resources, and the specific discussions around these impacts in modern studies. With the knowledge assembled from current literature, we explored the applicability of both established and novel hydrological and hydrogeological tools to accurately characterize the groundwater cycle in the anthropogenic environment. Our study was carried out at a test site in an urbanizing catchment on the Swiss Plateau, containing a shallow, unconfined fluvio-glacial aquifer. Emphasis was therefore placed on an urban area where the groundwater is actively exploited for municipal and agricultural water supply.

Our methods included an analytical water balance to estimate groundwater recharge using readily-available public data, followed by statistical analysis of chemical indicators to identify the sources and pathways of water into and out of an aquifer. With minimal public data, we were able to estimate historical patterns of groundwater recharge over the course of a decade, including an assessment of changes in the individual variables of the groundwater balance – notably storm runoff versus infiltration. To supplement public data for further analysis, a network of groundwater monitoring wells was installed across the most urbanized area of our study catchment, from which a database including physical, chemical, and isotopic variables was constructed. For chemical analyses, inorganic ions, with a long record of use, were analyzed along with organic micropollutants, which are a relatively novel tool specific to human environments. This data, combined with information on the layout of the river network and the sewer system, allowed us to evaluate potential interactions between groundwater, surface water, and the sewer network. These results have

demonstrated the suitability of our approach to capture groundwater dynamics in an urbanizing catchment.

Résumé

Comprendre la dynamique des ressources en eaux souterraines, soumises aux pressions de l'activité humaine, est devenue un sujet central de l'hydrogéologie du 21^{e} siècle. La disponibilité en eaux souterraines est définie à la fois en termes de quantité - le volume d'eau dans un aquifère – et en termes de qualité – le volume d'eau de qualité suffisante pour la consommation. L'aménagement des milieux naturels par les humains a eu des impacts sur ces deux aspects. Par la nature cachée des eaux souterraines, il est notamment difficile d'estimer leur disponibilité de manière précise. En outre, la complexité des activités humaines rend cette caractérisation encore plus difficile. De plus, le milieu humain lui-même est en train d'évoluer rapidement avec une augmentation constante de la population humaine, dont la plupart vit maintenant dans les villes. Cette croissance de la population conduit ensuite à une augmentation de l'aménagement des sols, et une demande de plus en plus importante de ressources en eaux. C'est pourquoi un nombre plus important d'études scientifiques sur le sujet des eaux souterraines dans le milieu humain apparaissent depuis peu.

Avec tout cela en tête, cette thèse a pour but d'identifier les impacts du milieu humain sur des ressources en eaux souterraines. Avec les connaissances recueilles dans la littérature, nous avons étudié la pertinence d'outils hydrologiques, établis et nouveaux, pour caractériser le cycle d'eau dans l'environnement anthropique avec précision. Notre étude a été réalisée comme une étude de cas dans un bassin versant en voie d'urbanisation, hôte d'une aquifère peu profonde et non confinée, sur le plateau suisse. L'accent a donc été mis sur une zone urbaine où les eaux souterraines sont activement exploitées pour l'approvisionnement municipal et agricole en eau.

Nos méthodes ont compris un bilan analytique d'eau pour estimer la recharge de la nappe phréatique, suivi d'une analyse statistique des indicateurs chimiques, pour identifier les sources et voies d'écoulement des eaux à l'entrée et à la sortie de la nappe phréatique. Pour notre bilan d'eau, nous avons utilisés des données publiques qui sont facilement accessibles. Nous avons démontré qu'avec une base de données minimale, il est possible d'estimer l'évolution historique de la recharge de la nappe phréatique, y compris une estimation des variables individuelles dans le bilan d'eau – notamment la relation entre le ruissellement et l'infiltration des précipitations. Ensuite, pour les analyses plus profondes, nous avons complémenté les données publiques avec l'installation d'un réseau de piézomètres dans le centre urbain du bassin versant. Avec ce réseau, nous avons construit une base de données comprenant des variables physiques, chimiques, et isotopiques. Ces données, en combinaison avec les informations sur le réseau fluvial et le réseau d'égouts, nous ont permis de déterminer toute communication éventuelle entre les eaux souterraines, les eaux de surface, et le système d'égouts. Ces résultats ont démontré l'aptitude de

notre approche pour la caractérisation des dynamiques des eaux souterraines dans des bassins versants urbains.

Zusammenfassung

Das Verständnis der Dynamik von Grundwasserressourcen, die dem Druck menschlicher Aktivitäten ausgesetzt sind, ist zu einem zentralen Thema der Hydrogeologie des 21. Jahrhunderts geworden. Die Verfügbarkeit von Grundwasser wird sowohl quantitativ definiert - wie viel Wasser in einem Grundwasserleiter gespeichert ist - als auch qualitativ - wie viel Grundwasser in ausreichender Qualität für den Verbrauch zur Verfügung steht. Veränderungen in der Landnutzung haben sich direkt auf diese beiden Facetten ausgewirkt. Aufgrund seiner verborgenen Natur ist die genaue Bestimmung der Menge des verfügbaren Grundwassers bekanntermassen schwierig, und die zusätzliche Komplexität aus menschlichen Stressoren verstärkt diese Schwierigkeiten nur noch. Hinzu kommt, dass die menschliche Gesellschaft selbst einem raschen Wandel unterworfen ist, mit einem stetigen Anstieg der menschlichen Bevölkerung, von der grössere Teil heute in Städten lebt. Diese Bevölkerungszunahme hatte zu einer Vergrösserung der für die anthropogene Nutzung bestimmten Landfläche geführt und erfordert immer grössere Mengen an Wasserressourcen für Trinkwasser, landwirtschaftliche Anwendungen und industrielle Prozesse. Folglich sind in der wissenschaftlichen Literatur immer mehr Bemühungen zum Thema Grundwasser in der menschlichen Umwelt zu verzeichnen.

Vor diesem Hintergrund befasst sich diese Arbeit mit der Identifizierung der Auswirkungen verschiedener anthropogener Landnutzungsmuster auf die Grundwasserressourcen, sowie mit den spezifischen Diskussionen um diese Auswirkungen in modernen Studien. Mit dem aus der aktuellen Literatur zusammengetragenen Wissen haben wir die Anwendbarkeit sowohl etablierter als auch neuartiger hydrologischer und hydrogeologischer Werkzeuge zur genauen Charakterisierung des Grundwasserkreislaufs in der anthropogenen Umwelt untersucht. Unsere Studie wurde an einem Teststandort in einem urbanisierenden Einzugsgebiet im Schweizer Mittelland durchgeführt, das einen flachen, ungespannten fluvio-glazialen Grundwasserleiter enthält. Der Schwerpunkt wurde daher auf ein städtisches Gebiet gelegt, in dem das Grundwasser aktiv für die kommunale und landwirtschaftliche Wasserversorgung genutzt wird.

Unsere Methoden umfassten eine analytische Wasserbilanz zur Schätzung der Grundwasserneubildung unter Verwendung öffentlich zugänglicher Daten, gefolgt von einer statistischen Analyse chemischer Indikatoren, um die Quellen und Wege des Wassers in und aus einem Aquifer zu identifizieren. Mit nur minimal wenigen öffentlichen Daten waren wir in der Lage, historische Veränderungen der Grundwasserneubildung im Laufe eines Jahrzehnts abzuschätzen, einschliesslich einer Beurteilung der Veränderungen der einzelnen Variablen der Grundwasserbilanz -

insbesondere Sturmabfluss gegenüber der Infiltration. Zur Ergänzung der öffentlichen Daten für die weitere Analyse wurde ein Netzwerk von Grundwasserbeobachtungsbrunnen im am stärksten verstädterten Gebiet unseres untersuchten Einzugsgebietes installiert, aus dem eine Datenbank mit physikalischen, chemischen und isotopischen Variablen aufgebaut wurde. Für chemische Untersuchungen wurden konventionelle Analysen anorganischer Ionen mit organischen Mikroverunreinigungen kombiniert, die ein relativ neuartiges, für die menschliche Umwelt spezifisches Werkzeug darstellen. Diese Daten, kombiniert mit Informationen über die räumliche Verteilung des Flussnetzes und des Kanalisationssystems, ermöglichten es uns, potenzielle Wechselwirkungen zwischen Grundwasser, Oberflächenwasser und dem Kanalisationsnetz zu bewerten. Diese Ergebnisse haben die Eignung unseres Ansatzes zur Erfassung der Grundwasserdynamik in einem urbanisierten Einzugsgebiet gezeigt.

Mots-Clés:

Qualité des eaux souterraines, Hydrogéologie urbaine, Utilisation des terres, Ruissellement, Recharge des eaux souterraines, Interactions des eaux souterraines – eaux de surface, Hydro-géochimie, Micropolluants organiques

Key Words:

Groundwater Quality, Urban Hydrogeology, Land Use, Surface Runoff, Groundwater Recharge, Groundwater – Surface Water Interactions, Hydro-geochemistry, Organic Micropollutants

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List of Acronyms

Chapter 2

AMD...Acid Mine Drainage
ASR...Aquifer Storage and Recovery
ASTR..Aquifer Storage Transfer and Recovery
BTEX...Benzene, Toluene, Ethylbenzene, Xylene
cDCE...cis-1,2 Dichloroethene
DNAPL...Dense Non-Aqueous Phase Liquid
EPMC..Emerging Pharmaceutical Manufacturing Country
LNAPL..Light Non-Aqueous Phase Liquid
MAR..Managed Aquifer Recharge
NAPL...Non-Aqueous Phase Liquid
OC...Organic Contaminants
PCE..Tetrachloroethene
SAT..Soil Aquifer Treatment
TCE..Trichloroethene
VC..Vinyl Chloride
WWTP...Wastewater Treatment Plant

Chapter 3

AET...Actual Evapotranspiration
API...Antecedent Precipitation Index
C_Q...Streamflow Coefficient
C_{qf}...Quickflow Coefficient
C_{Roff}...Runoff Coefficient
CN..Curve Number
CSO...Combined Sewer Overflow
GAP...Genetic Algorithm
GWR..Groundwater Recharge
HS...Hydrograph Separation
I_a..Initial Abstraction
k..API Decay Factor
M..Soil Moisture
MC..Monte Carlo
P...Precipitation
P_5...5-day Antecedent Precipitation
Q..Streamflow
Q_0..Upper Streamflow Component
Q_1...Intermediate Streamflow Component
Q_2..Lower Streamflow Component

qf..Quickflow
R_{off}..Surface Runoff
S_0..Maximum Potential Retention
SLZ..Lower Soil Zone Storage
SM..Soil Moisture
SME...Sahu-Mishra-Singh (method)
SP..Snow Pack
SUZ..Upper Soil Zone Storage
WWTP..Wastewater Treatment Plant
β...Fraction of Antecedent Precipitation Contributing to M
λ...I_a Coefficient

Chapter 4
ATR..Atrazine
BTZ...Benzotriazole
CAF...Caffeine
CSO...Combined Sewer Overflow
EDF..Empirical Distribution Function
HCA..Hierarchical Cluster Analysis
L..Distance Between Flow Boundaries
LOQ...Limit of Quantification
WWTP..Wastewater Treatment Plant
ϕ...Flow Potential

1. INTRODUCTION

1.1. Groundwater and the Human-influenced Water Cycle

In modern times, human activity has had significant influence on every environmental compartment on the planet. Fresh water resources, vital to life on earth, are no exception. Groundwater in particular serves as a principal source of freshwater supply for many regions, and is generally considered to be better safeguarded against pollution through filtering from subsurface sediments when compared to surface water. However, as aquifers are relatively long-term storage reservoirs, groundwater quantity or quality degradation can become long-term issues. The increasing stressors of climate change, industrial activity, and an expanding global population that is migrating to cities en masse have all led to an increased risk of pollution and depletion of groundwater resources (Burri et al., 2019; Han et al., 2017). It is essential to continue to improve our understanding of human-influenced groundwater systems so that the necessary steps can be made to protect them and secure their long-term availability.

The difficulty in characterizing groundwater arises largely from its hidden nature in the subsurface. While some direct observations of physical aquifer properties and dynamics are made possible via monitoring wells, soil cores, or geophysical surveying, much of what we understand comes from indirect observations (Figure 1-1). On top of natural environmental complexities, anthropogenic-influenced water cycles present additional challenges in hydrogeological characterization. In general, these challenges emerge from sources including induced changes in aquifer properties and differences from a natural water cycle (Han et al., 2017). The water balance as a whole is often artificialized, groundwater extraction is increased, and a myriad of chemicals that are applied for various purposes end up polluting aquifers (Barron et al., 2013; Scanlon et al., 2005). Often, groundwater risk assessment is based only on approximate knowledge, and unexpected difficulties will arise when the true state of the subsurface differs from an approximated conceptual model. Even the best risk assessments and land development practices are only as good as the knowledge on which they are based.

Anthropogenic land use is diverse. In order to get a grip on the array of human landscapes, it is useful to classify them into three global categories of agricultural, industrial, and urban land use. Each of these categories is defined by a set of basic shared characteristics. Agricultural landscapes are areas dedicated to cultivating plants and livestock, largely for food as well as for energy production. Industrial landscapes are dedicated to activities including mass production, raw material extraction, refineries, or major ports. Urban areas generally comprise large settlement areas, large population densities, commerce, and transportation infrastructure serving the city's inhabitants. While these three categories are helpful for conceptualization, it is important to keep in mind that large overlaps exist between categories, such as industrial-scale farming or urban industrial parks, among others. Many regions are in fact composed of a matrix of different land uses, particularly for cities. One thing that all of these categories have in common is their dependence on water.

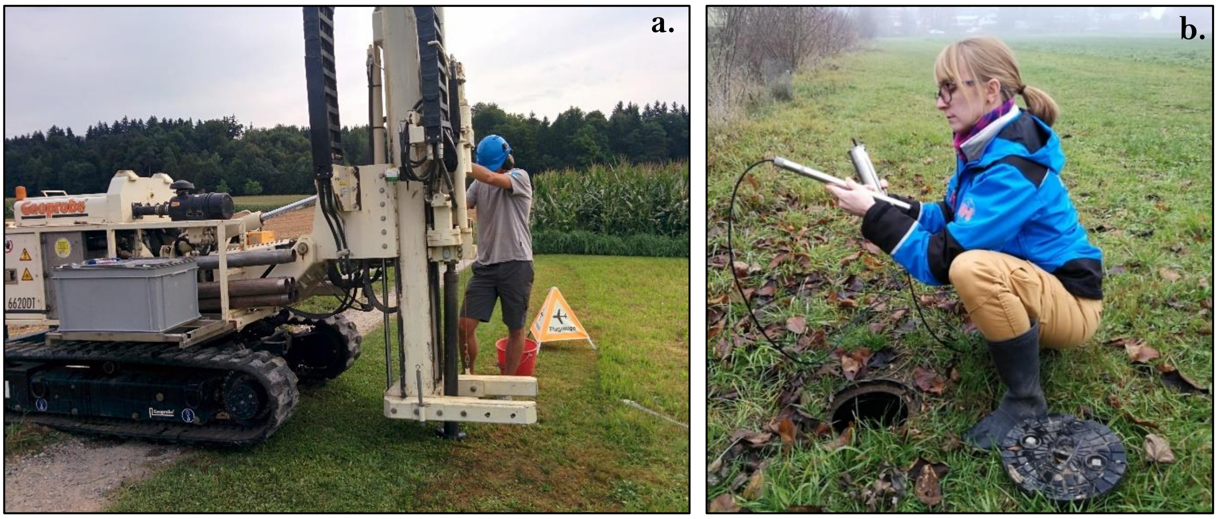

Figure 1-1. Groundwater monitoring wells allow us to directly observe and sample the subsurface. a.) installation of monitoring wells and soil core collection with a direct-push Geoprobe; b.) wireless sensors allowing for continual monitoring of basic groundwater conditions.

For practical reasons, most developed land is located in proximity to water resources. This is indeed an ideal situation as it secures ease of access and reduction of energy needs tied to importing water from afar. Further, when local aquifers are exploited for drinking water, issues are more visible in the community, who thus have a direct interest in protecting their resources. However, this same practical layout also poses a risk to these resources because of the impacts of land use. In many cases, land development has greatly outpaced research and understanding, leading to incomplete or fully absent risk assessments. Informal settlements in urban areas are a prominent example. Some solutions to land-use stressors have been presented, with water-efficient appliances, nature-based solutions, and effective remediation tools that certainly can offer considerable improvements in environmental protection (Kurth et al., 2015; Phillips, 2009). Still, issues persist in many areas due lack of funding for infrastructural improvements, uncontrolled or rapid urban expansion, and the unfortunate reality of short-term special interests taking priority over sustainable growth in the realm of decision-making (Baba and Ayyildiz, 2006; Gordalla et al., 2013; Masten et al., 2016).

Groundwater contamination risks from human land use are many. Raw wastewater can make its way into an aquifer directly via sewer leakage or indirectly via combined sewer overflow. Nitrates, phosphates, pesticides, herbicides, and biocides are carried with storm runoff into streams and into groundwater. Products from industrial parks such as NAPLs, VOCs, de-icing agents, corrosion inhibitors, and numerous others leach from the surface or through industrial effluent networks. These are without mentioning the legacy contamination issues that persist from activities over the past decades and even centuries (Burri et al., 2019). Further, all anthropogenic contamination may be compounded with natural geogenic contamination issues.

1.2. Groundwater Recharge in Urbanizing Catchments

Approximately 80% of fresh water resources in Switzerland come from groundwater, much of which is contained in unconfined aquifers in proximity to cities; of these resources, approximately 50% come from springs and 50% via pumping wells (Reinhardt et al., 2019). This pattern between human settlement and water resources is observed the world over. In order to define sustainable levels of groundwater abstraction, estimates of groundwater recharge are vital. As a result, the importance of understanding recharge and its influencing variables in urban environments is widely acknowledged, and the past few decades have produced numerous studies and knowledge gains to this end (Barnes et al., 2018; Barron et al., 2013; Foster et al., 1999; Gremillion et al., 2000; Ku et al., 1992; Lerner, 1990; Paul and Meyer, 2001; Schirmer et al., 2013).

Deforestation, impervious surfaces, buildings, water mains, wastewater canals, storm infrastructure, parks and gardens, agricultural plots, industrial centers, and water treatment plants are just a few of many components of urban landscapes that interact directly with groundwater bodies. For example, surface runoff, evapotranspiration, and groundwater recharge are often modified to a considerable extent due to an increase in impervious surfaces (Thomas and Tellam, 2006). Subsurface flow is altered by the presence of water distribution networks, storm drains, and sewer systems (Lerner, 1990; Rutsch et al., 2008). Rivers and streams are often straightened and canalized or dammed in and around the city limits, to the detriment of important riparian zones (Kurth et al., 2015). Groundwater – surface water interactions may be attenuated or reversed (Marsalek et al., 2007). All of these dynamics have consequences for groundwater recharge, and may carry risks.

Our interest here lies in unconfined urban aquifers, due to their diffuse and direct connection with conditions at the surface. A large number of tools and methods have been applied to estimate groundwater recharge (Healy, 2010), many of which are applied to estimate urban groundwater recharge. For example, Thomas and Tellam (2006) used a GIS-based model to estimate groundwater recharge and pollutant transport for the city of Birmingham, England. Their model was structured with land use data, geological maps, hydrological and meteorological data, and geochemistry to make estimates under different urban land cover types. Barron et al. (2013) applied the distributed, physically-based, surface water – groundwater coupled MODHMS model to study the effects of urbanization in a sub-catchment close to Perth, Australia. The authors accounted for artificial factors including irrigation and groundwater abstraction, and applied their strategy for predictions on future scenarios of urban development. Meriano et al. (2011) made use of stable water isotopes and hydrochemistry to investigate the relationship between storm runoff and groundwater recharge in an urban catchment near Ontario, Canada. The authors compared estimates from hydrograph separation with water table fluctuations, focusing on the importance of recharge in the midsummer months.

Many of these methods, at all levels of complexity, calculate recharge with a water balance equation of some form. For unconfined, predominately rain-fed aquifers, groundwater recharge can be expressed as a water balance as such:

$$GWR = P - ET - R_{off} \tag{1-1}$$

where GWR is groundwater recharge, P is precipitation, ET is evapotranspiration, and R_{off} is surface runoff. This seemingly simple balance integrates a majority of the factors controlling groundwater recharge for unconfined aquifers including climate, vegetation, geology, and soil types, which control evapotranspiration, runoff, recharge, and interactions between water bodies. All of these variables are further impacted by land use changes, which are therefore also integrated into the groundwater balance in its most simple form. The often-observed increases in surface runoff accompany the sealing of surfaces for roads, sidewalks, parking lots, homes and buildings, among others (Eshtawi et al., 2016). More recently, the interplay between urban evapotranspiration and infrastructure has been a point of investigation, with findings that ET dramatically decreases under impervious surfaces (Minnig et al., 2018). Many of these changes can be explicitly accounted for in a groundwater balance when estimating the input variables of runoff and evapotranspiration (Barron et al., 2013). The balance can further be expanded by adding terms for regional aquifer flow, percolation from lakes, and other natural phenomena, as well as artificial inputs and outputs including water mains or sewer leakage, managed aquifer recharge, or diversion of streamflow for hydroelectric power.

Figure 1-2. Groundwater characterization is a group effort that requires effective collaboration between different specialists. Here, a groundwater modeler accompanies field work.

Urban groundwater studies are also particular in that, in ideal cases, they often require collaboration between specialists in an array of domains. Field scientists, hydrochemists, and groundwater modelers have been working together for several decades at this point (Figure 1-2). Specialists in civil engineering, urban planning, solid waste and wastewater management, and agriculture are just a few of many additional voices that should regularly be included in comprehensive urban hydrogeology studies. More recently, an increasing number of studies in this direction have come about, a notable example being coupled models between groundwater and sewer networks (Karpf and Krebs, 2011; Wolf et al., 2006). It is only through collaborative efforts that thorough characterization and informed policy can succeed.

1.3. Tracers for Characterizing Groundwater Flow

Chemical and physical tracers, or indicators, are a useful tool in hydrogeology for identifying groundwater flow and associated processes, as well as studying the consequences of development on environmental functions and water resources (Cook and Herczeg, 2000). In the current text, our use of tracers does not include those artificially added to a water body in order to study its characteristics (dye or salt tracers, for example). We focus solely on tracers that are present in the environment. Tracers are capable of shedding light on water sources, flow pathways, and contamination, as well as identifying bio-geo-chemical controls tied to oxidation or reduction, microbial degradation, or denitrification, among others. As such, tracers are used to a wide variety of ends in the hydrological sciences and related fields, and have proven to be extremely valuable and versatile in their application.

Many tracer types lend themselves well to the various objectives within the urban hydrological sciences. They are used as stand-alone tools, combined for analysis of multiple tracer types, or used in tandem with groundwater balances or physical flow models. Statistical techniques are common tools in tracer analysis (Gotway et al., 1994). Techniques such as correlation analysis, principal component analysis, cluster analysis, or factor analysis are useful for quickly exploring multi-dimensional parameter spaces, identifying end members, and constructing mixing models (Barthold et al., 2011; Moeck et al., 2016; Tubau et al., 2014). More recently, semiparametric and nonparametric methods have become important tools for working with trace chemicals, where many measurements will fall below the limit of quantification (Helsel, 2012; Noack et al., 2014; Szarka et al., 2018).

In this work, we turn our focus to inorganic ions, stable water isotopes, and emerging organic contaminants, the latter collectively referred to as micropollutants. These tracers are often used to separate localized, line, and diffuse sources of recharge and of contamination (Katz et al., 2011; Minet et al., 2017); for hydrograph separation to quantify baseflow, quickflow, and other streamflow elements (Klaus and McDonnell, 2013); to determine groundwater – surface water interactions (Cook et al., 2018); to differentiate multiple groundwater plumes (Van Stempvoort et al., 2013); or to differentiate raw wastewater from treated effluent (Zirlewagen et al., 2016). The possibilities are seemingly endless. For example, Moeck et al. (2016) used a combination of inorganic, organic, and isotopic tracers to characterize groundwater flow in a managed aquifer recharge zone near Basel, Switzerland. The authors applied multicomponent statistical analyses to inorganic chemistry in order to identify water types and mixing, and validated these findings with isotopic signatures and micropollutant concentration ranges. Minet et al. (2017) applied water isotopes with nitrogen isotopes to explore sources and pathways of nitrates in groundwater in a rural area in southeast Ireland. Spearman correlations between isotope types were used to indicate processes including denitrification and mineralization, and differentiate point sources from diffuse sources. As a final example, Van Stempvoort et al. (2013) applied pharmaceuticals and Acesulfame as tracers to differentiate multiple wastewater plumes in two urban watersheds. Correlations between persistent compounds were used to identify single or multiple wastewater plumes, and emphasis was placed on the need to use multiple micropollutants as co-tracers to validate results.

Each tracer type has its relative strengths and drawbacks. Stable water isotopes are integrated into the water molecule itself, and are highly conservative in nature. Inorganic hydrochemistry is also relatively conservative, and can additionally be used to identify groundwater – surface water interactions or mixing of end-members (Cook et al., 2018). The hitch with stable isotopes and ions is that they have high background levels in nature and as such, are not inherently source-specific (Barrett et al., 1999; Gasser et al., 2010). Micropollutants, for their part, are a very source-specific marker compared to other tracer types, with zero background levels in the natural environment. The shortcomings in this case are that micropollutants are subject to degradation in the environment through many processes (Warner et al., 2019). As elucidated in the examples above, the best way to exploit the strengths of different tracer types is often to use them in combination (Moeck et al., 2017c).

Micropollutants as tracers are a relatively novel tool when compared to ions and isotopes, meriting some further detail. The class of micropollutants comprises a seemingly innumerable number of organic compounds (Postigo and Barceló, 2015), which can be overwhelming to work with. The specific research questions of a project are a first step to refine which compounds to target (Schirmer et al., 2011). Products that are suitable as tracers for municipal wastewater will differ from those used for agricultural irrigation and drainage, products used as source indicators may differ from those used as process indicators, and those used to indicate quality degradation will meet slightly different requirements (Table 1-1; Warner et al., 2019). Other important factors to refine target compounds include knowledge on local practices and the state of infrastructure, which will determine what products could be found in the environment.

Recharge Source	**Flow Path**	**Infrastructure**	**Marker**
Rainfall and Irrigation	Infiltration	Green spaces, paved surfaces, buildings	Pesticides and biocides
	Surface runoff		
Waste Sewers and Water Mains	Storm overflow	Drainage canals, septic tanks, sewer pipes, WWTP	Pharmaceuticals, lifestyle products
	Leakages		

Table 1-1. Overview of major urban water sources and pathways into groundwater, and the micropollutants commonly used to identify them. See Postigo and Barceló (2015), Schirmer et al. (2011), and Warner et al. (2019) for comprehensive information.

1.4. Objectives and Structure of Thesis

The purpose of this thesis is to investigate the nature of aquifer recharge, sources of groundwater flow, and risk of quality degradation in human-impacted environments using data-driven techniques. We approach this by way of quantifying groundwater reserves and identifying surface water – groundwater interactions as well as source-specific indicators of human influence. We make use of both public databases as well as data collected within the context of this study to carry out our characterizations, which include physical as well as chemical databases. As a first step, we review the topic of anthropogenic groundwater risks within the global context of current issues, research questions, and methods that are being discussed in modern literature. The next steps take these identified concerns to target an investigation of a field site within an urbanizing catchment in Switzerland. Specific research questions include:

- What are the sources of major risks towards groundwater quality and quantity in the modern anthropogenic environment?
- How do these risks manifest themselves in the different contexts found in real-world studies?
- How can we estimate groundwater recharge within the urban water cycle?
- How can we utilize hydrochemistry to illuminate sources of recharge and groundwater flow?
- What information do different tracer types offer for an aquifer system?

This thesis is presented in the following way. After the current chapter 1, chapter 2 is dedicated to assembling the contemporary state of knowledge between land use and groundwater quality. A review of currently identified risks from different land use types, human activities, and waste management is presented, along with how they behave in differing climates, aquifer types, and other environmental compartments. This is followed by an exposé of case studies that have addressed questions surrounding groundwater contamination in contemporary times. These highlighted studies are meant to act as a window into the variety of specific issues that different regions of the world are facing. This review is of use in order to identify appropriate methods for characterization and to identify where gaps in understanding persist.

Chapter 3 focuses on the physical aspects of the water balance as it relates to groundwater recharge, and is carried out as a case study. From our review in chapter 2, a recurring theme of surface runoff and groundwater recharge emerged, which we decided merited exploration at our study site. We apply a top-down water balance focusing on the runoff – recharge relationship, which is unequivocally impacted by land use change and has consequences for both water quantity as well as water quality. Our efforts investigate the utility and performance of empirical and conceptual methods that continue to be widely used today. Such methods are of interest as they are transferrable to most regions of the world due to minimal data requirements. Additional emphasis is placed on what should be changed with such methods so that they continue to integrate increases in knowledge, and better capture groundwater dynamics under land use change.

In chapter 4, we focus on the ability of environmental tracers to capture the characteristics of urban groundwater flow, within the same field site as in chapter 3. We made use of a groundwater monitoring network installed in the context of this study in order to monitor the groundwater, collect water samples, and construct an internal database on groundwater levels, hydrochemistry, and stable water isotopes. We analyzed the use of emerging organic contaminants – a.k.a. micropollutants – as appealing urban tracers due to the fact that they are very source-specific in comparison to more traditional environmental tracers. A targeted screening of micropollutants were carried out in both surface water and groundwater samples to work out the presence of a variety of recharge sources unique to urban areas. However, these tracers are relatively novel and are non-conservative. To strengthen our hypotheses drawn from their results, we sought to compare findings with the application of conservative tracers that have a longer track-record of use in hydrogeology. The interpretations gathered from these environmental tracers are analyzed alongside probabilistic groundwater flow fields in order to validate the results from hydrochemistry and water isotopes. With these analyses, we aim to shed light on human influence, sources of flow, groundwater – surface water interactions, and areas vulnerable to contamination.

This thesis is finished with a discussion of our overall findings in chapter 5. We also offer our suggestions for future research directions within the realm of anthropogenic hydrogeology.

2. A Review of Threats to Groundwater Quality in the Anthropocene[1]

2.1. Abstract

Awareness concerning sustainable groundwater consumption under the context of land use and climate change is gaining traction, raising the bar for adequate understanding of the complexities of natural and anthropogenic processes and how they affect groundwater quality. The heterogeneous characteristics of aquifers have hampered comprehensive source, transport and contaminant identification. As questions remain about the behavior and prediction of well-known groundwater contaminants, new concerns around emerging contaminants are on the increase. This review highlights some of the key contaminants that originate from anthropogenic activities, organized based on land use categories namely agricultural, urban and industrial. It further highlights the extensive overlap, in terms of both provenance as well as contaminant type, between the different land use sectors. A selection of case studies from literature that describe the continued concern of established contaminants, as well as new and emerging compounds, are presented to illustrate the many qualitative threats to global groundwater resources. In some cases, the risk of groundwater contamination lacks adequate gravity, while in others the underlying physical and societal processes are not fully understood and activities may commence without adequately considering potential impacts. In the agricultural context, the historic and current application of fertilizers and plant protectants, use of veterinary pharmaceuticals and hormones, strives to safeguard the growing food demands. In the context of a sprawling urban environment, waste, human pharmaceuticals, and urban pesticide outputs are increasing, with adequate runoff and sanitation infrastructure often lagging. Finally, industrial activities are associated with accidental leaks and spills, while the large-scale storage of industrial byproducts has led to legacy contaminants such as those stemming from raw mineral extraction. With this review paper, we aim to underscore the need for transdisciplinary research, along with transboundary communication, using sound science and adaptive policy and management practice in order to procure sustainable groundwater quality.

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2.2. Introduction

Groundwater quality degradation is a well-recognized phenomenon and has received considerable attention since the industrial revolution (Arias-Estévez et al., 2008; Spalding and Exner, 1993; Von Der Heyden and New, 2004). In spite of this, many aspects concerning the understanding and management of groundwater as a resource remain complex, and adequate information, in many cases, remains elusive (Famiglietti, 2014). In addition to natural heterogeneities, anthropogenic activities in all sectors have been shown to impact and alter the natural water cycle and subsequent groundwater quality (Figure 2-1). These changes can have wide-ranging impacts on ecosystem functioning and human health.

The vulnerability of an aquifer and its risk of contamination in the anthropogenic environment arises from the complex interplay of the natural dynamics of the hydrological cycle with the physical alterations of the earth surface, water resource exploitation, and waste emissions from anthropogenic activities. Physical changes to the landscape that can lead to increased risk include changes in surface roughness, surface sealing, topographic alterations, river canalization, or construction of artificial water bodies (Bhaskar et al., 2016; Han et al., 2017). In addition to changing land cover, anthropogenic activities include the extensive application of natural and synthetic chemical products. The use of such products has ensured high crop yields, improved human and animal health, sufficient energy, material production, and functional infrastructure.

However, many substances that are widely used today have been shown to be soluble, mobile, and persistent in groundwater, as well as toxic to environmental or human health (Wakida and Lerner, 2005). Many more products are of yet unknown risk, and the risk of chronic exposure to a cocktail of products in any environmental compartment has been thus far difficult to characterize (Kim et al., 2011; Musolff et al., 2010).

Figure 2-1. Sources of potential groundwater contaminants, as diffuse and point source inputs, from agricultural, urban and industrial settings and with respect to the dominant flow direction (arrows).

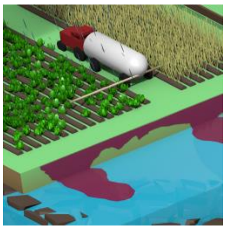
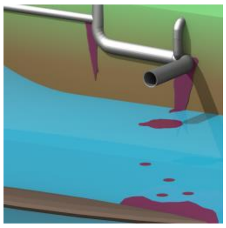
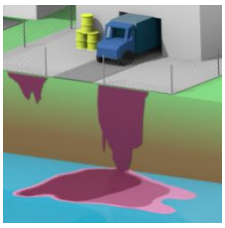
When an aquifer becomes contaminated with harmful chemical products, it may become unusable for decades. The residence time of contaminants within groundwater bodies can be anywhere from weeks to decades, depending on physico-chemical properties of compound and environmental conditions (Chapman and Parker, 2005; Freitas et al., 2015; Moeck et al., 2017a). In addition, the effects of groundwater contamination do not end with the loss of well-water supplies. Several studies have documented the migration of contaminants from disposal or spill sites to nearby lakes and rivers as groundwater passes through the hydrologic cycle (Conant et al., 2004).

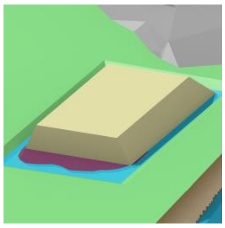
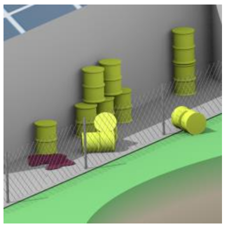
These issues are widely recognized in the scientific community. In many areas of the world, regulatory bodies have implemented concentration limits for a large number of contaminants in drinking water bodies, with nitrate likely being the most notable example. Still, groundwater contamination stemming directly from anthropogenic activities remains a persistent and ever-increasing concern (Lapworth et al., 2017; Wakida and Lerner, 2005). The current expansion of anthropogenic activities is often in direct contrast with what is needed to protect groundwater resources for future use (Howard, 2015; Khan et al., 2016).

In this article, we review some of the major controls on groundwater contamination from anthropogenic activity, and discuss several relevant contaminant classes from these activities. We follow by highlighting a number of case studies in literature that address historic and emerging issues in contaminant hydrogeology, as well as the diversity of issues that arise in different regions of the world. The effect of practices such as land development and waste production on groundwater in terms of pollutant class, sources, and pathways are discussed in order to underscore the myriad of issues that can arise when anthropogenic controls are present on top of natural controls. We focus on dynamics in three major land use types: 1) agricultural, 2) urban, and 3) industrial (Table 2-1), and the diffuse and point source manner in which they can introduce contaminants to groundwater sources (Figure 2-1). Due to their relevance in these environments, the following contaminant classes are included: nitrates, pesticides and biocides, pharmaceuticals and hormones, non-aqueous phase liquids (NAPLs), and acid mine drainage (AMD).

The urgent need for an improved understanding of contaminant dynamics in the built environment has been outlined in scientific literature and government directives alike (Bhaskar et al., 2016; Howard, 2015). This review attempts to underscore the complex interaction of groundwater contaminants, sources, and transport processes in heterogeneous environments. The pressing need to secure sustainable groundwater quality, and the call for transdisciplinary and transboundary actions as we move into 2020, are paramount (Montanari et al., 2013; UNDP Sustainable Development Goal 6, 2018).

Table 2-1. Major contaminants associated with the agricultural, urban and industrial land use categories and their threats to groundwater quality. Images of conceptual contamination pathways refer to Figure 2-1.

Land use Category	Potential contaminating compounds	Remarks on potential pathways and processes	Conceptual contamination pathways
Agriculture	Fertilizer (nitrates and phosphates) application as potential diffuse contamination	When nutrient load exceeds uptake capacity of plants, runoff or infiltration into groundwater bodies may result.	
	Crop protection (pesticides, herbicides etc.) as potential diffuse contamination	Agrochemicals, and their degradation products, can runoff and/or infiltrate into and remain in groundwater bodies for substantial amounts of times.	
	Use of veterinary products (antibiotics, hormones, etc.) as potential diffuse and point source contaminants	Antibiotics and hormones, although currently only detected in low concentrations groundwater, may pose a significant risk to the receiving environment.	
Urban	Wastewater as potential vector for point source and diffuse nitrate and pharmaceutical contaminants	Wastewater may enter groundwater bodies through sewer leakage, poor infrastructure, or via receiving streams down-gradient of wastewater treatment plants.	
	Runoff as potential vector for point source and diffuse nitrate, pesticide, road salts, etc. contamination	Products applied to urban surfaces readily leach into storm water and can reach groundwater at localized or diffuse infiltration points. In combined storm – sewer systems, untreated wastewater can also overflow as runoff.	

	Leachate from solid and liquid waste as potential diffuse contamination	Lack of adequate lining of landfills or inadequate sanitation infrastructure can threaten aquifers through the introduction of solid and/or liquid anthropogenic waste as leachate.	
	Managed aquifer recharge (MAR) and wastewater irrigation as vectors for diffuse nitrate and pharmaceutical contaminants	In many water-scarce regions, wastewater presents a valuable resource. However there is increasing concern regarding aquifers vulnerability underlying such systems, especially when these aquifers are considered as potential drinking water sources.	
Industry	Spills and leaks as potential point source for BTEX (benzene, toluene, ethylbenzene, xylene) contaminants	Subsurface heterogeneities, even in relatively simple porous aquifers, with horizontal bedding features overlying aquitards, compose complex transport processes, posing a significant challenge for the remediation of BTEX spills.	
	Runoff, leachate and precipitate as source and vector for diffuse contamination, and sever water chemistry alteration	Mining exposes minerals sulphates to surface reactions, resulting in radically altered pH conditions in associated waters . This phenomenon, known as AMD, may result in the precipitation or increased solubility of heavy metals.	

2.3. Natural Controls on Groundwater Contamination

In the context of understanding the propagation of solute fluxes in the subsurface, it is worthwhile to briefly recall the major controls on groundwater storage and quality in the natural environment. Groundwater quantity and quality is controlled by a water balance that can be characterized at several scales (local, regional, and global). Those controls deemed most prevalent to the water balance are discussed here. These underlying factors are important to keep in mind, as they will be built upon and frequently referred to in the construction of conceptual models for anthropogenic groundwater dynamics.

Natural groundwater occurrence and vulnerability depends first and foremost on regional weather conditions and climate oscillations (Gurdak et al., 2007; Randall and Mulla, 2001). In the case of fossil groundwater, this includes historical climatic conditions. The most important climatic parameters are precipitation, humidity and evapotranspiration (O'Driscoll et al., 2005). Precipitation or high humidity serve as major recharge for most aquifers, either through direct infiltration or through indirect runoff regimes (Jones, 2010). Evapotranspiration encompasses further climatic variables such as radiation, temperature, wind dynamics, and heat exchanges, all of which affect groundwater quantity and quality. For example in semi-arid and arid regions, rainfall is erratic and evapotranspiration is often high, resulting in reduced recharge and a concentrating effect of solutes within the unsaturated zone (McMahon et al., 2006).

Topography, vegetation cover, soil types and the underlying geology also play a major role in groundwater dynamics. Steeper slopes tend to increase surface runoff, and decrease groundwater residence time, whereas flat terrains tend to have decreased surface runoff accommodating increased infiltration. Soil types can vary dramatically within and across landscapes, depending on the underlying geology and land surface processes, and dampen or enhance recharge rates (e.g. O'Driscoll et al., 2005). Land cover, including flora (both living and decaying) and surface water bodies, are an additional determining factor for how much water is exchanged between surface and groundwater bodies. In the vadose zone, plant root systems can create preferential flow pathways, while dense floral cover can result in high evapotranspiration rates and reduced surface runoff.

Local and regional geology and tectonic deformation define the physical characteristics of an aquifer, and thus the natural dynamics of groundwater recharge and flow in the subsurface. Mineral-water interaction at the rock surface determines much of an aquifer's qualitative characteristics, such as hardness and pH, among others (Naicker et al., 2003). Sediment matrix characteristics such as the presence of confining layers, or grain size and pore spaces are all products of the parent geology combined with the weathering effects of climate. These physical matrix characteristics will influence aquifer storage capacity, including the rate and magnitude of recharge, flow and transport. Along with aquifer depth, these characteristics will also determine the average residence time of groundwater.

Soils and sediment regularly interact with solutes in all phases through chemical processes such as sorption, ion exchange, solute precipitation, and degradation (abiotic and biotic). In an aquifer, many such processes are controlled by pH-dependent redox conditions. In inorganic soils and sediments, redox reactions are generally retarded, while the presence of organic matter or bacteria in these layers tends to speed up reaction rates. As such, organic material in these layers can, to a large degree, regulate the contamination persistence (Jekel et al., 2015). In general confined aquifers tend to be oxygen-deficient, while unconfined, shallow or fissured aquifers tend to be oxygen-rich. Therefore, whether an aquifer is confined or unconfined will affect the cation exchange processes and reduction taking place. These factors determine the ability of the sediment matrix to degrade certain solutes that pass through its pores.

Hyporheic zones are the interface between surface water bodies and groundwater, and tend to be rich in organic matter and oxygen, resulting in an extremely reactive environment. Healthy riparian zones are able to strongly attenuate many potentially harmful solutes. Thick vadose zones and the presence of organic-rich layers are also very reactive and have the potential to sorb and degrade many chemical products, whereas thin vadose zones as well as highly permeable sands, gravels, presence of fissures or karstic features will do little to filter potential contamination (Pitt et al., 1999).

Groundwater recharge in shallow or unconfined aquifers normally occurs in a diffuse manner. Infiltration takes place relatively homogeneously in space, either over the entire wetted area or along preferential pathways. In confined, karstic, or fractured hard-rock aquifers, recharge and flow occur principally within networks of cracks, fissures, and other localized openings, so that both fast and slow recharge is often observed. Some flow pathways in these environments are active only after precipitation events or snow melt (Ballesteros et al., 2015). In fractured aquifers, the direction of flow might not coincide with the hydraulic gradient, as movement is also governed by fracture orientations in these settings (Graf and Therrien, 2007). As a result, in heterogeneous aquifers, water and solutes can spread in complex patterns by following both fast and slow flow pathways (Hunkeler et al., 1999).

Unconfined shallow and karstic aquifers alike are generally subject to the direct vertical inflow of surface waters. The quality of these infiltrating surface waters are therefore extremely consequential in these scenarios, as unconfined and karstic aquifers constitute a considerable amount of global groundwater reserves – approximately 25% of the global population is dependent on karstic groundwater (Ghasemizadeh et al., 2012; refer to Section 2.6.6 for contamination risks to karst systems). Contrarily, inflow to confined or deep aquifers is often indirect and may take years or decades. This fact can safeguard confined aquifers from degraded surface waters, but it can also present major remediation challenges once contaminated potentially compromising groundwater quality for decades due to long groundwater residence times (Chapman and Parker, 2005).

It can be seen that detailed knowledge on the nature of flow and chemical reactivity in groundwater bodies has been greatly developed over the last century, but the connection between hydrogeology and solute dynamics is still a developing science. The heterogeneity of most natural environments, combined with a lack of detailed aquifer information, makes a straightforward characterization of many systems nearly impossible (Hakoun et al., 2017). In general, highly complex systems are particularly vulnerable to contamination (Freitas et al., 2015; Wu and Hunkeler, 2013). Karstic aquifers for example are notoriously complex due to high spatial variations in porosity, making the data demand for proper characterization much more intensive (Ghasemizadeh et al., 2012).

2.4. Anthropogenic Controls on Groundwater Contamination

While the intrinsic vulnerability of an aquifer depends largely on the natural characteristics of its setting, contamination risk from anthropogenic activities depend predominantly on land use (Faye et al., 2004). Anthropogenic alterations are known to have significant impacts on every aspect of the water cycle, both by changing the magnitude of existing terms as well as the addition of new terms (such as leakages, extraction, or irrigation). Land development and land use practices significantly determine contaminant sources and the processes which control the contaminant propagation in the environment.

This review classifies land use into three broad categories (1. agricultural, 2. urban, and 3. industrial), which can be further split in a number of different ways. For example, to account for pastures versus croplands, residential areas versus streets, or primary material extraction sites versus production facilities. Another important example are road networks which connect the three defined land use categories. Although the density and expansion of road networks are generally higher in urban and industrial settings, they account for strong negative environmental impacts as they span across different landscapes (Ledford et al., 2016). Different land use categories rarely exist in isolation: residential areas may interface into pastures and fields, urban agricultural plots are a common feature in many cities, industrial parks may be large and set apart or they may be relatively small and within city limits, and intensive farming can bring elements of industrial activities into the agricultural setting. Current anthropogenic land use processes may also overlay sites of historical activities, including landfills or nuclear waste disposal facilities to name a few. In addition, there are relevant societal factors that define the specifics of land use activity and thus partially define risk of contamination. These include any prevalent human illnesses (refer to Section 2.6.5 for example) as well as regulations on the use of chemical and pharmaceutical products (see Table 2-2).

Thus, water quality experts who are looking to assess the risk of anthropogenic contamination to groundwater for a specific region, in addition to considering the natural setting, should not exclude the consideration of current local societal factors in context with existing and historic land use activities such as infrastructure and waste treatment technologies.

2.4.1. Land Development

It is estimated that since 2010, agricultural lands cover 30 - 40% of the world's usable land surface (FAO, 2019). Another 3% is occupied by urban and industrial landscape, including primary material exploitation (FAO, 2009). However, the density and intensity of activities are of equal, if not greater, importance to their spatial extent. For example, because urban areas comprise diverse land use features, high population densities, expansion of road networks, intense resource consumption, and high waste production, cities may pose an equivalent or even higher risk to groundwater contamination compared to adjacent agricultural areas (Han et al., 2017; Marsalek et al., 2007).

Changes to land cover are generally the first step in developing an area. This includes amending vegetation, topography, soil permeability, and surface water body characteristics, all of which feed in to the recharge and groundwater dynamics. Examples of the effect of these changes include thinning or clearing any existing vegetation, altering existing topography, wetland drainage, soil tillage, or addition of exotic vegetation types (usually for cultivation). Modification of vegetation stimulates change in evapotranspiration rates, and can either increase or decrease recharge, depending on the water demands of the dominant plant species and changes in solar radiation absorption or reflection. Deforestation, for example, leads to a decrease in plant transpiration, often stimulating increases in recharge (Brown et al., 2005).

Topographic alterations result from many different land uses. This includes creating artificial depressions or mounds for purposes such as flood control or installation of specific infrastructure. Perhaps one of the most prominent examples is excavation and tunneling in industrial mining operations. These excavations can create artificial surface water bodies, as well as mounds of discarded overburden or tailings. Tunnels can become preferential pathways when conditions become saturated.

Altering the physical characteristics of surface water bodies can change the direction of flow and the dynamics of interactions between water bodies. In catchments where rivers or lakes are present, groundwater-surface water interactions can be intensified, dampened, or reversed by river straightening and other alterations (Kurth et al., 2015).

Riverbed alteration also tends to stimulate a loss of riparian zones and cause deeper riverbed incision, which can decrease the capability of this important interface to favorably control mass fluxes from surface to groundwater or vice versa (Groffman et al., 2002).

In addition to changes stimulated by land development, artificial source and sink terms that arise from infrastructure must be added to the conceptual model of an anthropogenic water balance. Infrastructure includes road networks, buildings, pipelines, and drainage networks, among other elements. Heavily modified landscapes that have been built up with such elements change the water balance in significant ways, which in turn has an impact on solute mass fluxes and water quality (Strauch et al., 2008). The specific impact that infrastructure has on the local water balance and groundwater storage is highly variable and depends on the type and upkeep of each element as well as the effect of the ensemble of elements present (Han et al., 2017). A number of studies have found that anthropogenic solutes in groundwater are sourced directly from infrastructure (Bartelt-Hunt et al., 2011; Pitt et al., 1999).

Another class of infrastructure worthy of mention is the extensive networks of gasoline storage tanks and pipelines used in the industrial sector. These elements are potential sources of contaminating non-aqueous phase liquids (NAPLs) through leakages or accidental spills (refer to Section 2.6.6 for example). The broad distribution of petrol stations, and the abundant networks of above and underground tracks and pipelines carrying petroleum products illustrate a potential significant risk to groundwater quality.

Surface runoff is notably impacted by land development. This is consequential for quantity issues as well as quality, as runoff is a carrier for chemicals present in the atmosphere and leached from surfaces (Lesser et al., 2018; Wakida and Lerner, 2005). In agricultural areas, runoff is activated by storm events as well as by irrigation patterns. In urban and industrial areas, runoff is principally constrained by precipitation events only, and thus is only active during a storm and for a certain lag period following the storm. When surface runoff from the human environment infiltrates the subsurface, it tends to infiltrate in a more localized point- or line-source manner (Han et al., 2017). Because of these dynamics, the behavior of any solutes originating from runoff may be markedly different than the behavior from other sources such as wastewater contamination (discussed further in Section 2.4.3), which is largely weather-independent (Mutzner et al., 2016). It is sometimes possible to exploit these behaviors in order to detangle sources of contamination in mixed land use areas. In agricultural areas, however, the buildup of solutes in soil can create a nearly constant input over time so that temporal dynamics no longer provide insight on sources (refer to Section 2.6.3 for example).

Paved or compacted surfaces, including roads, building plots, and parking lots are one of the most common components found in the anthropogenic environment. These surfaces stimulate increases in surface runoff from storm events and snow melt, as well as major decreases in diffuse infiltration and evapotranspiration are common in urban and industrial environments (Marsalek et al., 2007). Increases in groundwater storage is sometimes observed in heavily paved catchments, despite the decreases in diffuse infiltration (Minnig et al., 2018). Decreases in storage may also be observed, and this is dependent on the relative magnitude in changed evapotranspiration, infiltration, as well as the presence of artificial recharge sources (Han et al., 2017). Looking forward, it is assumed that the spatial extent of impermeable surfaces will continue to expand as estimates have projected that nearly half of all urban infrastructure that will exist in 2030 has not yet been developed (Biello, 2012).

Many infrastructural elements have been designed with the sole purpose of controlling surface runoff in order to protect against flooding and water quality. Storm water infrastructure in particular is a decisive factor in controlling the location and infiltration rate of runoff especially in urban and industrial areas (Pitt et al., 1999). Two common infrastructural storm water systems include combined sewers, which are wastewater sewers equipped with drains so that storm runoff is collected into the sewer networks, followed by separated systems, which are more popular for modern city planning as they incorporate drains exclusive for storm runoff that release into nearby surface water bodies (Hensen et al., 2018). Combined sewers run the risk of overflow during heavy storms, releasing untreated wastewater along with storm runoff into the environment (wastewater infrastructure is detailed in Section 2.4.3). However, separate systems will drain storm runoff directly into surface waters, which in turn may be in direct communication with groundwater bodies. Separated systems may also run the risk of contaminating groundwater with untreated wastewater, either as a result of underground leakages into storm drains or through faulty or illegal pipe connections between storm water and wastewater networks (Panasiuk et al., 2015).

Other systems that handle storm runoff include retention basins which are permanent storm water storage ponds, detention basins which are temporary storage ponds that slow-release storm waters, or infiltration infrastructure (including basins, swales, and trenches) which direct storm water into groundwater in areas of high permeability. Contemporary efforts in green infrastructure have popularized further concepts such as rainwater harvesting to control the amount of runoff generated from storm events. Much of the literature concerning runoff dynamics and pollution is focused on surface water studies (Karn and Harada, 2001; Lee and Bang, 2000). However, groundwater pollution from storm runoff is a known phenomenon and several notable studies exist on the topic (Pitt et al., 1999; Voisin et al., 2018), including discussions on the efficacy of certain storm water infrastructure.

2.4.2. Land Use Practices

On top of development, many anthropogenic land use practices have the potential to influence groundwater quality. Chemical treatment of the land and infrastructure is a very common practice for purposes such as plant and infrastructure protection and pest control. The application of plant nutrients and plant protection chemicals is a widespread and ever-growing practice in the agricultural sector, and the resulting groundwater contamination is a ubiquitous and a longstanding issue (Gonçalves et al., 2007; Hakoun et al., 2017). Products used in the agricultural sector can reach groundwater along diffuse pathways through direct infiltration or in a more focalized manner through runoff (Kaczala and Blum, 2016). Alongside liquid chemical applications, the spread of manure in agriculture is also commonly practiced, and also acts as a pathway for a number of chemicals into the environment. The storage and effective pretreatment of manure is expensive so that direct application of untreated product is not an uncommon practice (Boxall et al., 2003).

Urban and industrial activities are known to practice chemical application for the purpose of pest control, or to optimize material properties. Pest control products in these environments are generally referred to as biocides. As opposed to agricultural products which are used almost exclusively outdoors, chemical products in the urban and industrial sector are applied both indoors and outdoors. This diversifies potential sources and pathways of these products into the environment, and has important implications for the biogeochemical processes that a product will undergo. Briefly, outdoor sources of contamination are subject to degradation via photolysis while on surfaces, followed by biodegradation in soils. Indoor sources will follow slightly different degradation pathways, particularly if they pass through a wastewater treatment plant. However, degradation in these environments is often only partial, leading to a multitude of transformation products. In addition, outdoor products may still end up in sewer networks in combined sewer systems which tend to result in focalized infiltration, either as point- or line- sources, into the groundwater environment (Hensen et al., 2018).

Within agricultural areas, the act of irrigation can influence local groundwater flow paths, as the artificial input of water tends to raise the local water tables or create shallow saturated lenses. These shallow saturated layers from irrigation can make soil and groundwater more susceptible to evapotranspiration, sometimes resulting in net losses of water as well as concentrating precipitated salts and contaminants in the uppermost soil layers (Gning et al., 2017). Refer to Section 2.6.2 for an example of this phenomenon.

Surface and groundwater exploitation can also be a consequential practice for water quality. Water is extracted for irrigation, drinking water supply, electricity generation, and during industrial operations such as mining. Mining and ore refining operations largely extract groundwater either in the process of decanting open pit mines where groundwater regularly infiltrates, or to dewater underground workings. Both abstraction and decanting of groundwater can alter natural groundwater flow and may lead to regional groundwater desiccation (Custodio, 2005). The process of groundwater rebound upon mining and pumping cessation is a well-known process with implications for groundwater quality (Henton, 1981). Indeed, water pumped from any water body has the potential to impact groundwater storage and stimulate changes in groundwater recharge pathways (Khan et al., 2016).

We re-emphasize that historical practices are often of equal importance as contemporary practices that pose a risk of contamination, particularly in the case of chemical applications. Depending on factors such as unsaturated zone thickness, permeability, climate cycles, and storage time, products applied directly at the surface can remain in soils and aquifers for decades (Baillieux et al., 2015). This means that groundwater contamination stemming from chemical application may remain an unsolved issue long after the application practice has ceased.

2.4.3. Waste Production

Because of the sheer magnitude of solid and liquid waste produced in the human environment, these two major contaminant sources are among the most commonly discussed in groundwater literature (Baba and Ayyildiz, 2006; Grimmeisen et al., 2016; Schirmer et al., 2013). The importance of proper waste handling for environmental protection and human health is widely acknowledged, but there are many cases of inadequate or deteriorating waste facilities around the world. Waste and wastewater infrastructure is quite heterogeneous on a global scale, so that risk of contamination is likewise variable (e.g. Laner et al., 2012; Okumu-Okot, 2012). It has been reported that globally, some 80% of wastewater is released into the environment untreated (WWAP, 2017).

Industrial activities collectively produce more waste than agriculture or urban activities combined (Park et al., 2005), with mining activities in particular generating the largest volume of waste handled in the world (ICOLD, 1996). Exponential industrial growth over the last decades within the raw materials, energy production, and engineering sectors has led to the release of an ever-increasing, diverse range of waste products into the environment, which has left its mark on groundwater quality (Manamsa et al., 2016; Musingafi and Tom, 2014). Refer to Section 2.6.7 for an example.

Concurrently, treatment of urban waste and wastewater remains a persistent issue when we consider that more than half of the world's population currently lives in cities (World Bank, 2018). According to the UN World Urbanization Prospects 2018, this number is expected to increase to nearly 70% by 2050. This brings about an acute risk for urban populations who find themselves in close proximity to poorly managed waste, and creates heightened risks for urban groundwater resources. Refer to section 2.6 for an example.

Solid waste

The presence, type, coverage, and upkeep of infrastructure such as landfills (including tailings facilities) may be among the most important factors determining the resulting quality of groundwater and the risk of contamination from solid waste products. Landfills are the most common method of solid waste disposal worldwide, and are still often the cheapest disposal option, especially for the large quantities of industrial waste (Han et al., 2014; Longe and Balogun, 2010). Although landfill leachate is a known source of contaminants in groundwater (e.g. Peng et al., 2014), solid lining of landfills is not enforced everywhere. In addition, landfills with poor or nonexistent lining dating from the industrial revolution are ubiquitous. Currently, areas without access to effective storage or disposal systems may rely on shallow underground disposal for their solid waste.

Liquid waste

For liquid waste, dedicated infrastructure includes drains, sewer networks, septic tanks, and pit latrines. Centralized wastewater collection systems, connected to an adequately functioning wastewater treatment plant (WWTP) with up-to-date treatment technology and regular maintenance are the preferred solution, as they generally have a better track record for keeping wastewater separated from the environment (Munz et al., 2017). Underground and above-ground septic tanks or French-drains are more common in suburban, semi-rural and rural environments, areas that are distanced from dense city networks. Although septic tanks have higher incidence of leakage than more centralized infrastructure, they still perform better than pit latrines, or direct emissions (open, decentralized waste disposal), which generally lack a proper impermeable barrier from soils into the environment. Developing countries are struggling to move away from open defecation (Figure 2-2), and although improvements are being made, many sanitary solutions are still based on water-dependent technologies, such as the flush system, which are difficult to implement in water scarce countries. The rapid population growth, particularly in India and China, calls for urgent solutions to sanitation deficiencies, as wastewater is often discharged without treatment.

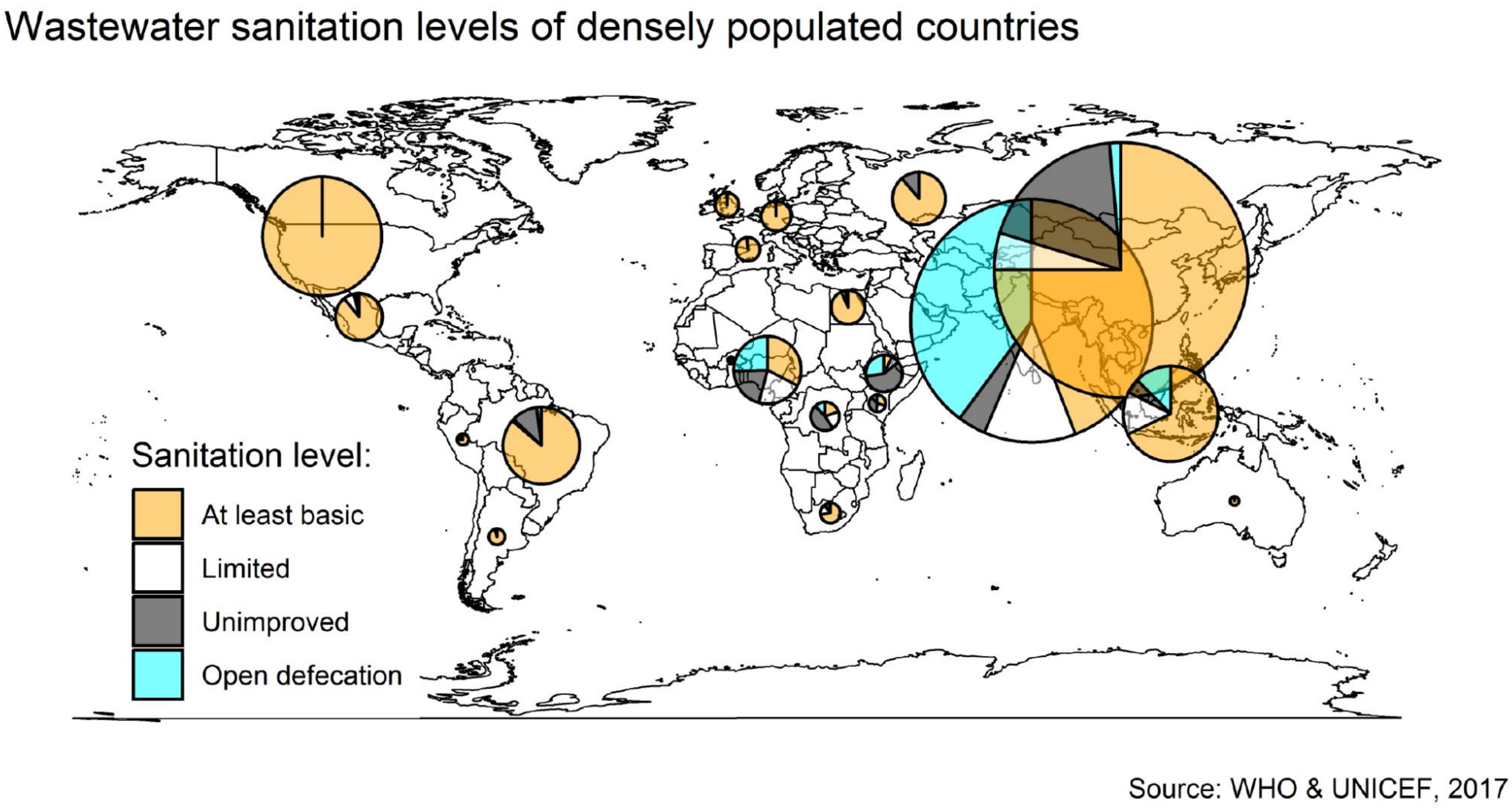


Figure 2-2. Wastewater sanitation levels of densely populated countries, with pie-sizes relative to populations size (note, the population of India and China is divided by 2 here for scalability), with their levels indicated as ranging from open defecation to at least basic sanitation (WWAP, 2017; https://aashdata.org/data/household).

In urban areas, wastewater can reach shallow groundwater via several routes, including direct leakage from infrastructure or infiltration from surface water runoff (Wakida and Lerner, 2005). Streams and rivers are common recipients of both treated and untreated wastewater, in which case they may act as line sources of contamination. Even where cities are serviced largely by centralized pipelines and WWTPs, treatment facilities are unable to completely remove all contaminants, and this is especially true for emerging organic contaminants (covered in more detail in Section 4). The effluent of treated water from these treatment plants will be a common source of these products, regardless of the treatment method (Lapworth et al., 2012). Wastewater infiltration can sometimes be identified as a source of groundwater contamination through the presence of a number of different chemical or biological indicators specific to anthropogenic activity (Panasiuk et al., 2015). Refer to Section 2.6.3 for an example of disentangling urban versus agricultural wastewater contamination.

Wastewater reclamation

The reclamation of used waters for a variety of ends (including for irrigation and use in industry) has been practiced to varying degrees for several centuries, especially in arid and semi-arid environments (e.g. Lesser et al., 2018). As issues of water security continue to increase, wastewater reclamation is an appealing practice that can safeguard a region's adequate supply (Tweed et al., 2007). With the variety of techniques in use for treating or storing reclaimed water improving, the risks of contamination stemming from imperfect or no wastewater treatment prior to its reuse is lowered (San-Sebastián-Sauto et al., 2018). This is in part also to the efficacy of soils used to filter out a large portion of contaminants that are present.

One such reclamation practice is that of managed aquifer recharge (MAR) that uses wastewater (MAR practices in general may use a variety of source waters). MAR can involve the intentional infiltration of wastewater into an aquifer via spreading, percolation, or injection for use such as water supply, ecosystem sustenance, or to control flow fields (Dillon et al., 2009; Bonilla Valverde et al., 2018). An example of existing MAR methods that is relevant to the present discussion is the practice of soil aquifer treatment (SAT), which involves soaking wastewater through the soil and vadose zone into (usually) unconfined aquifers, where it can be stored on a seasonal basis (Sharma and Kennedy, 2017). Other MAR methods such as bank filtration are practiced in more humid regions as well, as an answer to the issue of groundwater quality rather than quantity (e.g. Hiemstra et al., 2003). Apart from increasing water availability, MAR can be used to build up a local groundwater mound that serves as a hydraulic barrier to prevent inflow of contaminated water from areas upstream (Hendricks Franssen et al., 2011; Moeck et al., 2016).

Another common water recycling practice is crop irrigation with urban or industrial effluent. Many examples of long-standing wastewater irrigation practices can be found in places such as Asia (Tang et al., 2004), the Middle East and across Latin America (Bonilla Valverde et al., 2018). The arid Mezquital Valley in Mexico claims to be the world's largest and one of the oldest documented untreated wastewater irrigation systems (Lesser et al., 2018). While wastewater irrigation is an appealing practice as a means of water reuse, and is anticipated to become more important and widespread in the future, it is not without risk of contamination (Tang et al., 2004). Biological contamination such as coliforms are mostly filtered from wastewater as it passes through soil, but other products such as heavy metals, nutrients, and organic contaminants can persist for years or decades at these sites (Gallegos et al., 2015).

2.5. Major Contaminants of Groundwater

In this section, we offer details on the characteristics of a number of prominent groundwater contaminants. Many chemical compounds with contamination potential are well-characterized and regulated, but the continued development of new products coupled with poor knowledge of aquifer characteristics and groundwater quality is hampering sustainable water management in many areas (Mateo-Sagasta et al., 2017; Sorensen et al., 2015). In addition, many newer products on the market are of yet-unknown toxicity, especially at low concentrations or when found as part of a cocktail of other products (Munz et al., 2017; Andreas Musolff et al., 2010). Details on existing regulations (or lack thereof) for concentration limits in groundwater are available for many developed countries, and guidelines for drinking water quality are provided by the World Health Organization (Table 2-2). In many countries however, contaminants are either not regulated, or regulation limits are difficult to implement and are therefore overlooked and often not enforced (Knüppe, 2011). Table 2-2 gives an overview of some of the common contaminants regulated by industrialized, chemical producing countries.

Table 2-2. Contaminant regulations and restrictions from leading chemical producing countries with regard to drinking water

Parameter (µg/l)	WHO[1]	EU[2]	USA[3]	China[4]	Canada[5]	Switzerland[6]
1,2-dichloroethane	30	3.0	5.0	30	5.0	3.0
Alachlor	20	Banned (2006)	2.0			Banned (2012)
Aldicarb	10	Banned (2003)				
Aluminium		200		200	100	200
Antimony	20	5.0	6.0	5.0	6.0	5

Arsenic	10	10	10	5	10	10
Atrazine	100	Banned (2003)	3.0	2.0	5.0	Banned (2012)
Barium	700		2000	700	1000	
Benzo(a)pyrene	0.7	0.01	0.2	0.01	0.01	0.01
Boron	2400	1000		500	5000	1000
Bromate	10	10	10	10	10	10
Benzene	10	1.0	5.0	10	5.0	1.0
BTEX						3.0
Cadmium	3.0	5.0	5.0	5.0	5.0	3.0
Carbamazepine	no limits defined					
Chromium	50	50	100	50 (Cr^6)	50	50
Copper	2000	2000	1300	1000	1000	1000
Cyanide		50	200	50	200	50
Diclofenac	No limits defined					
Ethylbenzene	300		700	300	140	
Fluoride	1500	1500	4000	1000	1500	1500
Ibuprofen	no limits defined					
Iron		200	300 (recommended)	300	300	200
Lead	10	10	15	10	10	10
Manganese		50	50 (recommended)	100	50	50
Mercury	6.0	1.0	2.0	1.0	1.0	1.0
Metolachlor	10				50	
Nitrate	50000 (as NO3-)	50000 (as NO3-)	10000 (as N)	10000 (as N)	10000 (as N); 45000 (as NO3-)	40000 (as NO3-)
Nitrite	3000 (as NO2-)	500 (as NO2-)	1000 (as N)	1000	1000 (as N); 3000	100
Pesticides – Total		0.5				0.5
Pesticides (individual)		0.1				0.1
PAHs		0.1		2.0		0.1
Selenium	40	10	50	10	50	10

Simazine	2.0	Banned (2003)	4.0		10	Banned (2012)
Sulfamethoxazole	no limits defined					
Tetrachloroethene	40	10 (sum)	5.0	40	30	10 (sum)
Trichloroethene	20		5.0	70	5	
Toluene	700		1000	700	60	
Uranium	30		30		20	30
Vinyl chloride	0.3	0.5	2.0	5.0	2.0	0.5
Xylenes	500		10000	500	90	
Zinc			5000	1000	5000	5000

1 World Health Organization (WHO, 2011). Guidelines for Drinking-water Quality, Fourth Edition.
2 European Commission (2015). Drinking Water Directive (Council Directive 98/83/EC, amended 2015).
3 United States EPA Safe Drinking Water Act (USEPA SDWA, 2009). National Primary Drinking Water Regulations (EPA 816-F-09-004) ,
4 Ministry of Health of China (2007). National Standard of the People's Republic of China, Standards for Drinking Water Quality.
5 Health Canada Water and Air Quality Bureau, Healthy Environments and Consumer Safety Branch (2014). Guidelines for Canadian Drinking Water Quality.
6 Swiss Federal Department of Home Affairs (FDAH, 2016). Order on Drinking Water and Water in Publicly Accessible Bathing and Shower Facilities (RS 817.022.11).

Improving understanding on the extent and behavior of contaminating compounds in the ground, and the cumulative effect of a mixture of products remains a pressing topic for environmental scientists and decision makers (Botkin and Keller, 2011; Kunz et al., 2016; Moschet et al., 2014). Despite the complexity of solute transport, reactivity and potency in the subsurface, these are important factors which need to be understood in order to determine whether the regulation or mitigation of compounds, or the rehabilitation of aquifers, is effective in protecting or improving groundwater quality.

2.5.1. Inorganic Contaminants – Nitrogen

Nitrogen is an inorganic chemical that is naturally present in the environment. At high enough concentrations, it becomes toxic to environmental ecosystems and to human health. Several human activities may entail elevated levels of nitrogen in groundwater, including the application of plant fertilizer and the production of wastewater. Nitrate (NO_3^-) in particular is one of the most common contaminants measured in aquifers globally, and is the most mobile form of nitrogen (Spalding and Exner, 1993).

Persistence of nitrogen in the subsurface is principally governed by the biological reactions of nitrification and denitrification, which are in turn a function of environmental redox conditions. In the absence of oxygen, reducing conditions favor denitrification: the conversion of nitrate into nitrogen gas. In the presence of oxygen, ammonia or nitrite readily oxidize into the highly mobile nitrate. In such oxidizing conditions, nitrate becomes relatively inert due to the fact that it is negatively charged, and is thus unlikely to sorb to substances in the unsaturated zone such as clays (Fetter et al., 2017).

Recorded nitrate contamination of groundwater through agricultural land use has a relatively long history, and agriculture is assumed by-and-large to be the largest source of nitrates in the environment. It is estimated that 50–70% of all nitrogen applied to crops is lost from the soil-plant system through diffuse leaching (Green et al., 2008; Spalding and Exner, 1993). Although fertilizer application is being moderated in many countries, the global fertilizer production rate continues to increase (European Commission, 2008; FAO, 2018) , with 113 million tones consumed in 2014 (Figure 2-3). Additionally, many places where agricultural nitrogen application has been considerably reduced through regulations (e.g. Switzerland and the European Union), groundwater nitrate values often continue to exceed official drinking water limits (Decrem et al., 2007; European Commission, 2008). In some cases renewed concentration highs were measured post-remediation or regulation (Baillieux et al., 2015), with studies also reporting delays in response of groundwater quality post-regulation (Gutierrez and Baran, 2009; McMahon et al., 2006).

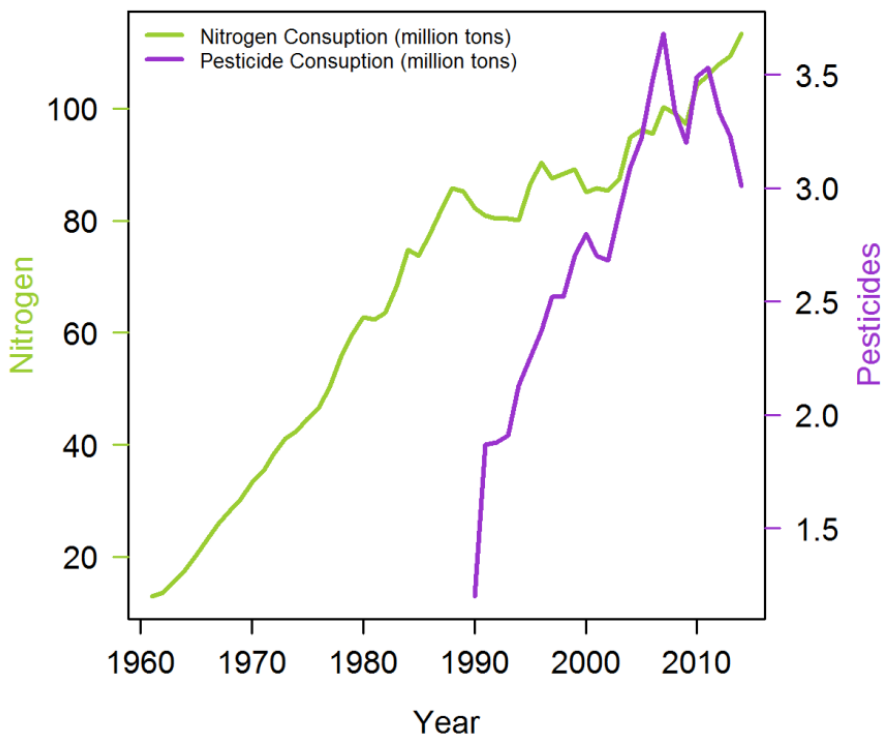


Figure 2-3. Total fertilizer and pesticide used globally in million tons per year from 1961-2014 (FAO, 2018, 2009). Note that although pesticides were already in widespread use, global monitoring data for pesticide consumption is only available post 1989.

Nitrogen contamination of groundwater is also a relevant issue in many cities (e.g. Appleyard, 1995; Tang et al., 2004). Globally, the magnitude of urban nitrogen contamination is smaller than its counterpart in agriculture, though the variety of urban sources are much higher. Nitrogen sources in urban areas include wastewater, solid waste, water supply, construction zones, urban parks and gardens, storm water, and atmospheric deposition (Wakida and Lerner, 2005). Groffman et al. (2004) hypothesize that this variety of sources and types of nitrogen released in urban environments will have an impact on the microbial communities involved in nitrogen transformation processes, potentially rendering them less efficient. Wastewater in particular is one of the most commonly discussed emitters of urban nitrogen. Wastewater nitrogen occurs most often in the form of ammonia, though it can be readily transformed into nitrates in the oxic conditions of some aquifers (Fukada et al., 2004; Musgrove et al., 2016).

2.5.2. Organic Contaminants

Organic contaminants (OCs) are a diverse class of products that have widespread use in agriculture, urban, and industrial environments. They include a range of hydrocarbons, pesticides, and pharmaceuticals, among others. These products can occur in groundwater either as pure compounds or a mixture of compounds, some of which are readily metabolized into stable transformation products (equally known as degradation products). Some OCs are partially or fully hydrophobic, therefore, they may occur dissolved in water or in a separate phase (Bhatt et al., 2007; Fetter et al., 2017). A large number of OCs have been linked to environmental degradation and risk to human health by researchers as well as policy makers (Fent et al., 2006; Gavrilescu et al., 2015).

Concentrations of measured organic contaminants in groundwater range from nanograms per liter to milligrams per liter (Conant et al., 2004; Hunkeler et al., 2004; Moeck et al., 2017b). Observable concentrations and attenuation rates of many organic contaminants can be attributed either to transformation products, to sorption, or to dilution (Schreglmann et al., 2013). Some compounds are easily degradable and therefore short-lived, while others are persistent and either become mobilized in the aqueous phase (the case for uncharged species), or sorb to soils (the case for charged species). Additionally, some degradation products have been found to have a higher toxicity than their parent compound (Banaszkiewicz, 2010; Sinclair and Boxall, 2003).

Pesticides

The recognition of pesticides as environmental contaminants was brought to people's attention in the early 1960s. Chemical pest control has become a staple of agricultural land development and is also widespread in urban and industrial development. Global monitoring data (starting from 1989) has shown a continued increase in pesticide consumption (Figure 2-3), with a maximum of 3 million tons consumed in 2007. However, as pesticide use has become more heavily regulated over the past two decades, in particular within Europe and North America (Table 2-2; European Commission, 2008; FQPA, 1996), a decline in global pesticide consumption is noticeable (see Figure 2-3). Despite regulations, pesticides remain a persistent issue for global groundwater resources (refer to section 2.6.2. for example).

Although groundwater pesticide contamination has been widely reported, current approaches in tracing the environmental degradation and making relevant predictions on their persistence are nonetheless limited (Elsner and Imfeld, 2016; Kunz et al., 2016). Characterizing the dynamics of these products in the subsurface is complicated due to the differences in degradation and sorption rates (the two most important processes governing pesticide persistence), which are a function of individual pesticide compounds as well as sediment and aquifer matrix characteristics (Arias-Estévez et al., 2008). Porous aquifers are generally better at filtering pesticides from the groundwater, while karstic aquifers are more prone to long-term pesticide contamination issues due to rapid flow and low sediment reactivity (Andreo et al., 2006).

Pesticide products are diffuse and ubiquitous in agricultural landscapes, and most major groundwater contamination studies for pesticides are carried out in these areas (e.g. Baran et al., 2008; Gonçalves et al., 2007; Hakoun et al., 2017). In addition, pesticides are the most commonly detected organic contaminants in urban groundwater (Stuart et al., 2011). In cities, pesticides are used in places such as urban parks and gardens, urban agricultural plots, on roads, rail tracks, and sidewalks, in building material (including insulation and paint) and in household protection products (Mutzner et al., 2016). It is known that storm water runoff is a major pathway of pesticides from agriculture, and the same is true of cities (Hensen et al., 2018).

There is a large amount of overlap in product use across environments – many products available on the market today are used outdoors in both agricultural and urban environments. This creates a challenging task of source identification in aquifers impacted by mixed land uses (refer to Section 2.6.3 for example). The detection of more specific products used in building materials may aid in defining urban versus agricultural sources in groundwater. For example, in many areas of the world, the herbicide *prometon* is generally only applicable to urban areas (Capel et al., 1999), and can therefore be used to clarify an urban signature. In addition, in many cases pesticides that reach environmental waters through sewer leakage and wastewater effluent – i.e. indoor sources – often follow slightly different degradation pathways and can thus be classified as largely urban in origin (Wittmer et al., 2011).

Historically utilized pesticides that are now banned (see Table 2-2) continue to be measured in groundwater bodies as persistent compounds, and it is not always clear precisely why this is the case (Gonçalves et al., 2007). Current approaches in tracing the environmental degradation and making relevant predictions of their persistence within groundwater bodies are limited (Elsner and Imfeld, 2016; Kunz et al., 2016). Concentration time series, parent-to-metabolite compound ratios, and compound-specific isotope analysis are some of the current approaches to determining pesticide contaminant sources and pathways in groundwater bodies (Schreglmann et al., 2013).

Pharmaceuticals

Pharmaceuticals as contaminants have become a primary concern in recent decades due to their prevalence in modern society, and are increasingly found in anthropogenically impacted surface and groundwater bodies in many regions (e.g. Barnes et al., 2008; K'oreje et al., 2016; Lesser et al., 2018; Loos et al., 2010; Peng et al., 2014). Pharmaceuticals pose a particular risk, as they are purposefully designed to be bioavailable, and have effects which could go beyond the intended recipient once they enter the environment (Kaczala and Blum, 2016).There are few concepts as to what it might take to remediate existing and future pharmaceutical problems in groundwater bodies (Horvat et al., 2012). And indeed, to date there are no, or only very limited, legislative limits on pharmaceutical concentrations in groundwater (Küster and Adler, 2014; see Table 2-2).

For reasons similar to pesticides, characterizing the propagation of pharmaceutical products in the subsurface is not a straightforward task. Laboratory-scale experimentation has shown that individual product's sorption coefficient will be a major determiner of persistence and mobility (Scheytt et al., 2005), and some product degradation rates have been shown to be highly dependent on soil and aquifer redox conditions as well (Banzhaf et al., 2012). Studies have suggested that characteristics of the soil-aquifer matrix are more important than the characteristics of individual pharmaceuticals in determining their degradation (Hebig et al., 2017). This would explain why many field-based experiments have come up with contradictory results on the persistence of specific products in the environment.

The discussion on pharmaceuticals in groundwater often revolves around urban-sourced contamination. Urban pharmaceuticals reach groundwater bodies in a point-source manner via wastewater emission, combined sewer overflow, or from leakages in wastewater infrastructure (Christoffels et al., 2016; Kolpin et al., 2002). Reclamation practices of municipal wastewater, such as MAR or wastewater irrigation (see Section 0), may present an additional risk of urban-sourced pharmaceuticals entering groundwater bodies. The presence of pharmaceuticals in urban environmental waters is highly variable on the global scale, and in addition to physico-chemical controls, is a function of wastewater infrastructure and local pharmaceutical consumption patterns (refer to Section 2.6.5 for example). Relevant societal factors include illnesses prevalent in local society, as well as product availability (i.e. prescription versus over-the-counter) (Mutiyar & Mittal, 2013).

Veterinary compounds in agriculture are another major source of pharmaceuticals into the environment, although they tend to be underrepresented in the literature (Bottoni et al., 2010; Kim et al., 2011). An abundant range of veterinary pharmaceutical compounds are used in the agricultural sector including antimicrobials, anthelmintics and ectoparasiticides, antifungals, hormones, anaesthetics, tranquilisers, euthanasia and anti-inflammatory products (Boxall et al., 2004). It is estimated that 50 - 90% of doses administered to livestock is excreted (largely unmetabolized) into the environment (García-Galán et al., 2010; Kaczala and Blum, 2016). Veterinary antibacterials, have been repeatedly detected in groundwater wells associated with animal feed lots (Batt et al., 2006). Hormones are detected less frequently than other veterinary pharmaceuticals, though they have been measured both in surface and groundwater samples (Bartelt-Hunt et al., 2011; García-Galán et al., 2010; Vulliet and Cren-Olivé, 2011).

In addition to direct excretion, the extensive application of animal manure to crop fields (see Section 2.4.2) is also considered a major route through which veterinary pharmaceuticals can enter groundwater systems (Boxall et al., 2003). Additionally, leachates from livestock burial pits is poorly described in association with groundwater contamination, though it may pose a threat to environmental and public health (Kaczala and Blum, 2016; Yuan et al., 2013).

NAPLs

Non-aqueous phase liquids (NAPLs), which are either slightly soluble or completely insoluble, make up a major subset of organic contaminants that have been detected frequently in anthropogenically-impacted groundwater. NAPLs can be classified as light (L) and dense (D), according to their density relative to water. Benzene, toluene, ethylbenzene, and xylene (BTEX) are a prominent example of LNAPLs, while chlorinated solvents and heavy crude oil are examples of DNAPLs.

The majority of NAPL pollution is a product of industrial environments, though issues are present in urban and agricultural environments as well, as some chlorinated compounds are used in pesticides or cleaning agents, and gasoline transport and storage networks are present in all anthropogenic environments (Baker et al., 2016; Bhatt et al., 2007). Landfills, leaking gasoline storage tanks and pipes, leaking septic tanks, and accidental spills are all potential sources of NAPLs in groundwater.

When infiltration to the saturated zone occurs, LNAPLs will accumulate on top of the groundwater table and generally flow in the direction of the hydraulic gradient. On the other hand, DNAPLs migrate vertically until the impermeable base of the aquifer is reached. This vertical migration tends to leave behind residual phase DNAPLs along its pathway. The direction of flow in this case may not coincide with the hydraulic gradient (Kueper and McWhorter, 1991; Parker and Park, 2004). The slow dissolution of lightly soluble NAPLs can result in contamination plumes that are larger and longer-lived than the measured spread of the pure product, further complicating characterization and remediation efforts (Soga et al., 2004).

Chlorinated solvents including tetrachloroethene (PCE), trichloroethene (TCE) are among the most common NAPL pollutants, found both in association with industrial and urban activities (Matteucci et al., 2015; Stroo et al., 2003). Highly chlorinated solvents such as PCE are persistent or degrade only slowly under aerobic conditions in aquifers (Hunkeler et al., 1999), while under reducing conditions partial or complete microbial dechlorination occurs (Fennell and Gossett, 1998; Picardal et al., 1995). Less chlorinated solvents such as TCE can also be biodegraded under aerobic conditions (Enzien et al., 1994; Palau et al., 2016). Dechlorination of PCE leads to the formation of TCE, cis-1,2 dicholorethene (cDCE), and vinyl chloride (VC) as intermediate products (Hunkeler et al., 1999). Typically, ethene (ethylene) is the end product of dechlorination (Fetter et al., 2017).

Natural subsurface heterogeneities, even in relatively simple porous aquifers, make the remediation of NAPLs a challenging task (Schnarr et al., 1998). Compared to porous aquifers, studies on the spatial and temporal distributions of NAPLs in karst aquifers are notably less prevalent yet significantly more complex (Yu et al., 2015). Depressions in karstic conduits may act as traps for DNAPLs (Wu and Hunkeler, 2013; Xu et al., 2018), making detection and remediation extremely difficult (Field, 2018).

2.5.3. Raw Mineral Extraction

Acid mine drainage (AMD) is a significant contaminant arising from mine waste such as tailings facilities. Tailings facilities compose dumps of crushed waste rock and liquid, and generally contain high proportions of so-called ‘byproducts’ of the host rock, such as pyrite (FeS_2). Leachate from tailings is often enriched with salts and heavy metals due to low pH and interactions between the solid and liquid phase, leading to the phenomenon of AMD. In more arid regions, where rivers derive their base flow from groundwater seepage, stream flow resulting from elevated groundwater levels can be composed almost entirely of AMD (Tutu et al., 2008).

Very low pH values can cause heavy metals to become soluble. This is a known environmental hazard emanating from many active and abandoned mine workings (Rösner, 1998). However, some studies do suggest that shallow or fractured aquifers can be remarkably effective at sorbing heavy metals from mine leachate, depending on pH, soil conditions, and leachate concentrations. For example, studies by Schwartz and Kgomanyane (2008) and Von Der Heyden and New (2004) showed that sorption of heavy metals from mine leachate occurred within 700 m down gradient from the polluting source due to ideal physicochemical conditions within the groundwater. In these cases, relatively high pH conditions of the groundwater (greater than 6) and H^+ surface complexation onto hydroxides and oxides of iron are believed to have facilitated the adsorption of heavy metals to the clays and organic material of the shallow unconfined groundwater.

However, the absence of carbonate or calcite in the underlying geology, or the cessation of lime addition to tailings facilities could reduce the groundwater's ability to buffer mine leachate. Just a small decrease in pH has been shown to result in an increase in soluble metal concentrations. Should leachate and groundwater pH decrease to below 5, markedly increased concentrations of aluminium and copper within the groundwater can be expected, adversely affecting the surface and groundwater quality and their related ecosystems (Ashton, 2010; Musingafi and Tom, 2014).

2.6. Case Studies Highlighting Current Threats to Groundwater Quality

2.6.1. Nitrate in Unsewered Cities

Nitrate pollution from wastewater is a particular threat in cities that overlie shallow aquifers and lack adequate underground sewer networks, and where urban wastewater is able to infiltrate in a relatively diffuse manner. A study by Faye et al. (2004) presents an analysis of the impact of various land occupations on the quality of the unconfined quaternary sand aquifer underlying the suburban area of Thiaroye, located on the Dakar peninsula in Senegal. According to the authors, land use is highly variable in Thiaroye and includes densely populated areas that are lacking centralized sewer networks, depending instead on septic systems that are not always properly constructed. As groundwater levels are very shallow in the Thiaroye region, consistent communication between surface activity and groundwater has been evidenced. Nitrate contamination in the regional groundwater is a longstanding issue, with values in excess of 500 mg/l having been recorded in groundwater at drinking water extraction points.

The authors used a GIS approach to combine data on the geospatial distributions of measured nitrate concentrations with information about soil type, groundwater characteristics, and land use. Three classes of spatial vulnerability were first assigned based on intrinsic aquifer characteristics. On top of vulnerability, spatial potential for pollution was also assigned to one of three classes based on land use features. Ratings for both steps were determined using a Boolean logic operation to avoid subjective assignment of classes. From their analysis, the authors deduce that nitrate concentrations are a good proxy for both aquifer vulnerability as well as other anthropogenic contamination on a regional scale. In evaluating their constructed vulnerability map, the authors point out that observed nitrate levels also depend intimately on contaminant loading and contaminant characteristics, which is more of a function of land use and layout rather than any climatic or hydrogeological factors.

2.6.2. Nitrate Accumulation and Long-term Leaching

In a study conducted on the High Plains aquifer of the United States, isotopic tracers of nitrate (^{15}N) and water (^{2}H, ^{3}H, ^{18}O) were used to assess the storage and transit time of nitrates in the subsurface (Figure 2-4). Sites were selected to compare unsaturated zones of rangelands (Figure 2-4a) with those associated with irrigated cropland sites (Figure 2-4b) where chemical where applied (Gurdak et al., 2007). McMahon et al. (2006) demonstrated how the mobilization of natural salts, as a result of irrigation return flow and long-term evaporative (ET) concentration near the base of the root zone, resulted in a larger accumulation of nitrate within thick unsaturated zones beneath irrigated sites. This accumulation accounted for as much as 60% of the nitrate found in groundwater reservoirs beneath irrigated croplands.

Although advective transit times in the unsaturated zone were estimated to range from 50 to 375 years (longer than any of the sites had been irrigated for), agrochemicals were detected in groundwater at 66% of the sites associated with irrigated crop sites. McMahon et al., (2006), suggests that transport occurs along multiple flow paths ranging from slow paths (associated with fine-grained sediments with little or no flow) to fast paths (associated with areas of focused recharge such as depressions, streams or playas). The authors concluded therefore that the amount of contaminants reaching the unconfined aquifer from the irrigated sites could increase, even if input was completely stopped, as the mass of historically accumulated compounds under irrigated fields continue to slowly travel downwards through the thick unsaturated zone. This storage of contaminants in sediments is one explanation for the continued excessive nitrate load measured in many groundwater bodies.

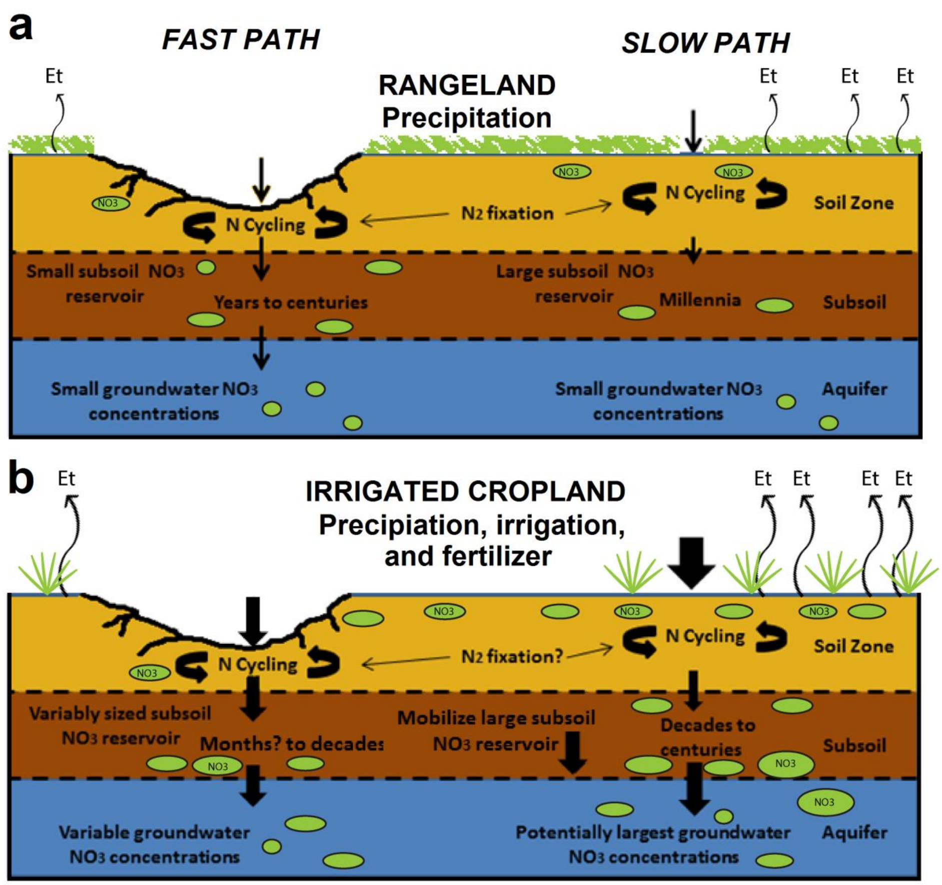


Figure 2-4. Conceptual models for the evaporative (ET) concentration and transport of NO_3^- from the land surface to the water table through the unsaturated subsoil to the aquifer, under a) rangeland conditions and b) irrigated cropland conditions in the High Plains of the United States (abbreviated from McMahon et al., 2006).

2.6.3. Pesticide Contamination in Urban versus Agricultural Settings

Due to the overlapping application practice of pesticides in the urban and agricultural settings, it can be difficult to detangle the exact sources of products detected in groundwater, particularly in cities with dense parks, gardens, and in close proximity to agricultural zones. Many products used in urban outdoor areas are the same products used in proximal agricultural zones. According to Sinclair and Boxall (2003), considering pesticides transformation products can be important in detangling pesticide sources in groundwater studies.

As an illustration of the similarities and differences between urban and agricultural pesticides, Barlow et al. (2012) measured 38 pesticides and their degradates in the shallow, largely unconfined, aquifer associated with urbanized areas in and around Memphis, Tennessee, USA. The authors made use of local criterion and usage patterns to identify products as 'primarily urban', 'urban and agricultural' and 'primarily agricultural'. In the Memphis aquifer, for example, the herbicide *simazine* was the most often detected primarily urban product, and its occurrence and concentration was reported to have increased through the duration of the study. *Atrazine* was the most often detected product of both urban and agricultural use. Other pesticides deemed to be primarily of urban use included *tebuthiuron*, *prometon*, *diuron*, *bromacil*, and *dieldrin*. The authors compared detected values from measurements in groundwater between 1994 and 2009 to outline changes in land use and product use patterns, thus highlighting the importance of obtaining knowledge on local usage patterns for stronger interpretation. For example, while *simazine* is primarily used in urban environments in Memphis, it is also known to be used in many agricultural contexts such as berry fields, orchards, and vineyards in other places in the US, as well as around the world. Further, the use of both *atrazine* and *simazine* was banned in the EU over a decade ago (refer to Table 2-2). In many countries today, including the United States, Australia, Brazil, and India, *atrazine* remains one of the most-used herbicides (Singh et al., 2018).

2.6.4. Veterinary Pharmaceuticals in Groundwater

Sulfonamides are commonly used veterinary antibiotics, usually allied in mixtures, that have low soil sorption tendency, are highly soluble, and have half-lives ranging between 5 - 40 hours (in serum). Sulfonamides have been repeatedly detected groundwater wells located down gradient from confined animal feeding operations (Batt et al., 2006; Karthikeyan and Meyer, 2006; Lindsey et al., 2001; Sacher et al., 2001). An investigation by García-Galán et al. (2010) in Catalonia (Spain) of 39 groundwater sites representing a variety of aquifers, including the fractured multilayer confined sedimentary Plana de Vic aquifer and the unconfined alluvial La Selva aquifer, found a 90% detection frequency of sulfonamides. Although the average concentration of sulfonamides detected was generally below 50 ng/l, highs of 3,461 ng/l were measured for *sulfacetamine* and 745 ng/l for *sulfamerazine*. These sulfonamides were measured predominantly in an aquifer from which 68% of the water was abstracted for agricultural purposes, but from which 20 % of the water was also designated for drinking water purposes. In the García-Galán et al. (2010) study, a strong correlation between sulfonamides and nitrates was established, justifying the consideration of this coupling of compounds an indicator of groundwater pollution stemming from animal origin.

2.6.5. Production and Consumption Patterns of Human Pharmaceuticals

As an example of a relatively extreme case of urban groundwater contamination from human pharmaceuticals, we highlight the publication by K'oreje et al. (2016). The authors carried out a study in the cities of Nairobi and Kisumu, Kenya to characterize the presence of pharmaceutical products in wastewater, surface water, and groundwater in what were deemed to be at-risk zones. The authors differentiated between multiple classes of pharmaceuticals, and made special mention of commonly used products at the city scale. In their study, they were able to identify major stresses on groundwater, due not only to

WWTP effluent, but also untreated wastewater discharges from septic tanks and pit latrines used in informal settlements along with effluent from pharmaceutical production facilities. Although concentrations measured in shallow groundwater wells in Kisumu were magnitudes lower than those of associated surface waters, anti-inflammatory, antibiotics and psychiatric drugs were measured (Figure 2-5). In particular, high concentrations of *nevirapine* (an anti(retro)viral drug) were measured in two out of the three groundwater wells assessed in Kisumu (1200 ng/l and 1600 ng/l for Well 1 and Well 2 respectively). This study is one of the first in identifying the persistence of anti(retro)viral drugs in groundwater. The authors note that HIV/AIDS is the leading cause of death in Kenya, hence a widespread consumption of anti(retro)viral drugs would lead to its prevalence in effluent and, under these circumstances, may find its way into shallow groundwater bodies.

This conclusion highlights the dependence of pharmaceutical presence on local consumption patterns. To emphasize this point further, in another study Rehman et al. (2015) discuss an important large-scale contribution of pharmaceutical products in the aquatic environment, one that is rarely discussed in western literature: pharmaceutical and precursor production facilities. The authors here point out that as a result of international economic relocation, some 20% of generic products on the global market are produced in India alone. Similarly, more than half of pharmaceutically active precursor ingredients are made in China. The authors coin the term 'EPMC' – emerging pharmaceutical manufacturing country, to refer particularly to Bangladesh, China, India, and Pakistan, where a proportionally large amount of pharmaceutical precursors and finished products are manufactured. For this reason, as well as for the fact that sanitation levels are limited and that nearly half of the global population resides in these regions (refer to Figure 2-2), these EPMCs stand out. The authors claim that one pharmaceutical production park in India, the Patancheru estate located in Hyderabad, produces more than 1500 m^3 of wastewater every day. Further, these countries possess low wastewater treatment capacities; the authors claim that only 2% of wastewater in Pakistan is treated, while the number rises to 24% in India. Due to these factors, urban groundwater in EPMCs are some of the most at-risk in the world for pharmaceutical contamination.

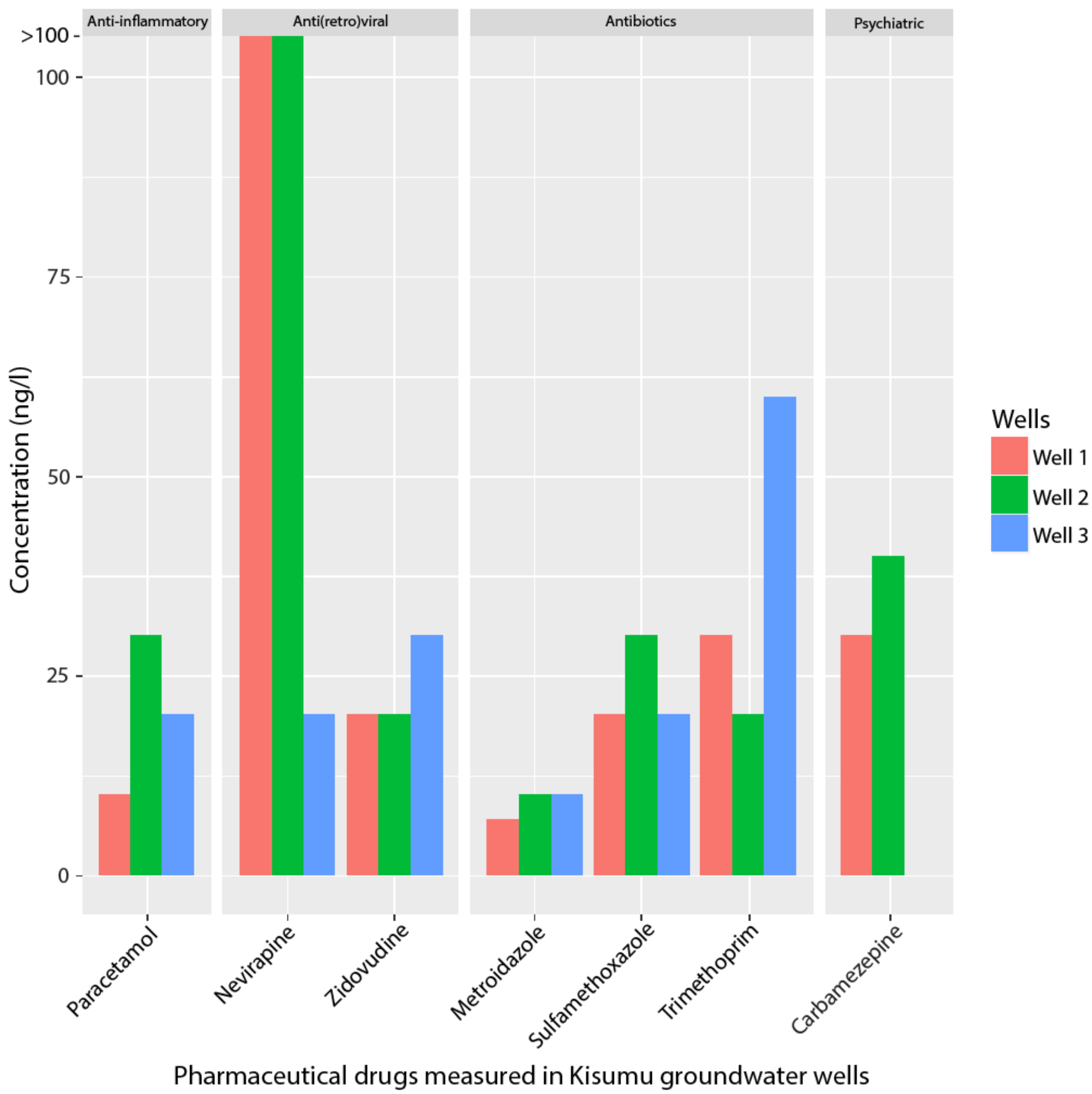


Figure 2-5. Concentration of pharmaceuticals detected in groundwater three wells in Kisumu, Kenya. Note that in Well 1 and Well 2, nevirapine concentrations were 1200 and 1600 ng/l respectively (adapted from K'oreje et al., 2016).

2.6.6. Chlorinated Organic Compounds in Karstic Systems

Yu et al. (2015) investigated the distribution patterns of chlorinated organic compounds in a karst aquifer in northern Puerto Rico, where PCE and TCE were some of the most commonly detected and persistent contaminants. They identified a decreasing trend in contaminant concentrations with depth and distance from source, but also a spreading of contaminants beyond the extent of known sources. They concluded that either unidentified waste disposal sites must exit, or that the transport of the contaminants through the karst system took place along unknown flow paths. A detailed description of these preferential pathways is typically impossible (Andreo et al., 2006; Kaufmann, 2016). When attempted, geophysical techniques (Al-fares et al., 2002; Chalikakis et al., 2011) and/or artificial and intrinsic tracer tests (Hillebrand et al., 2014; Maloszewski et al., 2002; Reh et al., 2015) are common methods to identify such pathways. However, even with the best methods, generally only a fraction of the flow and transport pathways can be identified (Göppert and Goldscheider, 2008; Robert et al., 2012).

Wu and Hunkeler (2013) studied the hyporheic flow in sediment filled karst conduits. They demonstrated that hyporheic flow is induced by conduit bends, even in the case of flat sediment surfaces. This can have strong implication for the storage and slow release of chlorinated solvents, but could also have a positive effect on water quality by filtration and due to biogeochemical transformation of solutes. They also noted that this hyporheic flow in karst sediments has received little attention so far.

2.6.7. Long-term Impacts of Mining

The Highveld coal fields in South Africa have been exploited since 1894, and provide insight into the long-term impacts of mining (McCarthy, 2011). The extensive historical mining in the Highveld has left a scarred landscape of abandoned and collapsing mines (Drebenstedt and Singhal, 2014), and has leached acidic water into the groundwater system for decades. In lieu of long-term open cast mining, surface water quality in parts of the Highveld has deteriorated to such a degree, with recorded SO_4^{2-} values exceeding 7,000 mg/l and pH < 2, that local coal-powered electricity supply utilities are forced to import water for use in their power stations. This process of AMD decanting from the groundwater to the surface water is expected to continue until all the pyrite (FeS_2) hosted in the bedrock of the exposed coal fields has been completely oxidized, with little or no effective mode of cessation or remediation currently at hand (McCarthy, 2011). As mining licenses continue to be issued in the Highveld, farmers downstream (an area famous for its fruit production), risk losing their license for agricultural export as surface and groundwater quality worsen.

In addition, AMD can have a negative effect on karstic systems. The Proterozoic Dolomites of the Malmani Subgroup in South Africa (a UNESCO World Heritage site known as the Cradle of Humankind) overlies the infamous gold- and uranium-rich Witwatersrand Supergroup; from which more than one third of the world's gold has been produced and which still contains six times more gold than the world's second largest gold field (Tucker et al., 2016). The Malmani karst system has experienced repeated long-term dewatering (as far back as 1903) as the underlying gold mines were pumped to keep the stopes and shafts dry, followed by rewatering as mines were abandoned and pumping ceased (Durand, 2012; Naicker et al., 2003). The massive discharge of contaminated groundwater (up to 80,000 m^3/day) has altered surface stream characteristics in the surrounding areas from non-perennial to sizable rivers and swamps contaminated with mine effluent containing aluminum, iron, nickel, zinc, cobalt, copper, lead, radium, thorium and uranium (Durand, 2012; Naicker et al., 2003). As AMD water continues to rewater ground- and surface water, the structural stability of the region is threatened, and the archaeological and palaeontological heritage site risks losing its UNESCO status. The exact number of abandoned mines and resultant AMD as a result of historic mining activities in South Africa remains poorly quantified and monitored (Fourie et al., 2010).

2.6.8. Managed Aquifer Recharge and Pesticides

When urban storm water or wastewater is intentionally used for recharge during managed aquifer recharge (MAR), the risk of contamination cannot be disregarded and should be assessed regularly. A study conducted by Shareef et al. (2014) does exactly this for the Parafield storm water harvesting site in Adelaide, Australia. The authors investigated the question of biogeochemical degradation capacity of select pesticides – *simazine* and *diuron* – under aerobic vs anoxic conditions, in order to investigate the behavior of these products as they move from their source waters into deeper, confined aquifers. The Parafield system harvests rain water from two urban storm water catchments, where it is pre-treated and then stored either in an aquifer storage and recovery (ASR) well or in an aquifer storage transfer and recovery (ASTR) system within a confined limestone aquifer (please refer to the original publication for more details on ASR and ASTR systems). The authors added either *diuron* or *simazine* to a simulated system under either aerobic vs anoxic conditions, and then monitored the concentration evolution of the two compounds over a series of two months. Comparing their results with other literature results, Shareef et al. (2014) concluded that a decrease in both product concentrations was due to biodegradation, with little degradation occurring from abiotic processes or hydrolysis. This identifies potential risk of persistence of select pesticides and other organic pollutants in anoxic aquifer systems.

2.7. Discussion

Over the past decades, many advances have been made towards better groundwater characterization, due in large parts to technological advances. Numerical modelling of flow and transport, isotope analysis, better analytical power for synthetic compounds, and improved geophysical methods are all greatly increasing our understanding of aquifer contamination (Baillieux et al., 2015; Botter et al., 2011; Brunner and Simmons, 2012; Clements and Denolle, 2018; Levison and Novakowski, 2012; McMahon et al., 2006). Still, great uncertainties persist in these methods and in our understanding (Montanari et al., 2013). Due to variability in the spatio-temporal scale of given processes, the comprehensive characterization of the links between the surface, unsaturated and saturated zones in response to land use changes and the associated contamination risk remains a challenge (Scanlon et al., 2005). Currently no single measure is able to describe the water quality for any one water body (Rickwood and Carr, 2009).

Uncertainty also results from a poor understanding of how our activities will impact groundwater, and this is particularly true for newer practices. For example, groundwater vulnerability to pharmaceutical loading in response to temperature change or disease outbreaks is poorly understood. With increasing numbers of studies detecting pharmaceuticals in groundwater bodies (e.g. Bu et al., 2013; García-Galán et al., 2010; Kaczala and Blum, 2016), the question concerning antibiotic resistance and proliferation of compounds in the aqueous environment should concern us. Further studies are needed concerning the consequence of these compounds, both in their individual concentrations and as cocktails, in the groundwater environment.

There exist many classes of anthropogenic products with contamination potential that were not discussed in-depth in this review. This includes plastics and plastic-associated chemicals (Teuten et al., 2009), musk fragrances (Teijon et al., 2010), deicing agents (Ledford et al., 2016), and flame retardants (Stepien et al., 2013), to name a few. In addition, processes such as shale gas exploitation (hydraulic fracturing), are among those which have come under scrutiny as a potential source of groundwater contamination (Gordalla et al., 2013). While the risk from such practices is gaining increasing attention in the environmental sciences, there are as yet few publications on this topic. Future studies are needed to illicit the impact of products used in emerging technologies in a more comprehensive way. In light of this, there is also a global need for effective early warning systems that are capable of anticipating risks associated with compounds used before they become "contaminants of emerging concern" (Dulio et al., 2018).

Furthermore, the scarcity of centralized and easily accessible data for most products is an issue, in particular for emerging contaminants. Information along the lines of product consumption by geographical region or by sector is not readily available to environmental researchers, stakeholders, or law makers. When planning a monitoring campaign, for example of certain products in groundwater, having prior knowledge on what products, and how much, are commonly used in a local or regional areas of interest, could be equally as useful as having knowledge of hydraulic conductivity or groundwater-surface water interactions. Emerging monitoring technologies including wireless technology, automated sensors, and new tracers have all added to the massive growth in data availability (Lovett et al., 2007), so that high quantity and quality data collection and data management should continue to improve the ability to monitor and exchange information in hydrogeology with related fields (Staudinger et al., 2019).

Although there is a general consensus among many experts that the threat of groundwater contamination is important to address, continued political indifference, social stigma, and disregard of ecosystem services results in an undervaluation of groundwater as a renewable resource (Knüppe, 2011). For example, in many developing countries, areas immediately surrounding and downstream of mining operations are often inhabited by poor communities with little access to service provision. These communities are dependent on local streams, wetlands and groundwater sources for their water supply, and many are at risk of acute metal toxicity from heavy metals (Dhakate and Singh, 2008; El Khalil et al., 2008; Hobbs et al., 2008). In order to address these and similar shortcomings, the link between groundwater, groundwater-dependent sectors and groundwater governance needs to be understood and communicated, both in policy and in practice (Montanari et al., 2013). However, it is important to note that in some cases, especially in the developing world, countries are cutting back on their monitoring investments (Harmancioglu et al., 2003).

In a world where water consumption is predicted to increase, water scarcity will continue to intensify and a dependence on water reuse will become common practice, the monitoring of pollutants in the effected environment will become imperative (Elsner and Imfeld, 2016; Friedler, 2001). It is up to the scientific community to clearly impress the importance of monitoring networks and the upkeep and development of long-term data sets on decision makers, while prioritizing the need for installation and maintenance of measuring systems in the face of resource constraints (Lovett et al., 2007). With conditions often changing faster than scientists or policy makers can anticipate, adaptive management strategies and interdisciplinary research provide a means to address sustainable resource governance under uncertain conditions.

2.8. Summary and Conclusion

This review highlights some of the key groundwater contamination issues that are sourced from anthropogenic activities. A selection of major contaminants are discussed, including established products as well as emerging contaminants. Case studies addressing unique issues regarding groundwater quality, contaminating sources, and highlighted contaminants are presented. The diversity of cases illustrates the variability of qualitative threat to groundwater in terms of a sustainable resource for the human population and to safeguard the environmental integrity. Intensive agriculture, urban sprawl, globalized pharmaceutical production and consumption, insufficient wastewater infrastructure, dwindling empirical data on water quality, and in some cases the insufficient emphasis of groundwater as a renewable resource, are all hampering the complex process of managing groundwater quality. Although advances in measuring, monitoring, and modelling groundwater are astride, the rate at which new contaminants and contaminating issues are entering the scene may outpace current progress. Transdisciplinary research and action may provide an opportunity in developing a comprehensive understanding of contamination dynamics and their effects on the groundwater system. This presents great opportunities for merged fields of research and transboundary communication.

3. Estimating Surface Runoff and Groundwater Recharge in an Urbanizing Catchment Using a Water Balance Approach

3.1. Abstract

In this study, we explore the relationship between surface runoff and groundwater recharge in the urbanizing Kempttal catchment on the Swiss Plateau with two empirical and conceptual top-down groundwater balances. Land use changes often have significant impact on the water cycle, changing groundwater – surface water interactions, groundwater recharge zones, and increasing risk of contamination. Groundwater resources in urban areas are often actively used for municipal water supply, thus highlighting the importance of accurately estimating the availability and determining sustainable use of these important water resource. Since runoff is the connecting route between surface conditions and subsurface conditions, and is significantly impacted by urban infrastructure, we assess runoff magnitudes and resulting groundwater recharge. We applied two empirical models to estimate surface runoff: 1.) an updated curve number-based pluviometric method, followed by 2.) a bivariate hydrograph separation, using public databases on precipitation and streamflow. We added modifications to each method in an attempt to better capture continuous soil moisture processes, and to explicitly account for runoff from impervious surfaces. Important differences between runoff estimates shed light on the complexity of the rainfall – runoff relationship, and highlight the importance of understanding soil moisture dynamics and their control on hydro(geo)logical responses in urbanizing catchments. These runoff results were then used as input in a water balance to calculate groundwater recharge for the shallow, unconfined aquifer within the study catchment. Two approaches were used to assess the accuracy of these groundwater balance estimates: a.) comparison to calculations of groundwater recharge using the conceptual HBV Light model, and b.) comparison to groundwater recharge estimates from other catchments of the Swiss Plateau that were found in literature. Satisfactory agreement was found between the empirical water balance and the HBV Light model, and recharge was estimated at approximately 40-45% of annual precipitation under average conditions between both methods. These conditions were found to closely echo those results from Swiss catchments of similar characteristics to our study area.

3.2. Introduction

Groundwater is among the most important reserves of freshwater on the planet, critical for drinking water resources as well as for healthy ecosystem functioning. Responsible management of groundwater is therefore essential for ensuring its long-term availability. Groundwater reserves are replenished through aquifer recharge, which is highly reactive to climate change and land development for many shallow aquifers. Unconfined shallow aquifers in particular are inherently vulnerable to short-term dynamics such as precipitation excess or deficit, or to quality degradation from the surface (Thomas et al., 2017; Vogt and Somma, 2013). This vulnerability translates into increased risk of groundwater contamination in areas impacted by human land use (Burri et al., 2019; Hale et al., 2014; K'oreje et al., 2016; Meyer et al., 2005; Scanlon et al., 2007). Because of this, significant energy has been dedicated to studying the changes in groundwater recharge and its influencing factors as a result of human activity (Barron et al., 2013; Ficklin et al., 2010; Lerner, 1990; Schirmer et al., 2013). As more than 50% of the world's human population is now living in cities, an increasing number of studies have been dedicated to investigating the numerous and complex changes in groundwater recharge in urbanizing environments (Minnig et al., 2018; Wakode et al., 2018).

Groundwater recharge is a result of many factors. Its accurate characterization therefore requires properly accounting for the individual environmental variables that contribute to its dynamics. Surface runoff in particular is one of several important contributing variables to shallow aquifer recharge, and acts as a direct link between surface water and groundwater bodies. Surface runoff is defined here as the excess precipitation and shallow soil moisture that flows at and near the land surface immediately following a storm event (Harbor, 1994). Like recharge, surface runoff dynamics have been shown to be heavily altered by human activity, often in very complex ways (Eshtawi et al., 2016; Harbor, 1994). Increases in the amount surface runoff are often observed in developed areas as a result of increased impervious surfaces, soil compaction, and drainage infrastructure (Eshtawi et al., 2016; Gremillion et al., 2000). While it is not the most significant variable in a water balance by magnitude, runoff plays a proportionally large role with regards to contamination risk, as it may carry pollutants from the surface into the subsurface through processes such as groundwater – surface water interactions, downstream infiltration, or re-use for irrigation (Foster and Chilton, 2004; Musolff et al., 2010). Contaminants that are mobilized by surface runoff include pesticides, herbicides, biocides, sewage and effluent, non-aqueous phase liquids, and volatile organic compounds, among others (Fischer et al., 2003; K'oreje et al., 2016; Wong and Kerkez, 2016).

As neither recharge nor surface runoff can be directly measured, both must be inferred indirectly with data that can be measured (Foster et al., 1999; Rammal et al., 2018). This can lead to great uncertainties in estimates, difficulties in characterizing runoff – recharge relationships in changing environments, and subsequent difficulties in effectively protecting and managing groundwater resources. Great efforts have been made to improve upon our understanding of these dynamics, and many different approaches of varying complexity have been implemented to study rainfall routing and groundwater recharge (Scanlon et al., 2002). Examples include empirical and conceptual water balances (e.g. Bergström and Lindström, 2015; Minnig et al., 2018; Wittenberg and Sivapalan, 1999); thermal, chemical, or isotopic tracers (Meriano et al., 2011; Solomon et al., 1993); timeseries analyses (Bakker and Schaars, 2019; Crosbie et al., 2005; Moeck et al., 2020); statistical and numerical modeling (e.g. Bakker et al., 2016; Brunner and Simmons, 2012; Döll and Fiedler, 2008; Moeck et al., 2017a), remote sensing and GIS (e.g. Sheffield et al., 2018; Tweed et al., 2007), as well as combined method approaches (Brunner et al., 2004; Hornero et al., 2016; von Freyberg et al., 2015a). In general, it has often been suggested to carry out estimations using multiple methods because of the uncertainties involved in all approaches (Healy and Cook, 2002).

While increases in computational power have enabled the development of fully distributed, physically-based numerical models, the use of empirical and conceptual models remain popular. This can be attributed to the large data requirements that are necessary for numerical modeling, while simple methods are more widely accessible due to minimal requirements and relatively straightforward parameterization (Bakker and Schaars, 2019). Because of this fact, it is of great interest to explore the performance of simplified approaches in different environments. In their most basic form, empirical and conceptual approaches to estimating elements of the groundwater balance generally require some combination of data on precipitation, groundwater levels, river discharge, and climatic data, which are some of the most widely available data in most parts of the world. These data types continue to become significantly more accessible on large spatial scales, due to the organization of free databases provided by local governments up to global organizations such as the Center for Global Environmental Research or the United Nations Food and Agriculture Organization (UN FAO). In addition, many small-scale published datasets from around the world (Moeck et al., 2020) are also freely available.

3.2.1. Quantifying Surface Runoff

Surface runoff can be quantified in a number of ways, most commonly with pluviometric methods or with hydrograph methods (Hernández-Guzmán and Ruiz-Luna, 2013; Kirchner, 2019; Rammal et al., 2018; Woldemeskel and Sharma, 2016). As far as pluviometric approaches, Curve Number-based methods are among the most common (USDA Natural Resources Conservation Service, 1986). These methods estimate event flow, i.e. surface runoff, using precipitation timeseries. The original Natural Resources Conservation Services Curve Number (NRCS-CN) method remains popular for estimating surface runoff in both research and engineering due to its suitability for small-scale applications, ability to apply it in ungauged catchments, low data requirements, and thorough documentation and case studies in literature (Ajmal et al., 2016; Minnig et al., 2018; Mishra and Singh, 2003; Soulis and Valiantzas, 2012; Thomas and Tellam, 2006; Wakode et al., 2018; Zope et al., 2017). Indeed, contemporary models of varying complexity continue to be developed using the original CN equations or aspects thereof (Verma et al., 2017). Examples are the GIS-based SARA model (Hernández-Guzmán and Ruiz-Luna, 2013), methods making use of remote sensing data (Zeng et al., 2017), the popular SWAT model (Arnold et al., 2012), and a model fusing the rational equation with the curve number (Wang et al., 2012). Modern adaptations of the method attempt to improve soil moisture accounting (e.g. Bartlett et al., 2016; Michel et al., 2005; Mishra et al., 2003; Sahu et al., 2010; Singh et al., 2015; Wałęga and Rutkowska, 2015), or to explore the proportionality concept that is of unclear origins (Hooshyar and Wang, 2016).

For hydrograph methods, river discharge is directly observable and can give a great deal of insight on storm runoff response and changing water dynamics within a catchment. Discharge, also called streamflow, is an integrated signal of all contributing waters leaving a catchment. In a bivariate model, river discharge is composed largely of slow-moving baseflow and the rapid-response of quickflow. Baseflow, conceptualized as groundwater discharge, has been found to be a significant component of streamflow, even during storm events, and even in some urbanized areas (Klaus and McDonnell, 2013; Meriano et al., 2011; Sklash and Farvolden, 1979). However, increases in quickflow are commonly observed in urban areas and drained agricultural lands, at times independent from the baseflow response in these areas. The ratios of these components are estimated in dry periods, wet periods, and during active storm events in order to identify the characteristics of catchment storm response. Hydrograph separation can be done with timeseries analysis of streamflow using digital recursive filters (Chapman, 1991; Li et al., 2014; Nathan and McMahon, 1990; Willems, 2009), or with more sophisticated methods using high-frequency chemical or isotope composition in addition to streamflow timeseries (Jasechko et al., 2016; Lyon et al., 2012; Penna et al., 2015; von Freyberg et al., 2017).

3.2.2. Quantifying Groundwater Recharge

Groundwater recharge for shallow aquifers is often determined via "top-down" water balancing, which uses data on surface conditions in order to estimate recharge (Arnold and Allen, 1999; Minnig et al., 2018; Seibert and Vis, 2012). Natural water balances are used to calculate the partitioning of precipitation into surface water, groundwater, and evapotranspiration. Major control factors for precipitation partitioning include climate, geology, geomorphology, precipitation intensity, and land cover, among others (Gannon et al., 2014; Stanton et al., 2013). These control factors will determine the amount of water that infiltrates, becoming potential recharge, the amount lost to evapotranspiration, and the amount that becomes surface runoff, which is a loss factor if it reaches the catchment outlet before it reaches the water table. In urban environments, water balances can easily be expanded to account for additional inputs such as sewer leakage, effluent, or irrigation. Recharge estimates from these water balances are only as good as the estimates of their individual variables, and thus are contingent on identifying and accurately quantifying the significant input and output variables.

3.2.3. Objectives

The objective of this chapter is to apply empirical and conceptual methods to quantify and explore runoff – recharge dynamics, and to assess the suitability of these methods to estimate groundwater recharge in a changing environment. This is carried out as a case study in a small catchment located on the Swiss Plateau that is undergoing active transition from an agricultural landscape into an urban landscape. Our study site mirrors the situation across Switzerland: approximately 80% of freshwater resources in Switzerland are sourced from groundwater, and aquifers within the unconfined fluvio-glacial sediments of the Swiss Plateau are highly exploited as a resource (Reinhardt et al., 2019). At our study catchment, nearly all of municipal and industrial water supply is sourced from a local, unconfined aquifer. The relative strengths and shortcomings of each of these methods, as well as their potential sources of differences, are discussed. With these comparisons, we are able to gauge the ability of these simplified methods to offer satisfactory characterization of the water cycle in a human-impacted catchment. For our study catchment, timeseries of streamflow, precipitation, and estimated evapotranspiration spanning decades are available from Swiss public repositories, and this available data was used for all of our calculations.

In this study, two timeseries approaches are used to estimate catchment surface runoff: 1.) an amended version of the NRCS-CN method, called the Sahu-Mishra-Eldho (SME) model after its authors (Sahu et al., 2012, 2010); followed by 2.) automated hydrograph separation (HS) using the popular recursive digital filter as outlined by Nathan and McMahon (1990), where we explore a wider range of filter parameters suited to urban environments. Surface runoff estimates from these two methods have independent data requirements, offering a useful comparison of their performance at our study area. For clarity, estimates using the SME method are referred to as surface runoff, estimates using HS are referred to as quickflow, and river discharge is referred to as streamflow.

Two approaches are then used to estimate groundwater recharge within this study: 1.) an empirical water balance using our runoff estimates as input, leading to two groundwater recharge estimates; followed by 2.) application of the conceptual HBV Light model. The

HBV Light model requires only air temperature, potential evapotranspiration, precipitation, and streamflow as data inputs. As a final validation step, we compare our results with recharge estimates found in the literature for similar Swiss catchments.

3.3. Case Study

The upper Kempttal catchment on the Swiss Plateau is located approximately 30 km east of the city of Zürich, Switzerland. The Swiss Plateau is a region of temperate climate characterized by rolling hills and valleys formed from a series of glacial periods. The catchment covers an area of approximately 35 km^2 with an increasing altitude from NW – SE: 520 m.a.s.l. at the lower outlet area (NW), and up to approximately 900 m.a.s.l. in the upper headwater area (SE). Before human settlement, the area was naturally dominated by forest. The catchment groundwater is exploited as the principal source of drinking water and agricultural water resources for the local population.

As a result of the alpine glacial origins of the valley, shallow geology is composed of unconsolidated fluvio-glacial sediments in the form of heterogeneous sandy loam and glacial gravels (Figure 3-1). Some areas are additionally intercut with lenses of impermeable glacial moraine and marl. Sands and sandy loam dominate the central valley and riparian zones. The bedrock is made up of an Upper Freshwater Molasse consisting of consolidated sandstone, conglomerates, and claystone. The unconsolidated sediments host a shallow, unconfined aquifer with a surface area of approximately 10 km^2. The deepest zones of the aquifer body are in the central valley and have been reported at 10 – 20 meters, with thinner portions between 1 – 8 meters on the valley edges (Krejci et al., 1994), though these estimates are uncertain. As determined with data that we collected from soil cores, 2D electrical resistance tomography, and a network of groundwater monitoring wells, the aquifer is covered by an average of 3 meters of unsaturated zone above the water table in the middle catchment (S-SE), and an average of 1 meter of unsaturated zone above the water table near the catchment outlet (NW). Groundwater recharge occurs mainly through precipitation, and the residence time of groundwater is assumed to be relatively short, on the order of months to two years (Krejci et al., 1994).

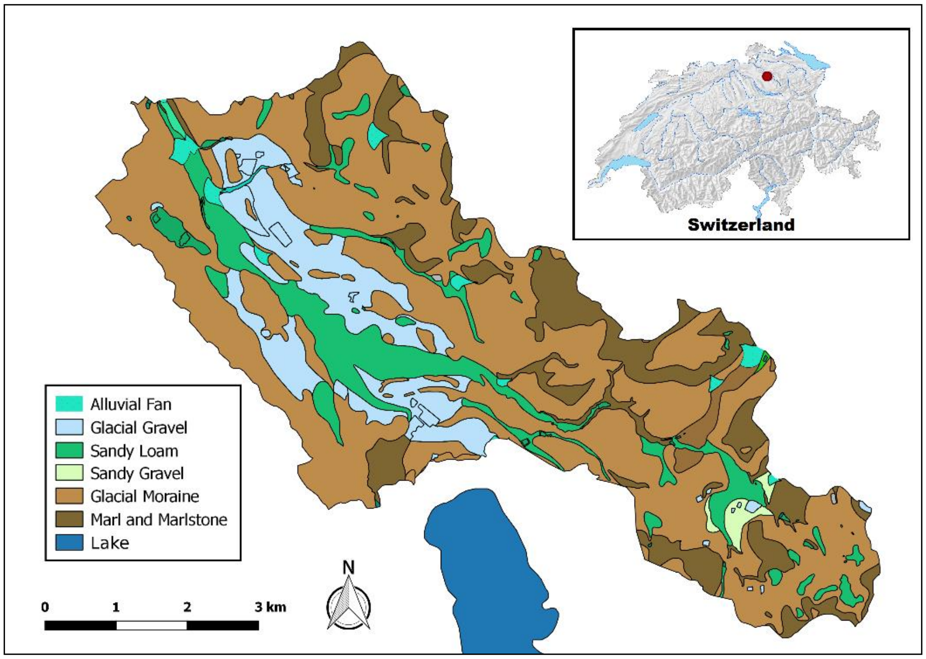


Figure 3-1. Shallow geology of the upper Kempt catchment. The aquifer is principally located within the glacial, loamy, and alluvial sediments of the catchment. Public sources: Swiss Federal Office of Meteorology and Climatology; Canton Zürich Office for Waste, Water, Energy, and Air (AWEL); Swiss Federal office for the Environment (FOEN).

The catchment contains a small tributary network feeding in to the Kempt river, which is heavily modified via canalization and deepening of the river bed in the central urban municipality of the catchment, Fehraltorf. The Kempt river has been shown to be somewhat intermittent and tends to react strongly to climatic conditions with high peak flows in wet seasons, and running dry along much of its stretch during particularly dry seasons. This latter phenomenon is compounded by a hydropower plant in the upper reaches of the Kempt. However, its intermittence is compensated in downstream areas by the presence of a wastewater treatment plant that emits treated effluent into the Kempt river close to its outflow point. This treatment plant is upstream of the main river gauging station, and is therefore an integral component of measured streamflow. This effluent may be conceptualized as an artificial form of baseflow present in the lower areas of the catchment.

The area has been dominated by agriculture for much of recent history, and agriculture remains the highest proportion of land cover today. Over the past several decades, expansion of urban centers and neighborhoods has accelerated. Sealed surfaces and drained areas make up approximately 10% of the catchment. The valley is currently made up of 53% agriculture, 25% forest, and 22% urban area (Federal Statistical Office of Switzerland GEOSTAT). Today, the entire catchment area has approximately 11000 inhabitants, and the most populated area is the municipality of Fehraltorf with 6300 inhabitants (GEOSTAT; Gemeinde Fehraltorf). The urban area is expected to sustain its growth over the decades to come due to its proximity to the city of Zürich.

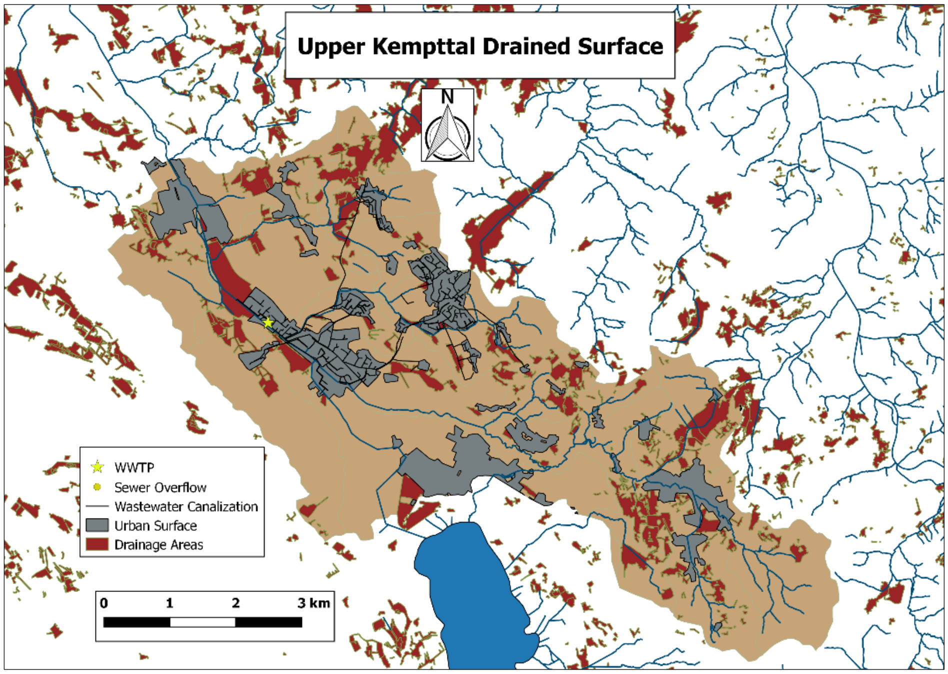


Figure 3-2. Urban surfaces and drained land in the upper Kempttal catchment. Public sources: Swiss Federal Office of Meteorology and Climatology; Canton Zürich Office for Waste, Water, Energy, and Air (AWEL); Swiss Federal Office for the Environment (FOEN).

Surface and underground drainage systems exist in several areas, with tile drains and ditches in some agricultural zones and underground storm drains in urban zones (Figure 3-2). Most storm drains are separated from the sewer network, though some central areas are still served with storm water systems combined to the sewer network. The latter systems can lead to combined sewer overflow (CSO) during heavy storms, when network flow capacity is exceeded. CSO leads to a release not only of storm runoff, but also of sewage. In the Fehraltorf urban center, CSO is known to occur during heavy storms (personal communication, Dr. F. Blumensaat, 2017). While the precise impact of the configuration of the drainage systems is difficult to characterize, their development has coincided with faster response times to storm events observed from streamflow, with peakier hydrographs that are characteristic of many developed areas (Bhaskar and Welty, 2015; Sheeder et al., 2002; USDA Natural Resources Conservation Service, 1986). Further, due to the canalization of much of the river network, groundwater – surface water interactions along the river are considered to be greatly attenuated, such that phenomena such as riparian subsurface runoff may be reduced.

Observation Data

For all of the calculations made in this study, the entire catchment area was assumed to contribute to runoff and groundwater recharge; differences in dynamic contributing areas was not explored. Table 3-1 gives a summary of the principal datasets used for the study methods, including data sources and the time period of the dataset. All public monitoring data sets are available on a daily time scale. Climate data was sourced from weather stations within 10 km of the catchment, and precipitation was calculated as an average from four gauging stations surrounding the catchment. Surface water data was collected from a single gauging station at the outflow of the catchment, immediately downstream of the wastewater treatment plant for the municipality of Fehraltorf.

Data Type	Source	Time Period
Precipitation (P)	MeteoSwiss	2007 – 2018
River discharge (Q)	AWEL	2007 – 2018
Evapotranspiration (ET)	MeteoSwiss	2007 – 2018
Air temperature (T)	MeteoSwiss	2007 – 2018
Groundwater levels (GWL)	AWEL; Our wells	2000 – 2018
Land cover	GEOSTAT; AWEL; FOEN	2015
Paved surface area	Canton Zürich	2015

Table 3-1. Summary of main databases used in the current study. Public sources: Swiss Federal Office of Meteorology and Climatology (MeteoSwiss); Canton Zürich Office for Waste, Water, Energy, and Air (AWEL); Swiss Federal Office for the Environment (FOEN).

Year	P (mm)	AET (mm)	Q (mm)
2007	1137.3	445.7	443.1
2008	1115.7	422.8	323.7
2009	1057.5	433.5	325.4
2010	1207.5	414.8	462.6
2011	961.1	514.2	305.7
2012	1329.5*	450.0	605.9
2013	1156.6	441.7	577.8
2014	1116.8	430.4	531.2
2015	891.6	554.8	452.0
2016	1268.4	403.8**	660.2*
2017	1048.6	475.6	438.9
2018	889**	554.9*	288.4**
12-year Ave.	**1094.7**	**462.0**	**451.3**

*Table 3-2. Annual sums of major water balance variables during the period of study. Precipitation is assumed to represent the maximum potential recharge, actual evapotranspiration AET is the principal precipitation loss factor, and Q is streamflow, which is an integrated signal of surface runoff and groundwater exfiltration. * and ** correspond to highest and lowest yearly values, respectively. Data courtesy of MeteoSwiss (2019).*

3.4. Materials and Methods

3.4.1. Surface Runoff

SME Method

The SME method was first proposed by Sahu et al. (2010) as an improvement of the NRCS-CN method (USDA Natural Resources Conservation Service, 1986). A brief introduction of the NRCS-CN method and its governing equations can be found in the supplementary information, with more detailed information found in Mishra and Singh (2003). The SME method is based on the same water balance as that of the original CN (equation S.I.1), and adaptations to the two fundamental hypotheses that underlie the method (equations S.I.2 and S.I.3). The authors adapted the estimation of soil moisture, while maintaining a relatively straightforward implementation and a restricted number of required parameters. The SME method has been applied in a number of case studies since its inception (e.g. Ajmal et al., 2015; Sahu et al., 2012; Wałęga et al., 2017), and like its predecessor, the only hard data requirement is a precipitation timeseries. A computer program was developed in Python to implement the SME model in our study.

The SME method decouples soil moisture from catchment potential retention, which are lumped in the original NRCS-CN method. Several simplifying assumptions are then applied in order to derive an expression for soil moisture, using a 5-day antecedent rainfall condition P_5 (see equation S.I.4 in the supplementary information). The principal assumption in formulating this soil moisture equation is that the catchment is completely dry prior to the 5-day antecedent precipitation window P_5. This assumption is, however, generally invalid for temperate regions, regions with regular winter snowfall, and for urban landscapes where impervious surfaces lead to prolonged soil moisture retention. Antecedent rainfall may be taken over longer time periods (P_x for $x > 5$) for calculations, but this does not resolve the issue of subjectivity in choosing an antecedent moisture window, and subsequent disregard of conditions prior to that window.

An alternative to the P_5 metric is the antecedent precipitation index (Fedora and Beschta, 1989; Kohler and Linsley, 1951), which we propose here to replace P_5. The antecedent precipitation index (API) applies an exponential decay factor over a rainfall timeseries, in order to estimate the amount of prior rainfall that may be contributing to current soil moisture conditions. APIs are regularly used as soil moisture proxies in rainfall – runoff modeling (e.g. Bennett et al., 2018; Descroix et al., 2002; Ma et al., 2014; Woldemeskel and Sharma, 2016). Various, closely related formulations are given in the literature, and a generalized form of the API is used in this study:

$$API = \sum_{t=1}^{T} P_{-t} * k^t \tag{3-1}$$

In equation 3-1, T is the total number of time steps in the series, t is the individual time step, and k (dimensionless) is a decay factor that is less than 1 (often in the range of 0.6 – 0.99 for temperate areas), which represents how quickly moisture is lost from a catchment through any process. P_{-t} is the amount of precipitation at prior time steps t. As t increases, the term k^t decreases in magnitude, approaching zero. In general, higher values of k represent a slow draining landscape and lower values represent a quickly draining landscape (Ali et al., 2010; Lee and Huang, 2013; Woldemeskel and Sharma, 2016). In reality, the decay factor is proportional to evapotranspiration and likely related to water table depth, and thus should vary seasonally (Pui et al., 2011). In practice, it is often taken as a constant through time, assumed to represent average annual conditions. Aside from determining the value of k, the API rids the need for the user to determine an arbitrary, fixed-window sum of antecedent precipitation.

For this study, values of k between 0.8 and 0.99 for daily time steps were considered suitable for a temperate catchment with urban surfaces. The calculated API was in fact relatively insensitive within this range, and without further information, a value of $k = 0.9$ was selected to calculate the API. The length of T for the API covered our entire timeseries (2007-2018). Due to the exponential decay factor, the point at which past precipitation becomes irrelevant to current moisture conditions is automatically determined.

The original SME equation for soil moisture, M, (equation S.I.4) is thus modified and expressed as:

$$M = \beta \left[\frac{(API - \lambda S_0)S_0}{API + (1-\lambda)S_0}\right] for \text{ API} > \lambda S_0 \tag{3-2}$$

where β (dimensionless) represents the fraction of antecedent precipitation that is contributing to soil moisture, S_o (units of depth) represents maximum potential retention of a catchment, and λ (dimensionless) is the initial abstraction (I_a) coefficient, where $I_a = \lambda S_0$. All of these parameters are fixed in time.

From the decoupling of soil moisture and maximum potential retention, S_0 is determined as a function of physical catchment characteristics including soil type, unsaturated zone depth, land cover, and vegetation types. Initial S_0 values can be approximated with values of S in dry conditions from the NRCS-CN method, and adjusted through calibration (Mishra and Singh, 2003; USDA Natural Resources Conservation Service, 1986). The value of S_0 is assumed to be reduced by the presence of subsurface infrastructure including sewers and water mains, as these lead to a loss of pore space in the soil. Likewise, the parameter λ is generally deduced from geological maps, drainage tests, soil cores, climatic factors, or other aspects of the current conceptual model for the site under study. Values of λ are referenced in literature between the ranges of $0.05 - 0.3$, and are closer to 0.05 in urbanized areas (Minnig et al., 2018; Mishra and Singh, 2003). Values of β may range between $0 - 1$, though more precise information on this parameter in literature is sparse. Further, the fraction β is most certainly affected by the use of the API in place of P_5, and is expected to be closer to 1 in this formulation of M due to the decay factor already inherent to the API.

In addition to the implementation of the API, in the present study we aimed to expand the representation of runoff beyond soil-controlled saturation-excess overland flow. This was done by explicitly accounting for sealed surfaces with a pre-processing of rainfall partitioning. Runoff over paved surfaces was decoupled from soil-controlled runoff dynamics by assuming that all precipitation falling onto sealed surfaces immediately becomes runoff. As 10% of the entire catchment is covered by paved surfaces, 10% of each day's precipitation was routed directly to runoff, and the remaining 90% of each day's precipitation was then used as input for SME calculations. With these added considerations, the following equation for runoff R_{off} is applied:

$$R_{off} = \frac{(0.9P - I_a)(0.9P - I_a + M)}{0.9P - I_a + S_0} + 0.1P, for\ \ 0.9P > I_a \tag{3-3}$$

where I_a essentially corresponds to rainfall interception, which is the fraction of precipitation that is lost from a catchment during a storm event through processes such as infiltration, canopy interception, or ponding at the surface (Lee and Huang, 2013; Van Dijk et al., 2015). In equation 3-3, the factors of 0.9 and 0.1 will change from catchment-to-catchment depending on the ratio of area that is covered by impervious surfaces. We carried out calculations on a daily basis and upscaled to weekly, monthly, and annual scale in order to explore storm-by-storm, seasonal, and annual runoff.

Hydrograph Separation

Hydrograph separation (HS) involves dividing a hydrograph – a timeseries of river levels or discharges – into its assumed subflow components. It is widely accepted that streamflow is composed of sub-flow components corresponding to quick, intermediate, and base flow, where baseflow corresponds to sustained streamflow during dry weather periods and is largely sourced from groundwater. In general, quickflow is considered as surface runoff during storm events. Intermediate flow is considered to be shallow subsurface runoff, largely from the riparian zone. Intermediate flow is more difficult to characterize and depends significantly on vadose zone soil moisture. When bivariate hydrograph separation is applied, intermediate flow is often lumped into quickflow and referred to as event-flow.

The basic approach for hydrograph separation uses recursive digital filters (RDFs) to separate quickflow and baseflow (Chapman, 1991; Nathan and McMahon, 1990; Willems, 2009). The RDF first proposed by Lyne and Hollick (1979), as outlined by Nathan and McMahon (1990) was applied with the EcoHydrology package available in R (Fuka et al., 2018) for this study. The filter is expressed as such:

$$qf_t = \alpha * qf_{t-1} + \frac{1+\alpha}{2} * (Q_t - Q_{t-1}) \tag{3-4}$$

where qf is quickflow (units of depth), Q is measured streamflow (units of depth), and α is the filter parameter (dimensionless). It can be seen from equation 3-4 that larger values of α lead to lower estimates of baseflow and higher estimates of quickflow, and vice versa.

In most applications, α is set at or near the value of 0.925 proposed by Nathan and McMahon (1990), which is considered standard practice. However, the original work by Lyne and Hollick (1979) suggested varying the filter parameter between $0.75 < \alpha < 0.9$, and more recent work by e.g. Li et al. (2014) has demonstrated that α can and does widely vary between $0 < \alpha < 1$ depending on baseflow dynamics and the underlying conceptual model. Knowledge of land cover, soil types, water table depth, and visual inspection of a streamflow hydrograph can be used as a preliminary assessment of potential value ranges of α. It is generally assumed that the lower end of the hydrograph recession curve should coincide with baseflow. Visual inspection of the upper Kempttal hydrograph show that values of $\alpha < 0.8$ begin to portray the expected behavior, which is much lower than the often-used 0.925 (e.g. Burns et al., 2012; Nathan and McMahon, 1990; Partington et al., 2012). For the current work, a range of values between $0.3 - 0.95$ were explored.

While we assume that the Kempt river is losing along much of its upper stretch (therefore minimal groundwater input to baseflow), we also know that baseflow is supplemented by wastewater effluent at the gauging station. Further, within the urban center, the riverbed is below the groundwater table. As the Kempt river gauging station is downstream of the WWTP, a higher quantity of baseflow (and thus a lower value for α) is deemed more appropriate to account for effluent. An example hydrograph from this exercise is available in the supplementary information. As with the SME method, we carried out HS calculations on a daily basis and upscaled to weekly, monthly, and annual scale in order to explore storm-by-storm, seasonal, and global runoff.

Streamflow, Runoff, and Quickflow Coefficients

The streamflow coefficient $C_Q = {}^{Q}/_{P}$ is a commonly used tool in hydrology to characterize the dynamics of river discharge response to storm events (Barron et al., 2013; Penna et al., 2015; von Freyberg et al., 2018). Similarly, coefficients using R_{off} or qf can be used to characterize the surface runoff response to storm events more specifically. The runoff coefficient is thus expressed as $C_{Roff} = {}^{R_{off}}/_{P}$, and the quickflow coefficient as $C_{qf} = {}^{qf}/_{P}$. We applied these coefficients in attempt to gain insight on the proportion of rainfall that contributes to a given storm event, the potential presence of runoff inputs additional to rainfall (i.e. pre-event water), and the catchment contributing area to runoff generation. These coefficients were explored as a function of both precipitation magnitude as well as antecedent precipitation conditions.

Uncertainty Analysis

Uncertainty in the parameters for both runoff methods were explored. First, the SME method is a relatively new approach as compared to the original CN method, and plausible ranges of parameter values are less documented. To address the uncertainty for this method, a Monte Carlo sampling approach was used to generate 10,000 random parameter combinations from a probability distribution of parameter values for S_0, λ, *and* β (Table

3-3, figure S.I.1), resulting in 10,000 runoff estimates. The lower and upper limits of S_o and λ were constructed to be larger than the ranges of these parameters found in literature for the original CN method (Minnig et al., 2018; Mishra and Singh, 2003; Sahu et al., 2012). It should be noted that during our construction of parameter ranges, S_o values greater than 300 mm led to very minimal surface runoff estimates, and values greater than 400 mm led to a complete absence of surface runoff. Finally, each parameter was allowed to vary independently during the sampling process.

With regards to hydrograph separation, the filter parameter α was similarly tested. In this case, a manual sampling of 20 random values between 0.3 and 0.95 was carried out Table 3-3).

Method	Parameter	Mean	Min	Max
SME	S_o	**150**	8.56	293.55
	λ	**0.10**	0.002	0.29
	β	**0.5**	0.01	0.99
HS	α	**0.62**	0.3	0.95

Table 3-3. Ranges of prior parameter values considered for SME and HS calculations.

3.4.2. Groundwater Recharge

Water Balance

The groundwater balance calculates GWR as the residual of relevant terms including precipitation (P), actual evapotranspiration (AET), and runoff (R_{off}). The most basic form was calculated in the current study:

$$GWR = P - AET - R_{off}, \text{ for } P - AET - R_{off} > 0 \qquad \textbf{(3-5)}$$

where the soil moisture element is integrated into calculations of AET and R_{off}. Using equation 3-5, GWR was estimated on a daily basis and upscaled to annual sums for the purpose of identifying long-term trends including dry years and wet years. GWR was estimated over the entire 35 km² catchment without differentiating between sub-catchments. We present recharge on an annual time scale. On daily and even monthly timescales, the right-hand term of equation 3-5 is often negative, signifying aquifer depletion. On the contrary, as recharge signifies increases in groundwater volume, the lower limit of GWR is 0.

The two estimates of surface runoff outlined in section 3.4.1 were used in turn as the R_{off} input. As AET inputs were available from public data, their uncertainties were not explored and the same AET dataset was used for water balance calculations. Further, quantitative input from sewer leakage or irrigation is expected to be minimal at our site and thus was not explored. Without precise information on points where the sewer and groundwater could interact, this is a difficult variable to quantify. Further, the vast majority of crop agriculture at in the Kempttal catchment is served with drip irrigation such that its input to the water balance is considered minimal.

HBV Light Model

HBV Light is a conceptual rainfall-runoff model developed by Seibert (1999) as an adaptation to the original HBV model developed by Bergström (1976). HBV Light is regularly applied by hydrologists to partition measured streamflow into its assumed sub-components. The model is freely available for download, currently through the University of Zürich (https://www.geo.uzh.ch/en/units/h2k/Services/HBV-Model.html). Thorough overviews of the model are available in literature (Bergström and Lindström, 2015; Seibert, 1999; Seibert and Vis, 2012). The HBV model is built around the following water balance equation:

$$P - AET - Q = \frac{d}{dt}(SP + SM + SUZ + SLZ + lakes) \quad \textbf{(3-6)}$$

where P is precipitation, AET is evapotranspiration, Q is river discharge, SP is snow pack, SM is soil moisture, and SUZ and SLZ are storage in upper and lower soil zones, respectively. All variables are in units of depth over a specified time step. In its simplest form, timeseries for precipitation, air temperature, river discharge, and potential ET (PET) are needed, where river discharge is fitted to calibrate model parameters. AET is then calculated from PET and air temperature within the model. The model may be solved in either a lumped-catchment manner or in a semi-distributed manner. Several built-in model structures are available to account for different catchment configurations. Structures are available that account for multiple groundwater bodies, snow packs, or a heterogeneous unsaturated zone. The standard, default model structure accounts for two layers of unsaturated zone on top of the saturated aquifer zone.

For this study, the standard HBV Light model structure was applied to the upper Kempt catchment for the years 2008 – 2016 to estimate groundwater recharge. We defined five different elevation zones and one vegetation zone to create a semi-distributed framework. Within the model, the variable given as recharge is conceptualized as all water infiltrating from the surface, with no differentiation between upper and lower soil zones. There are in fact three streamflow components accounted for in the model structure, labeled Q_0, Q_1, and Q_2, which account for unsaturated zone and shallow percolation contribution into streamflow (Q_0, Q_1), followed by baseflow that is connected to deep percolation (Q_2). Q_0 is calculated as 0 except during strong storm events and when soil moisture is above a pre-defined threshold, and is representative of shallow subsurface runoff. Q_1 is activated during most storm events as well as when soil moisture is above a second pre-defined threshold, and is representative of intermediate unsaturated zone flow. Therefore, for the purpose of our study, we subtracted Q_0 and Q_1 from the given recharge variable in order to calculate GWR that is consistent with our empirical water balance.

Built-in calibration methods are available to explore model uncertainty. Automatic sampling of parameter values between user-defined bounds can be carried out with either Monte Carlo (MC) random sampling or a genetic algorithm (GAP). Parameter sets are then evaluated by applying one or more objective functions between simulated and observed streamflow, and best-fit combinations are determined by optimizing the chosen objective function(s). Our model was calibrated between the years 2008 – 2012 and validated from 2013 – 2016, using both MC and GAP to find the best parameter sets. From these, the six best performing parameter sets were selected each from the MC and GAP simulations, for a total of six optimized estimates. Three objective functions were used to assess model performance: efficiency R_{eff}, log of efficiency $LogR_{eff}$, and the coefficient of determination R^2. Optimal values for each of these objective function is 1. Results only from the validation period 2013 – 2016 are presented in this study.

3.5. Results

3.5.1. Runoff Response to Rainfall

Streamflow Dynamics

The streamflow coefficient C_2 is plotted in Figure 3-3 as a.) a function of precipitation, and then as b.) a function of the API, over daily timesteps. The relationship is shown for days where P > 10 mm; amounts below 10 mm in one day were observed to generate little to no streamflow response (with the exception of periods with significant snowmelt), which has also been observed in previous studies of similar climate (Thomas and Tellam, 2006). Figure 3-3a reveals that C_2 has an inverse relationship with precipitation when taken on daily time steps. However, when C_2 is compared to the API (Figure 3-3b), a clear positive, exponential relationship is exposed. These relations suggest that antecedent catchment moisture characteristics have greater control on streamflow response than do absolute precipitation amounts or impervious ground cover.

The exponential increase in C_2 as a function of API may be an indication of variable catchment contributing areas (Meriano et al., 2011), which increase along with increased catchment soil moisture. For example, under dry catchment conditions, it is often assumed that the runoff contributing area is largely constrained to the riparian zone. Under wet conditions, the contributing area expands further inland, covering a larger portion of the catchment (Penna et al., 2015). In addition, pre-event soil moisture is more likely to be mobilized into streamflow when storms occur during wetter conditions. Conditions when $C_2 > 1$ may be an indication of greater pre-event water input, although this should be interpreted with care. $C_2 > 1$ could also be an artefact of the frequency of measurements, as streamflow recession generally occurs over longer periods of one day.

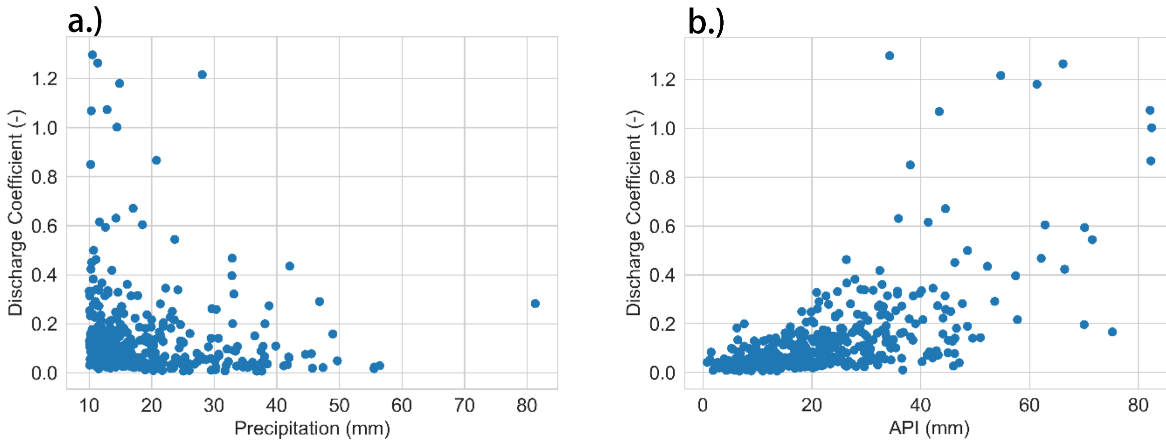


Figure 3-3. Streamflow coefficient C_2 with measured discharge Q as a function of a.) daily precipitation and b.) the API, respectively.

Comparing streamflow, precipitation, and the API exposes their relationships over the course of time (Figure 3-4), example year 2010; timeseries for all years available in the supplementary information). It can be seen that the two largest storms and river discharge peaks occur immediately following a mostly dry period with a low API. We can also see that snowmelt conditions during the month of March create a lag in streamflow response that is not captured by the API. It is interesting to note that during prolonged periods of increased soil moisture, resulting from consistent small storms, major peaks in streamflow are not always observed. A notable example in Figure 3-4 is the month of July, where the API is elevated from small storms, but streamflow exhibits no major peaks. This highlights the fact that storm characteristics also play a hand in runoff and streamflow response. Despite increases in sealed surfaces, it can be expected that much of the precipitation during small storms ends up infiltrating soils and recharging the aquifer rather than being lost to runoff.

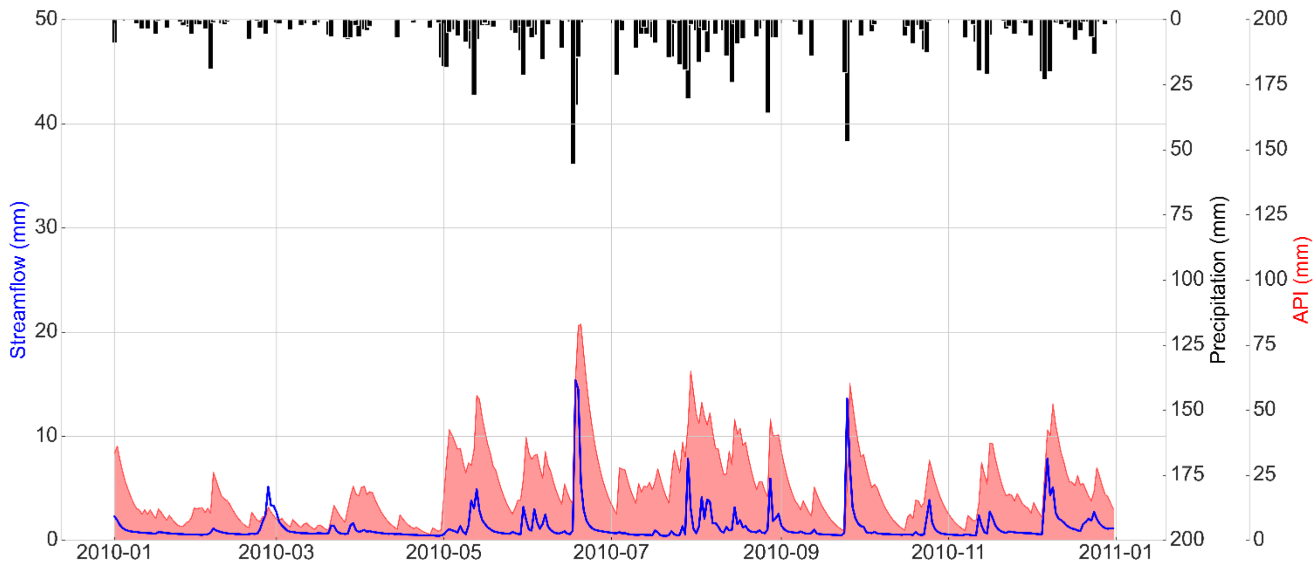


Figure 3-4. Daily timeseries of precipitation, river discharge, and calculated API. Timeseries for all years included in this study are available in the supplementary information.

Comparing Estimates of Surface Runoff

The surface runoff coefficient C_{Roff} was calculated using the average value of all SME surface runoff simulations as a function of precipitation. When C_{Roff} is plotted against precipitation and against the API (Figure 3-5), a similar pattern to those of Figure 3-3 emerges: an inverse relationship with precipitation, and an exponentially positive relationship with the API. Both graphs in Figure 3-5 suggest once again that immediate runoff from impervious surfaces, which are explicitly accounted for here, plays a minor role in surface runoff generation relative to antecedent moisture conditions, where the latter still largely dominates. And indeed, as the runoff response is calculated as instantaneous with pluviometric calculations, runoff lag times are not assimilated into the SME estimates. In this case, higher values of C_{Roff} for small amounts of precipitation is therefore not considered an artefact of measurement frequency muddled by lag times.

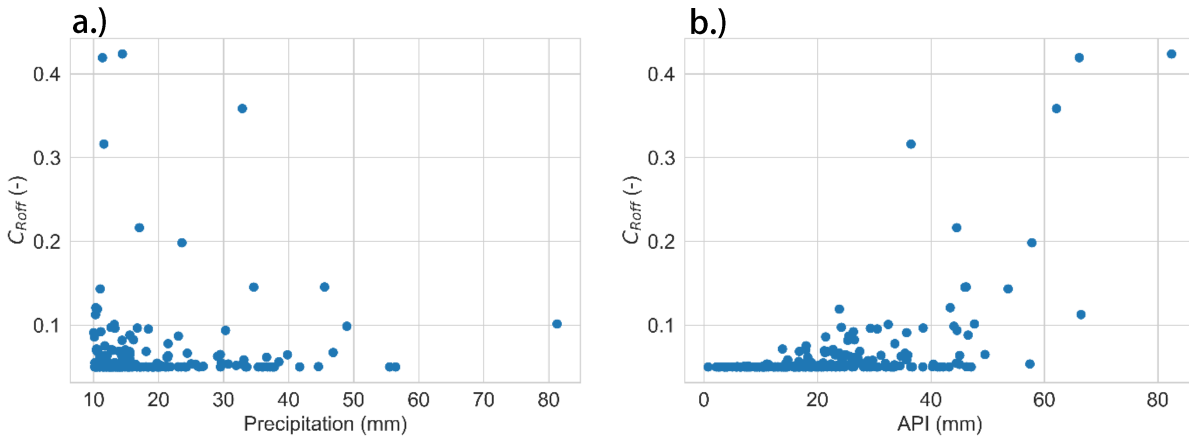


Figure 3-5. SME runoff coefficient (C_{Roff}) as a function of a.) daily precipitation and b.) the API, respectively. The mean SME runoff was used to calculate C_{Roff}.

The quickflow coefficient C_{qf} as a function of precipitation and then the API is shown in Figure 3-6. A major difference between C_{Roff} and C_{qf} is in their maximum values. Whereas C_{Roff} is below 0.5 even for the largest storms, the maximum value of C_{qf} surpasses 1 during large storms. Contrary to the discharge coefficient C_Q, lags in streamflow recession are assumed to have less of an impact, as much of the recession limb is filtered out when calculating qf from hydrograph separation. The possible explanation is again that the SME runoff is 'blind' to additional contributions to storm runoff, whereas HS quickflow integrates shallow pre-event water that may be contributing to the runoff response (von Freyberg et al., 2015b). As these contributions are inherently present in the hydrograph, C_{qf} is not subject to the constraint of precipitation amount as an upper threshold.

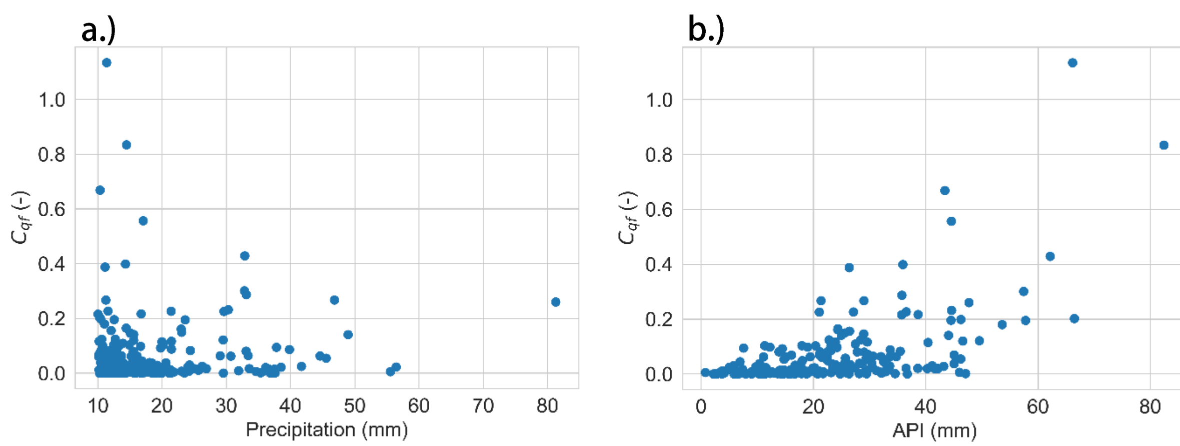


Figure 3-6. HS quickflow runoff coefficient (C_{qf}) as a function of a.) daily precipitation and b.) the API, respectively. The mean quickflow estimates were used to calculate C_{qf}.

Simulations of surface runoff timeseries for the example year 2010 are plotted on a weekly and monthly basis in Figure 3-7, where the solid and dashed lines represent the average of all simulations, and the shaded areas represent their respective standard deviations (timeseries for all years available in the supplementary information). The weekly time scale is used to compare results on a storm-by-storm basis, whereas monthly time scales are used to compare seasonal dynamics of each estimation. On a weekly basis, Figure 3-7 reveals that runoff estimates tend to agree well for more intense storms that elicit a larger runoff response. Greater uncertainties with regards to magnitude as well as response trends are present in consistent, low levels of precipitation, where soil moisture is high – for example, storms of early August 2010. This same tendency can be observed for all years (figures S.I.3.a and S.I.3.b in the supplementary information). Runoff estimates on a monthly basis show good agreement in general, although the SME estimates do not capture the same winter dynamics as those captured by HS estimates. During the month of August, discrepancies can be attributed to higher values of the API that are used for SME runoff estimates. They could also be an artefact of our direct routing of precipitation over sealed surfaces.

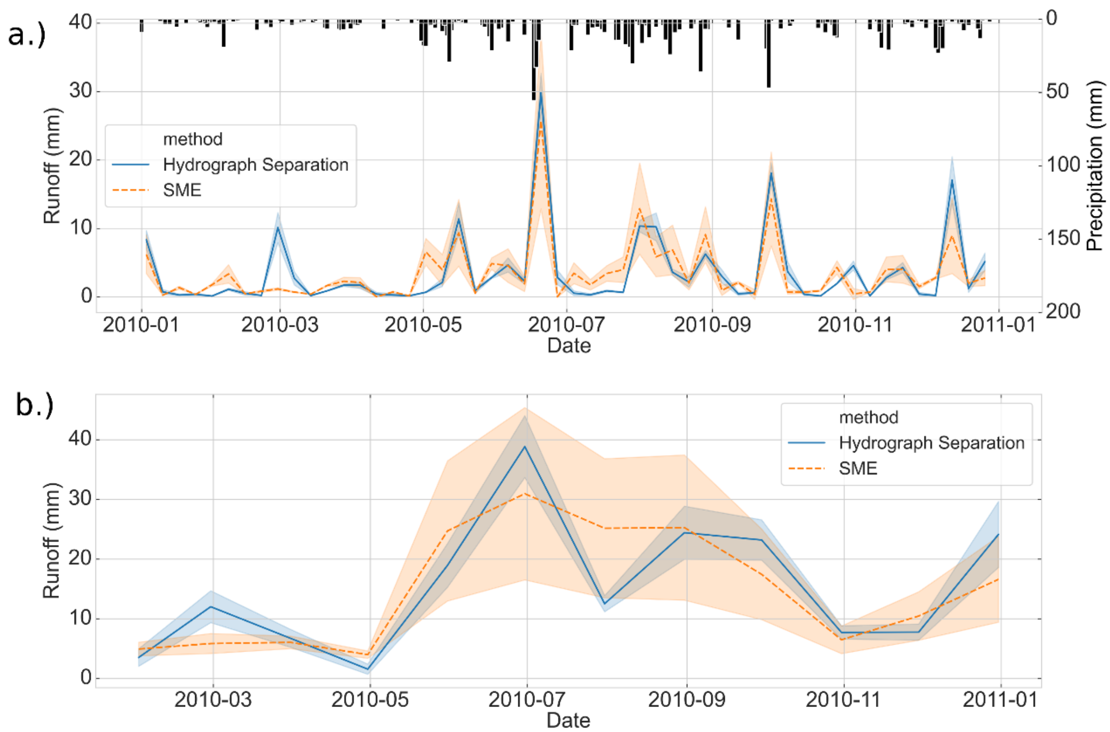


Figure 3-7. Timeseries comparison of surface runoff estimated from the SME method versus HS on a.) weekly and b.) monthly time steps. Additional timeseries over the entire course of study can be found in the Supplementary Information.

	SME		HS	
Year	**Mean**	**St.Dev.**	**Mean**	**St.Dev.**
2007	174.4	69.6	180.6	32.3
2008	163.5	65.8	106.2	20.1
2009	144.8	56.4	116.3	26.5
2010	178.0	74.3	181.4	32.4
2011	131.5	54.0	116.6	19.3
2012	196.9	85.9	237.8	52.1
2013	166.1	67.9	193.9	39.4
2014	156.4	64.6	200.8	36.6
2015	129.5	52.1	168.4	32.4
2016	192.5	84.8	249.8	52.5
2017	142.6	56.4	167.6	35.7
2018	118.4	47.9	94.0	19.7
12-year Ave.	**157.9**	**65.0**	**167.8**	**33.2**

Table 3-4. Average annual values of surface runoff (in mm) estimated via SME and HS.

A summary of the runoff simulations for both SME runoff and HS quickflow are given as annual averages in Table 3-4 and visualized in Figure 3-8. The average runoff estimates from the SME method are generally lower than quickflow estimates from HS during average and wet years, whereas average SME runoff estimates are generally higher during dry years. Higher SME runoff estimates during dry years can partially be attributed to the uncertainties surrounding consistent low levels of precipitation predominant in drier years, as opposed to large storm events. Higher estimates may also be due to the direct routing of precipitation over impervious areas into runoff, such that even moderate storms will lead to a small runoff response estimated using the SME method. It is interesting to note that higher SME runoff estimates are not clearly tied to particularly extreme values of AET (Table 3-2).

In the wet conditions of 2012 and 2016, the interquartile ranges of runoff estimates for each method individually are larger. The difference between each method during these wet years are also increased. On the contrary, in the more extreme dry conditions of 2011 and 2018, individual uncertainties are reduced, as are differences between the two methods. These reductions in uncertainties are partly due to the fact that when less rainfall occurs, or stream hydrographs do not contain many extreme peaks, the range of possible runoff estimates are also constrained. We see this clearly in Figure 3-7 on the monthly timescale, where periods of higher runoff are associated with higher uncertainties.

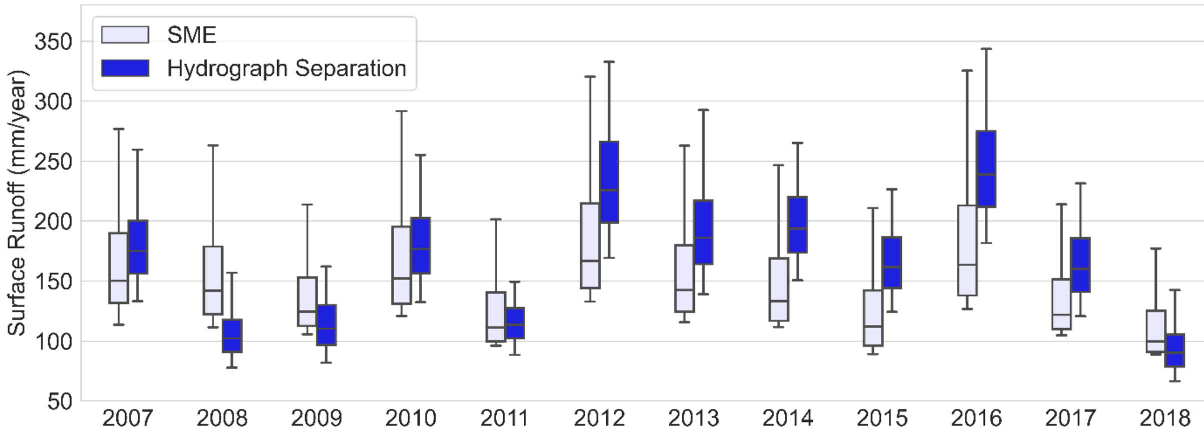


Figure 3-8. Total annual surface runoff estimated including all simulations for both methods for each year of the study period.

3.5.2. Annual Groundwater Recharge

Groundwater Balance of the Upper Kempt Catchment

As groundwater generally portrays a slower response time than surface runoff, we focused on annual estimations for the purpose of this study. Figure 3-9 shows the resulting comparative annual groundwater recharge calculated with our two runoff estimates, while the P and AET inputs were kept constant. The magnitude of the two resulting GWR estimates are generally in good agreement, and the inter-annual recharge trend is coherent between the two water balances as well. The largest difference between these estimates is on the order of 50 mm per year; a small and satisfactory difference. However, despite accounting for runoff uncertainty, there is a pattern of the HS quickflow input leading to lower recharge estimates between the years 2012 to 2018, consistent with higher runoff values in those years. This is a carryover effect to the fact that SME runoff estimates only account for losses from precipitation, where, HS quickflow integrates potential signals from pre-event soil moisture losses.

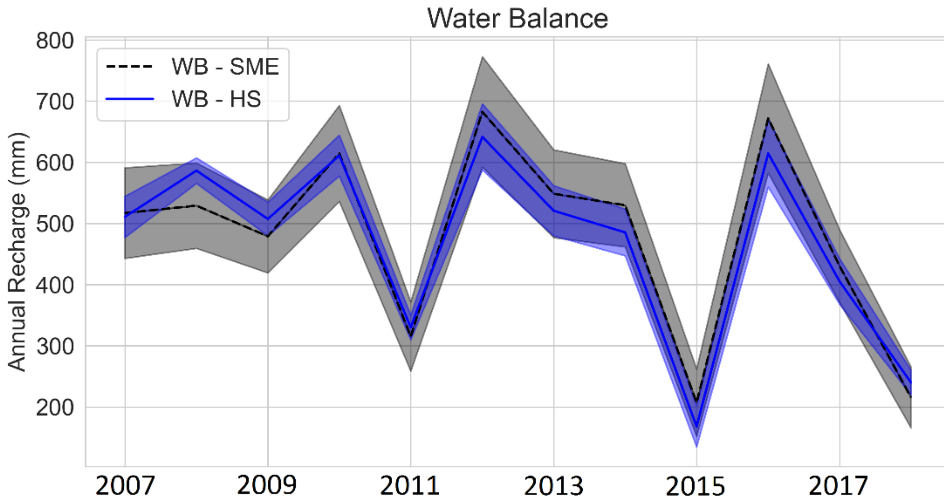


Figure 3-9. Annual timeseries comparing recharge estimates via water balance. Solid lines represent the mean value from all simulations, and shaded areas represent the standard deviation.

We then compare results from our water balance with estimates of groundwater recharge to the HBV Light model for the years 2013 – 2016, as all three methods are covered in this period. Table 3-5 lists the average annual estimates of groundwater recharge for all three methods. Figure 3-10 then shows the spread of these estimates, where the boxplots comprise all simulations for each method. In general, the average estimates between the water balance and the HBV Light model are also in good agreement. For the years 2013 and 2014, when annual precipitation was close to its 10-year average, the average difference between the lowest and highest recharge estimates is below 100 mm/year. However, differences increase for both the extremely dry year of 2015 and the wet year of 2016, reaching approximately 200 mm/year of difference in 2016. Regardless of these differences, estimates of groundwater recharge generally equate to 40-45% of annual precipitation recharging the aquifer from all methods. The exception to this is seen during the particularly dry years of 2015 (and of 2018), where recharge estimates dropped as low as 20% of annual precipitation.

	WB		HBV Light
Year	**SME**	**HS**	
2007	517.2	511.0	-
2008	529.3	586.7	-
2009	479.1	507.6	-
2010	614.6	611.2	-
2011	315.4	330.3	-
2012	682.7	641.8	-
2013	548.8	521.0	449.2
2014	530.0	485.6	456.7
2015	207.2	168.4	278.3
2016	672.0	614.7	478.2
2017	430.4	405.4	-
2018	215.7	240.1	-
Ave.	**478.6**	**468.7**	**415.6**

Table 3-5. Average annual groundwater recharge estimates from all methods.

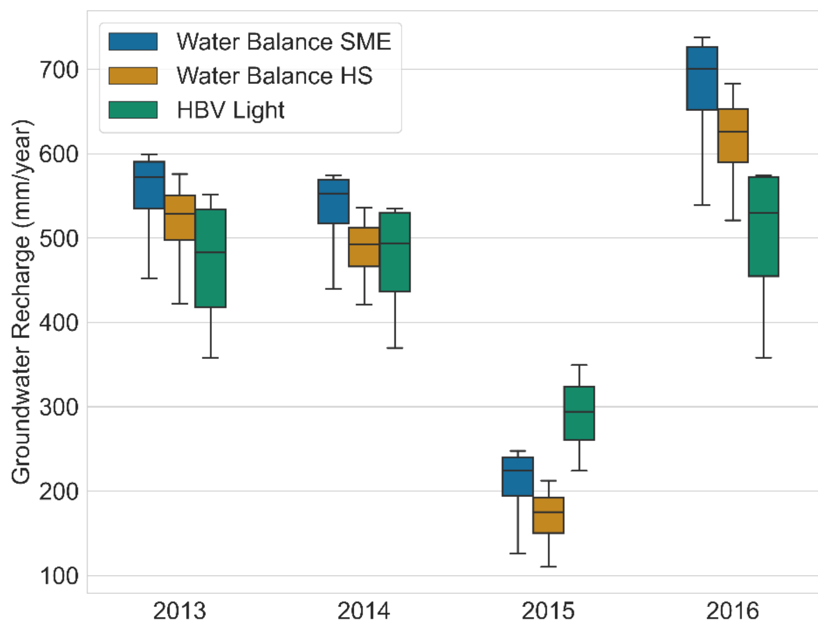


Figure 3-10. Comparison of annual recharge estimates with HBV Light model results for overlapping years 2013 - 2016.

It can be seen in Figure 3-10 that, despite a formal calibration in the HBV Light model against streamflow, with goodness-of-fit metrics > 0.6 (Table 3-6), there is a more significant spread in groundwater recharge estimates than is found with the water balance. This highlights the fact that simulations with satisfactory goodness-of-fit measures against streamflow can have lower goodness-of-fit values for other catchment criteria (McDonnell, 2003). This spread may also be tied to uncertainties in ET. Whereas AET estimates were used as inputs for the water balance calculations, PET is used as an input in the HBV Light model. The HBV Light model then calculates AET internally using soil moisture as a limiting factor. The differences between the AET and PET input datasets are on the order of 100 mm per year.

Daily Performance of HBV Light Simulations						
Goodness of Fit	**GAP**			**MC**		
R_{eff}	0.65	0.61	0.63	0.63	0.6	0.65
$LogR_{eff}$	0.73	0.69	0.67	0.68	0.79	0.70
R^2	0.65	0.61	0.64	0.64	0.60	0.65

Table 3-6. Final performance metrics of validation-period HBV Light simulations. Included are the three best GAP simulations alongside the three best MC simulations.

Groundwater Recharge Across Switzerland

In an attempt to further assess the relative performance of our GWR calculations, we compare our results with additional estimates of GWR found at a number of study sites across Switzerland. The studies listed in Table 3-7 were all carried out in catchments similar to ours, with similar aquifer types. One study is located between lake Neuchâtel and the Swiss Jura (Mdaghri-Alaoui and Eugster, 2001), another is located in the pre-Alps (von Freyberg et al., 2015a), and a final one in an urban watershed on the Swiss Plateau (Minnig et al., 2018).

Study	P [mm/y]	GWR [mm/y]	GWR [% P]	Notes
Mdaghri-Alaoui and Eugster (2001)	865	281 - 313	33 – 36%	Areuse River delta: 1990 - 1991
von Freyberg et al. (2015a)	1465	1037	71%	Rietholzbach: 2000 - 2012
Minnig et al. (2018)	947	374	40%	Dübendorf Municipality: 2009
This Study	**1095**	**415 - 480**	**38 – 44%**	**Kempttal Catchment: 2007 - 2018**

Table 3-7. Studies on groundwater recharge at three catchments in Switzerland in comparison to this study. Note: precipitation values for this study are averaged over the entire 12-year period.

The first study by Mdaghri-Alaoui and Eugster (2001) sought to determine the groundwater balance across one hydrological year in the Areuse river delta between lake Neuchâtel and the Swiss Jura. The Areuse delta is dominated by a mix of agriculture and settlement land use, with an aquifer dominated by alluvial sands and no significant portions of glacial gravels. The study area is approximately 100 m lower in elevation than the Kempttal. The authors used a soil column water budget approach, with data from two evapotranspiration estimates and calculations of hydraulic gradients. This area receives approximately 200 mm/y less precipitation than in the Kempttal, with recharge accounting for 33 – 36% of annual precipitation amounts.

A study by von Freyberg et al., (2015a) made estimates of groundwater recharge in the pre-alpine Rietholzbach catchment, in north-east Switzerland. The Rietholzbach is a small, agricultural catchment with similar subsurface geology as is found in the Kempttal catchment, and approximately 200 m higher in elevation. The authors compared five different methods of estimating groundwater recharge, including two 1D models, two soil moisture budgets, and water table fluctuations. Direct measurements of drainage from a large lysimeter was used to calibrate each method. The Rietholzbach receives an average of 400 mm more annual precipitation than in the Kempttal, and has no urban land cover. The percentage of rainfall to recharge of the aquifer was calculated to be 71%, the highest among all studies considered.

Finally, the study by Minnig et al. (2018) estimated groundwater recharge for the municipal area of Dübendorf, also in the canton of Zürich and within 20 km of the Kempttal catchment. Dübendorf has very similar subsurface geology as in the Kempttal, at slightly lower altitude, and with an urban area approximately double of that found in the Kempttal catchment. Annual precipitation in Dübendorf is reported to be only slightly less than precipitation in the Kempttal. In 2009, groundwater recharge equated to approximately 40% of precipitation. In prior periods, approximately 30% of rainfall was estimated to recharge the aquifer. Much of this increase was attributed to decreases in AET due to surface sealing. It should be noted that some of the estimated recharge in this study comes from sewer leakage and losses from water mains, in addition to precipitation.

While different approaches and assumptions were applied between our study and these three highlighted studies, our results are in close agreement with the studies in Dübendorf and in the Areuse river delta. Based on geographical proximity, climate, geology, and land cover, we expect our results to be closest to those found in Dübendorf.

3.6. Discussion

The results presented in this study have indicated that reasonable annual estimates of surface runoff and groundwater recharge for an urbanizing catchment can be obtained with an empirical and conceptual approach, where the HBV Light results served as a useful comparison of our results from the empirical water balance. Comparing our final annual groundwater recharge estimates with Swiss case studies found in literature further served as a useful tool to confirm that our results are within a credible range. However, greater uncertainties are tied to the surface runoff estimates on a storm-by-storm basis and on seasonal scales, highlighting the difficulty to capture specific processes that influence the runoff response. Such shorter time scales are less consequential for groundwater recharge, which has a comparatively slower response time than surface runoff. However, short time scales are extremely relevant for surface runoff, which can have response times as short as minutes, hours, or a few of days at most. Even if uncertainties in runoff are smoothed out over annual scales, shorter time scales are more consequential for related issues tied to combined sewer overflow, contamination, or flooding.

3.6.1. Assessment of Conventions in Estimation Methods

An important step in this study was to critically assess appropriate values of commonly used parameters in runoff estimation methods. To this end, some notable changes were made to the general applications of both runoff methods. For the well-known hydrograph separation using a recursive digital filter, we interrogated the commonly used value for the filter parameter $\alpha = 0.925$ by exploring a wider range of parameter values. The filter parameter has a direct relationship with runoff quantity – where smaller filter parameters lead to smaller runoff estimates in tandem with higher baseflow estimates. It has long been recognized that baseflow plays a large role in the storm runoff response, both in natural catchment areas and in many urbanized regions. In our opinion, variations in the filter parameter should regularly be included in uncertainty analysis when applying the RDF to a hydrograph. This parameter will also differ simply as a function of what individual studies are attempting to represent. For better granularity, multivariate hydrograph separations with stable water isotope analyses are needed.

Further, two modifications were made for our application of the SME runoff method. The first modification included the introduction of the API in place of the P_5 metric, which was introduced in an effort to avoid assumptions about catchment dryness prior to a user-defined window. The second modification, of rerouting a fixed percentage of rainfall directly into runoff, was an attempt to capture some of the runoff dynamics that are inherent in urban areas with impervious surfaces.

With the automated exponential decay factor implemented through the API, determining catchment wetness or dryness comes one step closer to being continuous and automated in the SME and other CN-based methods, while retaining an accessible approach. Inconsistencies in seasonal runoff are at least partially due to the fact that a constant value of the API decay coefficient k was used. In order to better capture seasonal variations, it is likely that k should be adjusted as a function of time, with lower values in summer and higher values in winter. In the summer months when ET is at a peak, it is reasonable to expect that the API coefficient will decrease due to quicker losses of soil moisture.

As far as the groundwater recharge methods, the definition of recharge in the HBV Light model had to be adjusted. HBV Light is commonly used as a tool in surface hydrology, where the definition of recharge – water infiltrating both the unsaturated zone and the saturated zone – in the model structure is less consequential. When applying this model as a tool to estimate recharge specifically to the *aquifer*, rather than simply applying it to the subsurface as a whole, the underlying conceptual model was adjusted in a way that the estimated fate of soil moisture in the unsaturated zone was filtered out of the recharge term. In our first iteration of the model, using the recharge estimate without filtering the soil moisture variables Q_0 and Q_1, we consistently ended up with estimates of more than 70% of rainfall becoming recharge.

3.6.2. Differences in Estimations as a Function of Data Input

In the process of interpreting surface runoff and groundwater recharge estimates from different methods, it is important to understand exactly what each approach represents. The result of any given method depends both on the model structure as well as the data that is utilized, and in this sense very few methods are explicitly equivalent. Even for simplified methods, it is always important to have a sound conceptual model of the system under study, in order to properly identify the physical processes may or may not be occurring. This information is particularly important for uncertainty assessment.

When comparing simplified pluviometric versus hydrographic methods to estimate runoff, many differences are drawn directly from the data input. Indeed, differences in even the most accurate of estimates are to be expected, as each data type only contains part of the story. Using precipitation as an input to this empirical model, there was no accounting for response time lags or the potential of additional inputs. As a result, the pluviometric calculations made here inherently assume an immediate response to rainfall, and that the amount of precipitation serves as the upper limit of potential surface runoff. While these assumptions may be approximately true in many cases, they should be kept in mind as a potential source of differences with a hydrograph. For its part, streamflow is an integrated signal of any present runoff inputs *and* their relative time lags. While this signifies that most of the information that is being sought is present in the signal, the difficulty lies in accurately identifying and separating these different signals. In addition, using a hydrograph to estimate storm runoff has an inherent assumption that all storm runoff is routed into the stream, which may not always be the case. However, the strength of comparing different approaches comes from the same source as their difficulties – there is a potential to use such discrepancies in estimates to identify system unknowns. For example, assuming accurate estimates are obtained between these two methods, their differences may be useful in further steps to identify additional inputs into the runoff response, identify runoff re-routing into infiltration basins rather than surface waters, or identify if the runoff response occurs in one pulse or in multiple phases.

3.6.3. Importance of the Runoff – Recharge Relationship

There are many important sources, processes, and interactions that impact groundwater recharge. For the current study, we were motivated by the fact that runoff carries particular importance with regards to water quality. This increased risk of quality degradation is notably relevant in human-impacted areas due to the cocktail of chemicals that are present in such environments. Pollutants carried with runoff from the surface can make their way into the groundwater in several ways: through the use of infiltration basins, through combined sewer overflow during storms, and through groundwater interactions with quality-impacted surface water, to name a few. Along these lines, acknowledgement of dynamic source areas should be included for a water quality point of view. The potential pollutants carried with storm runoff depend partly on which areas contribute to the runoff response.

In all cases, when studying the changes in the water cycle in a changing environment, it is important to keep in mind that relative changes of each input are occurring on top of the absolute changes of each. While the latter was the focus of the current study, it is nonetheless worth mentioning that increases in runoff do not necessarily signal a decrease in overall groundwater recharge. Particularly in urban areas, the observed increases in surface runoff that result from impervious surfaces are often accompanied by decreases in actual evapotranspiration due to these same impervious surfaces. In certain environments, depending on the level of urbanization, this can in fact lead to an increase in recharge rather than a decrease in these areas (Barron et al., 2013; Brandes et al., 2005; Minnig et al., 2018). While relative changes were beyond the scope of this study, the interested reader may refer to literature (Appleyard, 1995; Feng et al., 2012; Wittenberg and Sivapalan, 1999) for a more in-depth discussion on the feedback between ET, runoff, and recharge.

3.7. Summary and Conclusions

This study has compared multiple methods to estimate surface runoff and its impact on groundwater recharge in the small urbanizing Kempttal catchment on the Swiss Plateau. Simplified, straightforward methods were chosen in order to test their appropriateness in changing environments. Two approaches to estimate surface runoff – one pluviometric and one hydrographic – were applied, with modifications that attempt to better capture soil moisture accounting and to explicitly account for runoff from impervious surfaces. The results were used in a water balance to calculate groundwater recharge for the shallow, unconfined aquifer within the catchment. To evaluate the accuracy of these water balance estimates, we then compared them to additional estimates of groundwater recharge using the conceptual HBV Light model. Our recharge estimates were assessed against several literature studies from similar catchments in Switzerland. From these results, we were able to approximate a range of groundwater recharge estimates on a spatial scale, and gain insight on the sources of uncertainty in both runoff and groundwater recharge estimates.

4. Chemical Indicators and Conformal Mapping of Flow Fields for Groundwater Source Identification in an Urban Watershed

4.1. Abstract

Sources and flow pathways of groundwater were assessed in an urban watershed with a combined method approach using groundwater levels, hydrochemical data, and stable water isotopes. From a network of monitoring wells, groundwater levels were interpolated across the field site using a conformal mapping technique to construct groundwater flow nets. With supplementary information available on the sewer network and riverbed elevations, a map of relative levels was constructed in order to identify areas where rivers and sewers were submerged, or which areas sit above the water table. A multivariate hierarchical cluster analysis (HCA) was then applied to inorganic geochemistry data and validated against stable water isotopes, in order to deduce water signatures and locations of groundwater – surface water interactions. Organic micropollutants were used as source-specific indicators of anthropogenic impacts on the groundwater. These analyses were taken together in order to determine where interactions may be occurring and to characterize the impacts of urban activity on the groundwater. These methods were applied as a case study for a small urban watershed on the Swiss Plateau near the city of Zürich, Switzerland, where the local aquifer underlying the city is actively exploited for drinking water production. Each step of this analysis offers independent yet complementary information about local water dynamics at our field site. Similarities and differences between the results from each data type are discussed.

4.2. Introduction

Research into the water cycle of urban environments has become a major topic in hydrogeological studies over the past several decades. Changes in groundwater storage, recharge, flow pathways, sources and source zones, and other processes are inevitable consequences of the urbanization process. It is therefore of no surprise that urbanization can have major impacts on both groundwater quantity and quality. As urban aquifers all around the world remain a primary source of fresh water supply, it is critical to understand and to monitor water bodies in these areas in order to ensure their sustainable use and environmental protection. In the hydrogeological community, innumerable methods have been developed to measure the feedback between urban development and groundwater dynamics using a wide variety of physical, chemical, biological, engineering, and modeling techniques (Barnes et al., 2018; Foster and Chilton, 2004; Kalbus et al., 2006; Lerner, 1990; Minnig et al., 2018; Morris et al., 2007; Palau et al., 2016; Schirmer et al., 2013; Voisin et al., 2018; Wolf et al., 2006). Despite progress in the field, it has proven difficult to construct a generalized conceptual model of groundwater responses to the attributes of urban activity. The climate, type of aquifer, topography, natural vegetation are just a few of the many factors that determine the complex groundwater dynamics of the natural environment. On top of these natural complexities, the heterogeneous layout of urban areas, the history and progression of land development, the technologies and maintenance of urban infrastructure, and the specific activities associated with a given city will all leave an impact on the local water cycle, creating an exceptionally intricate system (Barnes et al., 2018; Howard, 2002; Marsalek et al., 2007). In these aspects, no two cities are the same.

There are continuous efforts to improve our understanding of hydrogeology in the human environment using both well-established and novel approaches. The use of natural physical and chemical indicators and tracers are a prominent example of an established tool for characterizing groundwater flow. Many different types of natural indicators are used to answer questions about the source and location of groundwater recharge, the residence time of groundwater, or characteristics of groundwater – surface water interactions (Cook and Herczeg, 2000). Inorganic chemistry and isotopes in particular have a long track record of use for a variety of objectives. For example, they are often used as inputs to multivariate statistical analysis to identify water types, sources of recharge, or water mixing (Thyne et al., 2004); measured at high frequency for multi-component hydrograph separation (Klaus and McDonnell, 2013); or used as tracers of wastewater contamination in water bodies (Kracht et al., 2007). More recently, a wider range of synthetic organic chemicals originating from specific human environments have been exploited as source and process indicators in groundwater and surface water (Postigo and Barceló, 2015; Schirmer et al., 2013; Warner et al., 2019). These include pharmaceuticals, lifestyle products, and a larger number pesticides, among others, and are collectively referred to as micropollutants. A handful of studies exploring the use of urban micropollutants in particular were carried out in the late 20th century (e.g. Eckhardt and Stackelberg, 1995; Hatcher and McGillivary, 1979), and their use has gained serious traction in the 21st century due to greater analytical power and process understanding (Barlow et al., 2012; Hollender et al., 2018; Kolpin et al., 2002; Andreas Musolff et al., 2010; Schirmer et al., 2011; Shan et al., 2020).

Most of these tracer types have shortcomings because of chemical instability, high background levels, or non-unique signals. In the case of micropollutants, their varied environmental degradation and complex application patterns certainly violate the condition of an ideal conservative tracer. However, their strength lies in the fact that they have little to no background levels in nature, and therefore offer unequivocal evidence of human influence. Both ions and isotopes are present in the natural environment, and are thus less source-specific than micropollutants, with higher background levels. However, both are more conservative in nature than are micropollutants. The shortcomings of individual tracer types can at least be partially circumvented with combined analysis of different tracer types, and by integrating information on the physics of groundwater flow for a stronger interpretation. These combined approaches allow researchers to better exploit the information to be gained from each method to tell a coherent story (Grimmeisen et al., 2017; Moeck et al., 2017c).

In order to improve catchment characterization, hydrogeological models are another appealing technique that can be used in tandem with chemical or isotopic tracers. Where tracer information reveals largely point-wise properties of water, modeling can weave this disjointed information into a single cohesive image. Many types of groundwater models exist, with fully distributed numerical models regarded as the most robust for representing complex systems. The drawback of complex numerical models is their demand for detailed, site-specific geological information and their relatively high computational cost, which makes it difficult to obtain exhaustive uncertainty estimates for their predictions (Ramgraber et al., 2020). Particularly in data-scarce environments, the available atmospheric and geological information may therefore not be sufficient to satisfy the requirements of these complex numerical models. In these cases, simplified analytical or quasi-analytical methods, for example interpolation, can be an attractive alternative to obtain probabilistic groundwater flow fields (Fong, 2015; Laga et al., 2019). These analytical methods therefore offer an extremely attractive option to apply in combined-method studies.

With this information in mind, this study makes use of chemical and isotopic tracers in tandem with a probabilistic, analytical flow model, with the objective of investigating groundwater dynamics in an urbanizing environment. In particular, we explore groundwater flow pathways, potential presence and impact of combined sewer overflow and leaky sewers, increases in surface runoff, storm infiltration dynamics, and groundwater – surface water interactions. Analytical flow fields were constructed with groundwater levels as data input, as well as information on sewer network and riverbed elevations. Data on stable water isotopes, inorganic chemistry, and organic micropollutants were collected in environmental water samples and applied as indicators of water body interactions, wastewater, and surface infiltration. Our investigations were carried out as a case study in a small urban watershed in proximity to the city of Zürich, located on the Swiss Plateau. This catchment is host to an actively-exploited aquifer, and to the local municipality of Fehraltorf, a town that has been actively undergoing transformation from agricultural fields into a more urbanized region over the past 20 years.

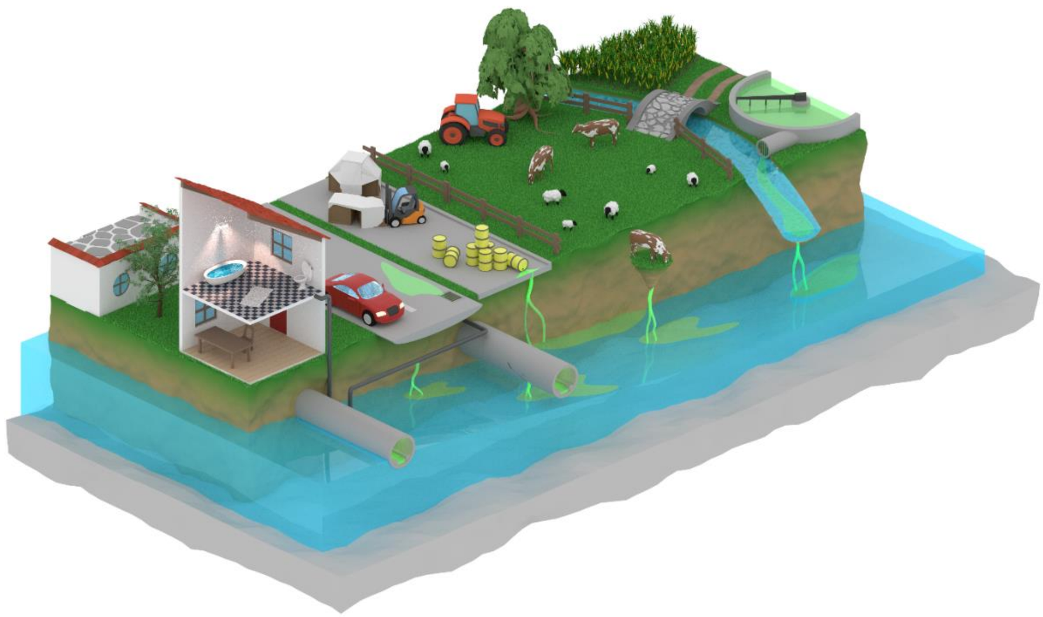


Figure 4-1. The heterogeneities of the urban environment can change groundwater flow and create new flow pathways. Households, sewer networks and water mains, outdoor sources, and wastewater are but a few of the relevant factors leading to such changes. Many of these changes pose potential threats of contamination.

To begin, probabilistic groundwater flow fields were generated using a conformal mapping technique and a network of monitoring wells. These flow fields were used estimate the pathways of groundwater towards a given well, as well as associated risks of interactions with urban infrastructure. Then, we applied a multivariate cluster analysis on ionic data in an effort to identify the dominating controls on water chemistry, and potential points of groundwater – surface water interactions. The ionic cluster analysis was assessed against stable isotope data in order to independently validate the findings. Finally, a nonparametric analysis of organic micropollutants was used to characterize the spatial and temporal distribution of human influence.

4.3. Site Description

The urban watershed in the town of Fehraltorf, Switzerland is located approximately 30 km east of the city of Zürich, Switzerland. This watershed is located within the Kempttal catchment that was used as a case study in chapter 3, and details about the entire catchment can be referenced in section 3.3.

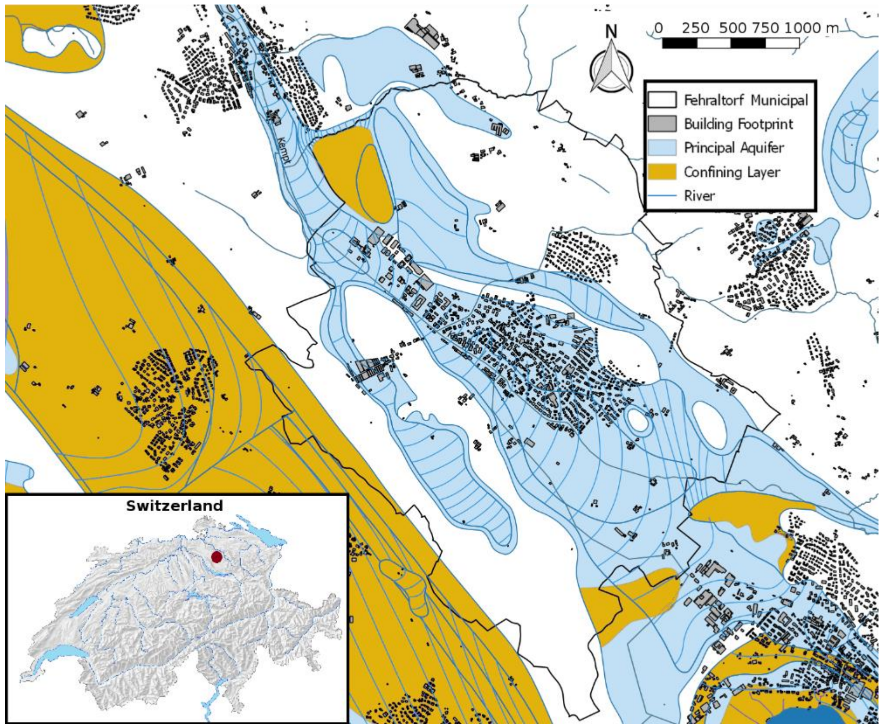


Figure 4-2. Fehraltorf municipality and aquifer. Data courtesy of Swiss Federal Office of Meteorology and Climatology; Canton Zürich Office for Waste, Water, Energy, and Air (AWEL).

The Fehraltorf municipality directly overlies the main aquifer of the catchment (Figure 4-2). This shallow, unconfined aquifer spans an area of approximately 10 km^2, with variable thickness. The deepest zones of the aquifer body are in the central valley and have been reported at 10 – 30 meters, with thinner portions between 1 – 8 meters on the valley edges (Krejci et al., 1994). As determined with internal data from soil cores, electrical resistivity tomography, and a network of groundwater monitoring wells, the aquifer is covered by an average of 1 - 3 meters of unsaturated zone above the groundwater table. Natural groundwater recharge occurs mainly through precipitation, and the residence time of groundwater is assumed to be relatively short, on the order of months to two years (Krejci et al., 1994; personal communication, M. Berg, 2019). The local aquifer is exploited as a principal source of drinking water and agriculture water resources in the area. Sewer network, storm drains, and canalization of streams (Figure 3-2, Chapter 3) are expected to have a direct impact on groundwater and surface water flow. Much of the urban area is served with separated storm water overflow, though some areas are still served with combined sewer and stormwater systems, which are known to overflow during heavy storms (personal communication, F. Blumensaat, 2017). At the outflow of Fehraltorf, a wastewater treatment plant (WWTP) emits treated effluent directly into the Kempt river.

4.4. Materials and Methods

4.4.1. Sampling, Storage, and Measurement

Groundwater and surface water samples were collected principally within the municipal limits of Fehraltorf. An overview of sampling points included in this study is given in Figure 4-3. During our project, a total of 20 wells were installed over the course of two drilling campaigns (August 2017 and April 2018). Wells were installed via direct push to depths ranging from 5 to 9 meters. The boreholes were secured with PVC lining and all were screened at the bottom two meters of their total length. Several wells have since been uninstalled due to very low hydraulic conductivity. A number of public wells were also sampled at least once during the study period. For these reasons, the number of samples collected from each well is varied.

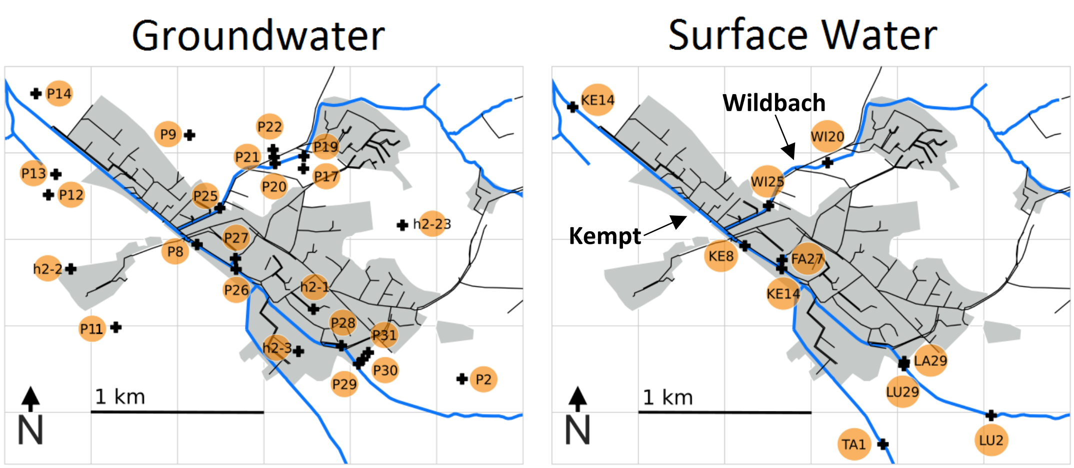


Figure 4-3. Location of a.) groundwater and b.) surface water sampling points. The main surface water bodies are the Kempt river running SE-NW and the Wildbach tributary running NE-SW. Not pictured are samples from catchment headwaters and Lake Pfäffikon to the SE, and sampling points downstream of the study area to the NW.

Grab samples were collected on a seasonal basis over the course of 10 campaigns between April 2017 and March 2019. Most groundwater samples were collected using a submersible pump with the widely accepted protocol of high pump rate and purging the well of three times its volume before collection. A smaller number of samples were collected via low-flow sampling (Puls and Barcelona, 1996). Surface water samples were taken from the principal Kempt river and the Wildbach tributary (Figure 4-3) as well as from a number of artificial ditches in the area. A field probe was used to measure EC, T, and pH in both groundwater and surface water at the time of sampling. Additionally, one-time samples were collected from lake Pfäffikon to the south-east, the catchment headwaters, and one public well downstream of the WWTP for reconnaissance of

boundary conditions and potential sources. In the end, a total of 105 groundwater samples, 48 surface water samples, and 1 sample from lake Pfäffikon were collected.
Samples were stored and measured with a similar method as outlined in other studies (Hollender et al., 2018; Moeck et al., 2017b). Briefly, for micropollutant samples, care was taken to reduce the risk of contamination in the field by using glass bottles and gloves during collection. Micropollutant samples were then stored frozen at -20 °C for a period of weeks to months before measurement via liquid chromatography tandem mass spectrometry. Inorganic ions were collected in plastic bottles and sent for measurement within 24 hours of collection via inductively coupled plasma mass spectrometry. Stable isotope samples were collected in small, tinted glass bottles with care taken to avoid headspace or small bubbles, and stored at 4 °C for a period of days to months before being sent off for measurement via laser spectroscopy. Error ranges were supplied by the laboratories for ions and isotopes. For micropollutants, quality control samples were included in analysis: laboratory blanks, field blanks, triplicate samples, and field spiked samples were taken on several occasions in order to assess measurement precision and error.

All tracer types were analyzed at least once in groundwater, surface water, and lake Pfäffikon. Headwater streams were only sampled for micropollutants and isotopes. To present these data in a concise manner, sampling campaigns are grouped by season to represent temporal dynamics. This was deemed justified, as sampling was low-frequency, increasing uncertainty. Further, patterns during the course of this study proved to follow similar trends from year to year. Seasons were separated as such: Spring from March – June, Summer from July – August, Fall from September – November, and Winter from December – February. It should be noted that only one summer campaign was carried out in 2018, which was among the driest summers since the year 2000.

4.4.2. Flow Net Generation Through Probabilistic Conformal Mapping

In order to interpolate groundwater levels and approximate the direction of flow, we applied conformal mapping to groundwater level data, an elegant method for the transformation of flow nets. The results from this analytical model were used to estimate the contributing area of individual monitoring wells, and to estimate the relative levels of groundwater to the elevation of surface water, sewers, or other infrastructure. This information is used, for example, to evaluate the characteristics of groundwater – surface water interactions, the risk of sewer leakages, and the probable source areas of groundwater recharge and flow. We implemented our calculations by developing a code in the Python programming language.

If we make the assumption that groundwater flow is primarily driven by the boundaries of the aquifer and that the medium is homogeneous and isotropic, then the resulting flow field is harmonic (i.e., it satisfies the Laplace equation for fluid dynamics). Because groundwater isopotential lines and the direction of flow are always perpendicular to one another, they can be jointly expressed as a complex number (equation S.I.9). Conformal mapping is an angle-preserving transformation that maintains this harmonic property as well as the perpendicular relationship between isopotential lines and flow direction. This means that complex flow nets can be produced by a transformation of simple flow nets to represent a given system.

We use two types of transformations in order to generate a flow net. First, we use a Schwarz-Christoffel mapping of a unit square into a unit disk (equations S.I.10, S.I.11; Fong, 2015). In a second step, we use a Möbius transformation to deform the flow net within the unit disk (equation S.I.12, Laga et al., 2019). An example of the process and its resulting flow net is shown in Figure 4-4.

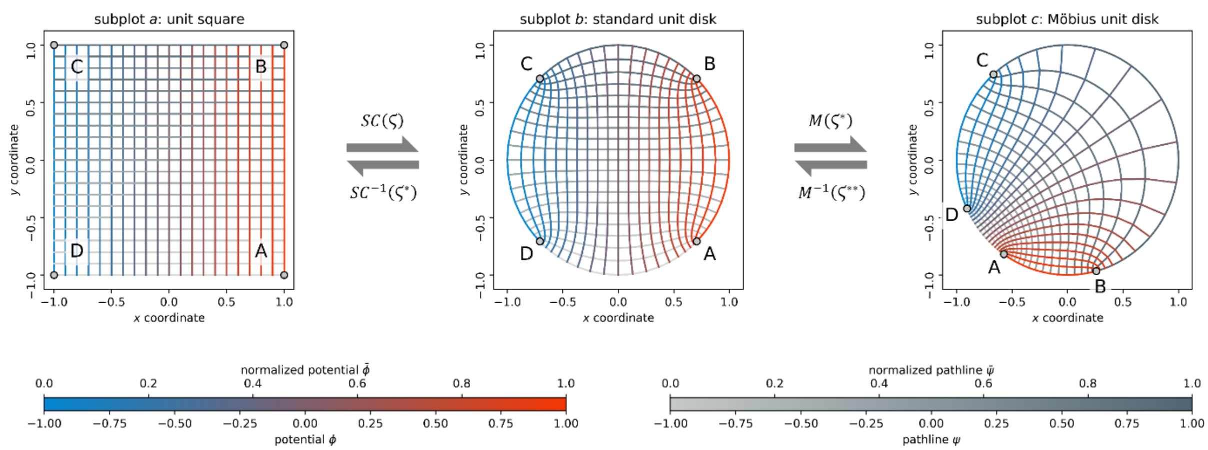


Figure 4-4. (a.) A simple, uniform (confined) potential flow net from right to left is defined in the unit square. (b.) A Schwarz-Christoffel transformation is used to map the square to the unit disk. (c.) Further applying a Möbius transformation by specifying three points and their images (A, B, and C) yields a distorted potential flow in the unit disk.

Bayesian Inference of Flow Nets

To obtain probabilistic estimates of the flow field, we use Markov Chain Monte Carlo (MCMC; e.g. Geyer, 1992). A few adjustments have been made in order to obtain flow paths over our area of interest: First, since the superposition of two harmonic functions yields another harmonic function, we use the superposition of two independent Möbius-transformed unit disks to create more complex flow nets. Second, since the aquifer over the domain of interest is dominated by two different geology types that create two different flow systems (Figure 4-2, section 4.3), we run two separate, independent MCMC chains for the north-eastern and south-western parts of the aquifer.

The parameters for the two layers of each chain are as follows: minimum potential ϕ_{min} in m a.s.l., maximum potential ϕ_{max} in m a.s.l., and the rotation of the control points A, B, and C to define the Möbius-transformed images on the unit disk (Figure 4-4c); the image of D is defined by the other points). Since our aquifer is unconfined, we also have an offset parameter ϕ_{offset} which controls the nonlinearity of the water table. The flow fields for each disk is thus defined:

$$\phi(x) = \sqrt{\left(\phi_{min} + \phi_{offset}\right)^2 + x\frac{\left(\phi_{max}+\phi_{offset}\right)^2-\left(\phi_{min}+\phi_{offset}\right)^2}{L}} \tag{4-1}$$

where $L = x_{max} - x_{min}$, the distance between the lower and the upper boundaries. Our inference method, MCMC, randomly proposes new flow fields, then accepts or rejects them with a probability based on the ratio of un-normalized posterior densities between a proposed and original sample (equation S.I.13.; Kruschke, 2015). For the proposal of new flow fields, we use an adaptive Gaussian proposal distribution with a diagonal covariance matrix. Its standard deviation is set to 10% of the averaged standard deviation of unique samples of the same type (e.g. rotation) in the current chain. We let each chain run for 10,000 steps. For the posterior, in this study, we assume uncorrelated Gaussian errors with a standard deviation of 0.25 m for the likelihood, with the measurements obtained from smoothed hydraulic head time series. The prior is defined in Supporting Information table S.I.1.

4.4.3. Multivariate Analysis of Inorganic Chemistry and Validation with Stable Water Isotopes

The multivariate statistical method of Hierarchical Cluster Analysis (HCA) was applied to our inorganic chemistry dataset in order to identify different water types by their ionic footprint. Multivariate statistics in general, and HCA in particular, offer useful tools for efficiently exploring a multivariate space. HCA is used in a number of fields including hydrochemistry and environmental studies, with varied objectives (Cloutier et al., 2008; Fitzpatrick et al., 2007; Moeck et al., 2016; Thyne et al., 2004; Yidana et al., 2018).

In this study, agglomerative HCA was used: each sample begins as its own individual cluster, and is then combined with the closest cluster in the multivariate space. This is carried out iteratively as clusters grow in size, eventually leading to a single cluster containing all clusters. These consecutive steps of clustering are often visualized as levels in a dendrogram, whereby sample linkage distances are portrayed in a graphical manner. This dendrogram can be cut at a certain level to obtain the desired number of clusters that sufficiently describe the differences of a system. The appropriate number of final clusters to explain a given system is somewhat subjective. We determined the number of clusters by reducing the within-cluster sum of squares between sample points, which generally stabilizes after a certain number of clusters. In addition, a minimum threshold value for the linkage distance, visualized as a phenon line, was set to 10 units.

For our application, each variable of the dataset (ion concentrations) was standardized to have a mean of zero and measured in units of standard deviation, ensuring that all variables are equally weighted for analysis. Samples were clustered into groups as a function of their Euclidean distances between pairs of individual data points within the multivariate space. Then, the distance between clusters was determined with the linkage criteria known as Ward's minimum variance method in order to progressively combine clusters. In essence, Ward's method applies the criteria that the variance within the merged clusters should remain as low as possible (Ward, 1963).

Six variables were used to carry out our HCA: Na^+, Mg^{2+}, Ca^{2+}, K^+, Cl^-, and NO_3^-. At each individual sampling location, the mean concentration over all sampling campaigns was used - this is justified due to the very low temporal variability of ion concentrations compared to their relatively higher spatial variability. Usually, a range of number of clusters might be equally valid in order to describe the variation of a system. For this reason, we explored using between 3, 4, or 5 clusters in order to best estimate how many clusters are sufficient to describe the water types in our environmental samples before settling on a fixed number of clusters. The resulting groups of our analysis were assessed against isotopic data for validation using an independent dataset. We applied HCA using the R programming language.

4.4.4. Micropollutants as Source Indicators

A total of 29 organic micropollutants were selected for targeted screening (table S.I.2.) in environmental samples. Different product types were chosen in an effort to identify different potential sources between groundwater and surface water, including agricultural runoff, combined sewer overflow (CSO), sewer leakage, or treated wastewater effluent. These included pharmaceuticals, lifestyle products, pesticides , multi-purpose (miscellaneous) compounds, and a number of persistent transformation products. These products can further be globally classified as so-called indoor products (those carried with municipal wastewater) and outdoor products (those applied directly to the land surface). However, some products have multiple sources: for example, Benzotriazole is widely applied for both industrial uses (antifreeze and de-icing agents) as well as for household use (anti-corrosives and dishwashing detergents), such that their source is not clear-cut and they do not lend well to outdoor vs indoor classification (Alotaibi et al., 2015). Details on all 29 compounds, including detection frequencies, are given in the supplementary information table S.I.2.

Four total measurement series were carried out over the study period. Lower and upper limits of quantification (LOQ) for individual compounds were determined separately for each measurement series by constructing a calibration curve from laboratory standards, and accounting for the variance in the standards. The LOQ can additionally be calculated by considering the average concentrations calculated in blank samples, or considering signal-to-noise (S/N) ratios (equation S.I.14. and S.I.15). We chose the highest LOQ determined between these three approaches as the most conservative estimate. A number of compounds were discarded due to poor analytical performance, significant presence in field blanks, or to high carryover rate between environmental samples and laboratory blanks. The remaining products were evaluated as a function of their detection frequency and concentration magnitudes in environmental samples.

Micropollutants used as indicators	
Pharmaceuticals & Lifestyle	**Acronym**
4-Acetamidoantipyrine*	4ACE
Atenolol	ATE
Atenolol acid*	ATEA
Caffeine	CAF
Hydrochlorothiazide	HCL
Lamotrigine	LAM
Sulfamethoxazole	SULF
Valsartan	VAL
Pesticides & Herbicides	**-**
Atrazine	ATR
Chloridazon-Methyl-Desphenyl*	CMD
Terbutylazine	TERZ
Miscellaneous	**-**
Benzotriazole	BTZ
5-Methyl-Benzotriazole	5MB

*Table 4-1. Subset of 13 measured compounds used for analysis. Compounds were measured in groundwater, surface water, and one lake water sample. * indicates a transformation product.*

From the targeted screening, a subset of 13 compounds were short-listed as suitable indicators at our site (Table 4-1). These comprised two groups of products: ubiquitous compounds, found dispersed across the study site, and non-ubiquitous products that were locally relevant and suggestive of discrete sources. Spatially ubiquitous compounds were defined as those detected in more than 50% of samples, with at least 20% of detects above the respective LOQ. The choice of a threshold to define ubiquitous compounds is somewhat fluid; in our case these thresholds marked the point at which different landscape compartments – hillslopes, riversides, sediment types, urban areas, agricultural areas – were represented. Finally, a number of non-ubiquitous compounds were defined as detected discretely through time, or at a limited number of sampling points. These detections and their locations are indicative of localized sources (Van Stempvoort et al., 2013).

Treatment of Censored Data

Censored data is defined as data that falls outside of the lower or upper LOQs, such that their exact values are unknown. In environmental sciences it is most common to have left-censored data, i.e. sample concentrations falling below the lower LOQ. Proper handling of censored datasets is particularly relevant for trace contaminants such as micropollutants, where concentrations are often on the order of ng/L – µg/L. A number of studies use substitution to handle these censored datasets (reporting a value of 0, 1/2 the LOQ, or as the LOQ itself), with the argument that such low concentrations are non-consequential. However, substitution or exclusion can lead to significant bias in final results and potentially incorrect interpretation when considering combinations or sets of compounds (Helsel, 2010, 2012). Several parametric, semi-parametric, and non-parametric methods exist to properly handle censored datasets, so that there is no need to discard or substitute values.

In the current study, micropollutant datasets were censored between 5 - 90% depending on the compound, and did not seem to closely follow any of the most-used theoretical distributions (LOQ values available in the supplementary information table S.I.3.). For this reason, the non-parametric Kaplan-Meier estimator was applied to calculate statistical distributions of the data (Kaplan and Meier, 1958). The application of the Kaplan-Meier estimator to environmental datasets has gradually been gaining in popularity (Blackwood, 1991; Gross et al., 2013; McGlynn and McDonnell, 2003; McGrory et al., 2017; Noack et al., 2014; Szarka et al., 2018). This method is not used to estimate the concentrations in individual samples, but rather to characterize the distribution of concentrations through space and time. Estimations are commonly presented as an empirical distribution function (EDF) that utilizes both censored and non-censored data to determine the cumulative probability of the set. We made use of these estimated summary statistics and empirical distributions to characterize individual compounds, and to compare differences between categories of micropollutant data. Because results are presented as an EDF, they can also be compared to the EDF of non-censored datasets in a straightforward manner. Further detail on the Kaplan-Meier estimator is available in the supplementary information.

In our study, the estimator was only applied to analyze ubiquitous compounds where more than 10 detections were available and censoring was below 30%. Due to low detection frequency and high censoring, non-ubiquitous compounds are reported simply via detection frequency, maximum concentration, and the location of detection. The concentration distributions between groups – namely, water types and seasons – are compared using the non-parametric Kaplan-Meier procedure. Then, the spatio-temporal detection profile of the different products is presented.

Kaplan-Meier calculations were implemented using the Lifelines package in the Python programming language (Davidson-Pilon et al., 2020). A standard error formula – the exponential Greenwood formula – was additionally used to calculate the 95% confidence interval of these distribution estimates (Hosmer et al., 2008; Sawyer, 2003).

4.5. Results

4.5.1. Source Areas and Pathways with Flow Nets

The probabilistic flow fields were first used to map the height of the groundwater table relative to the height of the river bed and the sewer system across for average annual conditions, determining if either system is submerged or not (Figure 4-5). The wells included in the figure (blue dots) are those that were used to interpolate the flow fields. It can be seen that the sewers running along the most urbanized reach of the Kempt have a high probability of being submerged, therefore groundwater infiltration may be occurring in faulty areas. The same can be seen for the sewer network for the downstream reach of the Wildbach tributary. With the exception of parts of the NE neighborhood sewer network, the rest of the system lies above the groundwater table, therefore sewer leakage may be occurring in those areas. Similar to this concept, the relative level of groundwater and surface water allows us to identify areas where surface water may be losing to groundwater, and vice versa. These relations allow us to constrain probable areas and directions of groundwater – surface water interactions.

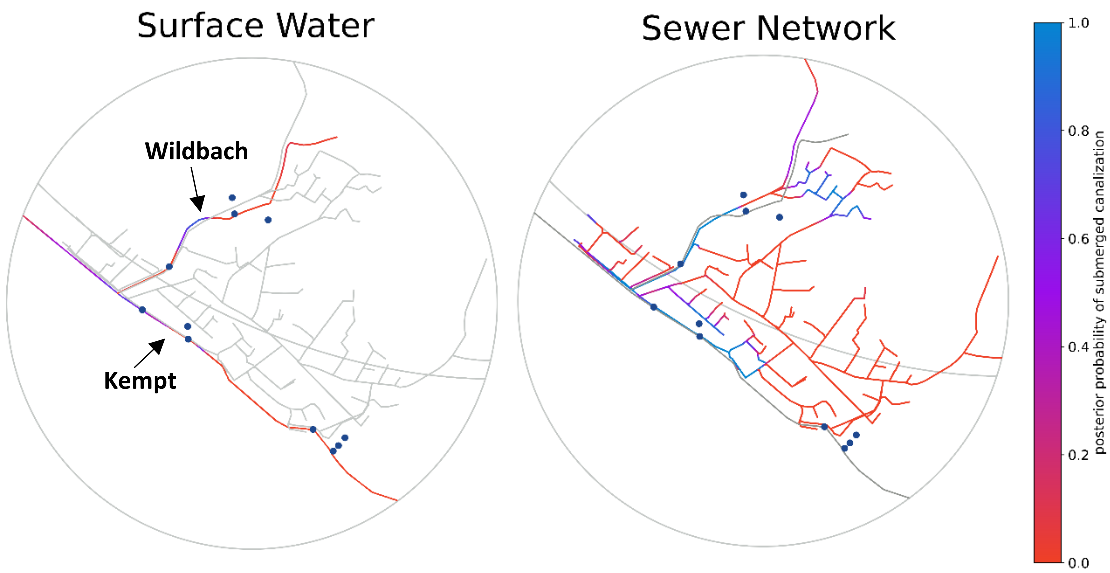


Figure 4-5. Probabilistic map of a.) the surface water and b.) the sewer network being above or below the groundwater table. Red areas are above the groundwater, and blue areas are submerged. Purple areas are at an interface and thus uncertain. Blue points are the wells used to calibrate the probabilistic maps.

Relative water level evidence suggests that, if the groundwater and surface water are connected, the Kempt river is losing to the groundwater in proximity to wells P26, P28, and P29 along the upper river reaches. The same can be said of all wells along the Wildbach. Well P8, however, is located in an area of transition in this regard. As far as the sewer network, it appears to be submerged in proximity to wells P8 and P26, but is above the groundwater in proximity to P28. The situation along the Wildbach is more variable. Groundwater at upstream wells P19 and P20 lie below the riverbed and canalization, whereas groundwater at well P25 is below the river level, yet likely above the sewer level.

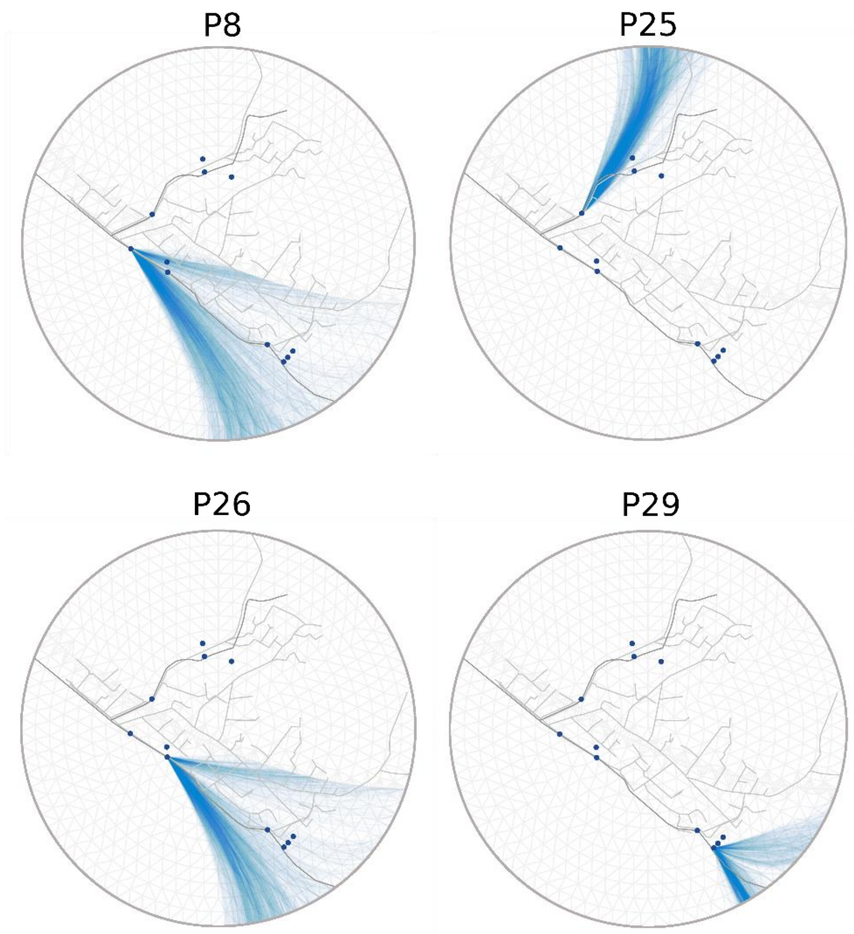


Figure 4-6. Estimated flow field contributing areas for individual wells. From top left: P8, P25, P26, and P29. Blue points are the wells used to calibrate maps.

Figure 4-6 displays the estimated flow pathways towards four representative wells of the field site, again based on average annual conditions (refer to supplementary information for seasonal variations in flow pathways at these wells). Wells in proximity to the riverside and sewer canalization are represented to assess any possible interactions at these locations. These flow pathways show the estimated expanse of groundwater contributing areas at each well, and also give an indication of potential interactions with surface waters or with sewers. In essence, the portions of surface water or sewer network that are crossed by these flow lines are those that could be contributing to a given groundwater well. With the exception of P29, the flow paths of all of these wells traverse the riverbed and sewer system both. P29 is located upstream of all canalization.

4.5.2. Water Signatures with Hierarchical Cluster Analysis

By assessing several dendrograms resulting from our HCA (figures S.I.9) we identified three sample clusters that were sufficiently distinct from one another to describe our field site. The geographical mapping of these groups in Figure 4-7 reveals that the three HCA clusters correspond well with effluent-impacted surface water (group 1), stream water (group 2), and groundwater (group 3). It should be noted that two samples collected further downstream of the WWTP (to the NW) are not pictured here for brevity, though they also clustered into group 1.

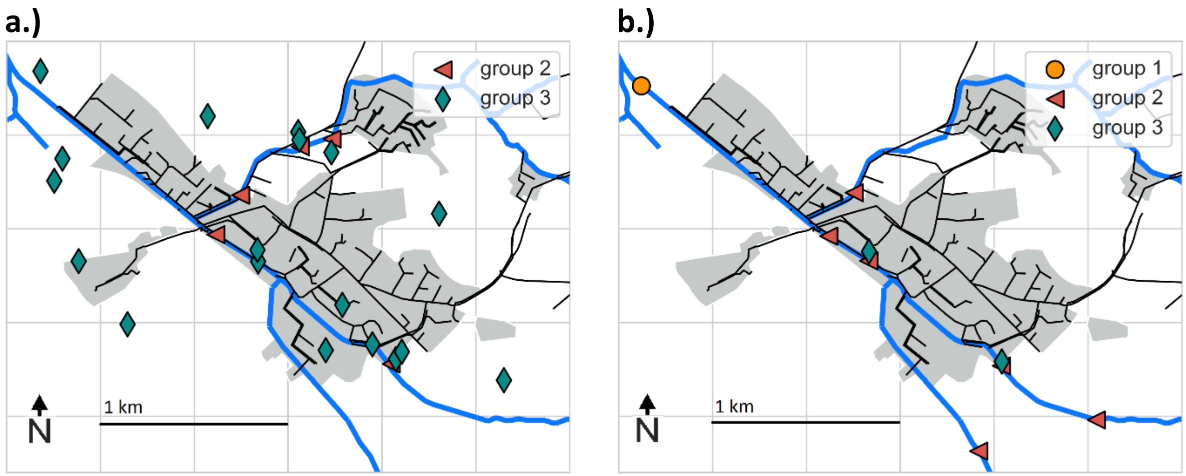


Figure 4-7. Spatial distribution of groups determined from HCA for a.) groundwater and b.) surface water. Sampling locations may be referenced in Figure 4-3.

We can see from this spatial distribution that several points of groundwater – surface water interactions are tentatively identified via their chemical signatures. In particular, we see that all riverside piezometers – P19, P20, and P25 – along the Wildbach tributary are clustered within group 2 corresponding to stream water. Two additional wells near the Kempt riverside – P8 and P29 – show similar evidence of stream infiltration. In comparison to the results presented from flow pathways, it is only P26 that does not show chemical evidence of surface water infiltration. Finally, two surface water points are clustered into the groundwater group 3. These are LA29 and FA27, which are both artificial drainage ditches that are approximately perpendicular to the direction of groundwater flow.

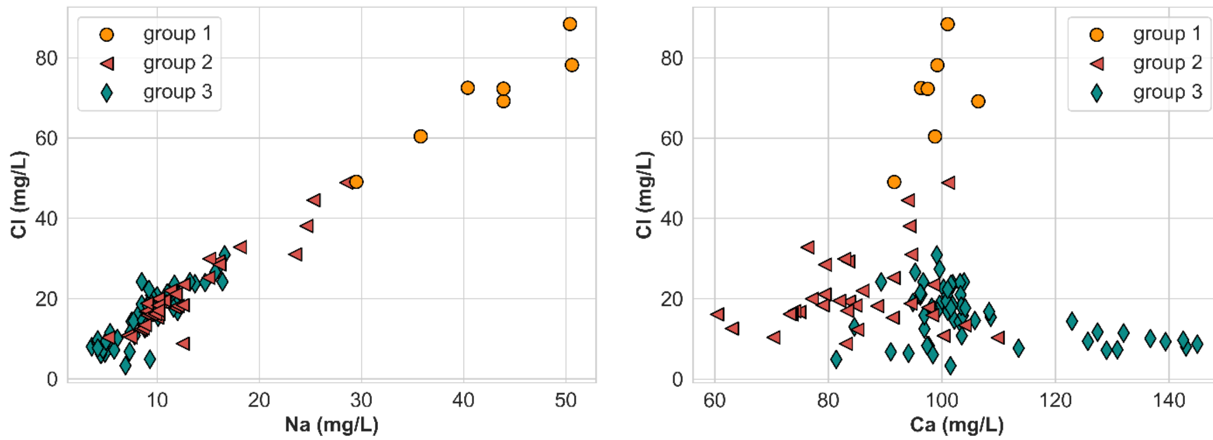


Figure 4-8. HCA groups represented on bivariate plots of major ion pairs Na-Cl and Ca-Cl.

Figure 4-8 shows the HCA groups as a function of specific ionic pairs measured in each sample - NaCl and CaCl. Note that these graphs plot samples from every individual sampling campaign, rather than the time-averaged measurements that were used to determine the groups. Group 1 is clearly dominated by an enrichment of the NaCl pair, which is coherent with the fact that effluent-impacted water bodies have increased levels of Cl^- (Gasser et al., 2010). On the other hand, Ca^{2+} in some studies is used as a hardness term tied to major aquifer minerals (Moeck et al., 2016; Thyne et al., 2004). Group 3 - largely pertaining to groundwater – indeed has the highest concentrations of Ca^{2+}, indicating prolonged contact with subsurface geology. Carbonate rich sediments observed at the catchment headwaters and in several wells during the drilling process support this assumption.

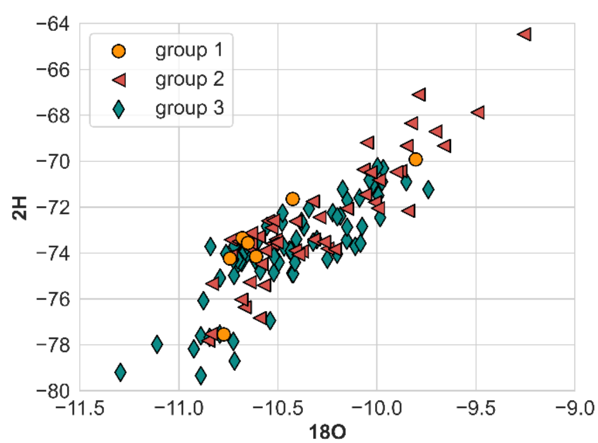


Figure 4-9. HCA groups plotted as a function of stable isotope pairs. Extensive mixing is evidenced, although group 2 and group 3 end members are identified.

Figure 4-9 plots the HCA groups as a function of the stable water isotopes ^{18}O and ^{2}H measured in each sample. Because the residence time of the groundwater is relatively low, communication between groundwater and surface water occurs rapidly such that isotopic signatures are similar between the two water types. A groundwater end member can nonetheless be differentiated from the surface water end member with these groups. The lowest isotopic values in Figure 4-9 correspond to inland groundwater wells on the valley edges, notably P9 and P22. The higher isotopic signatures correspond to stream samples LU2, LU29, and WI25. Effluent-impacted water samples, on the contrary, do not have a distinct isotopic signature, since water resources are largely extracted from the local aquifer. As far as the groundwater wells clustered into group 2 as identified via Figure 4-7, all are located in the central, well-mixed zone of the isotopic plot. Further, isotopic signatures at each sampling point are quite variable in time.

4.5.3. Source Indications with Micropollutants

Of the 13 micropollutants selected for analysis (Table 4-1, section 4.4.4), three proved to be spatio-temporally ubiquitous at our study site, with high detection frequency and high quantitation rates (<30% censoring) in both groundwater and surface water. All of these compounds proved analytically stable with very minor to no detection in field or laboratory blanks. These are Atrazine (ATR), Benzotriazole (BTZ), and Caffeine (CAF). The remaining 10 products proved non-ubiquitous, yet locally relevant in space or in time. All non-ubiquitous compounds were detected in abundance at sampling points downstream of the WWTP. Non-ubiquitous pharmaceuticals were detected at least once in monitoring wells and surface water along the Wildbach tributary (WI20, WI25, P19, P20, P25), at least once in monitoring wells near the center of the urban zone along the Kempt river (P8, P26, P27, P29) along with their corresponding surface water sampling points, and once at well P31. Non-ubiquitous pharmaceuticals were detected very sparsely at inland groundwater wells, with a few exceptions of censored detections.

Detection rates and summary statistics of the three ubiquitous compounds are given in Table 4-2 and Table 4-3, grouped respectively by water type and then by season. For all compounds the median value is available directly from the data, whereas lower percentiles and mean are estimated with the Kaplan-Meier estimator. With few exceptions, the data tend to be positively skewed – thus the median concentration gives a more realistic summary of the central tendency of the data. Detection frequencies and median concentrations between groundwater and surface water are generally of similar magnitude, however, censoring rates are overall more significant in groundwater. Note that the maximum detected concentration exceeds the upper LOQ for several compounds, so that the calculated mean in these cases is uncertain. However, these high maximum values are of great interest as they are strong indicators of proximity to sources. Further, two groups – namely BTZ and CAF during the Fall – have no censored values.

By Water Type							
Water Type	**Compound**	**Nr. Samples**	**Nr. Detects**	**Nr. Censored**	**Mean (ng/L)**	**Median (ng/L)**	**Maximum (ng/L)**
Groundwater	**BTZ**	105	105	12	492	14.9	32900.0**
	CAF	105	98	25	122	14.2	1360.0**
	ATR	105	99	4	16	13.6	57.6
River	**BTZ**	48	48	32	84	9.0	564.0
	CAF	48	47	6	79	26.9	617.4
	ATR	48	48	1	12	9.5	26.7

*Table 4-2. Detection profile of ubiquitous micropollutants in groundwater and in surface water. Summary statistics are estimated using the Kaplan-Meier estimator. Two asterisks ** indicate that the maximum value is above the upper LOQ and thus cannot be taken as an exact value. However, a general order of magnitude can be deduced at these points. Due to high censoring, summary statistics cannot be calculated for non-ubiquitous compounds.*

By Season							
Season	**Compound**	**Nr. Samples**	**Nr. Detects**	**Nr. Censored**	**Mean (ng/L)**	**Median (ng/L)**	**Maximum (ng/L)**
Spring	**BTZ**	57	57	5	116	12	3039**
	CAF	57	54	1	195	108	1360**
	ATR	57	56	2	15	14	33
Summer	**BTZ**	26	26	4	69	24	1399**
	CAF	26	26	6	29	7	264
	ATR	26	26	2	13	11	31
Fall	**BTZ**	14	14	0	2404	24	32900**
	CAF	14	14	0	136	19	814
	ATR	14	13	1	17	10	58
Winter	**BTZ**	58	58	18	155	15	2030**
	CAF	58	53	24	49	6	617
	ATR	58	54	1	14	10	37

*Table 4-3. Detection profile of ubiquitous micropollutants as a function of season. Summary statistics are estimated using the Kaplan-Meier estimator. Two asterisks ** indicate that the maximum value is above the upper LOQ and thus cannot be taken as an exact value. However, a general order of magnitude can be deduced at these points.*

The cumulative Kaplan-Meier EDFs for the three ubiquitous compounds are compared in Figure 4-10. All are plotted on a log-scale for the x-axis due to the skew of the data. The differing shapes of each curve strongly suggests that they have different sources. While the median values of all three are close, a significant divergence is observed at higher concentrations. The distributions of CAF and BTZ both display mild multi-modal patterns, i.e. there may be two or more populations (and therefore sources or degradation pathways) present in the distribution.

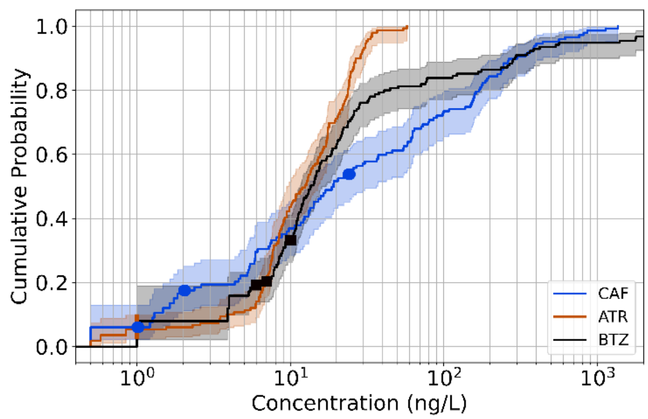


Figure 4-10. Kaplan-Meier distributions for the three ubiquitous compounds at our study site, including confidence intervals. LOQ values are marked with circles.

Kaplan-Meier empirical distributions are then assessed as a function of water type and then of season in Figure 4-11. The confidence intervals are not shown for seasonal curves in order to increase graphical visibility (confidence intervals may be referenced in the supplementary information).

For the most part, the distribution of compound concentrations is very similar in both water types as well as across seasons. Exceptions can be seen below the 25th percentile and above the 75th percentile, where differences are more evident. For example, while ATR is generally well-mixed in all categories, its maximum values are found in groundwater, and more censored values are found in surface water. ATR was banned in Switzerland in 2012, but it is still detected at quantifiable levels in groundwater due to its extreme resistance to degradation and high absorption rates to soils enriched with organic matter (Shan et al., 2020). Higher ATR values were detected in agricultural wells P2, P9, and P13, consistent with the fact that its major source is the subsurface. The seasonal stability of ATR concentrations do not give evidence of significant increases in groundwater exfiltration during wet seasons, nor significant dilution effects in the groundwater. The overall distribution between water types suggests nearly-uniform mixing between groundwater and surface water on seasonal scales. With a larger database and higher frequency sampling, ATR could be a candidate for baseflow estimation in the surface water.

Concentrations of BTZ downstream of the WWTP are, on average, an order of magnitude higher than those detected upstream. This validates that treated effluent is a definite source into the environment. However, its highest concentrations were found in inland groundwater wells – some with concentrations on the order of micrograms per liter – greatly exceeding the upper LOQ. This is highly indicative of localized outdoor sources, including direct infiltration and recharge, in addition to the indoor wastewater sources.

Multiple sources are also supported by the bimodal nature of its EDF curve in (seen more clearly in Figure 4-11). Maximum concentrations were detected in wells P9, P11, and P13, all of which are located in agricultural zones, far from the sewer network.

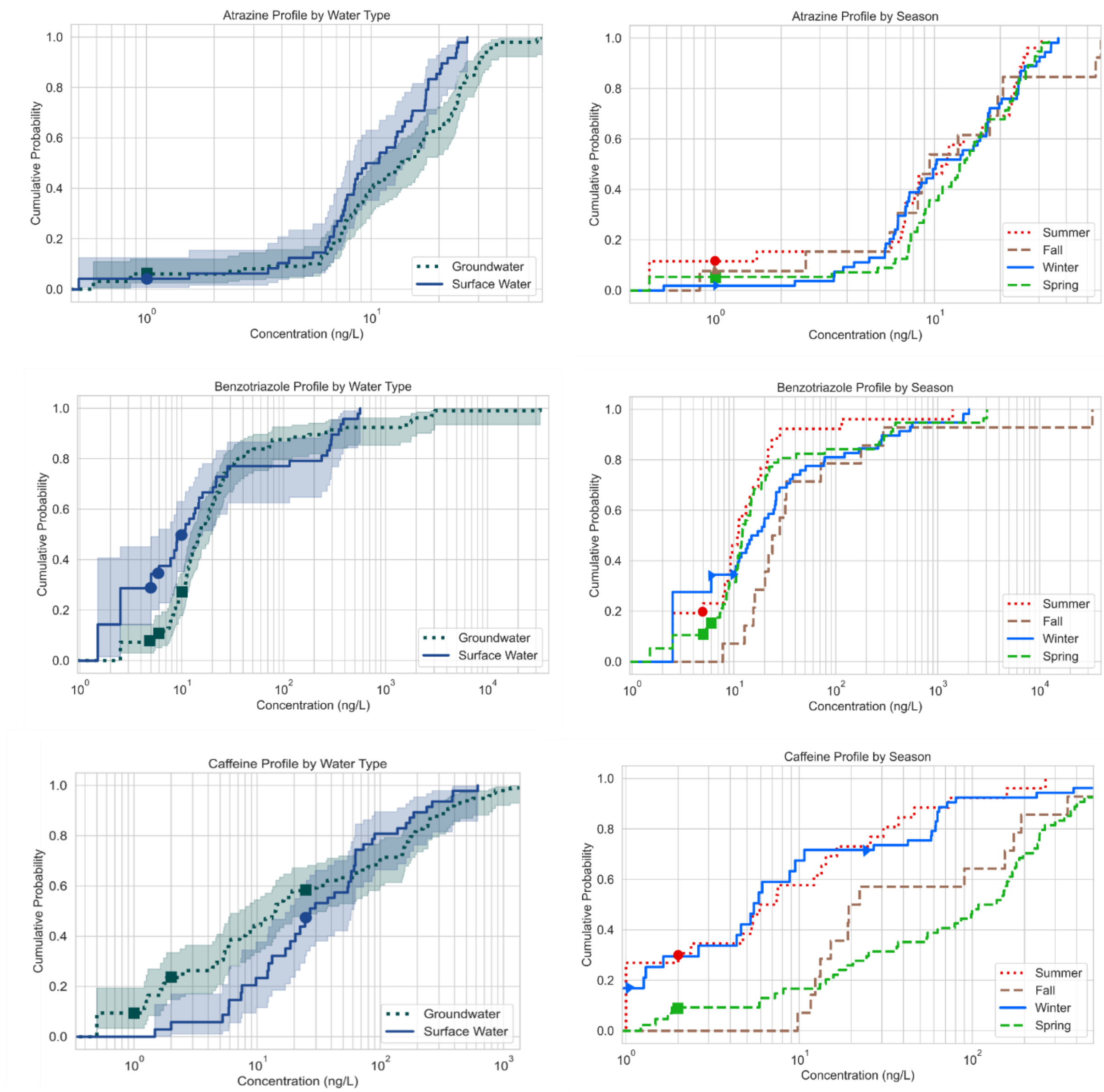


Figure 4-11. Kaplan-Meier distribution curves for ATR, BTZ, and CAF split into populations of water type and then of seasons. Symbols mark the LOQ values for each sub-population.

CAF was found at many sampling points, on the same order of magnitude both upstream and downstream of the WWTP, and between groundwater and surface water; in fact, localized maximum CAF concentrations were detected in groundwater upstream of the WWTP. CAF is known to be efficiently biodegraded in treatment plants, such that it has been applied as a tracer for raw, untreated wastewater instead of treated effluent (Buerge et al., 2006, 2003; Schirmer et al., 2011). The Kaplan-Meier curve in Figure 4-11 depicts a large difference in CAF concentrations between seasons, with no overlap in confidence intervals between spring and summer (figure S.I.12). Most of the seasonal variation is observed in groundwater, while only a select few surface water points – LU29, KE8, WI20 – portray this seasonality. This may offer distinct evidence that CAF is mobilized into groundwater with spring and fall precipitation. Seasonality of CAF and other wastewater micropollutant markers has been found in a number of additional studies (Buerge et al., 2006; Musolff et al., 2009). However, CAF should be interpreted with care when detected in isolation because of higher degradation rates and potential contamination of samples during sample preparation. Its indication of seasonal drivers for wastewater release must be validated with the presence or absence of additional urban products.

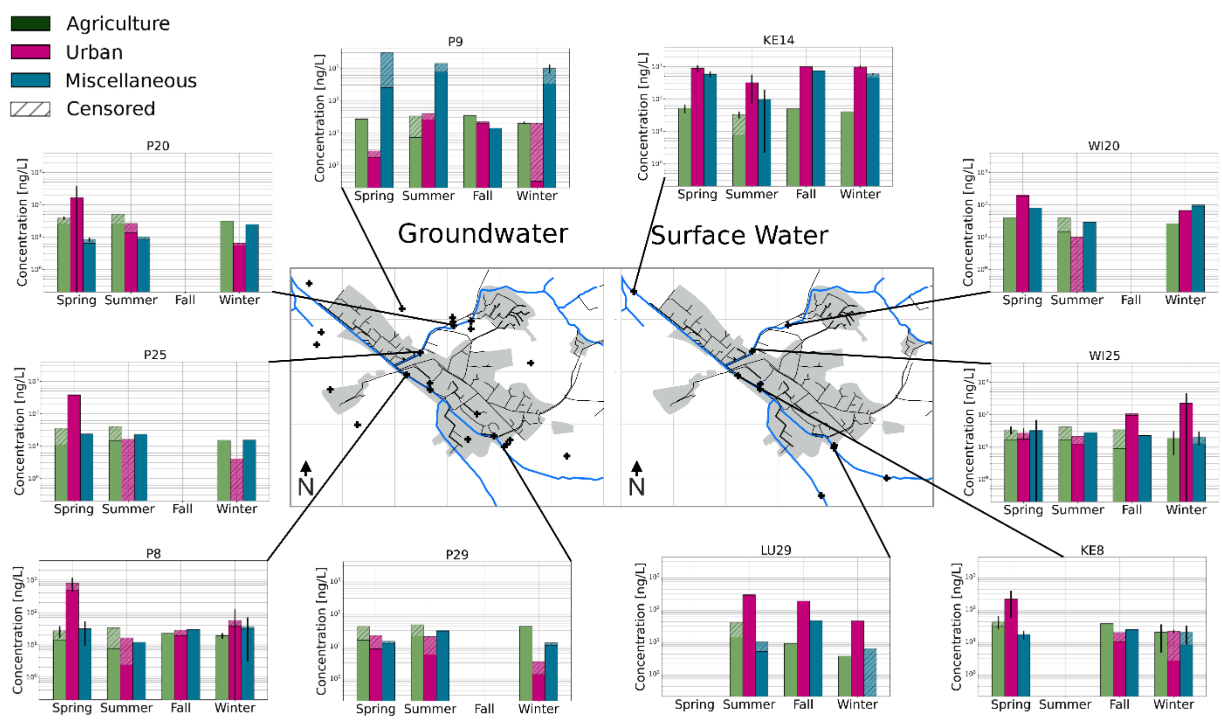


Figure 4-12. Micropollutant profile at select groundwater and surface water points on a seasonal basis. Average seasonal values across all sampling campaigns are used.. Error bars indicate the standard deviation of seasonal samples. NOTE: Seasons with no bars indicate no data available.

Figure 4-12 shows the total seasonal micropollutant profile for a select number of locations (profiles for all locations may be found in the supplementary information). Here, each of the 13 compounds (Table 4-1, section 4.4.4) are binned into the categories of agricultural (outdoor), urban (indoor), and miscellaneous products, and averaged seasonally. P9 is representative of the groundwater signature, and KE14 represents the signature of effluent-impacted waters as identified with HCA. Three corresponding groundwater/surface water locations are included – P25/WI25 and P8/KE8, P29/LU29

– to explore the potential groundwater – surface water interactions alluded from the flow fields and HCA groupings at these points. This seasonal averaging across all sampling campaigns was justified with the assumption that uncertainties due to low-frequency sampling greatly exceed the differences between seasons of different years.

The sum of agricultural products – ATR, CMD, and TERZ – are largely stable across the site and throughout the year, in both groundwater and surface water. This again indicates that the two water types are indeed closely connected at the catchment scale. BTZ also proved relatively stable with the exception of extreme values at wells P9 and P13, which indicate localized sources of surface infiltration. As alluded by the distribution of CAF, concentrations of urban micropollutants are significantly higher in spring than in other months in several locations, including a greater variety of compounds. The seasonal increase of urban products at KE14, on the order of 100s of ng/L, is in fact due to the increased presence of other pharmaceuticals rather than an increase in CAF concentrations. Further, the summer decrease in pharmaceutical concentrations is despite the fact that effluent made up a larger portion of streamflow at KE14 during the particularly dry summer covered in this study (2018). A similar seasonal pattern is observed at the two urban wells P8 and P25 with a greater variety of urban compounds detected along with significantly higher CAF concentrations – a testament to either sewer leakage or CSO. It should be noted that at the sampling points WI20, P19, and P20, the high-to-low spring-to-summer seasonality was also observed (figures S.I.13 – S.I.14).

4.6. Discussion

4.6.1. Flow Pathways and Points of Interaction

With results from the flow net generation, we were able to estimate the relative height of the water table to the stream bed and to the sewer system, and approximate the contributing flow areas for all groundwater wells. Potential interactions with groundwater arise when the generated groundwater flow pathways intersect either the stream or the sewer system. The relative groundwater levels then indicate the direction of such potential interactions by their differences in pressure heads. This information from flow nets offers preliminary indications of what *could* be occurring, however, flow fields alone cannot identify whether such interactions actually are occurring. Sewer leakage will only occur if a fault actually exists in the sewer canals. Likewise, groundwater – surface water interactions will only occur when the stream bed is actually permeable, creating a connected system.

The results from hydrochemical multivariate analysis therefore take us a step further in filling these information gaps. Through HCA, separate signatures for groundwater, surface water, and wastewater-impacted waters were identified and geographically validated. From this, where surface water signatures were detected in the groundwater (and vice-versa), stronger evidence of groundwater – surface water interactions is given. Likewise, the wastewater-impacted water signature in either surface or groundwater would give stronger evidence of such interactions actually occurring (no such signature was found in groundwater). When comparing these sample points back to probabilistic flow fields, it is also possible to deduce the actual surface water contributing areas to an individual well. When taken together, the information from flow nets and from HCA are therefore used to define a conceptual model of groundwater flow pathways and points of interaction.

Aside from the potential interactions identified with the groundwater flow field, however, no chemical indication of wastewater in groundwater was identified through HCA. We postulate that since the wastewater-impacted HCA group was identified using samples downstream of the WWTP, this sets a higher threshold for being able to identify wastewater sources. Therefore, small amounts of leakage or flashes of CSO would likely not be detected due to dilution in the environment. This is where micropollutants come into the picture as source-specific indicators.

4.6.2. Urban Micropollutants to Validate Flow Pathways

Even in trace amounts, urban micropollutants indicate the absolute presence of wastewater. With regards to underground sewer leakage, the extremely low concentrations detected in groundwater across our study site suggest that no major leakage is occurring, though minor leaking is probable. Minor leakage likely would not travel far in the groundwater, and thus remains a very localized source. It can also be expected that release from sewer leakage is approximately constant throughout the year. Increases in leakage may potentially be observed during high-flow conditions in sewers, including during storm events where runoff is diverted into the sewer network. Strong seasonal variations in urban micropollutants in groundwater are rather likely to be controlled by CSO and groundwater – surface water interactions. Because of the higher concentration magnitudes in surface waters, we conclude that CSO is likely a more important source of micropollutants into the environment than is sewer leakage.

We take the example of monitoring well P8 to illustrate the dynamics of wastewater in the groundwater. At P8, a larger number of different urban products were found for the springtime months, in addition to higher concentrations of CAF. However, the canalization in proximity to P8 is submerged. Because P8 has a surface water signature as determined by HCA, and because of the strong temporal indication from urban micropollutants, we hypothesize that the micropollutant signature at this well is indeed indicative of CSO that enters the groundwater by way of the surface water. Further, P26 is located in vicinity to P8, albeit separated by a CSO connection that is downstream of P26 and upstream of P8. At well P26, although higher urban micropollutant concentrations are found in spring, this is dominated by CAF, with few additional compounds. It is also noteworthy that the groundwater tables at both P8 and P26 show very little seasonal fluctuations. This could be indicative of groundwater infiltration into sewers, controlling their pressure heads. This is also consistent with the fact that sewers are submerged at these locations. These factors, when taken together, indicate that CSO is likely to be a more significant source of wastewater than is sewer leakage.

Similarly, all of the monitoring wells along the Wildbach display significant seasonality in urban compound concentrations (figure S.I.13 – S.I.14), and all have a surface water signature from HCA. Both the surface water and the sewer canals along the Wildbach are mostly above the water table at these locations, such that their sources are more difficult to differentiate. Further, their signatures are dominated by CAF alone, with very little presence of other urban compounds throughout the year. However, along the upstream Wildbach in wells P17 – P21, all storm drains are separated stormwater outlets such that CSO would not occur. Since the sewer network is not submerged, it is therefore possible that localized leakage is occurring. It is only at P25 where the posterior probability of submerged sewers is only 50%. Further, a CSO outlet is present upstream of this point and the surface water is not submerged, indicating probable CSO infiltration.

Significant levels of CAF were also detected at wells P2, P13, and P31 – wells in agricultural areas that far displaced from the sewer system – at significant levels during at least one season. At well P31, additional urban compounds were also detected, which means that further investigation in upstream wells is merited. These detections could be indicative of input from effluent from the upstream municipality of Pfäffikon, or from Lake Pfäffikon itself. A surface topographical divide as well as a clay ridge in the subsurface sediments exist between lake Pfäffikon and the aquifer, and from this we make the assumption that lake Pfäffikon has little to no impact at our study site. However, several small ditches have been dug in between the lake and the hillslopes of our catchment. These potential connections have not been explored at our study site as of this writing.

4.6.3. Suitability of Micropollutants

Even as their use increases in hydrogeological studies, discussion on the suitability of micropollutants as tracers continues. Among the commonly noted limitations are the non-conservative nature of micropollutants, high levels of censoring, and shortcomings of low-frequency sampling. Suggestions to circumvent the issue of non-conservation include using groups of compounds, accounting for multiple degradation products, or taking ratios of one compound to another (Warner et al., 2019). We addressed the issue of censoring here by applying the Kaplan-Meier estimator, demonstrating that important information can be gained even with higher levels of censoring. We were able to compare populations of water types and seasons without needing to estimate concentrations at individual sampling points and without arbitrarily substituting values. In addition to our findings, other studies have gone so far as to integrate censored data sets in model calibration (Lefrancois and Poeter, 2009). While seasonal grab sampling served as a reconnaissance of the micropollutant profile here, sampling frequency is still a noteworthy limitation and source of uncertainty in this study. Surface water flow and CSO in particular are extremely dynamic and fast-acting by nature, with 'pulses' of urban micropollutant concentration increases during overflow events being observed on the order of hours in surface water (Musolff et al., 2009). Samples separated by sewer hours can show very different micropollutant profiles. Further, the presence of baseflow are evidenced by ATR in the stream, but the precise dynamics of baseflow cannot be determined with grab samples. In this case, high-frequency sampling of ATR could shed light on these baseflow dynamics during dry periods and wet periods.

Finally, the use of micropollutants as indicators does require a certain level of working knowledge on the physico-chemical properties of different compounds, as well as the bio-geochemistry of soils and aquifer sediments. It has been shown that the degradation pathways of many micropollutants are strongly dependent on redox conditions as well as residence time, temperature, microbial communities, and other in-situ conditions (Banzhaf et al., 2012; Buerge et al., 2003; Hillebrand et al., 2012; Postigo and Barceló, 2015). This information can indeed be exploited in order to identify these processes in a catchment, and to differentiate pathways taken as a function of different levels of degradation. Without such information, these sources and pathways are less clear.

4.7. Summary and Conclusions

In this study we have investigated the anthropogenic water cycle in a small urbanizing watershed, using a combination of physical and chemical approaches. Each step of our study offered independent yet complementary information about local water dynamics at our field site. We were able to estimate flow pathways with conformal mapping, evidence surface water – groundwater interactions with HCA, evidence point sources of wastewater with urban micropollutants, and evidence infiltration outside of the urban center with agricultural and miscellaneous contaminants. The results of these analyses lead us to conclude that CSO is the dominant pathway of wastewater into the environment within the Fehraltorf urban area. The presence of pharmaceuticals and CAF upstream of the urban watershed area also suggest additional, unidentified sources of wastewater. Finally, the miscellaneous product BTZ gave evidence of both indoor sources and outdoor sources, and the pesticide ATR indicated thorough mixing between surface water and groundwater.

Differences between the results from each data type are partly explained by the different underlying controls represented by each. Flow pathways are determined physically via the interpolated water table, and indicate only the potential for different sources. Ionic and isotopic data are controlled by climate and geological factors, and indicate where surface water – groundwater interactions are actually occurring. In both of these cases, land use and activity are secondary controls. For its part, the presence of micropollutants is principally controlled by anthropogenic factors, where chemical degradation, climate, geology are secondary factors. Acknowledging the sources of these differences, when these independent analyses are taken together, a more cohesive image of the groundwater dynamics at this site becomes evident.

5. CONCLUDING REMARKS

This dissertation has presented an assessment of some of the real-word issues facing groundwater resources and availability in today's human environment. Due to the extent and complexity of the issue, chapter 2 was written to provide a comprehensive review of these issues and where they stem from. We contrasted anthropogenic versus natural controls on groundwater, and included specific details of impacts from different land use elements. We then explored some of the major groundwater contaminants that are released from human activity, and where they come from. Our list outlined a number of different inorganic and organic contaminants, and included information on contamination regulations in different regions of the world, in order to outline societal and political acknowledgement of these issues. The case studies presented were an effort to consolidate some of the important research currently being published. The topics of these case studies ranged from issues in un-sewered cities, long-term contamination, pesticides in agricultural versus urban settings, pharmaceuticals in urban versus agricultural settings, chlorinated organic compounds, and legacy contamination from mining sites. These studies cover different settings including shallow and deep aquifers, karstic environments, areas with extreme groundwater drawdown or re-watering, megacities and large-scale industrial areas, and areas of managed aquifer recharge.

5.1. Real World Case Study

From the review in chapter 2, we identified several recurring themes surrounding anthropogenic groundwater issues, including the importance of groundwater quantity for understanding issues of groundwater quality. We then moved to directly assess the applicability of different methods for on-the-ground field characterization to explore these identified themes in the Swiss context. A field site was set up in the urbanizing Kempttal catchment on the Swiss Plateau for our assessment, and served as the host for the case studies presented in chapters 3 and 4. The setting of this site – a shallow, unconfined aquifer, mixed urban and agricultural land use, developed infrastructure, and mostly efficient water utilities – was used to inform the design of a groundwater monitoring network within the urban watershed, and implement methods to characterize groundwater quantity and quality risks on the catchment scale as well as the urban watershed scale. The emphasis of these studies is on site characterization and method assessment, with no claim to predictive capacities.

Groundwater and surface water in urban areas was highlighted in chapter 2 as an important conduit connecting surface conditions and subsurface conditions. Therefore, in chapter 3 we tested the performance of two empirical methods that are often used in hydrology to calculate surface runoff, and their suitability to capture the dynamics of our study site. In this step we modified our calculations to explicitly account for sealed surfaces and hydrographic changes in quickflow. Surface runoff was then used as an input to estimate recharge with a groundwater balance. The performance of our groundwater balance was determined against the conceptual HBV Light rainfall – runoff model, and against results from similar field sites across Switzerland found in literature. The empirical results proved satisfactory against model and literature values, and highlighted the importance of soil moisture as a control for runoff in our catchment. At our field site, *changes* in the runoff – recharge relationship in particular is largely controlled by sealed surfaces, channelized rivers, and storm drains, and natural soil moisture is found to still largely dominate the catchment-wide runoff response. The characteristics of these relationships are directly relevant to the risk of contamination, as surface runoff is a carrier for many pollutants, and rainfall events may trigger the release of untreated wastewater into the environment.

The use of environmental tracers to characterize sources of groundwater was combined with analytical mapping of groundwater flow in chapter 4. Interpolated maps of groundwater flow lines around individual wells exposed probabilistic source areas and groundwater flow pathways. Relative levels between groundwater, surface water, and sewers were used to indicate the direction of any potential interactions that may be occurring. Using multivariate clustering, we used the inorganic chemical signature of water samples to identify locations where groundwater – surface water interactions are evidenced, as well as the signature of wastewater presence in environmental waters. From the large list of organic micropollutants in our targeted screening, a shortlist of ubiquitous and non-ubiquitous compounds relevant to our field site were additionally identified. These micropollutants were then used as source-specific indicators to validate the presence of wastewater, groundwater, and runoff infiltration at point locations across our monitoring site.

5.2. Future Studies

The research conducted here has outlined several topics of focus for future directions at this field site and those that are similar to it. Study in this area should continue in order to characterize changes in the factors impacting recharge – including surface runoff, evapotranspiration, and artificial inputs – during different phases of land use change and under different climatic conditions. These changes should be explored with all of our applied methods, both the physical water balance and the chemical indicator approach alike. Continued study should increasingly comprise integrated methods between hydrogeologists, urban engineers, and agricultural scientists in order to explicitly monitor the impacting factors. Field sampling, analytical methods, and numerical modeling alike would benefit from these collaborations. For example, in the context of this work, the use of micropollutants would greatly benefit from collaboration with sewer chemists and engineers. Such collaboration would help to identify additional site-specific compounds that are known to be present in the wastewater, and the locations of storm drains where sewer overflow is known to occur.

Specifically, a large unknown that persists in our characterization of surface runoff is the input of pre-event soil moisture during storm events, and the *exact* pathway of event precipitation from the surface into rivers or into localized infiltration points. To validate our empirical and conceptual approaches in a more concrete manner, applied, physically-based recharge models should be constructed as a comparative tool. This provides knowledge on the performance of our estimates in the Kempttal catchment and the general adaptability of widely used empirical models; knowledge that is transferrable to an extensive array of anthropogenic and hydrogeological settings.

To go further with chemical and isotopic indicators, the results here provide a blueprint on where to focus efforts. High-frequency sampling is time, labor, and cost-intensive, so this study has worked to identify where such efforts are merited: at locations where groundwater – surface water interactions were evidenced, where sewer leakage might be occurring, areas of infiltration and recharge source zones, and areas evidenced as localized sources of micropollutant release. High-frequency samplings are needed in both groundwater and surface water, unsaturated zone waters, sewage, and at points of combined sewer overflow are needed to characterize the temporal dynamics of such interactions. For example, high-frequency sampling of Atrazine, a tracer for groundwater, during storm events could be used to carry out a mass balance and quantify the baseflow response to these storms. High-frequency sampling of Caffeine and select pharmaceuticals, on the other hand, may be used to quantify the input of sewer overflow on a storm-by-storm basis.

Finally, there are areas specific to our study site that were not touched upon in depth, but may merit further investigation. These include the potential communication between lake Pfäffikon and the Kempttal aquifer, and potential inter-aquifer communication between the Kempttal aquifer and a shallow, yet largely confined, aquifer located high up in the south-eastern hillslopes of the area, on the border of the topographical divide. There is indeed a reasonable justification to the assumptions that no (or insignificant) input from these water bodies is present in the main aquifer under study. However, a large enough uncertainty of these factors exists such that in the least, a reconnaissance study should be carried out to validate whether communication is or is not occurring. Such reconnaissance could be carried out with geophysical campaigns near the divide of each water body, high-frequency isotopic studies, or integration of groundwater monitoring wells in those areas.

If they do prove to be occurring, this has implications for water quantity as well as water quality, the latter particularly from lake Pfäffikon.

The resources in the Kempttal catchment and the municipality of Fehraltorf, while generally a steadfast reserve, have proven sensitive to extreme climate. Significant groundwater drawdown during extreme dry years – of which there have been three such years in the past decade alone – has led to the real-world consequences of greater amounts of water imported from other areas. These consequences are not uncommon around the world.

5.3. Perspectives and Outlook

Securing groundwater resources is a pressing issue now more than ever. A growing population manifests as a growing demand for both land and water resources, demanding ever-increasing monitoring, remediation, and solutions for the future. Available resources are defined both by water quantity – how much is physically available – as well as water quality – how much is safe to consume by living beings? These two factors are interrelated and create a feedback loop between groundwater storage and pollution dynamics. Many issues have been outlined in this dissertation with regards to anthropogenic hydrogeology, and urban hydrogeology in particular. It is clear that for continued improvements in our understanding, additional and often times artificial variables to the groundwater cycle are present and must be accounted for in order to secure available resources. Effective management relies on concrete understanding of the dynamics of groundwater flow.

To meet the needs of our era in the real world, securing resources requires more than just scientific research. A truly transdisciplinary approach is necessary in order to tighten the link between understanding the issues, technological solutions, societal exposure to the issues, communication between stakeholders, effective regulations, and (hopefully) government implementation. Solutions should exist that are adaptable to many contexts, from developing countries to the first world. Research is at the foundation of better understanding and indeed is a central component to most of these facets. And this call to applied research is actively being answered to. Our increases in understanding as scientists, alongside ever-improving technologies, have given fruit to simple and effective approaches as well as powerful complex methods. Combined, these approaches have the power to improve nature-based solutions, more efficient appliances, agricultural tools, and more sustainable city planning. With this knowledge comes the power to secure groundwater resources to the best of our abilities in anticipation for the uncertain future to come.

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Supplementary Information for Chapter 3

Governing Principles of the Original Curve Number Method

A comprehensive description of the original CN method can be found in Mishra and Singh (2003). As a short overview, the foundation of all CN-based methods use empirically determined relationships between different watershed characteristics to estimate storm runoff in a catchment. The method is based on a water balance for partitioning precipitation (eq. S.I.1), as well as two fundamental hypotheses (eqs. S.I.2 and S.I.3):

$$P = R_{off} + F + I_a \tag{S.I.1}$$

$$\frac{R_{off}}{P - I_a} = \frac{F}{S} \tag{S.I.2}$$

$$I_a = \lambda S \tag{S.I.3}$$

$$R_{off} = \frac{(P - I_a)^2}{P - I_a + S}\ , for\ \ P > I_a \tag{S.I.4}$$

Where P is precipitation, R_{off} is runoff, F is infiltration, I_a is initial abstraction, S is the maximum potential soil retention under given moisture conditions, and λ is the initial abstraction coefficient. All variables are a function of depth per time step, with the exception of λ, which is dimensionless. The initial abstraction variable I_a acts as a threshold value above which runoff can be generated, so that the expression $P - I_a$ may be considered as the effective precipitation. I_a corresponds to loss factors such as canopy interception, short-term evapotranspiration, or ponding. The soil retention variable S is dependent on three discrete antecedent moisture conditions (AMCs) to represent dry, normal, and wet conditions. Equation S.I.2 is known as the 'proportionality concept' – an empirically-determined relationship stating that the ratio of actual runoff to effective precipitation (i.e. maximum potential runoff) is equivalent to the ratio of actual infiltration to maximum potential retention. Equation S.I.3 then proposes that the initial abstraction threshold is directly proportional to the maximum potential retention by a scaling factor λ.

As it reported that S can theoretically vary up to $+\infty$, the dimensionless curve number CN variable is determined via soil types and land use, using look-up tables that were constructed from empirically determined measurements. As mentioned, CN is also determined as a function of dry (AMCI), average (AMCII), or wet (AMCIII) antecedent moisture conditions. The CN S is determined as such:

$$S = \frac{25400}{CN} - 254 \qquad \textbf{(S.I.5)}$$

Many runoff methods apply these CN tables, even when the original equations are not applied.

Derivation of the Amended Curve Number "SME" Method

The authors of the SME method (Sahu et al., 2010) sought to amend the original CN equations to better account for the continuous nature of soil moisture, in place of the discrete moisture conditions used in the original equations. They partitioned the potential soil retention under different wetness conditions, *S*, into two values: one parameter representing maximum potential soil retention under dry conditions, S_0, and one variable to represent actual varying soil moisture conditions *M*. In this way, S_0 is a fixed value determined through catchment characteristics, and *M* is calculated as a function of antecedent precipitation. The proportionality concept is now represented in equation S.I.5, and the initial abstraction is represented in equation S.I.6:

$$\frac{R_{off}}{P - I_a} = \frac{F+M}{S_0} \qquad \textbf{(S.I.6)}$$

$$I_a = \lambda(S_0 - M) \qquad \textbf{(S.I.7)}$$

Finally, the expression for *M* is given as:

$$M = \beta\left[\frac{(P_5 - \lambda S_0)S_0}{P_5 + (1-\lambda)S_0}\right] for\ P_5 > \lambda S_0 \qquad \textbf{(S.I.8)}$$

As discussed in the main text, use of the P_5 metric creates an inherent assumption that a catchment is completely dry in the past days outside of the 5-day window. This assumption was deemed to be unsuitable for application in temperate to wet catchments, especially with larger urban areas where soil moisture is retained for longer periods of time.

For our implementation of the SME method, we carried out 10,000 Monte Carlo random samples of the parameters S_0, λ, and β as shown in Figure S.I.1. :

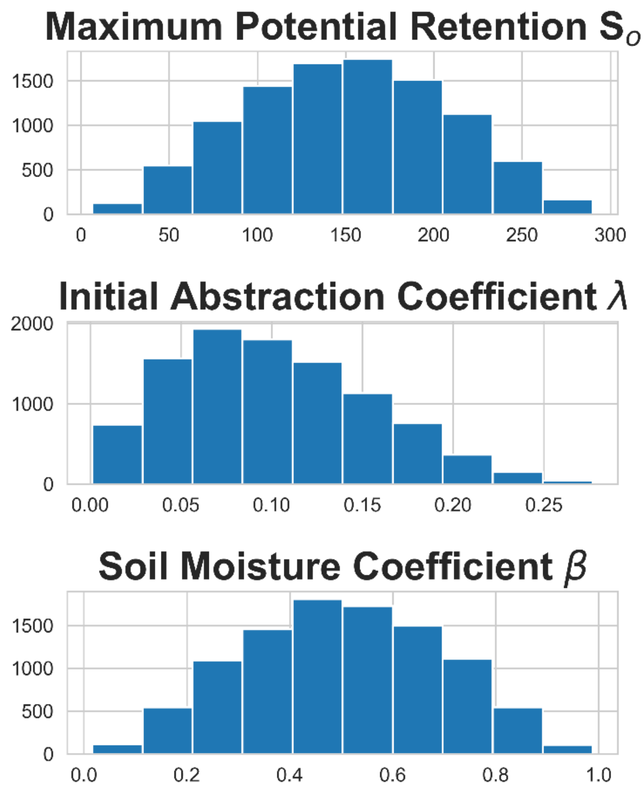

Figure S.I.1. Distributions of the three parameters used in SME calculations. These distributions were independently sampled 10,000 times for calculations.

Hydrograph Separation

Figure S.I.2 shows the resulting hydrograph separation from the digital filter (all separations averaged):

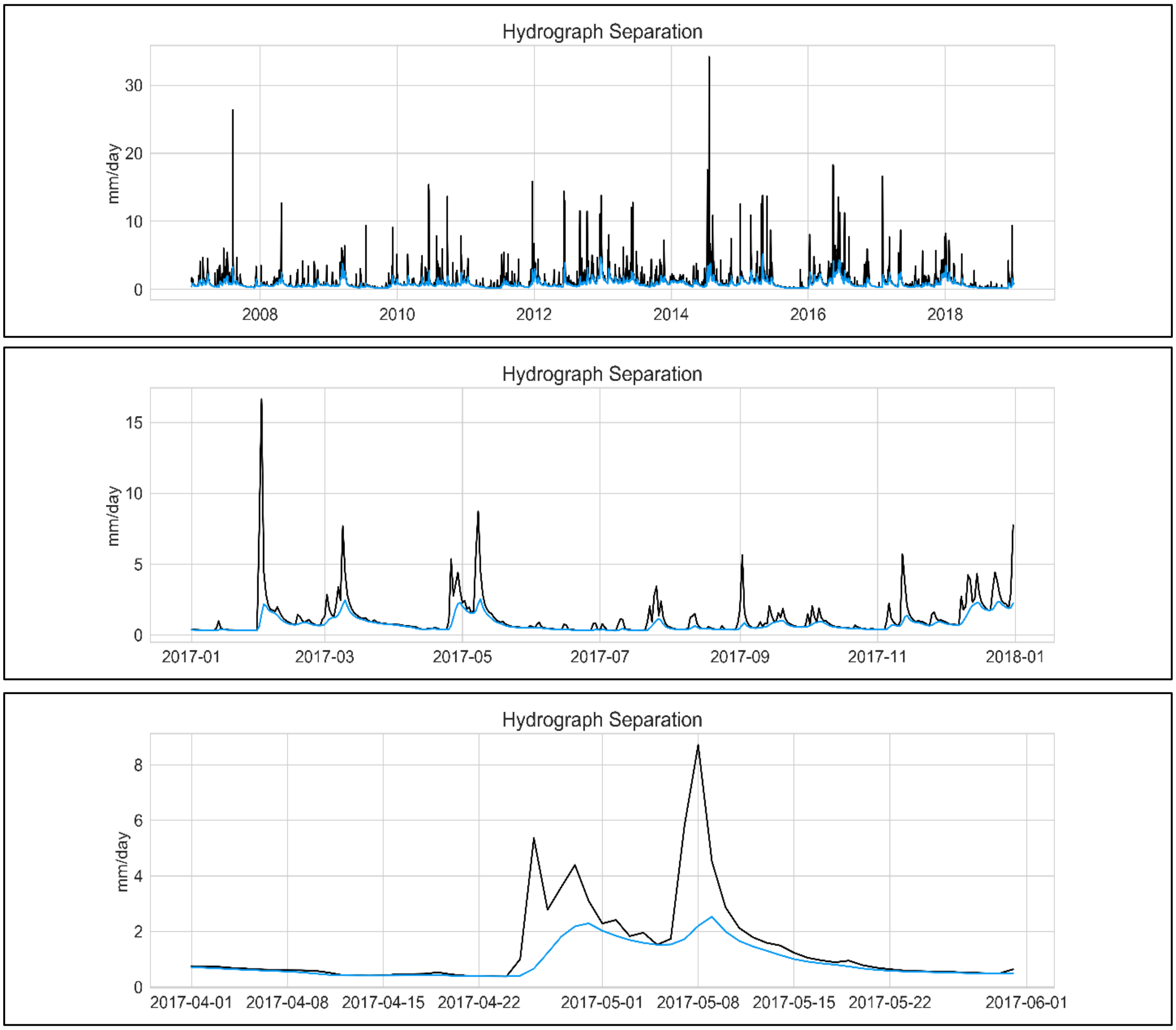

Figure S.I.2. Hydrograph separation into quickflow and baseflow over a.) entire timeseries, b.) yearly resolution for 2017, and c.) a two-month resolution for 2017.

In figures S.I.3.a. and S.I.3.b., the results of the two runoff calculations are compared on weekly and monthly basis for each calendar year of the study period. Figure S.I.3. displays the comparative daily timeseries of rainfall, streamflow, and the calculated antecedent precipitation index (API) for each calendar year of the study period.

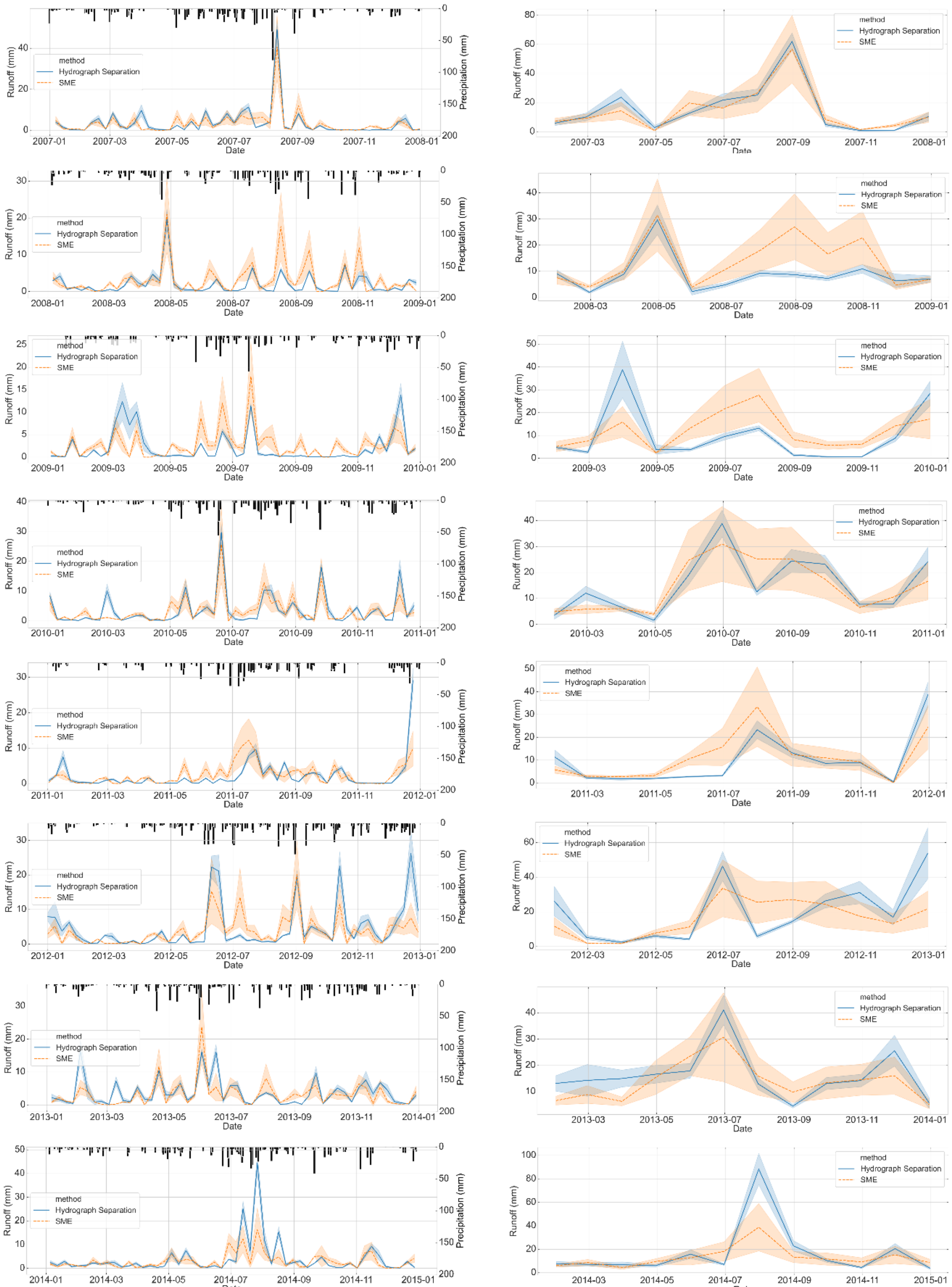

Figure S.I.3.a. Surface Runoff hydrographs estimated from each method for calendar years 2007 - 2014.

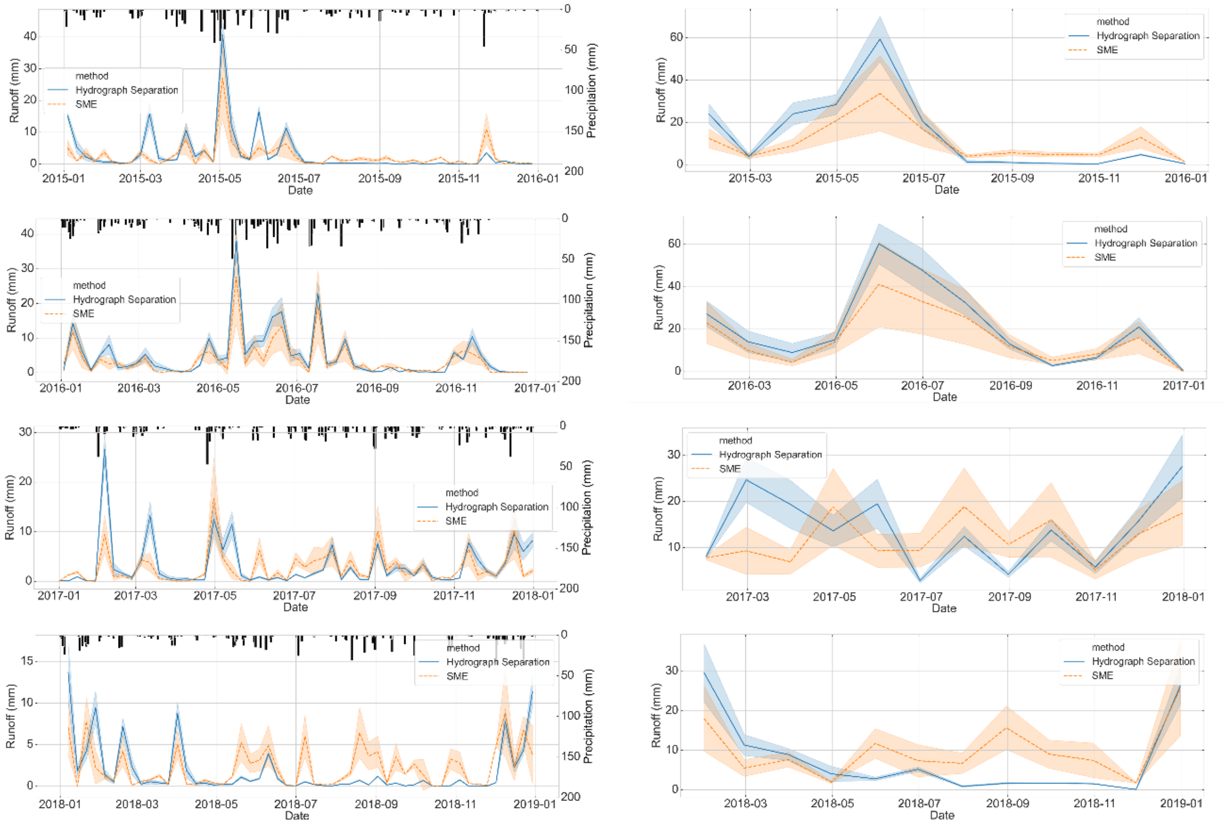

Figure S.I.3.b. Surface Runoff hydrographs estimated from each method for calendar years 2015 - 2018.

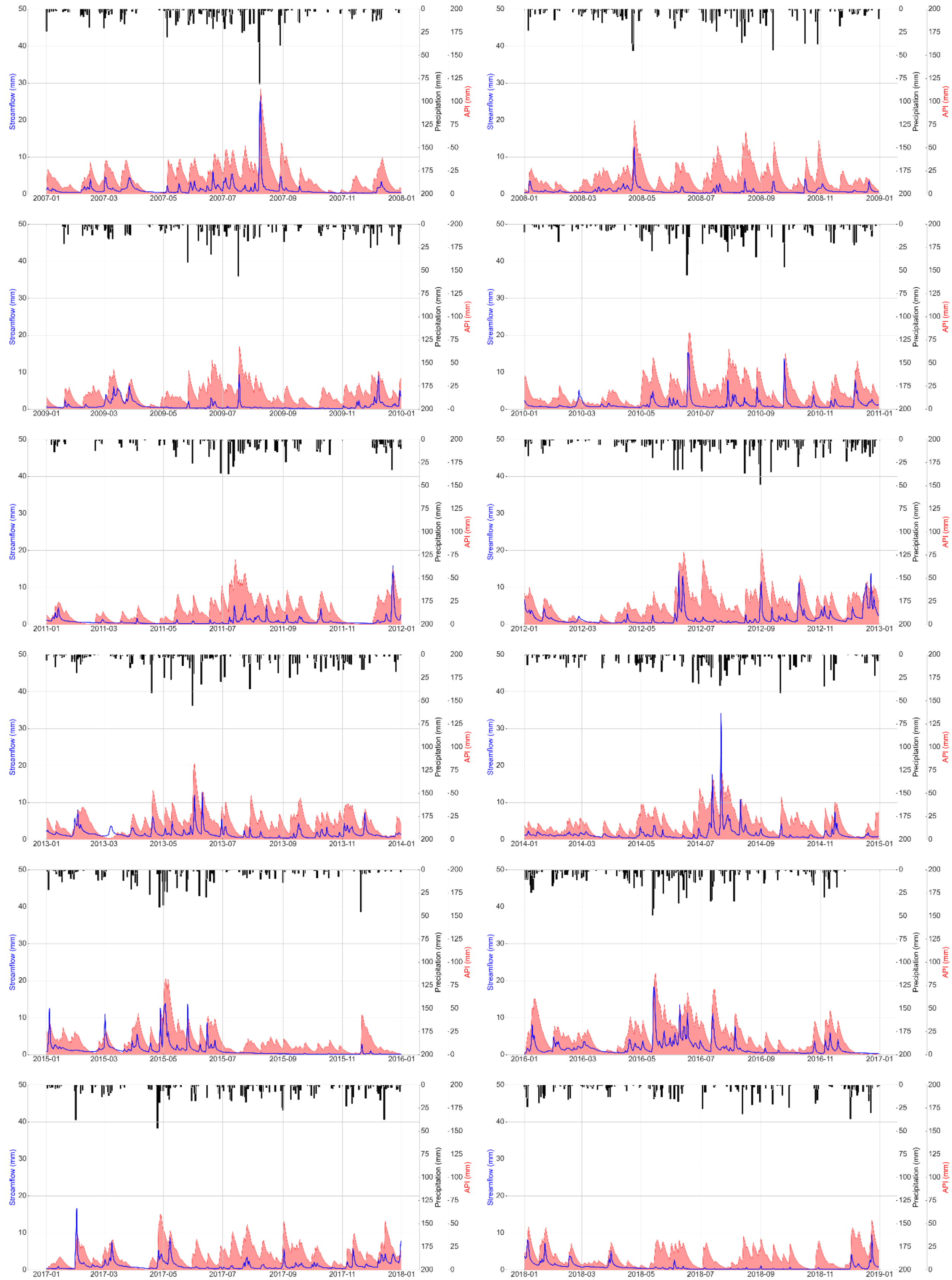

Figure S.I.4. Comparative daily timeseries of P, Q, and API from 2007 - 2018.

Supplementary Information for Chapter 4

Conformal Mapping

Because groundwater isopotential lines and the direction of flow are always perpendicular to one another, flow nets can be jointly expressed in terms of a complex number as the following function:

$$\varsigma(x,y) = \phi(x,y) + \psi(x,y)i \tag{S.I.9}$$

Where ϕ is potential, ψ is a pathline, and i is the imaginary number $i = \sqrt{-1}$.
The following equations define the Schwarz-Christoffel (SC) mapping from a unit square into a unit disk:

$$\varsigma^* = SC(\varsigma) = \frac{1-i}{-K_e} F\left(\cos^{-1}\left(\frac{1+i}{\sqrt{2}}\varsigma\right), \frac{1}{\sqrt{2}}\right) + 1 - i \tag{S.I.10}$$

as well as its inverse:

$$\varsigma = SC^{-1}(\varsigma^*) = \frac{1-i}{\sqrt{2}} cn\left(K_e \frac{1+i}{2}\varsigma^* - K_e, \frac{1}{\sqrt{2}}\right) \tag{S.I.11}$$

where ς^* is the transformed version of ς, $F(m,n)$ is the incomplete Legendre elliptical of the 1st kind with argument m and parameter n, $cn(m,n)$ is the Jacobi elliptic function with argument m and elliptic parameter n, and $K_e \approx 1.854$ is an evaluation of the incomplete elliptic integral of the first kind.

Möbius transformation (Laga et al., 2019) to deform the flow net inside the unit disk:

$$\varsigma^{**} = M(\varsigma^*) = \frac{a\varsigma^* + b}{c\varsigma^* + d} \tag{S.I.12}$$

where its parameters are obtained by the definition of three points on the unit circle and their images:

$$\begin{bmatrix} a & b \\ c & d \end{bmatrix} = \begin{bmatrix} w_2 - w_3 & w_1w_3 - w_1w_2 \\ w_2 - w_1 & w_1w_3 - w_3w_2 \end{bmatrix}^{-1} \begin{bmatrix} z_2 - z_3 & z_1z_3 - z_1z_2 \\ z_2 - z_1 & z_1z_3 - z_3z_2 \end{bmatrix}$$

The parameters for the inverse transformation $M^{-1}(\varsigma^{**})$ are $a^* = -d$, $b^* = b$, $c^* = c$, and $d^* = -a$.

MCMC accepts or rejects samples using a probability based on a ratio of un-normalized posterior densities between a proposed and original sample:

$$p_{accept} = \min\left(1, \frac{p(\theta^*)p(y|\theta^*)}{p(\theta)p(y|\theta)}\right) \tag{S.I.13}$$

where θ^* is the proposed and θ the original sample, $p(\theta)$ is the prior, and $p(y|\theta)$ the likelihood.

Parameter	Multivariate Gaussian		Von Mises		Exponential
	Mean μ	Covariance matrix Σ	location μ	scale κ	Scale λ
Rotation of control points A, B, C (north-west)	N.A.	N.A.	$\begin{bmatrix} -0.5 \\ 0 \\ 0.5 \end{bmatrix} \pi$	3	N.A.
Rotation of control points A, B, C (south-east)	N.A.	N.A.	$\begin{bmatrix} 0 \\ 0.5 \\ 1 \end{bmatrix} \pi$	3	N.A.
Potential limits ϕ_{min} and ϕ_{max}	$\begin{bmatrix} 530 \\ 530 \end{bmatrix}$	$\begin{bmatrix} 100 & 0 \\ 0 & 100 \end{bmatrix}$	N.A.	N.A.	N.A.
Potential offset ϕ_{offset}	N.A.	N.A.	N.A.	N.A.	0.1

Table S.I.1. Prior distribution for each layer of Möbius-transformed unit disks; in total, each full disk is composed of four sets of such parameters: One pair of two sets for the north-eastern aquifer, one pair of two sets for the south-western aquifer.

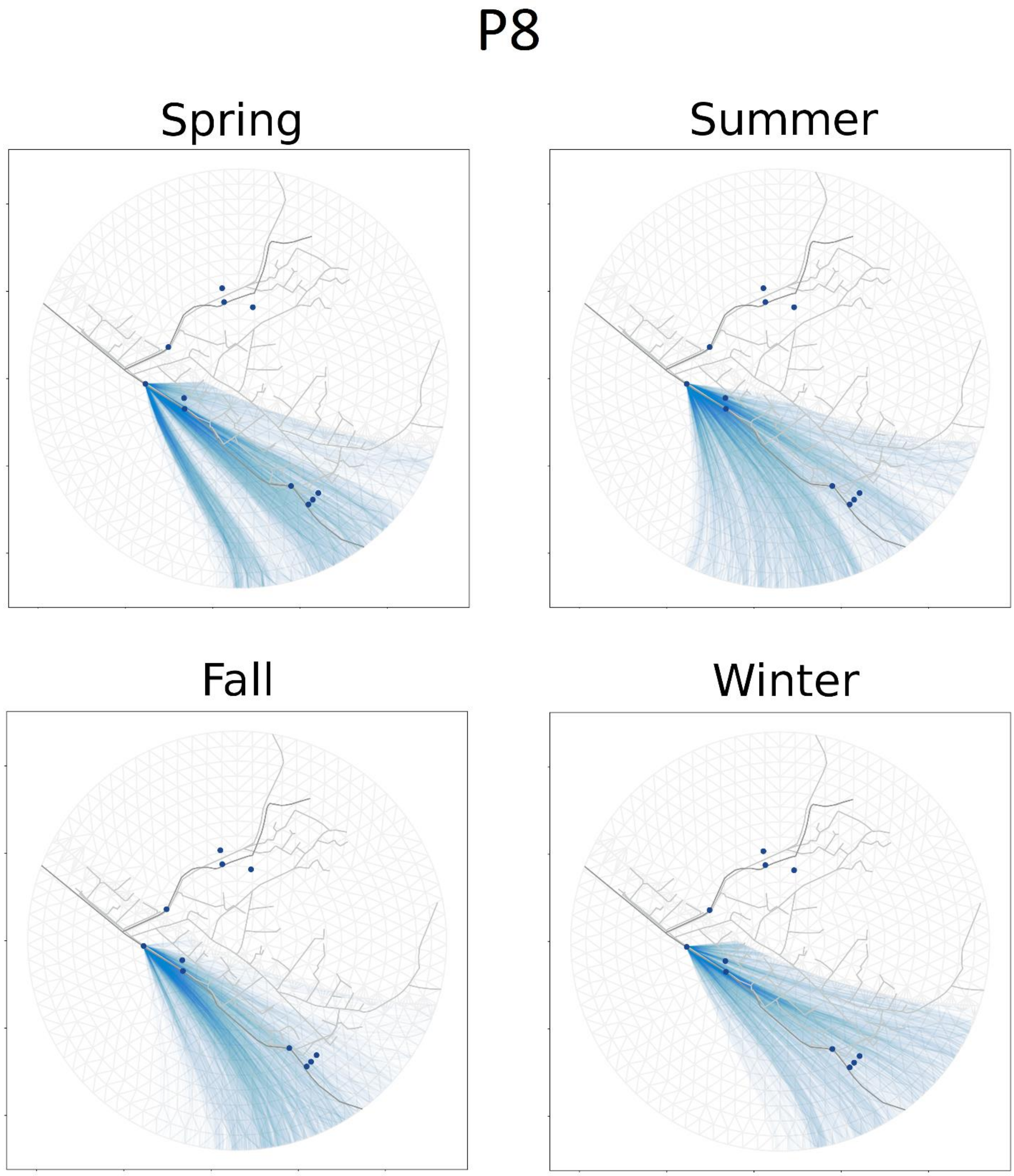

Figure S.I.5. Seasonal variation of flow fields and contributing areas for well P8

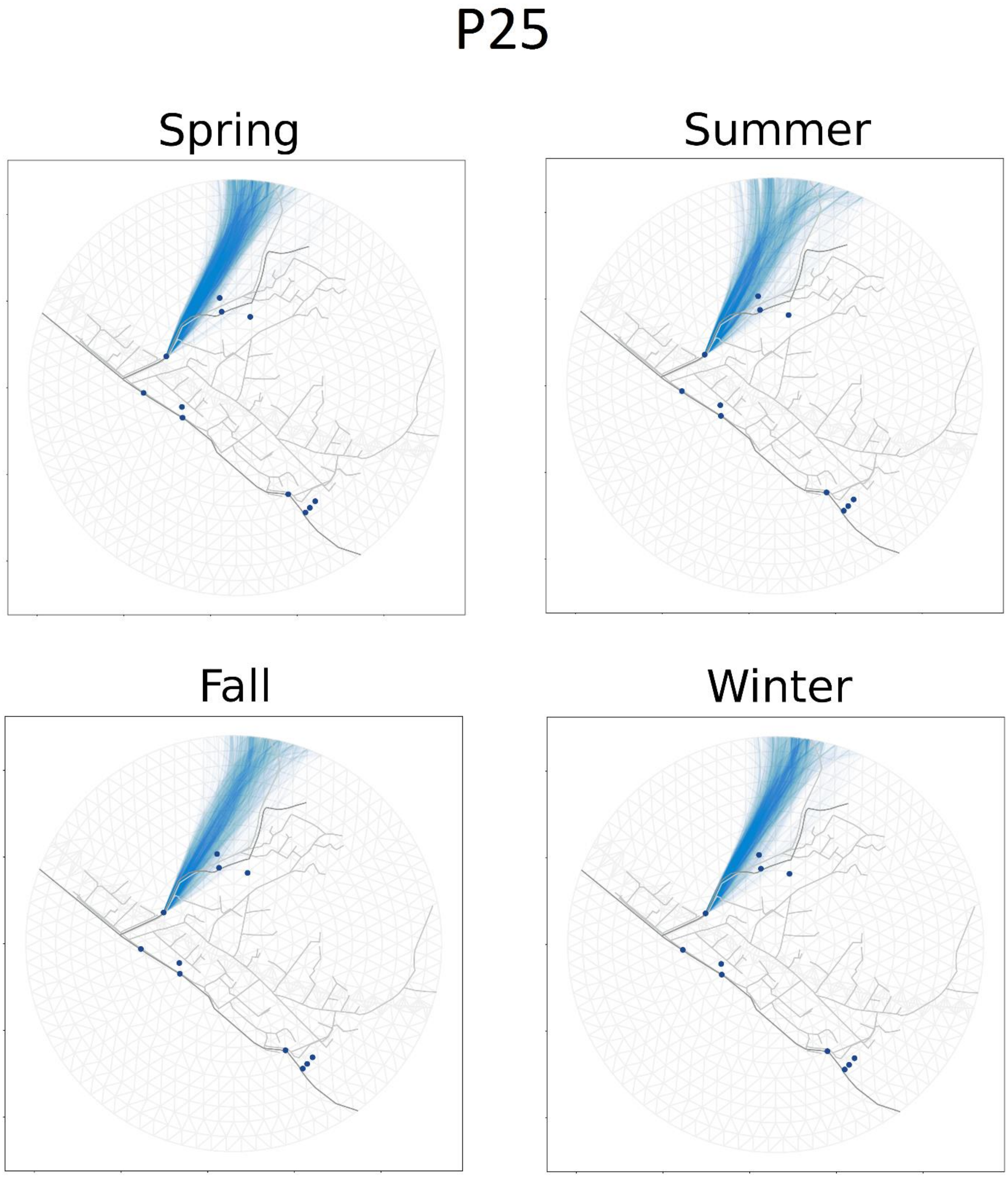

Figure S.I.6. Seasonal variation of flow fields and contributing areas for well P25

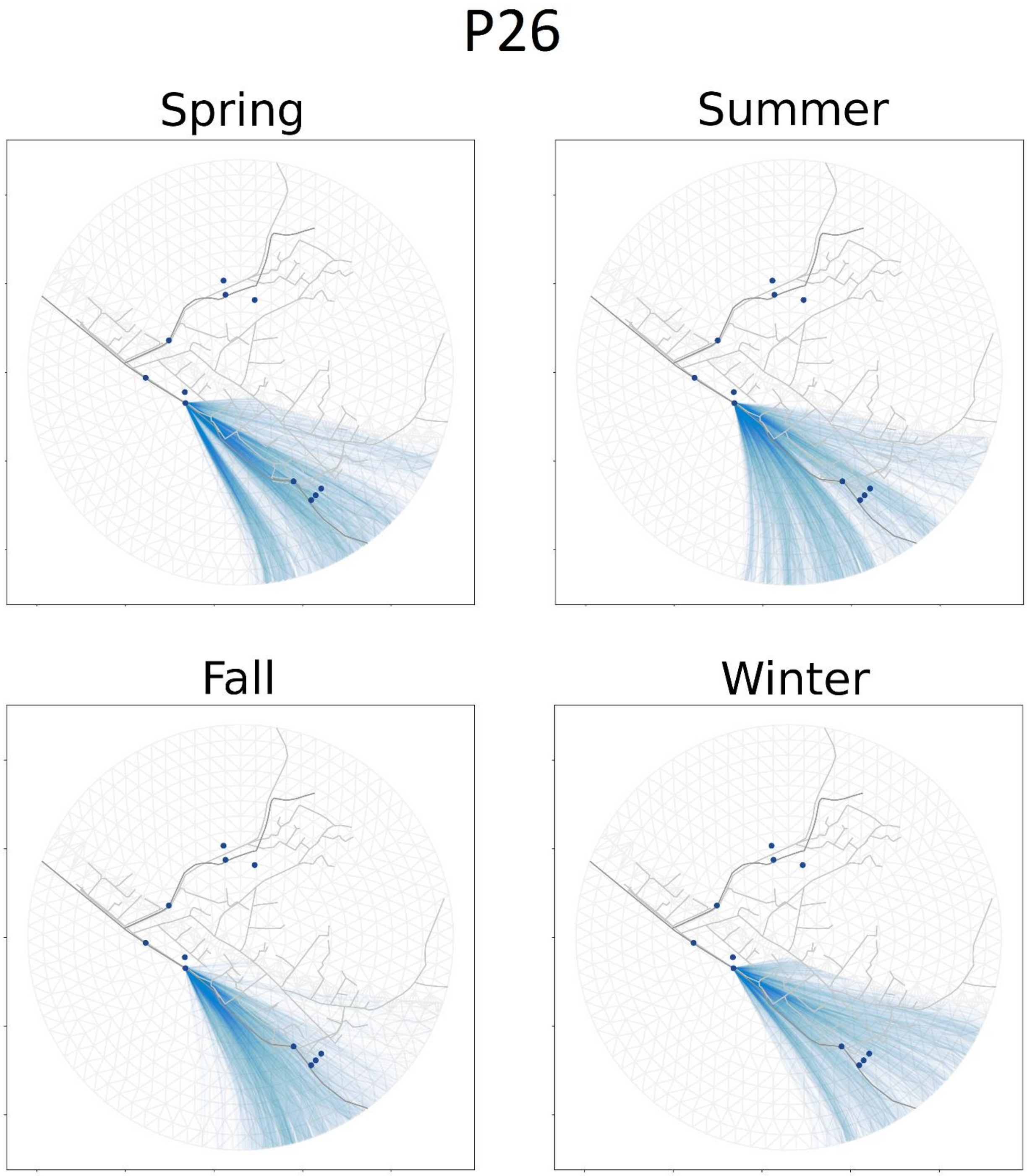

Figure S.I.7. Seasonal variation of flow fields and contributing areas for well P26.

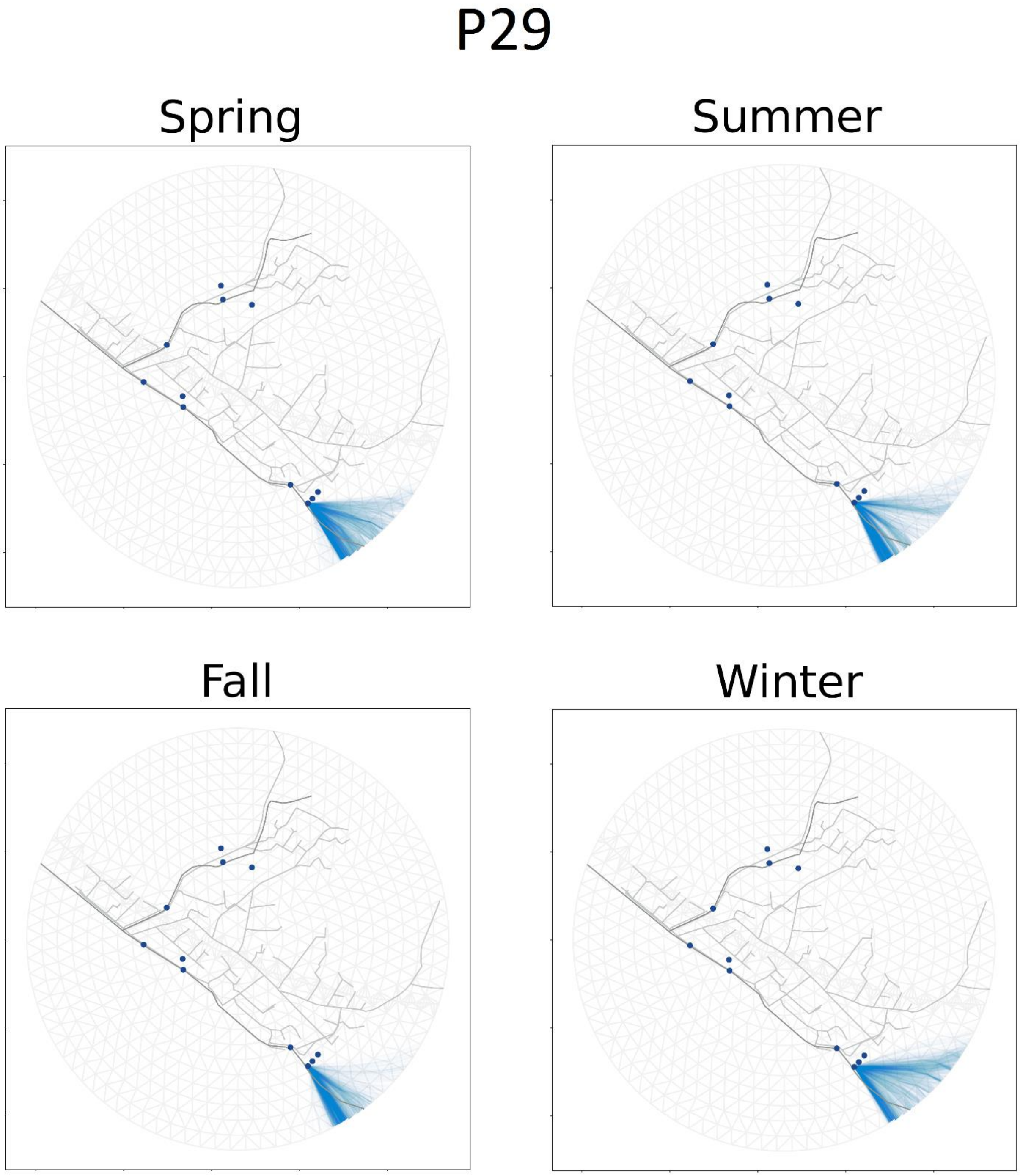

Figure S.I.8. Seasonal variation of flow fields and contributing areas for well P29.

HCA Dendrograms

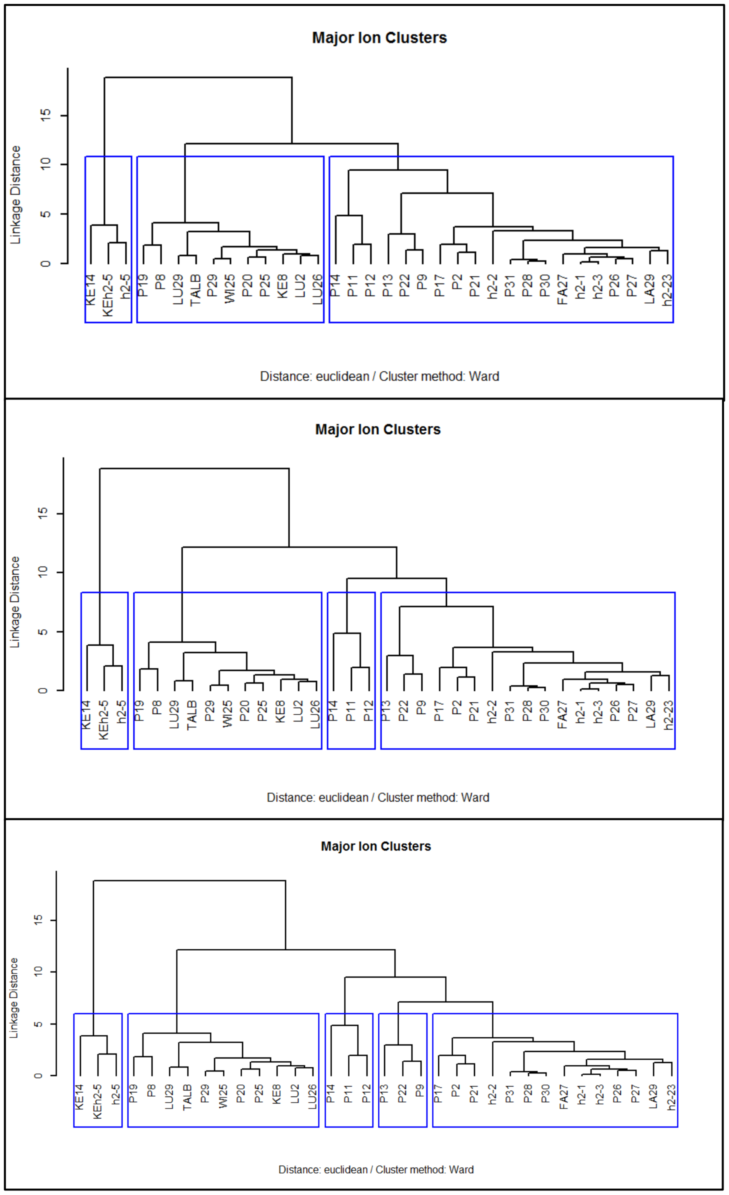

Figure S.I.9. HCA results exploring 3, 4, or 5 clusters, as shown as a dendrogram.

Micropollutants

Pharmaceuticals & Lifestyle	Acronym	Nr. Samples	Nr. Detects	% Censored	Notes
Acesulfame	ACE	133	35	74	High LOQ, High carryover rate into laboratory blanks
4-Acetamidoantipyrine*	4ACE	153	81	67	Included in subset of 13
Atenolol	ATE	153	28	57	Included in subset of 13
Atenolol acid	ATEA	153	51	56	Included in subset of 13
Caffeine	CAF	153	138	31	Included in subset of 13
Candesartan	CND	153	99	70	High carryover rate into laboratory blanks
Carbamazepine	CBZ	153	109	67	High carryover rate into laboratory blanks
Carbamazepine 10,11 dihydro	CBZ_dih	NA		NA	Analytically unstable
Carbamazepine-10,11-epoxide	CBZ_ep	153	91	69	Low detection frequency
Chlorothiazide*	CHL	NA		NA	Analytically unstable
Diclofenac	DIC	153	120	63	High carryover rate
Hydrochlorothiazide	HCL	153	49	47	Included in subset of 13
Lamotrigine	LAM	153	93	60	Included in subset of 13
N4-Acetyl-Sulfamethoxazole*	N4ACE	133	30	67	Very low detection frequency
Paracetamol	PAR	153	43	65	Low detection frequency, moderate carryover
Sucralose	SUC	133	35	34	High LOQ, low detection frequency
Sulfamethoxazole	SULF	153	98	67	Included in subset of 13
Valsartan	VAL	153	86	62	Low detection frequency
Valsartan acid*	VALA	133	76	51	Low detection frequency
Pesticides & Biocides	-	-		-	-
Atrazine	ATR	153	144	13	Included in subset of 13
Chloridazon-Methyl-Desphenyl*	CMD	153	129	36	Included in subset of 13
DCPMU	DCPMU	133	53	89	Very low detection frequency
Diuron	DCMU	133	70	83	Very low detection frequency
Terbutryn	TER	133	41	66	Very low detection frequency
Terbutylazin	TERZ	153	93	48	Included in subset of 13
Metolachlor	METO	133	62	89	Very low detection frequency
Mecoprop	MECO	NA	NA	NA	Analytically unstable
Miscellaneous	-	-		-	-

Benzotriazole	BTZ	153	146	27	Included in subset of 13
5-Methyl-Benzotriazole	5MB	153	135	55	Included in subset of 13

*Table S.I.2. Compounds measured in targeted LC-MS analysis over four measurement campaigns. Compounds were measured in groundwater, surface water, and one lake water sample. Results from CBZ_dih, CHL, and MECO (in red) were discarded due to extreme analytical instability. * indicates a transformation product.*

Table S.I.3. lists the lower limit of quantification (LOQ) and upper linear limit for each of the 13 subset compounds during each separate laboratory measurement series. These LOQs are the lowest *quantified* calibration samples from the laboratory calibration curve, and can thus be considered as the lower linear limit of quantification. LOQ estimates were additionally calculated by considering concentrations found in field blank samples, and sample signal-to-noise (S/N) ratios from the lowest calibration sample (equations S.I.14 and S.I.15). The linear limit of the calibration curve was used as the most conservative LOQ estimate, as estimates from blank samples and S/N concentrations were considerably lower than this linear limit. The linear goodness-of-fit parameter r^2 was consistently above 0.98 for all compounds across all measurement campaigns.

Compound	**October 2017**		**February 2018**		**August 2018**		**May 2019**	
Pharmaceuticals & Lifestyle	**Lower LOQ**	**Linear Limit**	**Lower LOQ**	**Linear Limit**	**Lower LOQ**	**Linear Limit**	**Lower LOQ**	**Linear Limit**
4ACE	1	1000	0.5	750	1	500	1	750
ATE	2	1000	5	750	1	750	1	500
ATEA	1	1000	1	750	1	750	2	750
CAF	5	1000	25	750	2	750	1	750
HCL	1	1000	1	750	1	750	1	750
LAM	5	1000	0.5	750	5	750	5	750
SULF	1	1000	0.5	750	5	750	1	250
VAL	2	1000	0.5	750	1	750	1	750
Pesticides	-	-	-	-	-	-	-	-
ATR	0.5	1000	0.5	750	1	250	1	750
CMD	1	750	0.5	750	25	750	1	750
TERZ	1	1000	0.5	750	1	100	1	500
Miscellaneous	-	-	-	-	-	-	-	-
BTZ	5	1000	10	750	5	750	6	250
5MB	1	1000	10	750	2	750	2	500

Table S.I.3. Lower and upper limits of quantification for each compound across all 4 measurement sequences, in nanograms per liter (ng/L). Limits were determined by constructing a calibration curve and accounting for variations in triplicate standard samples.

$$\mathbf{LOQ_{blank} = (average\ field\text{-}blank\ concentration) * 10} \quad \mathbf{(S.I.14.)}$$

$$\mathbf{LOQ_{S/N} = 10 * (S/N\ of\ lowest\ calibration\ sample)} \quad \mathbf{(S.I.15.)}$$

Sample Date	ID	Type	4ACE	5MB	ATE	ATEA	ATR	BTZ	CAF	CMD	HCL	LAM	SULF	TERZ	VAL
06/04/2017	KE14	SW	609.3	143.4	9.5	129.4	24.0	385.3	16.9	32.5	172.7	138.0	16.6	2.8	10.1
06/04/2017	h2-2	GW	<1.0	<1.0			3.4	10.5		16.1				<1.0	4.5
06/04/2017	h2-1	GW		<1.0			22.8	8.3	79.1	21.8		<5.0	<1.0	2.0	
06/04/2017	KE8	SW	2.8	3.5			26.7	10.9	25.2	25.7			<1.0	2.9	
06/04/2017	LU2	SW		<1.0			9.5	<5.0	62.9	8.2				1.1	
06/04/2017	h2-23	GW		<1.0			7.7	<5.0	37.2	5.6				<1.0	<2.0
09/10/2017	WI25	SW	<1.0	14.4	<1.0	<1.0	6.8	7.8	89.8	25.0	1.4	<5.0	<1.0	2.0	2.3
10/10/2017	P15	GW		3.9			57.6	31.9	15.2	9.6		<5.0	<1.0	5.4	
10/10/2017	P13	GW		13.9			8.7	71.1	191.5	<1.0					
10/10/2017	P12	GW		9.7			0.8	176.2	154.0	<1.0					
10/10/2017	P11	GW		96.4			2.6	>1000	814.0	10.0				5.3	
10/10/2017	P9	GW		1.2			9.5	12.7	19.3	24.4			<1.0		<2.0
10/10/2017	P14	GW		<1.0				15.5	11.7						
11/10/2017	TALB	SW		13.9			19.5	20.2	13.2					4.2	
11/10/2017	LU2	SW	1.0	15.7			6.3	28.1	173.2					2.4	<2.0
11/10/2017	LU26	SW		8.1			12.8	21.9	12.4	9.7				2.6	<2.0
11/10/2017	KE8	SW	<1.0	7.1			17.9	16.0	9.8	15.4		<5.0	<1.0	2.4	<2.0
11/10/2017	KE14	SW	439.7	448.2	13.8	173.8	20.5	291.3	22.3	26.2	131.1	173.7	16.2	2.7	13.5
11/10/2017	P8	GW	<1.0	5.7		<1.0	8.4	23.8	19.1	12.9		<5.0		1.2	<2.0
11/10/2017	P2	GW		3.7			54.4	32.6	354.3	9.5		<5.0	<1.0	5.3	
17/01/2018	P13	GW	1.5	<10.0			6.6	25.2	563.2	<0.5	<1.0	<0.5		<0.5	
17/01/2018	WI20	SW	3.4	89.3		<1.0	6.8	<10.0	57.7	17.8	<1.0	1.7		1.4	2.2
17/01/2018	KE8	SW	<0.5	20.8		<1.0	6.5	<10.0	<25.0	5.7				2.1	
17/01/2018	P9	GW		<10.0			7.4	50.5	<25.0	11.3			<0.5	<0.5	
17/01/2018	P14	GW		<10.0				26.0	<25.0	<0.5		<0.5			
17/01/2018	P2	GW		<10.0			34.1	<10.0	<25.0	<0.5		<0.5	<0.5	3.2	
17/01/2018	P8	GW	<0.5			1.6	6.0	13.2	<25.0	11.1	<1.0			0.8	0.7
31/01/2018	WI25	SW	<0.5	18.9			7.7	<10.0	383.8	<0.5	1.2	<0.5	<0.5	1.3	1.0
31/01/2018	P9	GW		<10.0			7.6	260.1	<25.0	13.0		<0.5	<0.5	<0.5	
31/01/2018	LU2	SW	<0.5	<10.0			4.3	<10.0	<25.0	<0.5		<0.5	<0.5	1.2	
31/01/2018	S16	SW	<0.5	<10.0			7.4	<10.0	<25.0	6.5		<0.5		1.0	
31/01/2018	P8	GW	<0.5	<10.0			6.0	14.2	<25.0	9.5				0.8	0.6
31/01/2018	PFL1	Lake	81.7	64.9	<5.0	28.5	3.5	167.9	234.9	<0.5	3.6	50.4	10.5	5.8	8.8
31/01/2018	P14	GW		<10.0				14.9	<25.0					<0.5	

31/01/2018	P2	GW		<10.0			34.0	11.0	<25.0	6.5		1.0	<0.5	3.5	
31/01/2018	P13	GW	<0.5	<10.0			17.6	<10.0	80.1	<0.5				<0.5	
31/01/2018	S15	SW	16.6	<10.0			20.2	<10.0	617.4	16.0	<1.0	<0.5	<0.5	1.8	
14/02/2018	P2	GW	<0.5	<10.0			36.7	11.2	<25.0	4.8		1.2	<0.5	3.5	<0.5
14/02/2018	P11	GW		<10.0			0.6	278.5	61.4	<0.5		<0.5		<0.5	
14/02/2018	P13	GW		<10.0			16.2	<10.0	64.2	<0.5		<0.5		<0.5	<0.5
14/02/2018	P9	GW		<10.0			6.8	>750.0	<25.0	9.4		<0.5	<0.5	<0.5	
14/02/2018	P8	GW	0.6	<10.0			6.8	17.1	<25.0	9.6		<0.5		0.8	0.6
14/02/2018	KE14	SW	449.1	158.7	11.9	138.8	17.5	282.9	<25.0	21.2	103.9	99.2	29.8	1.8	29.7
14/02/2018	h2-3	GW		<10.0			25.8	<10.0	<25.0	46.4		<0.5	<0.5	2.2	
14/02/2018	KE8	SW	2.4	<10.0			15.1	<10.0	<25.0	18.6		<0.5	<0.5	1.7	
14/02/2018	h2-1	GW		<10.0			24.7	<10.0	<25.0	49.8		<0.5	<0.5	<0.5	<0.5
14/02/2018	h2-23	GW					13.1	<10.0	<25.0	10.6		<0.5	<0.5	<0.5	
14/02/2018	P14	GW	<0.5	<10.0		<1.0	6.3	<10.0	<25.0	59.3			<0.5	<0.5	
14/02/2018	LU2	SW	<0.5	<10.0			3.8	<10.0	<25.0	<0.5		<0.5		1.0	<0.5
15/03/2018	WI25	SW	<1.0	7.1	<1.0		9.1	8.4	20.4	<25.0		<5.0	<5.0	<1.0	<1.0
15/03/2018	KE8	SW	<1.0	3.9	<1.0	<1.0	13.0	8.9	237.7	<25.0	<1.0	<5.0	<5.0	2.2	7.6
03/05/2018	PW1	Pore Water	<1.0	9.8		<1.0	8.9	10.5	15.7	<25.0	<1.0	<5.0	<5.0	<1.0	<1.0
28/05/2018	P27	GW	<1.0	<2.0	<1.0		23.7	11.7	149.7	<25.0	<1.0	<5.0	<5.0	2.7	<1.0
28/05/2018	P8	GW	<1.0	3.3	<1.0	<1.0	7.5	10.9	400.1	<25.0	<1.0	<5.0	<5.0	1.1	<1.0
28/05/2018	P8	GW	<1.0	3.5		<1.0	7.6	10.6	443.0	<25.0	<1.0	<5.0	<5.0	1.1	<1.0
28/05/2018	P14	GW	<1.0	<2.0		<1.0	<1.0	12.1	>750.0	<25.0		<5.0		<1.0	<1.0
28/05/2018	WI25	SW	<1.0	57.4		<1.0	7.8	13.5	5.9	<25.0	<1.0	<5.0	<5.0	6.3	<1.0
28/05/2018	P13	GW	<1.0	2.4			12.5	11.4	>750.0	<25.0	<1.0	<5.0		<1.0	<1.0
28/05/2018	P8	GW	<1.0	3.6	<1.0	<1.0	6.6	12.1	>750.0	<25.0	<1.0	<5.0		<1.0	<1.0
28/05/2018	KE8	SW	<1.0	2.7		<1.0	24.3	11.9	388.9	<25.0		<5.0	<5.0	3.5	<1.0
28/05/2018	P25	GW		8.8		<1.0	8.5	14.5	369.7	<25.0	<1.0	<5.0	<5.0	1.8	<1.0
28/05/2018	KE14	SW	<1.0	124.7	25.7	217.2	21.8	348.2	55.1	37.1	172.5	140.7	30.2	3.1	12.1
28/05/2018	P28	GW	<1.0	<2.0		<1.0	23.5	12.3	36.5	<25.0	<1.0	<5.0	<5.0	1.8	<1.0
28/05/2018	P14	GW	<1.0			<1.0	<1.0	7.6	<2.0	<25.0	<1.0	<5.0	<5.0	<1.0	<1.0
29/05/2018	P30	GW	<1.0	<2.0	<1.0	<1.0	15.6	11.0	14.2	<25.0	<1.0	<5.0	<5.0	1.6	<1.0
29/05/2018	WI20	SW	<1.0	64.5	<1.0	<1.0	5.5	14.7	186.6	<25.0	<1.0	<5.0	<5.0	9.4	<1.0
29/05/2018	P20	GW	<1.0	<2.0	<1.0		22.1	5.5	7.2	<25.0	<1.0	<5.0	<5.0	2.0	<1.0

29/05/2018	**P14**	**GW**	**<1.0**	**<2.0**	**<1.0**	**<1.0**	**<1.0**	**13.0**	**>750.0**	**<25.0**		**<5.0**		**<1.0**	**<1.0**
29/05/2018	**P29**	**GW**	**<1.0**	**<2.0**			**13.0**	**11.9**	**8.1**	**<25.0**	**<1.0**	**<5.0**	**<5.0**	**2.0**	**<1.0**
29/05/2018	**P21**	**GW**	**<1.0**	**<2.0**			**20.9**	**4.0**	**179.3**	**<25.0**	**<1.0**	**<5.0**	**<5.0**	**1.8**	**<1.0**
29/05/2018	**P19**	**GW**	**<1.0**	**<2.0**			**21.0**	**5.4**	**98.4**	**<25.0**	**<1.0**	**<5.0**	**<5.0**	**<1.0**	**<1.0**
29/05/2018	**P17**	**GW**	**<1.0**	**<2.0**		**<1.0**	**17.1**	**<5.0**	**169.9**	**47.3**	**<1.0**	**<5.0**	**<5.0**	**<1.0**	**<1.0**
29/05/2018	**P31**	**GW**	**<1.0**	**<2.0**			**30.8**	**14.4**	**99.6**	**<25.0**		**<5.0**	**<5.0**	**<1.0**	**<1.0**
02/07/2018	**P26**	**GW**		**<2.0**	**<1.0**		**25.5**	**8.7**	**16.5**	**<25.0**	**<1.0**	**<5.0**	**<5.0**	**<1.0**	**<1.0**
02/07/2018	**LA29**	**SW**	**<1.0**	**5.1**		**2.1**	**8.5**	**1.0**	**37.4**	**<25.0**		**<5.0**	**<5.0**	**1.6**	**<1.0**
02/07/2018	**WI20**	**SW**	**<1.0**	**18.1**			**7.0**	**10.8**	**<2.0**	**<25.0**	**<1.0**	**<5.0**		**7.6**	**<1.0**
02/07/2018	**WI25**	**SW**	**<1.0**	**14.6**		**<1.0**	**8.4**	**13.1**	**12.1**	**<25.0**	**<1.0**	**<5.0**		**7.8**	**<1.0**
02/07/2018	**P20**	**GW**	**<1.0**	**<2.0**			**23.7**	**8.1**	**13.4**	**<25.0**	**<1.0**	**<5.0**	**<5.0**	**2.2**	**<1.0**
02/07/2018	**LU29**	**SW**	**<1.0**	**4.8**	**<1.0**	**<1.0**	**11.7**	**<5.0**	**264.0**	**<25.0**	**<1.0**	**<5.0**	**<5.0**	**2.0**	**<1.0**
03/07/2018	**P8**	**GW**	**<1.0**	**2.6**		**<1.0**	**7.3**	**9.6**	**<2.0**	**<25.0**	**<1.0**	**<5.0**		**<1.0**	**<1.0**
03/07/2018	**P8**	**GW**	**<1.0**	**2.5**		**<1.0**	**8.1**	**9.3**	**<2.0**	**<25.0**	**<1.0**	**<5.0**		**<1.0**	**<1.0**
03/07/2018	**P31**	**GW**	**<1.0**	**<2.0**	**<1.0**	**<1.0**	**30.9**	**14.3**	**4.7**	**<25.0**	**<1.0**	**<5.0**	**<5.0**	**2.8**	**<1.0**
03/07/2018	**P8**	**GW**	**<1.0**	**2.6**		**<1.0**	**7.4**	**9.3**	**2.4**	**<25.0**	**<1.0**	**<5.0**	**<5.0**	**<1.0**	**<1.0**
03/07/2018	**P21**	**GW**	**<1.0**	**<2.0**			**16.6**	**<5.0**	**5.9**	**<25.0**	**<1.0**	**<5.0**	**<5.0**	**1.4**	**<1.0**
04/07/2018	**P30**	**GW**	**<1.0**	**<2.0**			**22.0**	**15.4**	**46.1**	**25.8**	**<1.0**	**<5.0**	**<5.0**	**1.7**	**<1.0**
04/07/2018	**P30**	**GW**	**<1.0**	**<2.0**	**<1.0**	**<1.0**	**22.5**	**23.5**	**30.6**	**26.6**	**<1.0**	**<5.0**	**<5.0**	**1.6**	**<1.0**
04/07/2018	**P29**	**GW**	**<1.0**	**<2.0**		**<1.0**	**17.6**	**28.4**	**5.4**	**<25.0**	**<1.0**	**<5.0**	**<5.0**	**2.4**	**<1.0**
04/07/2018	**P14**	**GW**	**<1.0**	**<2.0**		**<1.0**	**<1.0**	**<5.0**	**<2.0**	**<25.0**	**<1.0**	**<5.0**	**<5.0**	**<1.0**	**<1.0**
04/07/2018	**P8LF**	**GW**	**<1.0**	**2.1**		**<1.0**	**6.4**	**7.9**	**<2.0**	**<25.0**	**<1.0**	**<5.0**	**<5.0**	**<1.0**	**<1.0**
04/07/2018	**KE14**	**SW**	**263.6**	**47.8**	**12.6**	**87.8**	**10.8**	**114.4**	**29.7**	**<25.0**	**40.1**	**42.6**	**13.6**	**2.5**	**<1.0**
16/07/2018	**FURT1**	**SW**	**<1.0**	**<2.0**			**0.5**	**<5.0**	**7.5**	**<25.0**	**<1.0**	**<5.0**		**<1.0**	**<1.0**
16/07/2018	**LWier1**	**SW**	**<1.0**	**<2.0**		**<1.0**	**<1.0**	**<5.0**	**7.4**	**<25.0**	**<1.0**	**<5.0**		**1.1**	**<1.0**
07/08/2018	**P21**	**GW**	**<1.0**	**<2.0**	**<1.0**		**23.2**	**11.2**	**5.3**	**<25.0**	**<1.0**	**<5.0**	**<5.0**	**<1.0**	**<1.0**
07/08/2018	**P19**	**GW**	**<1.0**	**<2.0**		**<1.0**	**26.6**	**11.1**	**<2.0**	**<25.0**	**<1.0**	**<5.0**	**<5.0**	**<1.0**	**<1.0**
07/08/2018	**KE14**	**SW**	**38.2**	**8.0**	**1.4**	**6.1**	**1.5**	**21.6**	**72.9**	**<25.0**	**6.4**	**13.4**	**<5.0**	**<1.0**	**1.9**
08/08/2018	**P25**	**GW**	**<1.0**	**4.6**		**<1.0**	**11.4**	**18.3**	**<2.0**	**<25.0**	**<1.0**	**<5.0**	**<5.0**	**3.1**	**<1.0**
08/08/2018	**P13**	**GW**	**<1.0**	**<2.0**		**<1.0**	**24.5**	**21.3**	**157.9**	**<25.0**		**7.5**		**<1.0**	**<1.0**
08/08/2018	**P9**	**GW**	**<1.0**	**<2.0**		**<1.0**	**7.2**	**>750**	**25.8**	**<25.0**		**<5.0**	**<5.0**	**<1.0**	**<1.0**
08/08/2018	**P17**	**GW**	**<1.0**	**<2.0**		**<1.0**	**13.6**	**17.3**	**14.2**	**40.6**	**<1.0**	**<5.0**	**<5.0**	**2.3**	**<1.0**
29/01/2019	**KE14**	**SW**	**582.4**	**221.1**	**9.8**	**112.0**	**17.2**	**>250**	**62.7**	**23.7**	**112.8**	**82.0**	**52.5**		**63.0**
29/01/2019	**FA27**	**SW**	**<1.0**	**2.7**			**23.8**	**27.9**	**26.9**	**14.9**	**1.8**		**<1.0**		
29/01/2019	**P31**	**GW**		**<2.0**			**29.2**	**19.9**	**<1.0**	**20.4**			**<1.0**		
29/01/2019	**LU29**	**SW**					**3.5**	**<6.0**	**42.4**						
29/01/2019	**P30**	**GW**					**24.2**	**33.0**	**<1.0**	**22.5**			**<1.0**		
29/01/2019	**P26**	**GW**					**32.0**	**25.9**	**5.8**	**24.6**			**<1.0**		
29/01/2019	**KE14**	**SW**	**619.3**	**233.0**	**10.3**	**119.1**	**17.9**	**>250**	**62.7**	**24.2**	**119.2**	**85.6**	**54.2**		**68.5**
29/01/2019	**P2**	**GW**					**30.2**	**121.6**	**4.3**	**7.3**					

29/01/2019	P11	GW						>250	71.4	7.9					
29/01/2019	P8	GW	18.3	3.3		24.9	5.9	44.7		8.4	2.2				30.6
29/01/2019	P25	GW	<1.0	4.8			5.0	10.3	<1.0	9.0			<1.0	<1.0	<1.0
29/01/2019	KE14	SW	576.0	219.1	<10.0	105.7	17.4	<6.0	61.2	23.3	107.8	79.3	48.3		70.2
29/01/2019	P8	GW	32.9	5.9		48.3	10.1	77.7	0.5	15.2	4.6				66.8
29/01/2019	P29	GW		<2.0			10.2	10.5	1.3	29.9			<1.0		<1.0
29/01/2019	P8	GW	30.9	5.8		47.0	9.9	76.2		14.9	4.2				63.6
29/01/2019	WI25	SW	2.3	5.9			8.7	<6.0	58.2	18.1					<1.0
29/01/2019	P27	GW					24.8	11.8		15.8			<1.0		
29/01/2019	KE8	SW	<1.0	2.3			7.5	<6.0	5.2						
29/01/2019	P28	GW		2.0			24.1	18.9		22.1			<1.0		
30/01/2019	P20	GW					19.8	24.6	5.5	11.5			<1.0		
30/01/2019	P9	GW					9.2	>250	1.6	15.9			<1.0		
30/01/2019	P14	GW						37.8	4.6						
30/01/2019	P9	GW					8.5	>250	1.3	13.7					
30/01/2019	P22	GW					9.9	25.6	6.1	38.2					
30/01/2019	P21	GW					24.1	13.6	9.5	23.4					
30/01/2019	P13	GW					2.3	<6.0	8.8	38.4					
30/01/2019	P17	GW					13.5	20.0		22.8			<1.0		
30/01/2019	P22	GW					15.7	35.5	10.7	53.5					
30/01/2019	P19	GW					17.5	21.8	2.6	13.4			<1.0		
25/03/2019	LA29	SW					6.4	<6.0							
25/03/2019	P30	GW		<2.0			10.9	8.5		12.7			<1.0		
25/03/2019	P20	GW		<2.0			17.2	7.3	300.3	10.3		8.5	<1.0		
25/03/2019	P2	GW		<2.0			14.5	23.7	1.2				<1.0	1.7	
25/03/2019	P31	GW		<2.0			33.3	21.1	262.1	16.3		6.6	<1.0		
25/03/2019	P22	GW		<2.0			15.1	7.8	176.2	42.7		<5.0			
25/03/2019	P31	GW		<2.0			29.5	20.4	223.3	14.5		5.8			
25/03/2019	P17	GW		<2.0			16.3	15.7	195.8	37.0		5.2	<1.0		
25/03/2019	P28	GW		<2.0			28.8	22.2	339.0	22.2		9.4	<1.0		
25/03/2019	P31	GW		<2.0			26.1	18.6	243.2	14.2		5.6			
25/03/2019	LA29	SW		<2.0			7.6	<6.0	1.5	6.3			<1.0		
25/03/2019	P19	GW	<1.0	<2.0			28.6	6.4	244.5	13.5		7.6	<1.0		
26/03/2019	P9	GW					9.0	>250	1.8	20.8			<1.0		
26/03/2019	h2-5	GW	2.1	89.2		3.3	11.9	77.5	13.2	20.8	32.1	65.6	1.5		
26/03/2019	KE14	SW	371.4	446.0	7.8	93.7	12.7	235.6	54.4	15.8	79.0	98.9	37.9		21.6
26/03/2019	KE14	SW	399.0	470.5	9.0	104.8	14.1	>250	162.1	18.0	94.8	119.9	42.3		28.4
26/03/2019	KE14	SW	402.9	466.8	8.6	104.8	15.2	>250	86.0	17.9	85.5	109.3	44.2		28.1
26/03/2019	KE8	SW		9.0			10.9	14.8	137.9	7.0		5.1			

26/03/2019	**WI25**	**SW**		**6.5**			**8.4**	**<6.0**	**24.5**	**18.1**					**1.6**
26/03/2019	**FA27**	**SW**		**4.6**			**17.5**	**9.0**	**5.9**	**9.7**			**<1.0**		**<1.0**
26/03/2019	**P14**	**GW**		**<2.0**				**27.1**	**244.2**			**9.8**			
26/03/2019	**P8**	**GW**	**16.1**	**5.7**		**24.6**	**9.5**	**40.8**	**156.2**	**12.0**	**2.6**	**5.7**			**26.3**
26/03/2019	**P9**	**GW**		**<2.0**			**10.4**	**>250**	**108.2**	**23.9**		**6.1**	**<1.0**		
26/03/2019	**P26**	**GW**		**15.7**			**31.2**	**15.6**	**158.4**	**25.2**		**<5.0**	**<1.0**		**<1.0**
26/03/2019	**P27**	**GW**		**4.8**			**26.1**	**18.7**	**151.7**	**15.9**		**5.7**	**<1.0**		
26/03/2019	**P9**	**GW**					**7.8**	**>250**	**1.7**	**18.7**			**<1.0**		
26/03/2019	**KEh2-5**	**SW**	**414.7**	**<2.0**	**8.9**	**112.2**	**13.7**	**>250**	**18.6**	**27.3**	**93.8**	**103.6**	**42.6**		**26.4**

Table S.I.4. Summary of concentrations measured in all samples over the course of study. GW = groundwater, SW = Surface water. Numbers preceded by < signify values below LOQ, and above LOD. Changes in LOQ result from separate measurement series. Blank cells indicate values below the limit of detection (LOD).

Table S.I.4. lists the comprehensive results for each individual sample across all sampling and measurement campaigns. It should be noted that values listed < numerical LOQ are in fact between the limit of detection (LOD), as determined from the laboratory concentration curve, and the LOQ. No peaks were detected below the LOD.

	Oct-17		**Feb-18**		**Aug-18**		**May-19**	
	h2-2	**KE14**	**P14**	**PFL**	**WB20**	**P30**	**P20**	**P27**
4ACE	1.0	134.2		59.3		89.8	124.5	100.0
5MB	101.4	105.6	88.2	116.8	38.9	46.9	112.2	109.6
ATE		115.5	96.3				126.3	107.0
ATEA		104.8		104.5			106.7	88.9
ATR	103.8	113.2	79.3	96.4	120.7	75.9	130.4	109.9
BTZ	113.5	113.2	123.3	67.1		52.0	106.5	83.7
CAF		105.7	102.1		251.3		88.2	141.5
CMD	105.8				114.2			97.6
HCL		108.3	103.8	99.0			102.8	
LAM		115.3	96.7	85.4			128.8	109.3
SULF		94.1		80.5			92.1	92.5
TERBZ	97.5	101.7		95.5	111.1	91.6		
VAL	89.2	80.7	92.9	94.2				

Table S.I.5. Calculation of relative recoveries of each compound (in percentage) across each measurement series (equation S.I.16).

Table S.I.5. lists the relative recoveries (RR) of each compound, calculated from two spiked samples (listed in the second row) for each measurement series. Relative recoveries are determined by comparing environmental samples spiked with a laboratory standard of known concentration with their un-spiked counterparts (equation S.I.16.).

$$\% RR = \frac{[C_{spiked}] - [C_{unspiked}]}{[C_{calibration\ standard}]} * 100 \qquad \text{(S.I.16.)}$$

Kaplan-Meier Estimators – Survival Analysis

The Kaplan-Meier estimator is a common method used for censored datasets in medical sciences – hence its categorization as 'survival analysis' – but in fact can handle censored datasets for any application. It can handle both left-censored data (values below the lower LOQ) and right-censored data (values above the upper LOQ). The principal conditions for using the Kaplan-Meier method are as such: at least 3 detections and 50% or fewer censored observations should be available, multiple reporting limits must be present, and the lowest measured value should be uncensored. Small data sets are however associated with greater uncertainty, and the fewer the samples, the less censoring there should be. In our case, the condition of multiple reporting limits was met due to the fact that a different LOQ was determined for each of four measurement sequences, and for each compound individually. When these conditions of multiple LOQs or uncensored lowest value are not met, it is possible to apply Efron's bias corrector, which essentially treats one censored data point with the lowest LOQ as an un-censored value. This requires substitution, albeit only at one censored data point instead of at all censored data points, keeping bias as low as possible.

The survival function is expressed as a product function $\prod$:

$$S(j) = \prod_{j=1}^{k} \frac{b_j - d_j}{b_j} \qquad \text{(S.I.17)}$$

where S are the incremental survival probabilities, computed for each value j, b is the number of all observations at and below each detected concentration, and d is the number of uncensored concentrations. This incremental probability is conceptualized as the probability of "surviving" to the next lowest uncensored concentration, accounting for the number of data points below that concentration (Helsel, 2012).

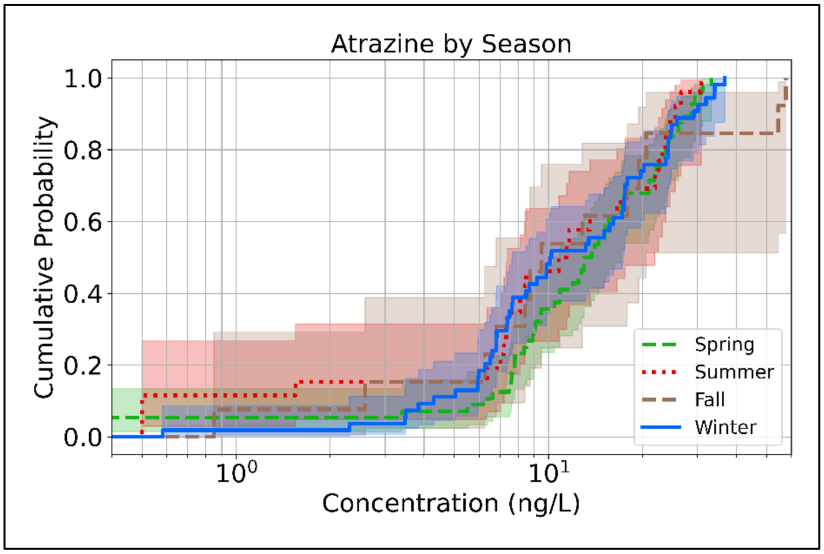

Figure S.I.10. Kaplan-Meier curve of Atrazine as a function of season, including confidence intervals. Only the upper percentiles of fall are clearly separated from the other seasonal curves.

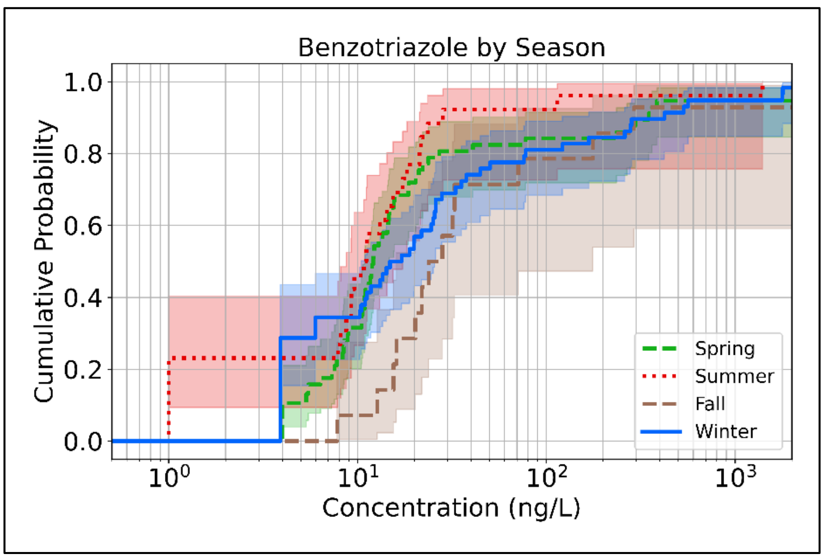

Figure S.I.11. Kaplan-Meier curve of Benzotriazole as a function of season, including confidence intervals.

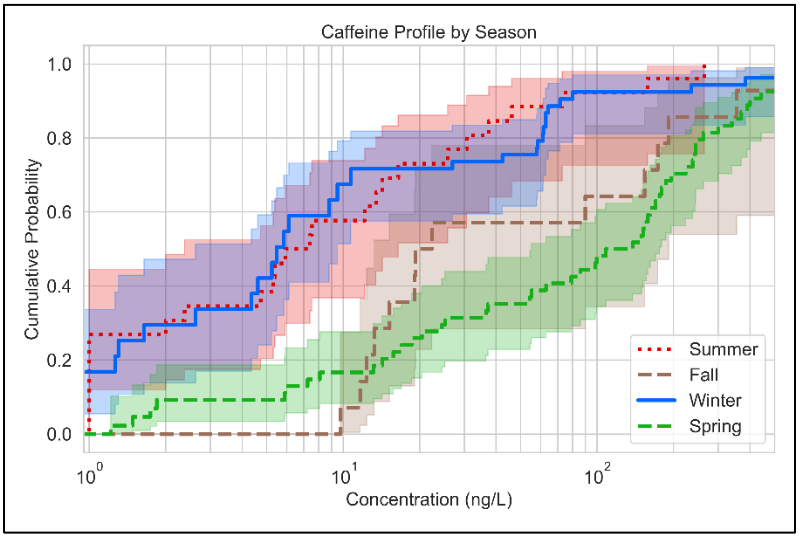

Figure S.I.12. Kaplan-Meier curve of Caffeine as a function of season, including confidence intervals. Despite overlaps in confidence intervals, spring and fall are clearly separated from summer and winter.

Spatio-Temporal Micropollutant Patterns

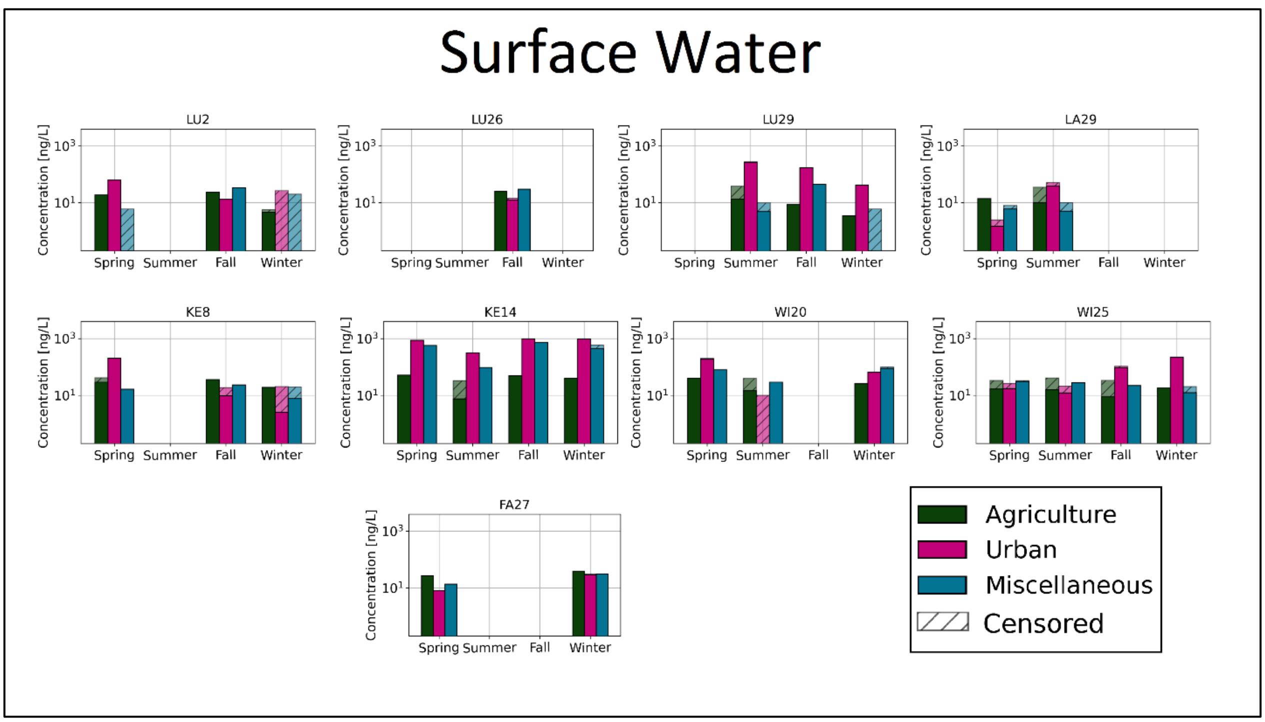

Figure S.I.13. Seasonal micropollutant profile at each sampled surface water point. Note that for seasons where bars are absent, no measurement was made.

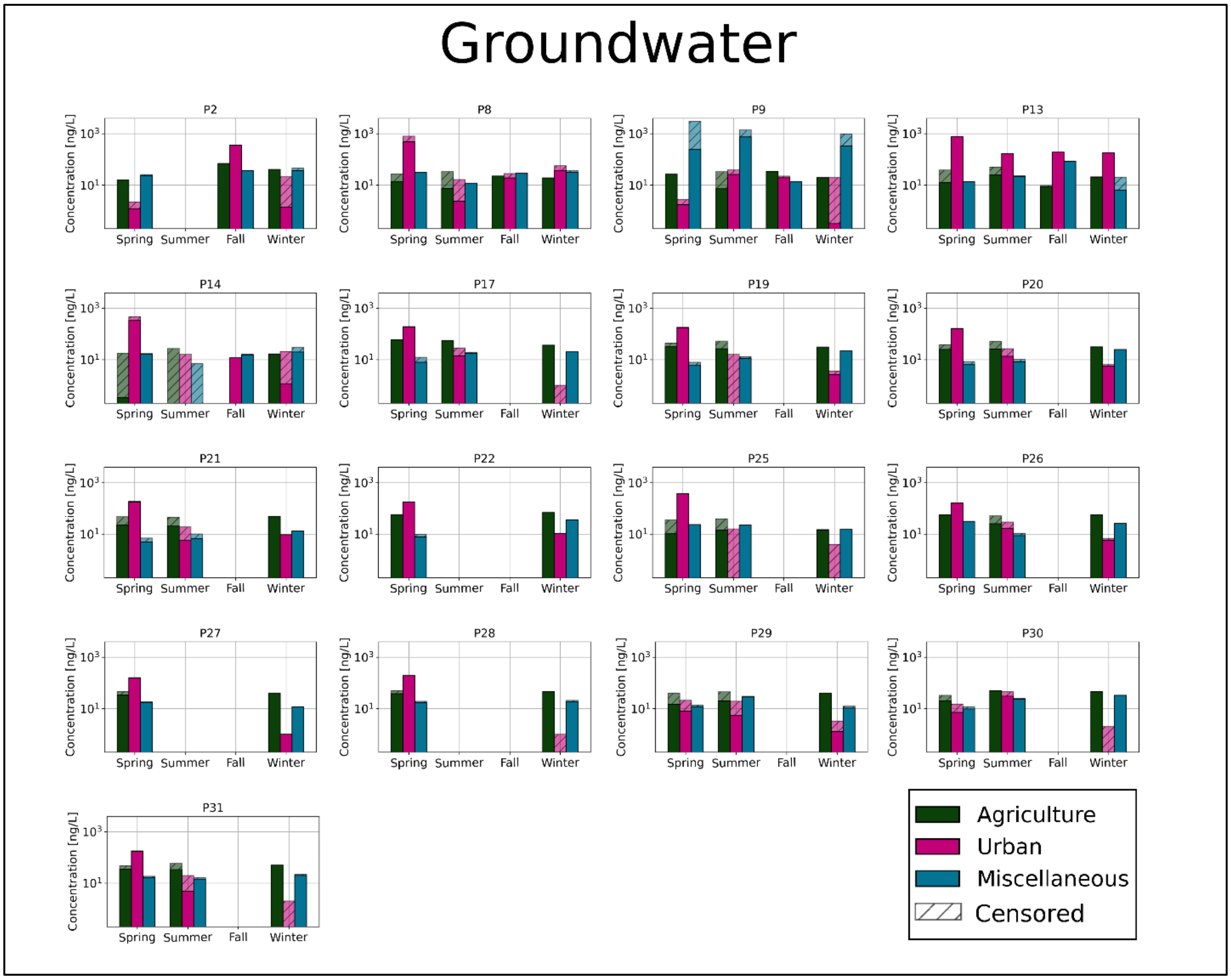

Figure S.I.14. Seasonal micropollutant profile at each sampled surface water point. Note that for seasons where bars are absent, no measurement was made.