https://doi.org/10.35662/unine-thesis-2917

DISSERTATION

Characterizing Groundwater Quality, Recharge and Distribution under Anthropogenic conditions

Presented to the Faculty of Science of the University of Neuchâtel to satisfy the requirements for Doctor of Philosophy in Science

By:

Nicole Marianne Burri
2021

PhD Committee:

Prof. Dr Mario Schirmer
Prof Dr Daniel Hunkeler
Dr Christian Moeck
Prof Dr Grzegorz Malina

Faculté des Sciences
Secrétariat-décanat de Faculté
Rue Emile-Argand 11
2000 Neuchâtel – Suisse
Tél : + 41 (0)32 718 21 00
E-mail : secretariat.sciences@unine.ch

IMPRIMATUR POUR THESE DE DOCTORAT

La Faculté des sciences de l'Université de Neuchâtel autorise l'impression de la présente thèse soutenue par

Madame Nicole BURRI

Titre:

"Characterizing Groundwater Quality, Recharge and Distribution under Anthropogenic Conditions"

sur le rapport des membres du jury composé comme suit:

- **Prof. tit. Mario Schirmer**, directeur de thèse, UniNE
- **Prof. Daniel Hunkeler,** rapporteur, UniNE
- **Dr Christian Moeck,** rapporteur, Eawag, ETH domain, Dübendorf
- **Prof. Greg Malina**, rapporteur, Częstochowa Univ. of Technology, Poland

Neuchâtel, le 24 août 2021

Le Doyen, Prof. A. Bangerter

Die Quelle der Thur

Auf dem Küheboden bei Unterwasser lebte ein wohlhabender Bauer. Seine Tochter hatte sich mit dem Nachbarssohn verlobt und stieg eines Tages hinauf auf die Alp Laui, um ihre Freundin, die Sennerin, zur Hochzeit einzuladen.

Unterwegs sprach sie ein fremder, ausgesprochen freundlicher Jüngling an, umschmeichelte sie und hielt inständig um ihre Hand an. Die junge Frau wusste kaum wie geschah, vergass ihren Bräutigam und gelobte dem Fremden, seine Frau zu werden. Nach einem heftigen Streit mit ihren Eltern, lief sie bei einbrechender Nacht davon und eilte auf die Alp, zu ihrem Geliebten, der sie innig küsste.

Doch als die Braut die Augen wieder aufschlug, lag sie in den Armen vom abgrundtief hässlichen, bösen, uralten Berggeist vom Säntis. ‘Du gehörst jetzt mir und du bist nicht etwa die Erste’, höhnte dieser, ‘auch deine Tränen werden von nun an die Quelle der Thur speisen, damit sie niemals versiege’. Seither sind viele Jahrhunderte verflossen und die Thur fliesst munter weiter. Denn es heisst, der Berggeist finde immer wieder ein Mädchen, das seinem Zauber erliege.

-Toggenburger Saga

The Source of the Thur River

Once upon a time, a wealthy farmer living below Alp Laui, near the source of the Thur River, had a daughter who was engaged to the neighbour's son. One day, the daughter climbed up to Alp Laui to invite her friend to the wedding.

On her way up the mountain, a strange endearing young man approached the daughter, and flatteringly asked her to marry him. The young woman, swept off her feet hardly knew what happened. She promptly forgot her bridegroom and vowed to become the stranger’s wife. That evening, after a fierce quarrel with her parents over the arrangement, the daughter ran away from home, up to Alp Laui, and into the arms of her lover.

Embracing her, he kissed her tenderly as she closed her eyes. But when the daughter opened her eyes again, she found herself in the arms of the ancient, evil, mountain spirit of the Säntis. 'You belong to me now’ he sneered, 'your tears will be the source that feeds the spring of Thur River so that it will never run dry’. Many centuries have passed since, and the Thur River continues to flow, for it is said that the spirit of the Säntis Mountain will always find a girl willing to succumb to his magic.

-Legend from the Toggenburg

Table of Contents

Acknowledgments

The journey that was my PhD was made possible by a great number of people and various institutions. Of the people who have made it possible I would firstly like to thank my parents, who have always supported me no matter the shape or size of my dreams, I would like to thank them for their enduring love and encouragement. Secondly, and with all my heart, I would like to thank my husband Nic Grech-Cumbo, for all his support and understanding, for being my anchor in the storm, and most importantly for sticking it out with me. I am most fortunate to be surrounded by such a loving and supportive family.

A heartfelt thank you goes out to my supervisor Mario Schirmer, both for giving me this opportunity and for his endless support and guidance. Your support, integrity, and generosity is something I will carry with me from here onwards as something to aspire towards in my own work. My deepest gratitude also goes out to Christian Moeck for all his time and input into my work; it would not have been possible without you. Furthermore, I would like to thank all of my colleagues in the Hydrogeology group and by extension the W+T Department at Eawag, for all of the stimulating discussions, lunch hours spent at the river, and generally supportive atmosphere. A special thank you to my office mates Robin Weatherl and Max Ramgraber for their humour, great scientific discussions, support, and shared love of coffee. I would also like to thank Lisa Hoffman for her work and contributions to this research, and Sandra Pool for all her insightful comments and suggestions. In addition, I would like to thank Reto Brit, Rosi Siber and Caroline Stengel for all their patience and technical support.

A sincere thank you to Daniel Hunkeler from the Centre for Hydrogeology and Geothermics at the University of Neuchâtel and Grzegorz Malina from the Department of Hydrogeology and Engineering Geology at the AGH University in Krakow for taking precious time to review my dissertation, and for adding input and value to this work. My gratitude also goes to the members of the of the Department of Environmental Affairs of the cantons Thurgau and St. Gallen, in particular to Sherin Hohl and Andreas Scholtis for their time and efforts in the field.

The hours of work which went into this dissertation would have been so much harder without the support of my extended South African family and friends. Thank you for your tireless encouragement, photos, and tales from home to keep me motivated. In addition, I would like to thank both my old and new friends in Switzerland, who have all become like family to me. Thank you for getting me through the tough (and for a South African often much too cold) times in Switzerland with the provision of great food, laughter, and excellent company.

Lastly, I would like to acknowledge the Swiss Federal Institute of Aquatic Science & Technology (Eawag) for providing such a fantastic working environment, as well as the Swiss National Science Foundation who provided the funding for this research project (grant agreement No 200021_169003).

Summary

Awareness concerning sustainable groundwater management is gaining traction and calls for adequate understanding of the complexities of natural and anthropogenic processes and how they affect groundwater quality and availability. This research project aimed to investigate different qualitative impacts on groundwater, and provide assessment methodologies that can be employed to ensure sustainable quantitative groundwater use. The study site, situated in north-eastern Switzerland, included groundwater systems located in minor and major alluvial deposits associated both with high elevation and plains regions. The Thur River catchment presents a study area that is both well investigated and of a large enough size (~1700 km^2) to be considered a mesoscale catchment. Specific objectives of this research project included 1) the determination of the major controls on groundwater contamination, 2) the assessment of the spatiotemporal variability of groundwater recharge, in a manner applicable to other catchments, and 3) the monitoring of groundwater in an adaptive and event-based manner. These research objectives were addressed by first reviewing historic and current qualitative threats to groundwater concerning anthropogenic processes and how they affect groundwater quality globally. Secondly, the spatiotemporal groundwater recharge in the mesoscaled Thur catchment was estimated, based on open-source data and software. Finally, variabilities of source water contributions to aquifers located in the Thur catchment were determined using environmental tracer data from sampled sites. The structure of this dissertation spans three different scales ranging from global, to mesoscale, and to localized sampling, and covers subsequent different levels of data availability.

In order to illustrate the many qualitative threats to groundwater resources, some of the key contaminants originating from anthropogenic activities, namely agricultural, urban, and industrial, were presented in the form of a review. Furthermore, a selection of case studies describing the continued concerns of both established, as well as new and emerging contaminants were presented. As demands on groundwater continue to increase, in addition to groundwater quality, it is also imperative to consider the sustainable management of groundwater quantity. For this, knowledge concerning a catchment's spatiotemporal groundwater recharge, and the dominant water sources controlling surface-groundwater dynamics, is vital. In many regions however, groundwater recharge remains challenging to quantify, whether due to hydrogeological process complexities or limited observation data. Gridded components from readily available remotely sensed and ground-based data, including precipitation, actual evapotranspiration, and hydrological discharge data (separated into quick- and baseflow), were used to generate spatiotemporal groundwater recharge maps over a 20-year period (2000 - 2019) using open source software. Results from the gridded groundwater recharge estimates agreed well with estimates from other studies, and overall, recharge was shown to account for 29% of total precipitation in the Thur catchment. Results highlighted the importance of precipitation to groundwater recharge, with prolonged periods of drought having a negative effect on groundwater recharge, while periods of above average rainfall had a buffering effect on the Thur catchment's groundwater resources.

River water represents a connection between the surface and sub-surface environment. Between 2017 and 2020, Thur River water was collected during extreme events (high- and low flow), and analysed for its conservative tracer ($\delta^{18}O$ and $\delta^{2}H$) content. These event-sampled surface waters were analysed in conjunction with groundwater and rainwater samples to characterize the spatiotemporal water dynamics in the Thur catchment. Using a

cluster and three end-member mixing analysis, the spatiotemporal variability of different source water components contributing to the Thur catchment's aquifers were identified. Source water variabilities of aquifers were found to be dependent on both elevation and geology, with different water sources dominating different regions of the Thur catchment. A surface water-type was found to be a dominant source in the high elevation regions, while a groundwater-type dominated the middle elevation regions, and a rainwater-groundwater mix the low elevation regions. A clear shift towards groundwater signatures during dry event conditions was observed in the event-sampled river water, with groundwater making up an overall average of 30% of the surface water sampled in the Thur catchment.

This research project highlighted key contaminants that originate from anthropogenic activities, as well as the complexities involved in understanding the underlying physical processes and factors governing groundwater quality, including climate, geological settings, topography, and land use. Pertinent case studies emphasized persistent uncertainties concerning contaminant degradation processes, contaminant pathways, and subsequent contamination risks to groundwater quality. Where groundwater quantity is concerned, this study demonstrated the value of remotely sensed data in estimating the spatiotemporal recharge of a mesoscale catchment, in particular where observation data is limited, but also emphasised the importance of continued ground-based monitoring networks. Finally, investigations demonstrated the variability of river and groundwater source components in the Thur catchment, where event-based samples provided a relatively inexpensive insight into the surface-groundwater characteristics of a mesoscale catchment.

Résumé

La prise de conscience concernant la gestion durable des eaux souterraines gagne du terrain. Elle implique une compréhension adéquate de la complexité des processus naturels et anthropiques et de la manière dont ils affectent la qualité et la disponibilité des eaux souterraines. Ce projet de recherche visait à étudier les différents impacts qualitatifs sur les eaux souterraines et à fournir des méthodologies d'évaluation qui peuvent être employées pour assurer une utilisation quantitative durable des eaux souterraines. Le site d'étude, au nord-est de la Suisse, comprend des systèmes d'eaux souterraines situés à la fois dans des régions d'altidude et dans des plaines alluviales. Le bassin versant de la rivière Thur est une zone à la fois bien étudiée et d'une taille suffisamment grande (~1700 km^2) pour être considérée comme un bassin versant à méso-échelle. Les objectifs spécifiques de ce projet de recherche comprenaient 1) la détermination des principaux contrôles de la contamination des eaux souterraines, 2) l'évaluation de la variabilité spatio-temporelle de la recharge des eaux souterraines, d'une manière applicable à d'autres bassins versants, et 3) la surveillance des eaux souterraines d'une manière adaptative et basée sur les événements. Ces objectifs de recherche ont été abordés en examinant d'abord les menaces qualitatives passées et présentes pour les eaux souterraines, es processus anthropogéniques et la façon dont ces derniers affectent la qualité des eaux souterraines à l'échelle mondiale. Ensuite, la recharge spatio-temporelle des eaux souterraines dans le bassin versant de la Thur a été estimée sur la base de données et de logiciels libres. Enfin, la variabilité des contributions des sources d'eau aux aquifères situés dans le bassin versant de la Thur a été déterminée en utilisant des données de traceurs conservateurs provenant de sites échantillonnés dans tout le bassin versant. La structure de cette thèse s'étend sur trois échelles différentes, allant de l'échelle globale, à la méso-échelle, et à l'échantillonnage localisé, et couvre ensuite différents niveaux de disponibilité des données.

Afin d'illustrer les nombreuses menaces qualitatives qui pèsent sur les ressources en eau souterraine, certains des principaux contaminants issus des activités anthropiques, à savoir agricoles, urbaines et industrielles, ont été présentés sous la forme d'une revue de littérature. En outre, une sélection d'études de cas décrivant les préoccupations continues au sujet des contaminants établis, ainsi que des contaminants nouveaux et émergents, a été présentée. Alors que la demande en eaux souterraines continue d'augmenter, il est impératif de considérer non seulement leur qualité, mais aussi la gestion durable de leur quantité. Pour cela, il est crucial de connaître la recharge spatio-temporelle des eaux souterraines d'un bassin versant et les sources d'eau dominantes qui contrôlent la dynamique des eaux de surface et des eaux souterraines. Dans de nombreuses régions, la recharge des eaux souterraines reste difficile à quantifier, que ce soit en raison de la complexité des processus hydrogéologiques ou de données d'observation limitées. Composantes maillées à partir de données de télédétection et de données au sol facilement disponibles, y compris les précipitations, l'évapotranspiration réelle et les données de décharge hydrologique (séparées en débit rapide et débit de base), ont été utilisés pour générer des cartes spatio-temporelles de recharge des eaux souterraines sur une période de 20 ans (2000 - 2019). Les résultats de la grille d'estimation de la recharge sont en accord avec les estimations d'autres études, et dans l'ensemble, la recharge représente 29% des précipitations totales dans le bassin versant de la Thur. Les résultats ont mis en évidence l'importance des précipitations pour la recharge des eaux souterraines, les périodes prolongées de sécheresse ayant un effet négatif, tandis

que les périodes de précipitations supérieures à la moyenne ont un effet tampon sur les ressources.

L'eau des rivières représente une connexion entre l'environnement de surface et de subsurface. Entre 2017 et 2020, l'eau de la rivière Thur a été collectée lors d'événements extrêmes (haut et bas débit), et analysée pour son contenu en traceurs conservateurs ($\delta^{18}O$ et $\delta^{2}H$). Ces eaux de surface échantillonnées lors d'événements ont été analysées conjointement avec des échantillons d'eaux souterraines et d'eaux de pluie pour caractériser la dynamique spatio-temporelle de l'eau dans le bassin versant de la Thur. En utilisant une analyse de « clustering » et une EMMA (« End-Member Mixing Analysis »), la variabilité spatio-temporelle des différentes sources d'eau contribuant aux aquifères du bassin versant de la Thur a été identifiée. La variabilité des sources d'eau des aquifères s'est avérée dépendre à la fois de l'altitude et de la géologie, avec différentes sources d'eau dominant différentes régions du bassin versant de la Thur. Un type d'eau de surface s'est avéré être une source dominante dans les régions de haute altitude, tandis qu'un type d'eau souterraine dominait les régions d'élévation moyenne, et un mélange d'eau de pluie et d'eau souterraine les régions de basse élévation. Un changement clair vers des signatures d'eau souterraine a été observé dans l'eau de rivière échantillonnée pendant des conditions d'événement sec, avec l'eau souterraine constituant une moyenne globale de 30% de l'eau de surface échantillonnée.

Ce projet de recherche a mis en évidence les principaux contaminants qui proviennent des activités anthropiques, ainsi que la complexité des processus physiques sous-jacents et des facteurs qui régissent la qualité des eaux souterraines, notamment le climat, la géologie, la topographie et l'utilisation des terres. Des études de cas ont souligné les incertitudes persistantes concernant les processus de dégradation des contaminants, les voies de contamination et les risques de contamination subséquents des eaux souterraines. En ce qui concerne la quantité d'eau souterraine, cette étude a démontré la valeur des données de télédétection dans l'estimation de la recharge spatio-temporelle d'un bassin versant à méso-échelle, en particulier lorsque les données d'observation sont limitées, mais a également souligné l'importance des réseaux de surveillance continue au sol. Enfin, les investigations ont démontré que les échantillons basés sur les événements permettent de fournir un aperçu relativement peu coûteux des caractéristiques des eaux de surface et souterraines d'un bassin versant à méso-échelle.

Zusammenfassung

Das Bewusstsein für eine nachhaltige Grundwasserbewirtschaftung nimmt zu und erfordert ein angemessenes Verständnis der komplexen natürlichen und anthropogenen Prozesse und deren Auswirkungen auf die Grundwasserqualität und -verfügbarkeit. Ziel dieses Forschungsprojekts war es zu untersuchen, wie sich verschiedenen Einflüsse auf die Grundwasserströmungssysteme auswirken und welche Bewirtschaftungsstrategien eingesetzt werden können, um eine nachhaltige qualitative und quantitative Grundwassernutzung zu gewährleisten. Das sich in der Nordostschweiz befindende Untersuchungsgebiet umfasst Grundwassersysteme, die sowohl in alpinen Lagen als auch in Auengebieten liegen. Das Einzugsgebiet der Thur stellt ein gut untersuchtes Studiengebiet dar und ist gross genug (~1700 km^2), um als mesoskaliges Einzugsgebiet betrachtet zu werden. Spezifische Ziele dieses Forschungsprojekts waren 1) die Bestimmung der wichtigsten Einflussfaktoren auf die Grundwasserverschmutzung, 2) die Bewertung der räumlich-zeitlichen Variabilität der Grundwasserneubildung in einer Weise, die auf andere Einzugsgebiete übertragbar ist, und 3) die Überwachung des Grundwassers in einer adaptiven und ereignisbasierten Weise. Diese Forschungsziele wurden angegangen, indem zunächst historische und aktuelle qualitative Bedrohungen des Grundwassers in Bezug auf anthropogene Prozesse und deren Auswirkungen auf die Grundwasserqualität weltweit untersucht wurden. Zweitens wurde die räumlich und zeitliche Grundwasserneubildung im Einzugsgebiet der Thur auf der Grundlage von Open-Source-Daten und -Software abgeschätzt. Schliesslich wurden die variierenden Quellwasserbeiträge zu den Grundwasserleitern im Thur-Einzugsgebiet mit Hilfe von konservativen Tracerdaten bestimmt. Die Struktur dieser Dissertation umspannt drei verschiedene Skalen, von der globalen über die Mesoskala bis hin zur lokalen Probenahme, und deckt anschliessend verschiedene Ebenen der Datenverfügbarkeit ab.

Um die vielen qualitativen Bedrohungen für das Grundwasser zu veranschaulichen, wurden die wichtigsten, aus der Landwirtschaft, den Städten und der Industrie stammenden anthropogenen Verunreinigungen in Form eines Überblicks vorgestellt. Darüber hinaus wurde eine Auswahl von Fallstudien vorgestellt, die die anhaltenden Probleme sowohl mit etablierten als auch mit neuen und aufkommenden Schadstoffen beschreiben. Da die Anforderungen an das Grundwasser immer weiter steigen, ist neben der Grundwasserqualität auch eine nachhaltige Bewirtschaftung der Grundwassermenge zwingend erforderlich. Hierfür ist das Wissen über die räumliche und zeitliche Grundwasserneubildung eines Einzugsgebietes und die dominierenden Wasserquellen, die die Oberflächen-Grundwasser-Dynamik steuern, entscheidend. In vielen Regionen ist es jedoch schwierig, die Grundwasserneubildung zu quantifizieren, sei es aufgrund der Komplexität der hydrogeologischen Prozesse oder aufgrund begrenzter Beobachtungsdaten. Gerasterte Parameter aus frei verfügbaren Fernerkundungsdaten und in-situ Beobachtungen, einschliesslich Niederschlag, tatsächlicher Evapotranspiration und hydrologischen Abflussdaten (getrennt in Schnell- und Basisabfluss), wurden verwendet, um räumlich-zeitliche Grundwasserneubildungskarten über einen Zeitraum von 20 Jahren (2000 - 2019) zu erstellen. Die so abgeschätzten Werte der Grundwasserneubildung stimmen gut mit Schätzungen aus anderen Studien überein. Insgesamt wurde gezeigt, dass die Neubildung 29% des Gesamtniederschlags im Thur-Einzugsgebiet ausmacht. Die Ergebnisse unterstreichen die Bedeutung des Niederschlags für die Grundwasserneubildung, wobei sich längere Trockenperioden negativ auf die Grundwasserneubildung auswirken, während Perioden mit überdurchschnittlichen

Niederschlägen eine puffernde Wirkung auf die Grundwasserressourcen des Thur-Einzugsgebiets haben.

Flusswasser stellt eine Verbindung zwischen der Oberfläche und der unterirdischen Umwelt dar. Zwischen 2017 und 2020 wurde Thur-Flusswasser während extremer Ereignisse (Hoch- und Niedrigwasser) gesammelt und auf seinen Gehalt an konservativen Tracern ($\delta^{18}O$ und $\delta^{2}H$) analysiert. Diese ereignisbezogen-entnommenen Oberflächenwässer wurden zusätzlich zu Grund- und Regenwasserproben analysiert, um die räumlich und zeitliche Wasserdynamik im Thur-Einzugsgebiet zu charakterisieren. Mit Hilfe einer Cluster- und Drei-Endglieder-Mischungsanalyse wurde die räumliche und zeitliche Variabilität der verschiedenen Wasserkomponenten identifiziert, welche zu den Grundwasserleitern des Thur-Einzugsgebietes beitragen. Welche Komponente dominiert, hängt grundsätzlich von der geographischen Lage im Einzugsgebiet, als auch der Höhenlage und der Geologie ab. Ein Oberflächenwasser-Typ wurde als dominante Komponente in den hochgelegenen Regionen gefunden, während ein Grundwasser-Typ in den Regionen mittlerer Höhe dominierte und ein Regenwasser-Grundwasser-Mix in den niedrig gelegenen Regionen. Eine klare Verschiebung hin zu Grundwasser-Signaturen während trockener Bedingungen wurde im Flusswasser beobachtet, wobei das Grundwasser im Durchschnitt 30% des beprobten Oberflächenwassers im Einzugsgebiet der Thur ausmachte.

Dieses Forschungsprojekt beleuchtete nicht nur die wichtigsten anthropogenen Grundwasserschadstoffe, sondern auch die komplexen physikalischen Prozesse und Faktoren, welche die Grundwasserqualität bestimmen, einschliesslich Klima, geologische Eigenschaften, Topographie und Landnutzung. Einschlägige Fallstudien betonten die anhaltenden Unsicherheiten bezüglich der Abbauprozesse von Schadstoffen, Schadstoffpfaden und die daraus resultierenden Kontaminationsrisiken für das Grundwasser. In Bezug auf die Grundwassermenge zeigte diese Studie den Wert von Fernerkundungsdaten bei der Abschätzung der räumlich-zeitlichen Neubildung eines mesoskaligen Einzugsgebiets, insbesondere bei begrenzten Beobachtungsdaten, betonte aber auch die Wichtigkeit fortgesetzter bodengestützter Überwachungsnetzwerke. Schliesslich zeigten die Untersuchungen die Variabilität der Fluss- und Grundwasser-Komponenten im Thur-Einzugsgebiet, wo ereignisbasierte Beprobungen einen relativ kostengünstigen Einblick in die Oberflächen-Grundwasser-Charakteristika eines mesoskaligen Einzugsgebietes liefern konnten.

List of Figures

List of Appendix Figures

List of Tables

List of Appendix Tables

List of Abbreviations

AET	Actual Evapotranspiration
AET_{corr}	Corrected Actual Evapotranspiration
AMD	Acid Mine Drainage
An	Andelfingen
Ap	Appenzell
ASR	Aquifer Storage and Recovery
ASTR	Aquifer Storage Transfer and Recovery
BTEX	Benzene, Toluene, Ethylbenzene, Xylene
cDCE	cis-1, 2 Dichloroethene
DEM	Digital Elevation Model
DNAPL	Dense non-aqueous phase liquid
CRDS	Cavity Ring Down Spectroscopy
EC	Eddy Covariance
Elvn	Elevation
EMMA	End-Member Mixing Analysis
EPMC	Emerging Pharmaceutical Manufacturing Country
ε	Component Error
ET	Evapotranspiration
f	Fraction
FA	Flow Accumulation
FA_{norm}	Normalized Flow Accumulation
FOEN	Federal Office for the Environment
Fr	Frauenfeld
GMWL	Global Meteoric Water Line
GPCP	Global Precipitation Climatology Project
GPM	Global Precipitation Measurement
GW	Groundwater
Ha	Halden
He	Herisau
Jon	Jonschwil
LAS	Large Aperture Scintillometers
LAI	Leaf Area Index
LMWL	Local Meteoric Water Line
LNAPL	Light Non-Aqueous Phase Liquid
MAR	Managed Aquifer Recharge
asl.	above sea level
MOD	MODIS
Mog	Mogelsberg
Mos	Mosnang
NAPL	Non-aqueous phase liquid
NAQUA	National Groundwater Monitoring
OC	Organic Contaminants
P	Precipitation
PAHs	Polycyclic Aromatic Hydrocarbons

PAM	Partitioning Around Medoids
PCA	Principal Component Analysis
PCE	Tetrachloroethene
PM	Penman-Monteith
Q	Discharge
$\mathbf{Q_q}$	Quickflow
$\mathbf{Q_{q\text{-}dis}}$	Spatially Distributed Quickflow
$\mathbf{Q_b}$	Baseflow
R	Recharge
RS	Remote Sensing
RSOI	Reduced Space Optimal Interpolation
S	Storage
s	Source
SAT	Soil Aquifer Treatment
Stg	St. Gallen
SW	Surface Water
TCE	Trichloroethene
TRMM	Tropical Rainfall Measuring Mission
VC	Vinyl Chloride
V-SMOW	Vienna Standard Mean Ocean Water
Wae	Wängi
WWTP	Wastewater Treatment Plant

1. Introduction

1.1 Concerning the complex nature of hydrogeological settings

The heterogeneous nature of most subsurface environments makes it difficult to characterize and understand the of processes of groundwater (Hakoun et al., 2017). Local and regional geology define the physical and chemical subsurface characteristics, and subsequent aquifer traits, including the natural dynamics of groundwater recharge, groundwater flow, and groundwater discharge to and from the subsurface. Depending on the underlying geology and land surface processes, soil types and sediment matrix characteristics can vary dramatically within and across landscapes, either dampening or enhancing groundwater recharge rates (e.g. O'Driscoll et al., 2005). In the vadose (or unsaturated) zone, the root systems of plants can create preferential flow pathways, while in cases where dense floral cover is present, elevated evapotranspiration rates and reduced surface runoff can be expected, all of which adds further complexity to the subsurface environment. The chemical interaction of minerals and water at both the sediment and the rock surface interface determines the qualitative characteristics of the groundwater (Naicker et al., 2003). These physical subsurface characteristics will influence an aquifer's storage capacity, including groundwater recharge rates flow and transport capacity, as well as groundwater residence time. Subsequently, groundwater quality and quantity is controlled by a water balance that can span from the local, to regional, and to the global scale.

A host of methods exist that attempt to characterize and predict groundwater within the context of the hydrogeological cycle, with data sets such as those obtained from gauged drainage basins (generally < 100 km^2 in size) often being a vital source of information. However, the complex nature of the hydrogeological setting, along with the restrictive nature of scale and time which need to be accounted for when dealing with heterogeneous landscapes, result in many methods falling short of being able to characterize groundwater adequately, especially under rapidly changing anthropogenic conditions (Brunner et al., 2007; Howard, 2015; Schirmer et al., 2013). As a result, assumptions are made concerning temporal trends and spatial characteristics, for example many methods as well as models assume that historical data is adequate when predicting future conditions, or that the information derived form a gauged catchment's behaviour can be applied to other basins with similar hydrological characteristics (Sivapalan et al., 2003).

In spite of these complexities, over the past several decades, the hydrological community has seen major advancements in process understanding, improved scaling theories, and data processing, largely as a result of new technological advancements such as computing power, satellite observations, sensor technologies, and the use of environmental tracers (Bierkens and Wada, 2019; Elsner and Imfeld, 2016; Hrachowitz et al., 2013b; McDonnell et al., 2007; Melsen et al., 2016; Palau et al., 2016; Sivapalan et al., 2003; Xu and Beekman, 2018). In spite of these advances, extrapolation from the observed to the inferred is to an extent inevitable when dealing with large heterogenic catchments or when making future predictions. Subsequently, in an attempt to understand these systems, where either processes or results cannot be validated through observations, a "black-box" approach is often applied, resulting in an inherent level of uncertainty (Hrachowitz et al., 2013b; Sivapalan et al., 2003). Unsurprisingly, there is a need for methods based on physical processes understanding rather than interpolated processes, especially where mesoscale (typically 10 – 10^4 km^2) catchments are concerned, as these are often of high relevance to water management. However, no matter at what scale you work at, an important concept to bear in mind is one of water balance, at the soil, atmosphere, and vegetation interface (Sivapalan et al., 2003).

Although technological advances have greatly improved our understanding of the hydrogeological environment, groundwater resource assessment, modelling, and management at catchment scales, a lack of data continues to be lamented (Brunner et al., 2007). And while certain models promote water management in a comprehensive, holistic, way (e.g. Integrated Urban Water Management (IUWM; Mitchell, 2006), MODFLOW (United States Geological Survey, 2018), Hydrogeosphere (Brunner and Simmons, 2012), etc.), it is not certain that these techniques adequately incorporate the unique processes and characteristics of groundwater recharge, storage, flow attributes, groundwater distribution and quality; aspects that all merit special management considerations (Brunner et al., 2007; Howard, 2015; Schirmer et al., 2013). While infinitely valuable, classical hydrological measurements provide only point-source data, obtained for example at weather or gauging stations (Brunner et al., 2007; Schirmer et al., 2013). Although small-scale process-understanding is necessary in order to predict for example water quality developments, regional hydrological models require distributed input data, simplification, and generalization. Subsequently parameter estimation and calibration are therefore often necessary at the large catchment scale (Kirchner, 2009; Sood and Smakhtin, 2015). However, precisely what kind of simplification or generalization should be applied remains elusive, and perhaps they are dependent on the objectives in question.

In terms of ground-based monitoring, technological advancement allows for ground-based variables such as river level, surface and groundwater temperature, electrical conductivity (EC), chemical data, and groundwater level measured at fixed locations over given intervals, to have their values transmitted via GSM (Global System for Mobile Communications) to data bases (e.g. Taffahi et al., 2013). Due to its high efficiency and cost-effectiveness, the automated transmission of measured data has provided a significant advance in the field of environmental monitoring (Lovett et al., 2007). However, although automated data transmission ensures easy and rapid access to measured data, this type of monitoring can fail in cases were the monitoring stations are located in remote places, are tampered with by the public, or where electricity supply is limited or intermittent. To overcome this limitation of data collection, adaptive monitoring schemes that allow event-driven sensor measurements and sampling have to be applied (e.g. Horsburgh et al., 2011, 2010).

In Switzerland an important source of hydrogeological data (especially discharge and precipitation) forms part of the on-going monitoring efforts conducted by federal authorities (e.g. Swiss Federal Office for the Environment (FOEN), MeteoSwiss, etc.), as well as the Cantonal authorities (in particular where groundwater characteristics are concerned). Although this existing data is essential for model calibration and application, it is often disseminated and with its large heterogeneity, the characterization of the internal catchment-wide processes of mesoscale catchments in Switzerland remain challenging (Viviroli et al., 2009).

1.2 Groundwater quality under anthropic conditions

Escalating waste emissions, land use change, and other human population growth-related challenges are affecting global air, soil, and water quality resulting in ever increasing, and sometimes conflicting, demands on recourses (Diamond and Hodge, 2007; Montanari et al., 2013; United Nations, 2007). Large-scale utilization and alterations of the global hydrological cycle have dramatically altered the natural runoff and recharge characteristic of many rivers and aquifers (Antrop, 2004; Haase, 2009; Rost et al., 2008), making the management, supply, and protection of freshwater resources a matter of global importance. Globally groundwater is an important source of drinking water. In Switzerland up to 80% of potable water is derived directly from groundwater sources, with 40% derived from alluvial aquifers (https://www.bfs.admin.ch; Vogt et al., 2009). In addition to it being a source of drinking water, groundwater is also used as a source of water in agricultural, urban, and industrial practices (Schirmer et al., 2013). Furthermore, many important ecological functions such as flood and drought mitigation and ecosystem maintenance are also dependent on the occurrence groundwater sources (Famiglietti, 2014; Taylor, 2014).

The orders-of-magnitude slower flow velocity of groundwater, compared to surface waters in rivers and streams, is an advantage in terms of the filtering process, storage, and subsequent utilization of subsurface water (Kirkby, 1969; Martinec, 1975). This has led to the realisation of the importance of retention areas, which are now recognized as playing a vital role in groundwater recharge (Kurth et al., 2015; Schirmer et al., 2014). Groundwater availability during dry periods can be significantly enhanced for example, if channelized river reaches can be restored in such a way that more river water can infiltrate into aquifers during high water levels, or if river bank filtration can be induced through the pumping of production wells screened in river-connected aquifers during dry periods (Bauser et al., 2010; Dillon, 2005; Dillon et al., 2009; Hiscock and Grischek, 2002; Tufenkji et al., 2002). In this manner peak flow can be significantly dampened (e.g. Van Liew, 2004), and groundwater may then become available as drinking water or for irrigation during times of high demand when low surface water conditions prevails. Subsequently, particular interest has recently been drawn to the research of restored river reaches (Kurth et al., 2015; Kurth and Schirmer, 2014; Schneider et al., 2011).

In light of this, the monitoring and management of water quality is fundamental, if the process of groundwater abstraction and recharge (whether managed or natural) is to be sustainable. A review was conducted as part of this research project which outlines threats, vulnerabilities, and monitoring requirements regarding historic and current groundwater contaminants, while also presenting research which attempts to address these and future threats to global groundwater quality. Relevant and real-world case studies, fundamental in framing the threats to groundwater quality, while conceptualizing current research gaps in the holistic management of groundwater, are presented. The review, presented in Chapter 2, takes a look at global water quality concerns associated with agricultural practices, industrialization, as well as more recent issues concerning population growth and clean water availability within the urban environment. This review brings together many different studies, conducted under various climatic and geological conditions, and provide a comprehensive picture of the threats to groundwater quality within the anthropogenic environment.

1.3 The spatiotemporal nature of groundwater recharge

More than ten decades of hydrological research has shown that the inherent heterogeneity of the hydrological cycle is extremely difficult to model and predict (Beven, 2001; Beven and Kirkby, 1979; Bonell and Gilmour, 1978; Dunne and Black, 1970; Horton, 1933; Kirchner, 2009; Kirkby and Chorley, 1967; Whipkey, 1965; Winsemius et al., 2008; etc.), forcing the simplification of complex processes for the sake of conceptualization (Hrachowitz et al., 2013a; Sivapalan et al., 2003). The management of water as a resource is further complicated by the fact that water resource management is often fragmented, and intrinsic hydrological links, for example the relation between surface water and groundwater or physical, chemical, and biological water qualities, are viewed as separate entities rather than a holistic system (Braune and Xu, 2008; Montgomery et al., 2007). This is further complicated by the fact that ecological, economic, and social values of the hydrological cycle are highly complex (as demonstrated in Chapter 2), and are expected to become more so with increasing anthropogenic pressures (Hering et al., 2012; Schirmer et al., 2013). Taken together, this reduces the confidence with which decision makers are able to manage water quality and availability sustainably into perpetuity.

Characterizing a catchment's spatiotemporal water balance holistically is crucial for the sustainable utilization and management of freshwater resources. However, this requires an understanding of the climatic, topographic, geological, biotic, and anthropogenic factors, as well as the mode in which these interact with the hydrological cycle, all incorporated into a single framework encompassing small to very large-scale basins (Sophocleous, 2002). In the early 1960's, eutrophication and acid rain became a phenomenon of interest, and the focus of surface-groundwater interaction intensified (Winter and Rosenberry, 1995). As environmental issues came to the forefront in the 70s, and later in the 80's and 90's, ecosystem loss became a pressing issue, after which the focal point turned to environmental protective legislation resulting an explosion of environmental studies which included studies focusing on the hydrological cycle in an effort to restore streams and manage riparian systems more effectively (Montgomery et al., 2007; Sophocleous, 2002). The accurate estimation of groundwater contribution to the global water cycle, although still hampered by the lack of continuous and reliable hydrogeological data (Fredrick et al., 2007), has since benefited from tools which better manage large data bases, models which more adequately predict subsurface flow, and technologies which address the spatiotemporal dynamics; all of which is applicable to water managers.

Understanding the spatiotemporal characteristics of surface and groundwater on a scale applicable to groundwater management, is vital to sustainable water resource stewardship. In order to develop solutions for the purpose of predicting water surplus and shortage, it is necessary to understand how the overall hydrogeological system works; the co-evolution of topography, soils, vegetation, and hydrological functions in relation to the underlying geology and lithology, changing climate, and seasonality are key in developing an understanding of how potential changes to the catchment would affect its response (Dunne and Black, 1970; Fenicia et al., 2010; McDonnell, 2017; Montanari et al., 2013; Sivapalan et al., 2003; Wagener and Montanari, 2011). For this, data, models, and real-time monitoring systems are key ingredients in the process of understanding, predicting, and subsequently sustainably managing a catchment's water resources (Montgomery et al., 2007). Although numerical models have begun to explore deeper geological links between groundwater, surface flow, and evapotranspiration (e.g. Beven and Binley, 1992; Condon and Maxwell, 2019; Hrachowitz et al., 2013; Molin et al., 2020; Sivapalan et al., 2003), the compartmentalized storage of water within a catchment has yet to be considered, and as such a comprehensive understanding of groundwater and surface water interactions, and the subsequent effects on water quantity and quality, remain elusive (McDonnell, 2017; Schneider et al., 2011).

Groundwater recharge is dependent on the amount of precipitation, temperature fluctuation, vegetation type and distribution, topography, soil characteristics, and underlying geology, as well as anthropogenic land and water utilization (Milly, 1994; Rodriguez-Iturbe et al., 1999). Subsequently climate change, changing land utilization and surface processes are a growing concern when characterizing groundwater bodies and predicting their sustainability. According to Bormann and Diekkrüger (2003) ‘new measurement techniques aiming at catchment responses on local to regional scales, considering the spatial variability within the catchment, have to be developed’ (p 1331). The combination of point measurements with validated regionally distributed measurements (e.g. remote sensing data) can improve hydrological models. The Thur catchment represents an opportunity to conduct catchment wide recharge studies, suitable for relatively ungauged basins, and at a scale applicable to water managers. The objective of the third chapter of this project was to use readily available datasets and open source tools to estimate the spatiotemporal groundwater recharge across a mesoscale catchment over a 20 year period.

Chapter 3, demonstrates the use of point measurements in combination with regionally distributed satellite observations, by way of a gridded parsimonious water balance assessment, to determine groundwater recharge for the Thur catchment in a spatiotemporal manner. The third chapter of this project demonstrates the use of remotely sensed MODIS ET data in conjunction with existing federal point- and grid-based databases to determine groundwater recharge using the following equation:

$$\boldsymbol{R = P - AET - Q_q + Q_b}, \tag{1}$$

where R is groundwater recharge, P is precipitation, AET is actual evapotranspiration, Q_q is quickflow, and Q_b is baseflow (Figure 1-1). Although seemingly simple, Eq. 1 integrates and takes account the major water inputs and outputs of a catchment. These factors include direct or indirect measurements of precipitation, temperature, vegetation, land use characteristics, and runoff, all of which govern processes of surface- and groundwater interaction: vital in the recharge process of unconfined aquifers. Findings in Chapter 3 indicate that a remotely sensed water budget presents a holistic starting point for monitoring a mesoscaled catchment’s recharge, in particularly - where direct observations are limited. However, the importance of continued ground-based monitoring of groundwater characteristics is emphasized.

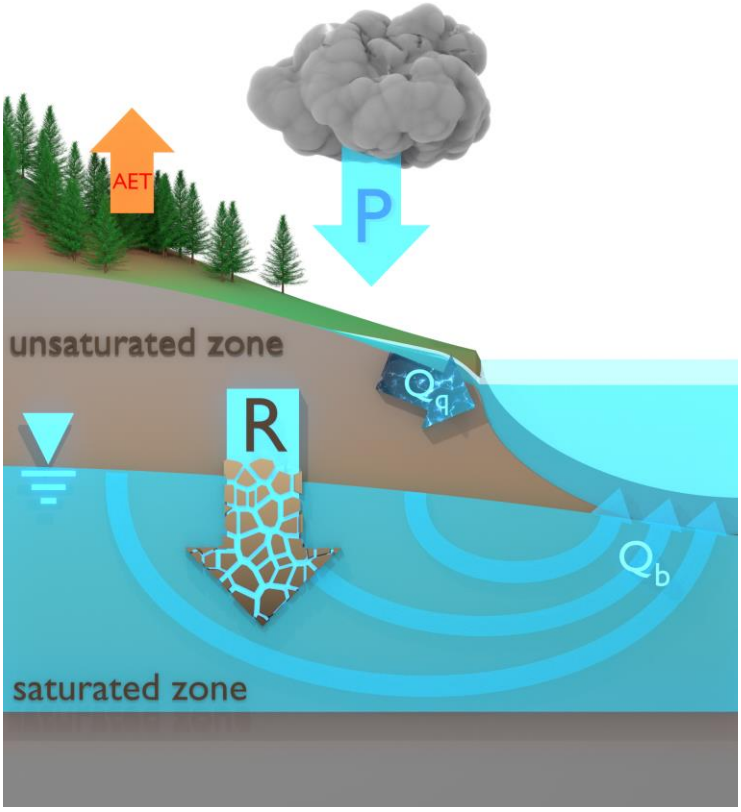


Figure 1-1: Schematic diagram of water balance components P, AET, Q_q, and effective recharge (R), which upon water reaching the water table, will give rise to the Q_b component measured as part of total discharge (Q), shown in a one dimensional soil column.

1.4 The use of environmental tracers in characterising a mesoscale catchment's water dynamics

Although long-term, high quality ground-based data is available for the Thur catchment, this is often not the case, especially where developing countries or remote regions are concerned. In such cases, where little or no ground-based data exists, initial attempts at gaining insight into a catchment's surface-groundwater dynamics would perhaps involve setting up a few automated sampling stations or the collection of *in situ* grab-samples. In an attempt to best capture the range of conditions (such as floods, droughts, freshwater availability, circulation, distribution, and quality), grab sampling is often conducted in a manner which aims to capture periods representative of a catchment's extreme events (either highflow or lowflow conditions).

The Thur River was event sampled during high- and lowflow conditions, with samples collected biannually over a period of three years at 11 surface water sites along the length of the Thur River, and 24 groundwater sites associated with either the Thur River or its three major tributaries (Murg, Sitter, and Necker Rivers). Chapter 4 investigates the Thur catchment's spatiotemporal surface- groundwater dynamics, however, unlike studies such as the likes of Pool et al. (2017) and Wang et al. (2019), where dozens or more high-frequency data points were available, this study considered the perspective of having but a few samples at your disposal, as would be the case in an ungauged catchment. The Thur River is a highly dynamic river system, displaying variable discharge values, which ranged between 3 – 605.2 m^3/s over the course of the three-year sampling period. The 11 sample sites located along the length of the Thur River were sampled bi-annually; once during times of intense rainfall (Figure 1-2 a and b) and once capturing dry conditions (Figure 1-2 c and d). Groundwater sites were sampled mostly during spring and autumn, but as access to the sites were dependent on local authorities, the sampling events could not be matched to the surface water event sampling campaigns. The groundwater monitoring sites sampled in the cantons Thurgau and St. Gallen, are themselves a product of their environment, with monitoring well designs varying from regular observation wells, to wells where casings have to be elevated to well above 3 m in order to avoid the floodwaters during the Thur River's highflow, to large diameter manholes which often house drinking water infrastructure (Figure 1-3a, b, and c).

In order to address the variability of surface-groundwater dynamics in the Thur catchment, both in terms of temporal and spatial distribution at the mesoscale, water samples were analysed for their stable water isotope composition ($\delta^{18}O$ and $\delta^{2}H$), and major ion content. The spatiotemporal variability of different source water components contributing to the Thur catchment's aquifers and river waters was investigated by conducting a cluster analysis of the isotope concentrations of the surface river water, groundwater and supplemental rainwater samples. This was followed by a three end-member mixing analysis (EMMA) conducted using a combination of environmental tracers, from the surface water, groundwater and rainwater samples. The characteristics of the event sampled river water was also explored in isolation, in order to determine the extent to which they are able to describe contributing sources and their spatiotemporal variability. Findings highlighted the variability of river and groundwater source components in the Thur catchment, with different source waters dominating different regions of the Thur catchment. While the use of event based samples was shown as being effective in providing a relatively inexpensive insight into the surface-groundwater characteristics of the mesoscaled Thur catchment.

Figure 1-2: Highflow (a and b) and lowflow (c and d) sampling of sites Thur09 (a and c) and Thur05 (b and d) in the Thur River during May and July 2019 respectively.

Figure 1-3: Groundwater monitoring wells along the Thur River range from a) regular monitoring wells installed at ground level, b) boreholes with elevated casings to protect loggers from floodwaters, c) large-diameter borehole.

1.5 Objectives and structure

The objective of this research project was to determine the controls on groundwater contamination, assess the spatiotemporal variability of groundwater recharge in a manner applicable to other catchments, and monitor groundwater source and flow in an adaptive and event-based manner in the Thur catchment in Switzerland. The structure of this dissertation spans three different scales from global (Chapter 2), to mesoscale (Chapter 3), to localized sampling (Chapter 4), and covers different subsequent levels of data availability. On the onset of this research project, a literature review was conducted on the topic of anthropogenic threats to groundwater quality within the context of global issues and current studies. Following this broad global overview, catchment scale and then field specific studies concerning water quantity and distribution were conducted within the mesoscaled Thur catchment. In order for the methods to be applicable to other catchments, the spatiotemporal groundwater recharge in the Thur catchment was estimated using publicly available datasets and open-source software. Where sampling is concerned, environmental tracer data from a handful of surface and groundwater sites located in the Thur catchment was used to determine the spatiotemporal variabilities of source water contributions to the various aquifers located in the Thur catchment as well as the Thur River itself.

Specific objectives addressed in this research project include:

- A detailed review of the major threats concerning groundwater quality in the modern anthropogenic environment, with current and pertinent case studies provided.
- Estimation of groundwater recharge rates within a mesoscale catchment, using a combination of remotely sensed evapotranspiration and ground-based river discharge data.
- Characterization of the surface-groundwater dynamics in the Thur catchment through the analysis of tracer values from groundwater and event sampled surface water, using a cluster and three end-member mixing analysis.

Following this introductory chapter, the dissertation presents the above mentioned research questions as three separate chapters, where Chapter 2 is dedicated to reviewing global anthropogenic threats to groundwater quality, while Chapters 3 and 4 focus on the physical aspects of groundwater recharge and surface-groundwater interaction in the Thur catchment in Switzerland. The final chapter (Chapter 5) provides some concluding remarks, briefly recapping the overall findings, along with some of the uncertainties and limitations concerning the research outcomes in Chapters 2, 3, and 4 of this dissertation. Based on these findings and limitations, some future research directions concerning both global and regional groundwater quality and quantity are presented. Chapter 5 ends on a final note highlighting some personal perspectives acquired over the course of this research project, concerning groundwater security under rapidly changing anthropogenic conditions.

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.

[1] This chapter has been published in Science of the Total Environment: Burri, N.M.*, Weatherl, R.*, Moeck, C., Schirmer, M., 2019. A review of threats to groundwater quality in the Anthropocene. Sci. Total Environ. 684, 136–154. https://doi.org/10.1016/j.scitotenv.2019.05.236
**Equal contribution from first and second author*

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).

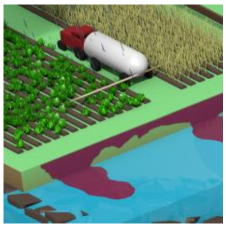
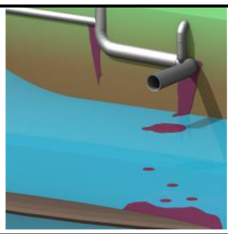
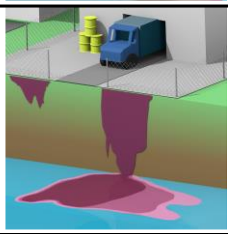
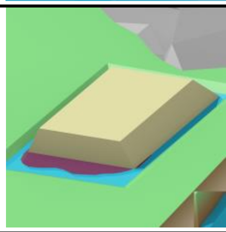
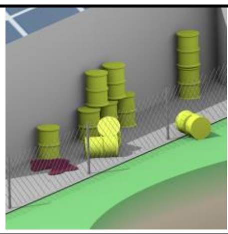
When an aquifer becomes contaminated with harmful chemical products, it may become unusable for decades. The residence time of contaminants within groundwater bodies can be anywhere from weeks to decades, depending on physico-chemical properties of compound and environmental conditions (Chapman and Parker, 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 1

Land use Category	Potential contaminating compounds	Remarks on potential pathways and processes	Conceptual contamination pathways
Agricultural	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 components 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 2.6.2 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 examples) 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 2.6.2 for examples). 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 examples).

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 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 2.6.3 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.

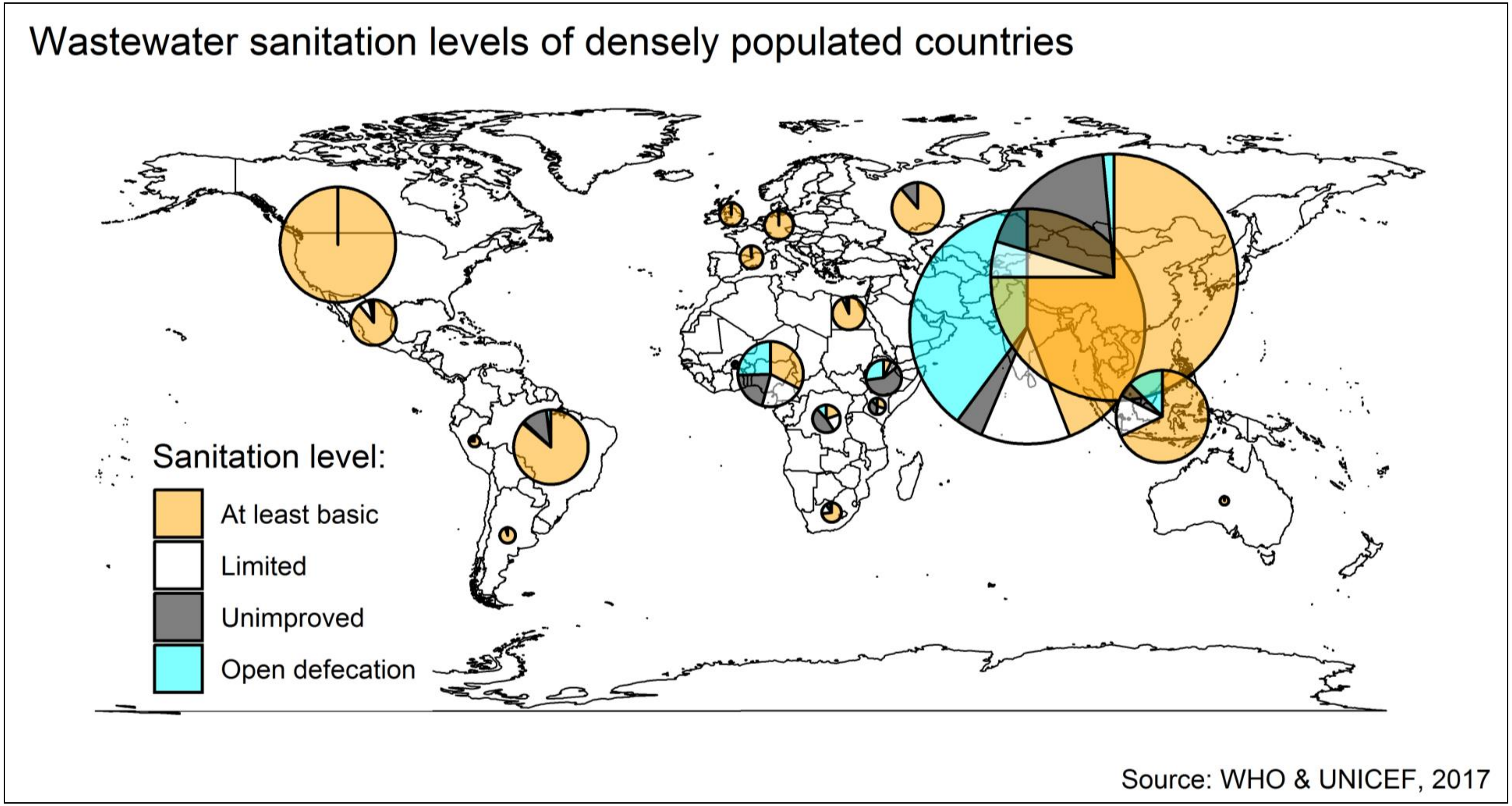


Figure 2-2: Wastewater sanitation levels of densely populated countries, with pie-sizes relative to populations size (note, the population of India and China is divided by 2 here for scalability), with their levels indicated as ranging from open defecation to at least basic sanitation (WWAP, 2017; https://aashdata.org/data/household).

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 2.5). 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.

2.4.4 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; 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 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	5.0
Arsenic	10	10	10	5	10	10
Atrazine	100	Banned (2003)	3.0	2.0	1.8	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						
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)		50	50
Mercury	6.0	1.0	2.0	1.0	1.0	1.0
Metolachlor	10				7.8	
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 (FDHA, 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).

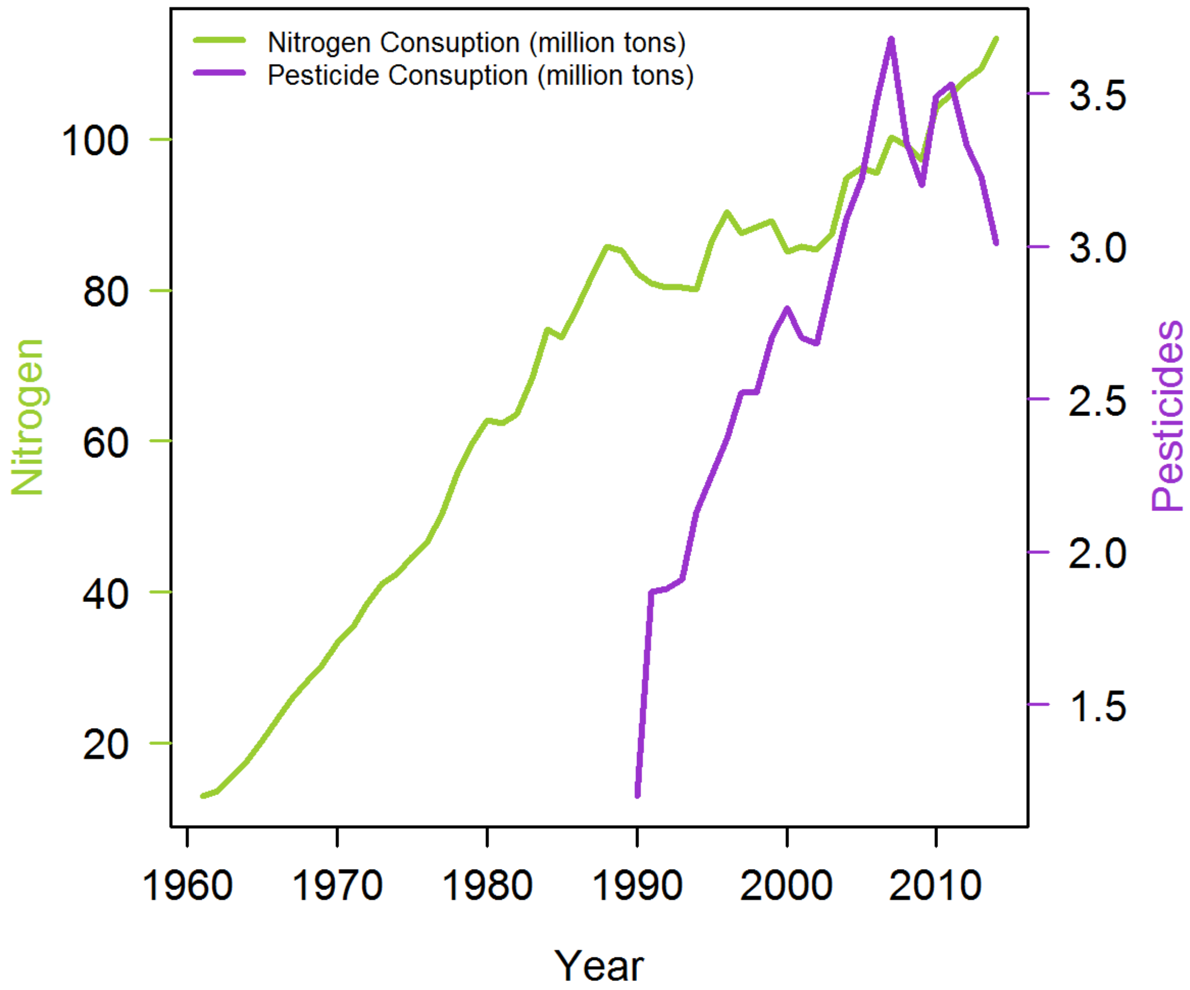


Figure 2-3: Total fertilizer and pesticide used globally in million tons per year from 1961-2014 (FAO, 2018, 2009). Note that although pesticides were already in widespread use, global monitoring data for pesticide consumption is only available post 1989.

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; 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 examples). 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).

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 sorption coefficients 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 2.4.4), 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 examples). 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 the 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.

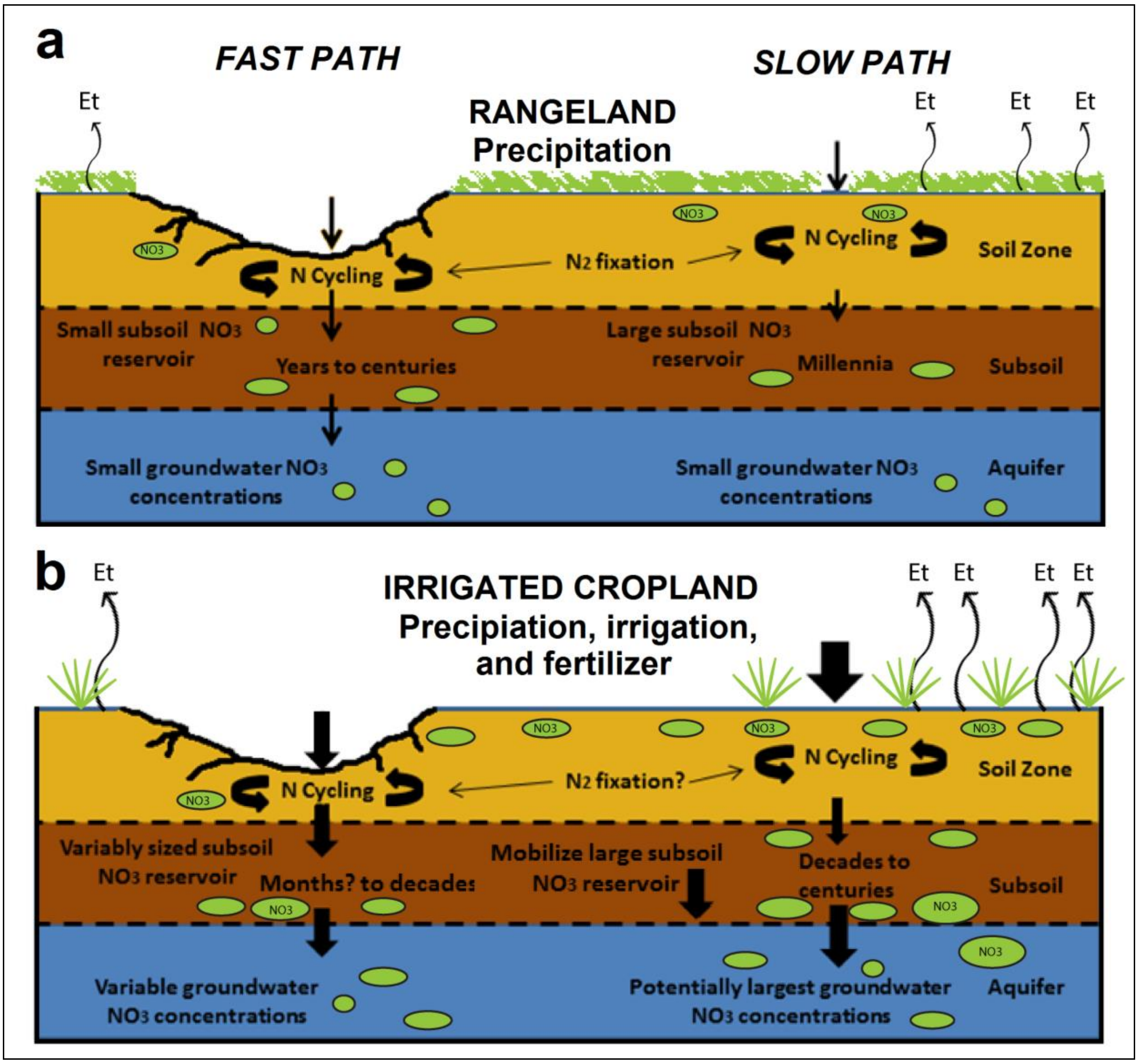


Figure 2-4: Conceptual models for the evaporative (Et) concentration and transport of NO_3^- from the land surface to the water table through the unsaturated subsoil to the aquifer, under a) rangeland conditions and b) irrigated cropland conditions in the High Plains of the United States (abbreviated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

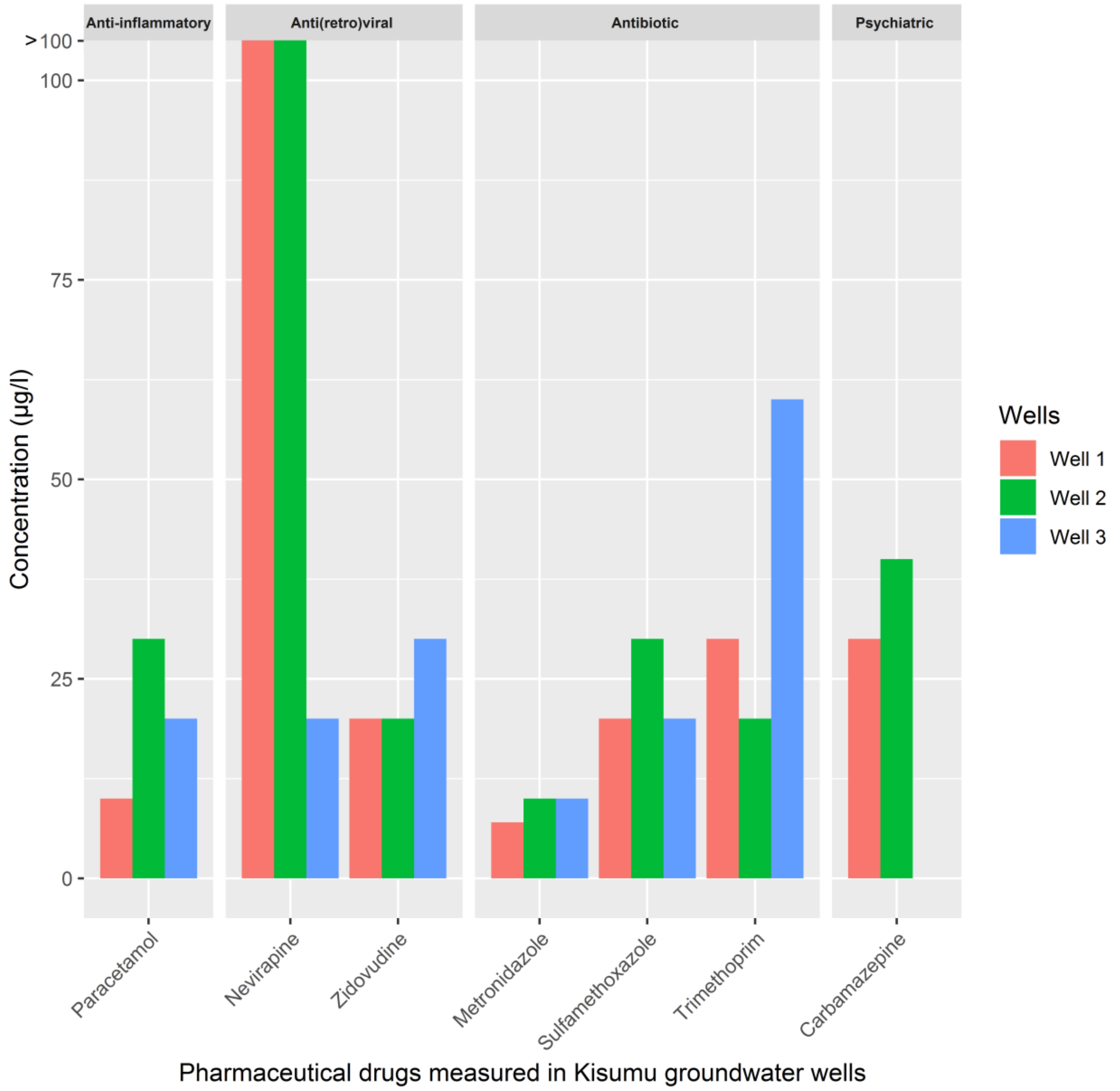


Figure 2-5: Concentration of pharmaceuticals detected in groundwater three wells in Kisumu, Kenya. Note that in Well 1 and Well 2, *nevirapine* concentrations were 1200 and 1600 ng/l respectively (adapted from K'oreje et al., 2016).

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.

2.6.1 **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.

2.6.2 **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.

2.6.3 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 (Durand et al., 2010).

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 spatiotemporal 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 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. Estimates of Groundwater Recharge Rates in a Mesoscale Catchment using a combined approach of Remotely Sensed and Ground-Based Data[2]

3.1 Abstract

Groundwater recharge is an important component of a catchment's water balance. However, recharge is challenging to quantify due to the complexity of hydrogeological processes and limited observations. Although remotely sensed data present an attractive and promising tool in hydrological studies, in particularly because of the spatiotemporal availability of many remotely sensed products, its application for calculating a water budget for mesoscale catchments (typically 10 – 10^4 km^2) remains limited. When coupled with ground-based observations, remotely sensed data can be utilised to provide a more complete understanding of the hydrogeological system. This study investigated spatiotemporal variations in groundwater recharge using a combination of satellite image products in conjunction with ground-based runoff data in the Thur catchment: a mesoscale (~1700 km^2) catchment in Switzerland. Gridded components from readily available precipitation data, actual evapotranspiration estimates from MODIS, and hydrological discharge data separated into quick- and baseflow, were used to generate spatiotemporal groundwater recharge maps over a 20 year period (2000 - 2019). Closure of the water balance found that short-term (monthly) data displayed a moderate correlation of total input vs. total output values; an improved correlation was obtained with medium- (seasonal) to long-term (annual) data intervals, suggesting that the Thur catchment is in a steady state. Groundwater recharge maps were generated and a pixel-wise linear regression performed for the 20 year period. At the 95th percentile, only 4% of the whole catchment area experienced significant change in recharge. Examination of the gridded water balance components during different hydrological years (e.g. wet vs. dry years), emphasized the limiting effect of precipitation on recharge whereas evapotranspiration remained relatively constant over the same 20 years. Temporal anomalies stressed the effects of hydrological wet years preceding hydrological drought years in terms of recharge deficits. This study highlights the potential of remotely sensed data in hydrogeological research, but emphasises the importance of continued ground-based monitoring networks; the lack of which is a limiting factor in water management where mesoscale or smaller catchment sizes are concerned.

[2] This chapter has been submitted to the Journal of Hydrology: Regional Studies and is currently under review: Burri, N.M., Moeck, C., Schirmer, M. Groundwater recharge rate estimation using remotely sensed and ground-based data: a method application in the mesoscaled Thur catchment.

3.2 Introduction

One of the most important functions of a catchment is its ability to store and release water; a characteristic that can buffer against severe weather events, seasonal changes, and climate variability (Berghuijs et al., 2016; Datry et al., 2017; Staudinger et al., 2017). Groundwater recharge (R) indicates the existence of renewable groundwater resources and is therefore an important component in catchment studies (Döll and Fiedler, 2008; Jasechko et al., 2014; Mohan et al., 2018). Recharge is also one of the least understood water balance components, largely because it varies in space and time and is difficult to measure directly (Minnig et al., 2018; Scanlon et al., 2002; von Freyberg et al., 2015). Climate change, evolving land utilization, abstraction, and anthropogenic impacts are a growing concern when characterizing groundwater bodies and predicting their sustainability (Burri et al., 2019; Condon and Maxwell, 2019; Han et al., 2017; Oki and Kanae, 2006; Sridhar et al., 2014). Therefore, monitoring and understanding a catchment's water balance is essential to the sustainable management of water resources. In many parts of the world, in their simplest form the components which make up a catchment's water balance are precipitation (P) as primary input, and evapotranspiration (ET) as predominant output (Crosbie et al., 2015; Dhungel and Fiedler, 2016; Reitz et al., 2017). However, in mountainous regions, stream or river discharge (Q); which can be further divided into quick, event-based surface flow (or quickflow, Q_q) and typically slow subsurface flow (or baseflow, Q_b) contributions, often makes up the majority of water output (Spreafico and Weingartner, 2005; Viviroli et al., 2007; Zappa et al., 2017). All of these components can be related through a water budget equation which, in its simplest form, reflects the rate of change of water into and out of a closed catchment in a steady-state:

$$\boldsymbol{P - ET - Q \pm \Delta S = 0}, \qquad (2)$$

where $\pm\Delta\boldsymbol{S}$ is the change of storage.

According to Healy and Scanlon (2010), "the universal concept of mass conservation of water implies that water balance methods are applicable over any space and time scale" (pp.15). However, the components that make up Eq. 2 are often far from simple to determine. They are traditionally limited to point or plot scales (~10^{-2} m^2 to ~10^1 m^2) and single components of Eq.2 (Ruth et al., 2018). The above mentioned components vary in space and time, and although linked through large-scale interrelationships, have very different spatiotemporal characteristics (Creutzfeldt et al., 2014). Hence, temporal and spatial scaling, whether up- or down-scaling, presents an additional challenge when determining a catchment's water dynamics (Anderson et al., 2007; Cui et al., 2018; Hong et al., 2009; Kalma et al., 2008).

A key variable of Eq. 2, and the major net loss component from the terrestrial water budget is ET; the sum of evaporation (from ground surface) and transpiration (from plant surfaces). The complex interacting components which result in ET are difficult to quantify, whether via field-based measurements, or via remotely sensed technology (Zhang et al., 2016). As a result, ET typically has the greatest uncertainty of the components presented in Eq. 2 (Velpuri et al., 2013), and remains one of the most difficult components to measure accurately (Ferguson et al., 2010; Hirschi et al., 2017). Over the past decade, a growing multitude of high quality, publicly available, products provided by on-board satellite sensors, have been contributing towards a growing understanding of global surface processes (Bhanja et al., 2016; Chen et al., 2016; Cui et al., 2018; Landgrebe, 1997; Pekel et al., 2016; Sheffield et al., 2018; Spiliotopoulos et al., 2017). Remotely sensed multispectral data enables the retrieval of real-time information concerning the spatial and temporal characteristics (e.g. net radiation, surface temperature, and reflectance) associated with processes such as land use change, vegetation cover, flood inundation, and glacier and sea ice movement (Cui et al., 2018; Gleason et al., 2018; Hong et al., 2007; Venter et al., 2018; Zhang et al., 2011). Remotely sensed data is an attractive option for monitoring atmospheric, surface and near-surface attributes as it is able to 1) integrate heterogeneous spatial variations at different resolutions, and 2) provide relatively long time series of routinely generated products, enabling the progression from point to regionally distributed information (Kalma et al., 2008).

Currently, remotely sensed ET products, derived from computational surface-energy balance models that stem from multispectral satellite-sensed characteristics (i.e. net radiation, surface temperature, and vegetation properties), offer perhaps one of the most attractive global estimates of actual ET measurements. As a result, this type of data has been used to improve model predictions and to close the water balance leading to a significant reduction in uncertainty (Anderson et al., 2011; Bastiaanssen et al., 1998; Irmak et al., 2012; Nishida et al., 2003; Tang et al., 2010; Wang and Xie, 2018). Although remote sensing (RS) is a very attractive and promising tool, particularly because of the long temporal and large spatial availability of many remotely sensed products, its application in mesoscale catchment studies (typically $10 – 10^4$ km^2) is still limited, primarily because of a mismatch in spatial scale (Becker and Nemec, 1987; Gleason et al., 2018). Most often the pixel resolution of available RS data are too large to be useful where regional water resource management is concerned (Armanios and Fisher, 2014; Sun et al., 2018), resulting in very few studies which have attempted to apply RS data to mesoscale catchments. In addition, although RS components for an entire water budget are readily available, reproducible methods for handling the necessary data are not prominent in literature (e.g. Rajib et al., 2018).

When coupled with ground-based data, remotely sensed observations have been shown to provide a more complete understanding of the hydrological system (Becker, 2006; Gleason and Durand, 2020; Pavelsky, 2014), and are therefore potentially more applicable in calculating the water balance of a mesoscale catchment. Although groundwater components generally have flow velocities that are orders of magnitude slower than surface water flow velocities (Berghuijs and Kirchner, 2017; Gabrielli et al., 2018), according to Brunner et al., (2007), recognizing that localized water occurrences, such as shallow unconfined groundwater bodies, are driven by surface processes (many of which can be inferred from RS data) is key to using satellite data as part of a water management tool. However, both surface and subsurface movement and storage of water is dependent on precipitation, temperature fluctuations, vegetation type and distribution, anthropogenic land and water utilization, as well as topographic, lithological, and soil characteristics (Sophocleous, 2002; Wada et al., 2010).

Discharge (Q), an approximated value of river flow and velocity, can typically be high resolution measurements at a specific point. However, many regions have sparsely instrumented or completely ungauged catchments, especially at local or regional scales, where remotely sensed methods remain limited (Gleason et al., 2018). In the presence of unconfined aquifers, Q typically represents a combination of surface runoff and contributing subsurface components to and from the catchment (Sophocleous, 2002). Quantifying subsurface contributions of Q is often problematic as knowledge of hydraulic conductivity and hydraulic head is needed and the knowledge of these factors are limited by subsurface heterogeneity and the number and depths of measuring locations (Alley et al., 2002).

Over longer time scales, change in a catchment's water storage is often assumed to be small relative to the volumes of the other components of Eq. 2, and for systems with no inflow from or outflow to adjacent catchments, the water budget can be assumed to be balanced. Where a catchment is in a steady-state in terms of water input and output, ΔS would be equal to zero (Healy and Scanlon, 2010). It is therefore common, both within the fields of research and water resource management, to estimate recharge from water budget calculations (Dages et al., 2009; Healy et al., 2007; Rodríguez-Huerta et al., 2020; Tilahun and Merkel, 2009; WFD-CIS, 2016).

This study investigates the application of satellite derived products, used in conjunction with ground-based discharge data, as a "soft" measure to determine spatiotemporal water distribution and estimate groundwater recharge within the mesoscaled Thur River catchment in Switzerland. The Thur River represents a dynamic system free of any major natural or artificial reservoirs, and with its mesoscale catchment (~1700 km^2) provides a unique opportunity to explore the potential of using readily available RS data to evaluate monthly, seasonal and annual groundwater recharge for the years 2000 – 2019. Previous research in the Thur catchment focused either on localized field-based studies (Chittoor Viswanathan et al., 2016; Kurth et al., 2015; Kurth and Schirmer, 2014; Paillex et al., 2017, 2005; Schirmer et al., 2013; Schneider et al., 2011; Vogt et al., 2011), or involved the use of lumped modelling approaches to simulate its large-scale processes (Abbaspour et al., 2007; Dal Molin et al., 2020; Doulatyari et al., 2017; Rössler et al., 2019; Viviroli et al., 2009). The aims of this study are as follows:

i) assess the spatiotemporal variability of gridded water balance components in the Thur catchment for the years 2000 – 2019 using only open source software and readily available RS data in combination and ground-based data, to estimate groundwater recharge,
ii) identify variability in environmental processes during different hydrological years (e.g. wet vs. dry years) in a mesoscale catchment,
iii) explore the results in terms of spatiotemporal distribution in the Thur catchment,
iv) examine method uncertainties and provide possible strategies for sustainable groundwater management in the Thur catchment.

3.3 Study area and its hydrogeological setting

The Thur River, located in the north-eastern part of Switzerland (Figure 3-1), has an approximate catchment size of 1700 km^2. The Thur River (a tributary to the Rhine) is the longest river in Switzerland free of any major natural or artificial reservoirs along the length of its course (~130 km), resulting in preannounced seasonality streamflow variability. Three major tributaries: the Murg, the Necker and the Sitter flow into the Thur River, and based on available data from active stream discharge stations, the Thur catchment can be divided into nine (9) sub-catchments (Figure 3-1a).

The headwaters of the Thur River arise in the southern, glacier-free, limestone-dominated, pre-alpine region of the catchment near Mount Säntis, where vegetation is sparse and soils are generally shallow (Figure 3-1b). Here, productive groundwater occurrences are confined largely to small fluvio-glacial gravel and sand deposits hosted largely within valley bottoms (dark blue, Figure 3-1b), and fractured-rock (dark green, Figure 3-1b) (Gurtz et al., 1999). Average depth to groundwater in this southern region is 3.5 m. The Pleistocene molass-sandstones, marls, and conglomerates located predominantly in the northern region of the Thur catchment are highly productive in terms of groundwater, and host one of the largest groundwater systems in Switzerland where average depth to groundwater is 1.4 m (Abbaspour et al., 2007; Keller, 1992). Abstraction rate estimates from the largest aquifer in the Thur catchment (approximately 64 km^2 in size) are in the order of 16 million m^3/y, which amounts to approximately 9.4 mm of water abstracted from the groundwater annually (Baumann, 2009; https://umwelt.tg.ch/, last access: 11 September 2020). When compared to the annual precipitation values (see below), this amounts to ~0.01% of the annual water input into the Thur catchment. Subsequently, abstraction rates were omitted from the water balance calculation in this study.

Land use in the Thur basin is dominated by agriculture (~ 60%), with large areas of pasture (Figure 3-1c). Forests make up 30% of the land surface, and the remaining ~10% includes barren land, surface waters, and urban areas. Elevation in the Thur catchment varies from 2502 to 363 m asl. (Figure 3-1d), with an average slope inclination of 7.9º (Melsen et al., 2016). The hydrological regime of the Thur catchment is characterized by its variable morphological and climatic elements. Streamflow in the Thur River can fluctuate by up to two orders of magnitude in the space of a few hours, with recorded discharge rates at the Andelfingen (An) discharge station ranging from 3 - 1130 m^3/s (mean discharge of 47 m^3/s) (Doulatyari et al., 2017; Gurtz et al., 1999).

On average, precipitation in the Thur catchment varies from 700 mm/y in the low elevation northern region, to 2700 mm/y in the southern mountainous region (Figure 3-1e) (http://www.meteoswiss. admin.ch/). The lowest average evapotranspiration rates (~400 mm/y) are found in regions of high elevation, with higher average ET is associated with the lower reaches of the Thur valley (~500 mm/y), (Figure 3-1f). The highest average evapotranspiration rates (~ 600 mm/y) are associated with the central region of the Thur catchment (~ 700 m asl.) (https://lpdaac.usgs.gov/), here land use is associated with mixed pasture, agriculture, and forestry (Figure 3-1e).

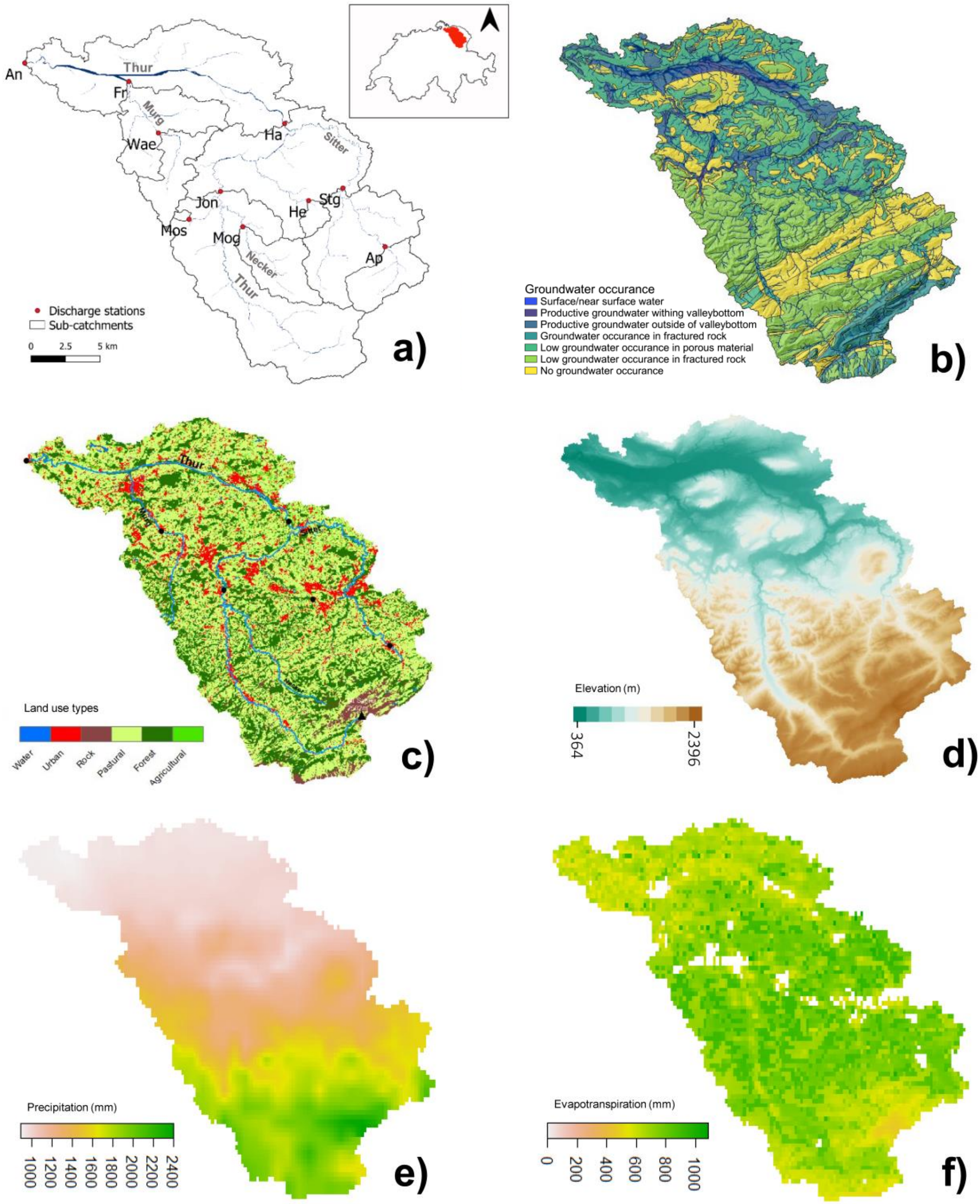


Figure 3-1: Characteristics of the Thur catchment's a) major drainage lines, gauging stations, and sub-catchments, b) groundwater occurrence, c) land cover classification d) topographic variability (m), e) mean precipitation values (mm/y), and f) mean actual evapotranspiration rates (mm/y) (BFS GEOSTAT 2009; FOEN 2020; Federal Office of Topography; MeteoSwiss; Running, et. al., 2019). White areas in figure f) represent no data areas for MODIS ET data.

3.4 Data and methods

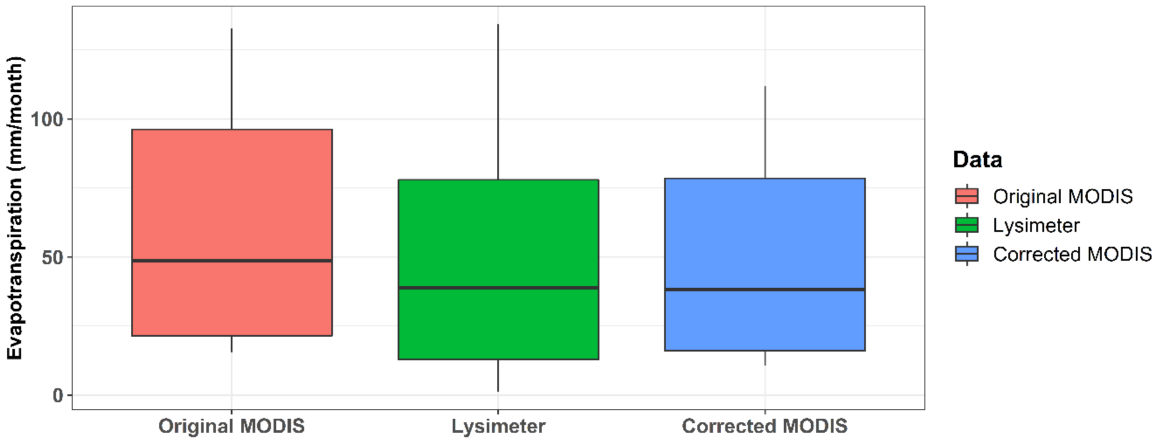
This section describes in detail the gridded and ground-based data employed in this study, as well as the methods applied to calculate groundwater recharge in the Thur catchment. Through employing open source software for the gridded water balance computations, the presented workflow is anticipated to be readily transferrable and applicable to other catchments.

3.4.1 Methodology

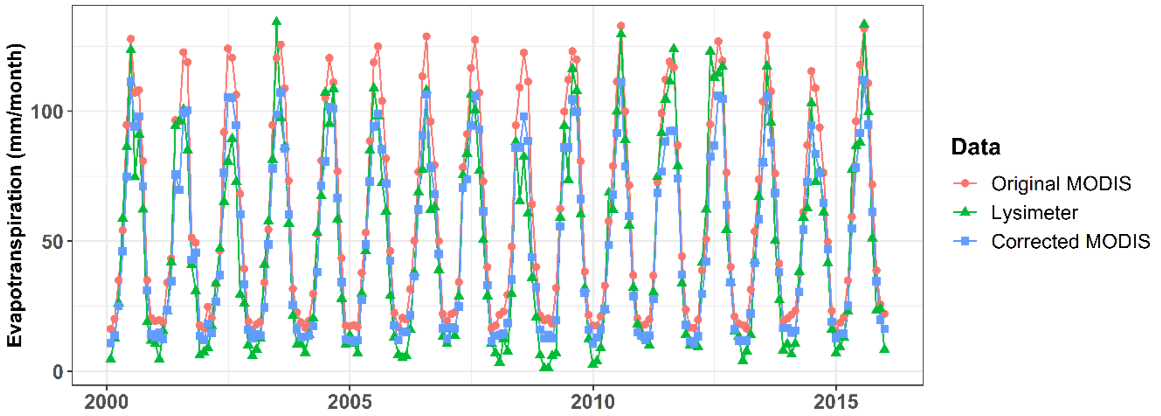
MODIS data

The Mosnang (Mos) sub-catchment (Figure 3-1a), also known as the Rietholzbach research catchment, is a well-instrumented catchment with a long history of both atmospheric and hydraulic data collection. Readily available long-term AET data from studies conducted in the Mos sub-catchment for the years 1976 to 2015 (Hirschi et al., 2017; Moeck et al., 2018; Seneviratne et al., 2012) were used in this study to evaluate the accuracy of MOD ET data used in calculating the Thur catchment's water budget.

The large weighing lysimeter setup in the Mos sub-catchment is the only independent long-term AET data available for the Thur catchment, rendering it necessary in verifying the expected AET values, in spite of its area representing only a fraction of the entire Thur catchment. As such, the mean MOD ET pixel values for the Mos sub-catchment were compared to the available lysimeter values from the study conducted by Seneviratne et al. (2012). When comparing the MOD ET values to lysimeter values, an overestimate in the MOD ET data was evident (Figure 3-2a). Where the lysimeter AET values ranged between 1.20 and 134.2 mm/month for the period from 2000 and 2015, the MOD ET values ranged from 15.52 to 132.79 mm/month for the same period. In order to account for this, the MOD ET values were adjusted (hereon referred to as AET_{corr}) by a correction factor of 0.71. This factor was estimated by inversely fitting the MOD ET data to the measured lysimeter values, while seeking to reduce the daily mismatch. Overall, fitted results are in good agreement with the observed lysimeter data (Figure 3-2b). In addition, AET_{corr} values were compared to expected MOD ET values as described by Mu et al. (2011) at a latitude of approximately 47.5º (the latitude of the Thur catchment), which were in line with the lysimeter values.



a)



b)

Figure 3-2: Comparison of original MOD ET values, lysimeter values and corrected MOD (AET_{corr}) values a) as a boxplot and b) a temporal plot showing seasonal trends for the years 2000 – 2015.

Baseflow from total discharge values

Baseflow separation is a method whereby total stream discharge (Q) is separated into precipitation event-based surface discharge components (often referred to as quickflow) (Q_q), and baseflow components (Q_b) (Eq. 3). Baseflow (Q_b) is usually associated with subsurface processes, cannot be attributed to a single precipitation event, and has been taken as a quantitative variable of groundwater discharge to rivers by many authors (Blume et al., 2007; Duncan, 2019; Fendeková and Fendek, 2012; Hall, 1968; Healy and Scanlon, 2010; Hellwig and Stahl, 2018; Nathan and McMahon, 1990; Reitz et al., 2017; Sutcliffe et al., 1981). Baseflow represents a part of the groundwater which returns to the surface water; a process through which many rivers and lakes are fed, and aquatic ecosystems are maintained during dry periods (Aeschbach-Hertig and Gleeson, 2012; Gurdak, 2017). Infiltration to recharge subsurface storage increases baseflow, but due to AET baseflow can also be reduced as temperature gradients and trees absorb water from the ground. Using a digital filter method available in the EcohydRology R package, with three passes and filter parameter set to 0.925 as proposed by Nathan and McMahon (1990), base- and quickflow was estimated from the available Q data in order to estimate baseflow from total streamflow in the Thur catchment:

$$Q = Q_q + Q_b \quad (3)$$

A baseflow index was generated for each sub-catchment (refer to Table S 1 and Figure S 1 of Appendix I: Supplementary Information to Chapter 3). In addition, a baseflow separtation method comparison was conducted (after Zomlot et al., 2015) using the free online automated Web-Based Hydrograph Analysis Tool (WHAT), to compare three separation methods: 1) the Eckhardt recursive digital filter (Eckhardt, 2005; Lim et al., 2005) with filter parameter set to 0.98 and 0.925, 2) the local minimum method, and 3) the one parameter method. On average, the ammount of baseflow contribution derived from the different methods varied by up to 22% (refer to Figure S 2 of Appendix I: Supplementary Information to Chapter 3). Using a recursive digital filter method with filter parameter set to 0.925 was the most conservative approach, resulting in an average monthly baseflow contribution of 43%.

Spatially gridded discharge

In order to evaluate the discharge volumes (in mm) in the Thur Catchment on a spatial basis as part of the water balance, point measurements of stream volumes weighted based on a topographically-based top-down flow accumulation (FA) algorithm generated using SAGA GIS (Conrad et al., 2015). Refer to Supplementary Figure S3 for a comparison of FA weight ranking methods. The FA raster was based on a flow routing algorithm (after Seibert and McGlynn, 2007; Tarboron, 1997) generated from a 25 m raster DEM (Source: Federal Office of Topography) which was pre-processed using Wang and Liu's, 2006 fill sink process (Wang and Liu, 2006). The FA raster was resampled using bilinear interpolation to match the 500 m x 500 m raster resolution of the MOD ET data, and then normalized (FA_{norm}) to create a weighting factor between 0-1:

$$\boldsymbol{FA_{norm}} = (\boldsymbol{FA} - \boldsymbol{FA}_{\mathbf{min}})/(\boldsymbol{FA}_{\mathbf{max}} - \boldsymbol{FA}_{\mathbf{min}}), \tag{4}$$

before being multiplied by the temporally aggregated quickflow (Q_q) values of each sub-catchment, in order to represent spatially distributed quickflow ($Q_{q\text{-}dis}$) for the Thur catchment:

$$\boldsymbol{Q_{q-dis}} = \boldsymbol{Q_q} * \boldsymbol{FA_{norm}} \tag{5}$$

The resulting product, although based on an algorithm which laterally connects adjoining downstream pixels, was used purely to represent discharge volumes spatially as input into the water budget calculation (Eq. 7; Figure 3-3). As such, each pixel value does not represent actual measured Q_q at the pixel location, but rather each $Q_{q\text{-}dis}$ pixel merely represents a portion of the precipitation into that cell which ultimately produces the measured downstream Q_q response.

Recharge estimates from the water balance equation

In cases where a catchment represents a steady-state system, the terrestrial water budget is equal to all inputs into minus all outputs out of the system. This implies that over long time periods (e.g. annual), storage (ΔS) calculated from Eq. 2 does not change, and baseflow can be defined as representative of effective groundwater recharge (Reitz et al., 2017; Wolock, 2003). Assuming a steady-state system for the Thur catchment (with inflow and outflow via groundwater negligible), Q was separated into its quick- and baseflow components using a Q_b-conservative digital filter method, where Q_b would represent the minimum effective groundwater recharge:

$$Q_b = P - AET_{corr} - Q_q \tag{6}$$

Assuming reasonable uncertainties and that component errors are minimal or constant (refer to Section 3.4.5), the water available for recharge (R) in the Thur catchment was described using the gridded component values as follows:

$$R \approx Q_b = P - AET_{corr} - Q_{q-dis}\ , \tag{7}$$

where the gridded spatiotemporal R values represent the value of water which would result in the modelled Q_b response derived from downstream measured Q values.

According to Creutzfeldt et al. (2014), the spatiotemporal variability and availability of water in a catchment is controlled by underlying processes of different spatial characteristics. Any change in trend (representing both the direction and rate of change) can be determined by the slope of a linear regression model (De Jong et al., 2011). Gridded values of R were assessed using a pixel-wise ordinary least-squares linear regression for the 20 years from 2000 – 2019, at the 95% significance level; determining changes in recharge characteristics in the Thur catchment over a twenty year period (refer to Section 3.5.3).

Workflow

Using the open-source statistical program R (R Core Team, 2018), grid-based computations were conducted for the Thur Catchment at the 500 m x 500 m resolution, with each independently estimated input variable representing a water balance component (in rates per unit area) for the years 2000 – 2019. The work process for the data processing is illustrated as a flow diagram in Figure 3-3. This method relates the water balance components P, AET_{corr} and $Q_{q\text{-}dis}$ in a spatiotemporal manner to estimate catchment-wide R over time. No lateral transfer was considered between the individual pixels, but rather mapping the vertical exchange of water entering (via precipitation) and leaving (via evapotranspiration and discharge) each pixel to estimate the recharge component of each cell.

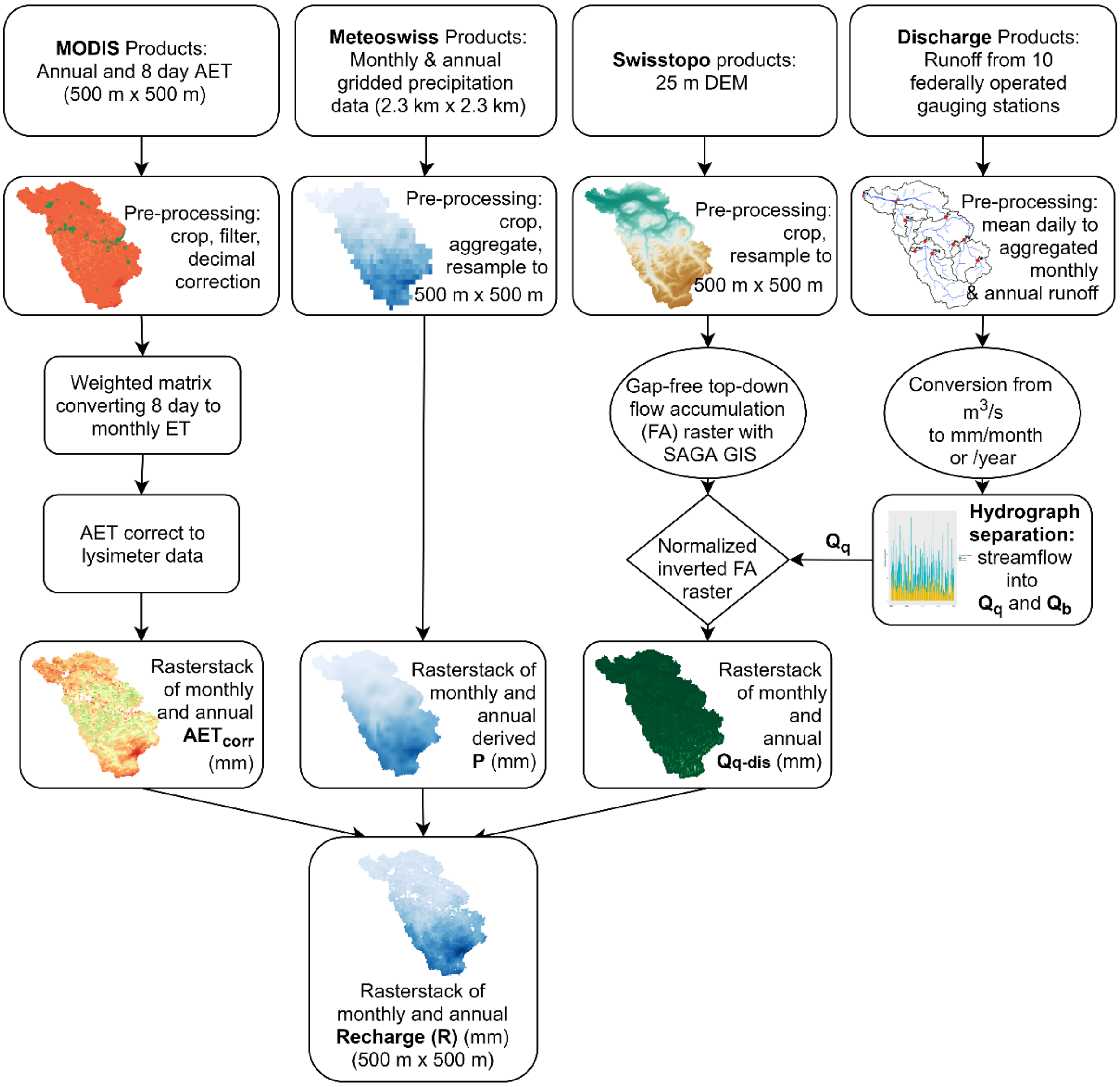


Figure 3-3: Flow chart showing work process in R studio with input data from MOD ET (AET), MeteoSwiss (P), FOEN (Q), and DEM (source: Federal Office of Topography) used in determining gridded recharge (R) in the Thur catchment for the years 2000 – 2019.

3.4.2 Precipitation product

Precipitation, being the primary flux in most hydrological cycles, requires high resolution data in order to reliably estimate water availability and distribution within a catchment. Although an array of remotely sensed rainfall data is available (e.g. Global Precipitation Climatology Project (GPCP), Tropical Rainfall Measuring Mission (TRMM), Global Precipitation Measurement (GPM), etc.), these all have a relatively low resolution (~10 – 250 km^2) when considering a mesoscale catchment with a high topographic variability (Sun et al., 2018). Thus, long-term gridded precipitation data, interpolated from 73 Swiss national stations located within or close to the Thur catchment, was used for this study (©MeteoSwiss, 2016).

The MeteoSwiss product consists of continuous high-quality measurements, interpolated from a network of ground based radar and gauge data using the Reduced Space Optimal Interpolation (RSOI) method; specifically developed for regions with a complex orography

(Begert et al., 2007; Schiemann et al., 2010). The interpolation errors for the Swiss Plateau region has a relative standard error of +/- 20% (MeteoSwiss, 2013), and the resulting gridded data has a 2.3 km x 2.3 km resolution. The gridded MeteoSwiss annual (January – December) and monthly rainfall data (RhiresY v1.0 and RhiresM v1.0) represents accumulated precipitation, including both rainfall and snowfall equivalent (in mm per month and per year). The MeteoSwiss data was resampled using bilinear interpolation to match the resolution of the MODIS ET data and used as input in the water budget calculation (refer to Section 3.4.1).

Although a substantial portion of the Thur catchment is under agriculture (Figure 3-1c), high annual precipitation rates resulting in wet environmental conditions in the catchment, renders the irrigated amounts as relatively insignificant when compared to the relatively high water surface water availability (Kanton Thurgau Amt für Umwelt et. al., 2008). Therefore, although seasonal water shortage (e.g. summer drought periods) are recorded locally (discussed in Section 3.5.3), it is assumed that the effect of irrigation is negligible in the sense of the Thur catchment's total water balance. Additionally, relatively little variation in precipitation characteristics, such as season, frequency, and duration of dry and wet days, appears across the Thur's different sub-catchments (Dal Molin et al., 2020).

3.4.3 Evapotranspiration product

Calculations of actual ET (AET) are generally local measures from Eddy Covariance (EC) towers, Large Aperture Scintillometers (LAS), or lysimeters. These methods are often regarded as the most accurate and reliable determination of AET (Baldocchi, 2003; Brotzge and Crawford, 2003; Rana and Katerji, 2000; Schrader et al., 2013; Xu and Chen, 2005). However, due to the spatial heterogeneity of AET, upscaling of point information to a regional scale is challenging, and models have been employed to compensate for the lack of observations and fill spatial gaps (de Graaf et al., 2017; Döll and Fiedler, 2008; Orth and Seneviratne, 2015; Wada et al., 2016).

Remotely sensed products offer feasible alternatives to obtaining AET measurements at regional scales (Bhattarai et al., 2016; Zhang et al., 2008). The Moderate Resolution Imaging Spectroradiometer (MODIS) on board the Terra satellite, has been acquiring 36 spectral bands (wavelengths) of the globe every 8 days since December 1999 (https://terra.nasa.gov/about/mission). The MODIS sensors were designed to detect electromagnetic bands which include spectral signatures of atmospheric water vapour as well as vegetation indices and land cover change from which continuous biophysical variables including land surface temperature, albedo, soil moisture, and leaf area index (LAI) can be deduced (Running et al., 2019, 1994). From these variables, a regional composite ET product is estimated, at a 500 m x 500 m resolution, using the Mu et al. (2011) improved ET algorithm which is based the Penman-Monteith (PM) equation (Monteith, 1965). When estimating groundwater recharge, it must be noted that a percentage of the AET determined by the MODIS ET algorithm may stem directly from the groundwater, especially during dry conditions. According to Luo et al. (2016), where depth to water table ranges between 3 – 6 m, this percentage may range between 15% and 23% for coniferous forests, depending on the soil type. However, were depth to water table is between 1 – 2 m, the effect of groundwater loss via transpiration is limited (Luo et al., 2016).

The MODIS ET product has well-documented quality assessment protocols, reproduces basin-scale AET response with acceptable uncertainty (Khan et al., 2018; Velpuri et al., 2013), has good temporal resolution, and is freely and easily accessible to researchers and governments. In light of this, the improved gap-filled annual (January – December) and 8-day (MOD16A3GF and MOD16A2GF respectively) MODIS (hereon referred to as MOD) ET data was used as the evapotranspiration component in this study. The full series was obtained from the Land Processes Distributed Active Archive Centre (LP DAAC) for the years 2000 to 2019 (https://lpdaac.usgs.gov/) [Accessed on 2019-11-19]. The MOD ET image tiles were pre-processed and clipped to the Thur catchment for ease of use (refer to Section 3.4.1).

3.4.4 Discharge product

While the MeteoSwiss P and MOD ET products are in gridded spatiotemporally varying quantities, Q is measured at a point as a flux through a stream channel (Tang et al., 2010). Ten (10) federally operated gauging stations are located in the Thur catchment (Figure 3-1a; Table 3-1). All stations are located along free-flowing systems and have continuous data for the period 2000 - 2019 (with the exception of the Halden (Ha) station, where October - December 2019 was absent – refer to Proportion of baseflow (Q_b) to total streamflow (Q) in Appendix I: Supplementary Information to Chapter 3 for details). Available stream discharge time series were obtained from the Swiss Federal Office for the Environment (FOEN) and quality checked prior to use.

The Andelfingen (An) site represents the discharge for the entire Thur catchment, with 9 sub-catchments located upstream of it. The next biggest sub-catchment is represented by the Ha site, which drains approximately half of the Thur catchment. For the 2000 – 2019 period, the high elevation sub-catchment Appenzell (Ap) displayed the highest average Q value (1375.5 mm/y), while the low elevation Frauenfeld (Fr) station displayed the lowest average discharge value (556.89 mm/y) (Table 3-1). For the years 2000 – 2019, hourly discharge (m^3/s) was converted to monthly, seasonal, and annual (January – December) volumes of water (mm), by aggregating the mean hourly discharge and dividing it by the discharge station's upstream area. Seasonal data was based on winter (December, January, and February), spring (March, April, and May), summer (June, July, and August), and autumn (September, October, and November) aggregates.

Table 3-1: Gauging stations located in the Thur catchment with site names and abbreviated IDs used in this study, along with number of catchments located upstream from station, area of upstream catchments, elevation of stations, and average stream discharge (Q) for the years 2000 – 2019

Site	ID	Code*	Upstream catchments	Downstream stations	Area (km^2)	Elevation (m) at catchment outlet	Average Q (mm/year)
Andelfingen	An	2044	9	0	1702	363	846.68
Appenzell	Ap	2112	1	3	74	772	1375.50
Frauenfeld	Fr	2386	2	1	213	394	556.89
Halden	Ha	2181	6	1	1085	461	1063.36
Herisau	He	2305	1	2	17	680	1059.03
Jonschwil	Jon	2303	3	2	493	534	1259.92
Mogelsberg	Mog	2374	1	3	88	610	1132.85
Mosnang	Mos	2414	1	3	3	670	993.74
St. Gallen	Stg	2468	2	2	261	582	1189.93
Wängi	Wae	2126	1	2	79	470	693.18

* Code of the gauging station, as defined by the Federal Office for the Environment, FOEN

3.4.5 Sensitivity of gridded water balance components

Although using independent components as input reduces the propagation of errors (Healy and Scanlon, 2010), the accuracy of recharge from a water budget calculation depends entirely on the uncertainties of each of the components used in the calculation. For example, previous studies have shown that in some cases MOD ET products result in an over estimation when compared to ground-based values (Miranda et al., 2017; Ruhoff et al., 2013; Velpuri et al., 2013; Zhao and Liu, 2014, also see Section 3.4.1). Terrain complexity, the distribution and number of measuring stations, along with time series availability and measurement frequency can affect the precision and representativity of measurements taken (Coxon et al., 2015; Schiemann et al., 2010; Turnipseed and Sauer, 2010). This is particularly true when measuring precipitation, where amounts can vary greatly in both seasonal and spatial distribution, especially over complex terrain (Schiemann et al., 2010; Sun et al., 2018).

Although the input components stem from independent sources, they are highly inter-dependant. However, assuming that they are unbiased and normally distributed, the variance (σ^2) of the individual components can be calculated in order to assess the degree of estimation error:

$$\boldsymbol{\sigma^2}_{\boldsymbol{\varepsilon}} = \boldsymbol{\sigma^2}_{\boldsymbol{P}} + \boldsymbol{\sigma^2}_{\boldsymbol{AETcorr}} + \boldsymbol{\sigma^2}_{\boldsymbol{Qq-dis}} \quad (8)$$

Here, confidence intervals (CI) were calculated and explored for recharge estimate using 100,000 random component values generated within a realistic component value range within which each component was varied by a fixed amount based on estimated data errors. The range of precipitation value error was based on a +/- 20% relative standard error suggested by MeteoSwiss (2013), while the error range for AET_{corr} was set at +/- 25% (based on the findings of Miranda et al., 2017; Ruhoff et al., 2013; Velpuri et al., 2013; and Zhao and Liu, 2014) as well as our own assessment (refer to Section 3.4.1). The specified error for Q is +/- 3% (after Spreafico and Weingartner, 2005), with higher errors indicated during increased or peak flows. In order to account for the high streamflow variability of the Thur River and its tributaries, the relative standard of error for $Q_{q\text{-}dis}$ was increased to 5% for this study.

3.5 Results

This section evaluates the individual water balance components, some of which were derived from ground-based data, and presents results from the Thur catchment's gridded water balance. Spatiotemporal recharge over a 20 year period was investigated, and the monthly, seasonal, and annual variability in the water balance components in the Thur catchment were examined.

3.5.1 Baseflow from total streamflow

The results of the digital filter baseflow separation were plotted as monthly data at seasonal intervals (Figure 3-4a). When considering the ratio of Q_b to total streamflow (Q), the significance of Q_b becomes evident for all of the sub-catchments in the Thur catchment, with average contributions of Q_b ranging from 31% – 57% (refer to Supplementary Table 1 for baseflow ratios). Along steeper slopes, flow velocities are higher and recharge capacity is generally limited, favouring surface runoff and instream discharge, resulting in elevated Q_q values. Whereas gentler slopes experience both slower flow velocities as well as greater storage capacities, resulting in a higher contribution of Q_b to total streamflow (Anderson et al., 1978; de Lavenne et al., 2019; Moeck et al., 2020; Van Loon and Laaha, 2015). The high elevation sub-catchments of Ap, He, Mos, Mog, and Stg displayed a greater proportion of Q_q relative to Q_b, while the sub-catchments Wae and Fr, located in the lowland region of the Thur catchment, displayed a relatively high proportion of Q_b in relation to Q_q. Although the entire Thur catchment experienced a predominance of Q_q during the winter, summer, and autumn months (with the highest Q_q values occurring during the summer), on average Q_b continued to make up 45% of the total discharge value and displayed a predominance of 53% of the total streamflow during the spring months. When lumping seasonal Q_q and Q_b values on a yearly basis, elevated contributions of Q_b during the dry summers of 2003, 2015, and 2018 are highlighted; making up as much as 55%, 65%, and 60% respectively of total flow recorded at the end of the dry (summer) months in the Thur River (Figure 3-4b). Please refer to Figure S 1from Appendix I: Supplementary Information to Chapter 3 for monthly Q_q and Q_b values from all of the sub-catchments. Twenty years of hourly quickflow values were fed into the gridded workflow (refer to Section 3.4.1), in order to evaluate the spatiotemporal R values (after Eq. 7) in the Thur catchment and its sub-catchments.

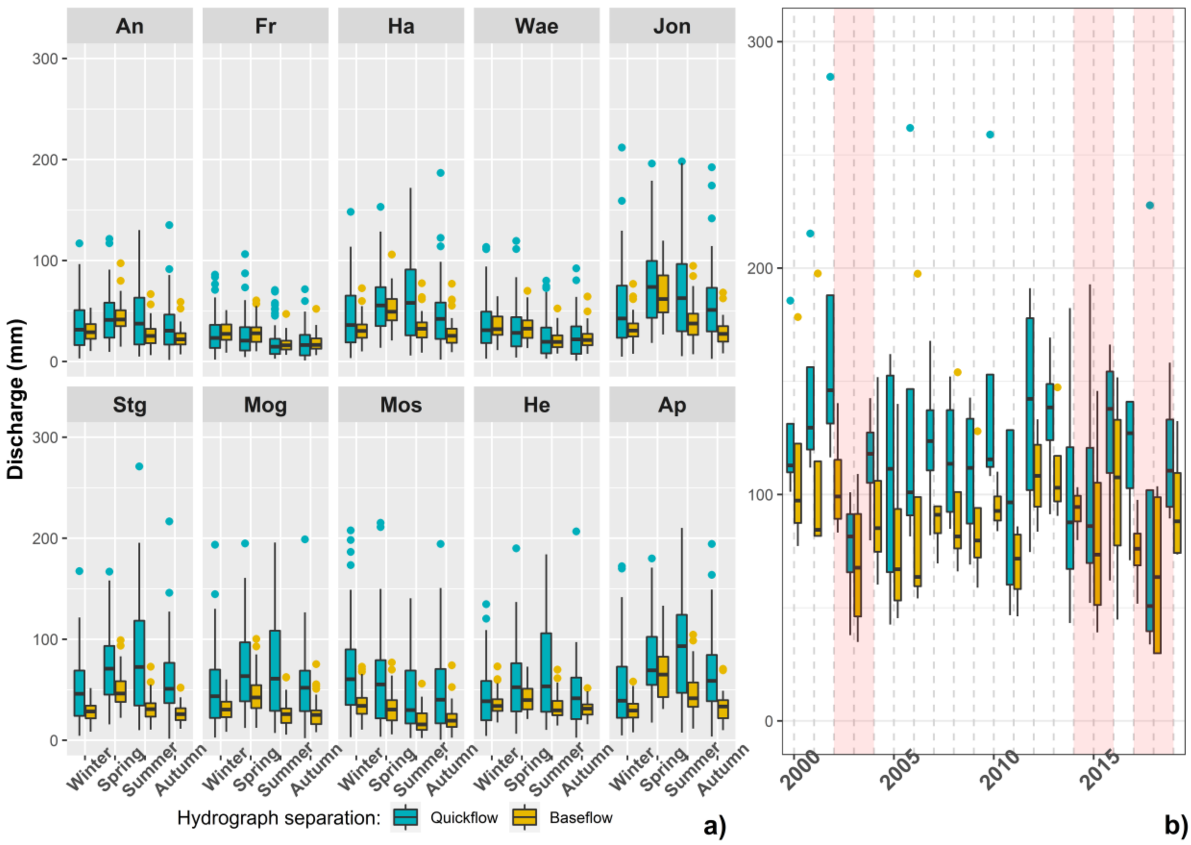


Figure 3-4: a) Monthly quick- (Q_q) and baseflow (Q_b) from total streamflow values (Q) in the Thur catchment (An) and its sub-catchments (listed in increasing order of elevation from top left to bottom right) grouped into seasonal intervals, and b) Seasonal Q_q and Q_b values for the entire Thur catchment grouped into yearly intervals for the period 2000 – 2019, with drought years 2003, 2015 and 2018 indicated in red.

3.5.2 Water balance in the Thur catchment

In order to determine the extent of water balance closure in the Thur catchment (after Eq. 6), mean monthly, seasonal and annual input values (P) were correlated with output values (AET_{corr}, plus the modelled Q_q, and Q_b values). Monthly values indicated a relatively good correlation, with R^2 equal to 0.65 (Figure 3-5a). The correlations improved were seasonal (Figure 3-5b) and annual (Figure 3-5c) data was used, with R^2 equal to 0.8 and 0.88 respectively. This suggests that over longer time periods (e.g. seasonal to annual), the assumption that the Thur catchment is in a steady-state, and ΔS negligible, becomes more valid.

The lack of complete closure might be attributed either to time-lags in groundwater to surface water, or to measurement errors and uncertainties in the water balance components. For instance, precipitation can have a relative standard error of +/- 20% as suggested by MeteoSwiss (2013). Moreover, in the high elevation reaches of the catchment uncorrected solid precipitation amounts (e.g. snow) can have a strong impact (Dal Molin et al., 2020; Schmucki et al., 2014; Zappa et al., 2003), and potentially limit the complete closure of the water balance. For example, although some grouping was evident in the monthly data (Figure 3-5a), with spring and summer values plotting predominantly above and autumn and winter values predominantly below the input vs. output correlation line, an improved grouping was evident in the seasonal values (Figure 3-5b). The impact of snow storage and melt is further advocated with most spring and summer data plotting predominantly above the correlation line (Franz et al., 2010; Meeks et al., 2017). However, a more systematic investigation is required to understand this process in detail and thus this outcome should not be over-interpreted in the context of this study.

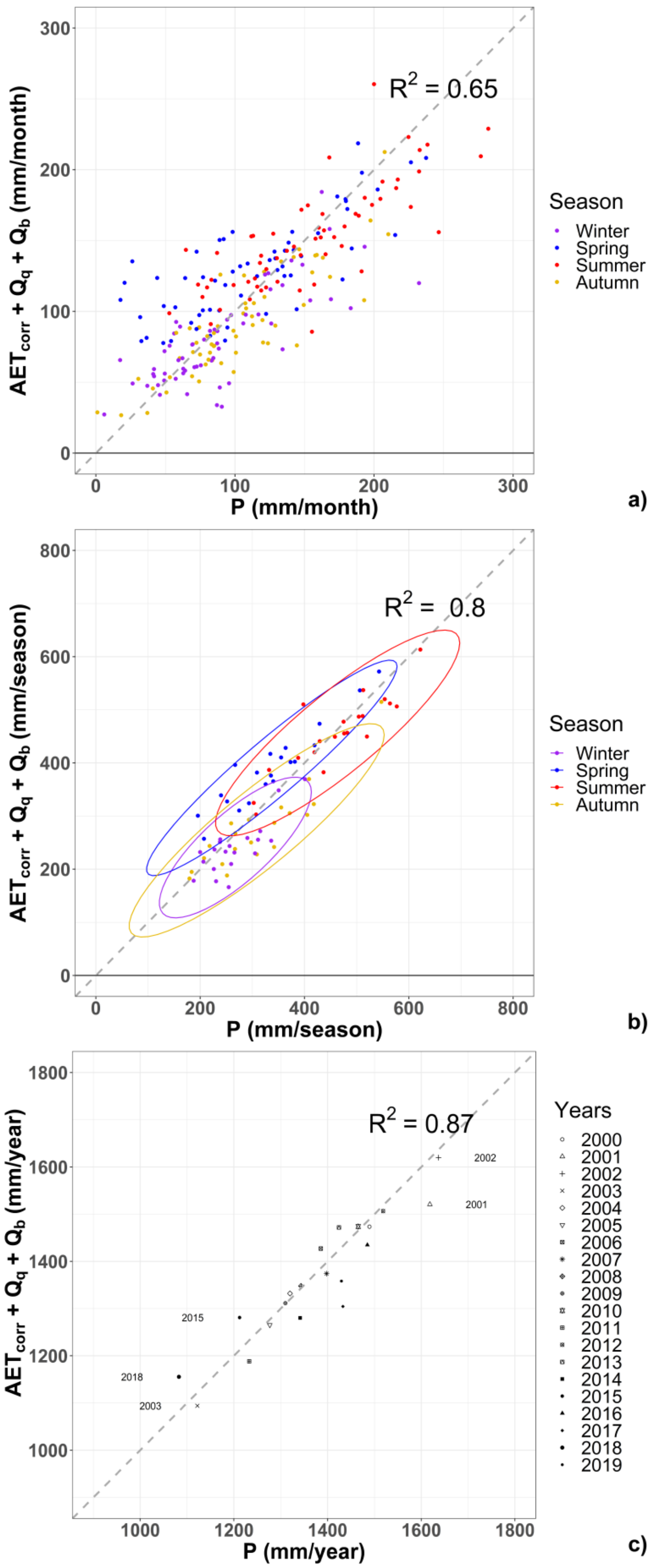


Figure 3-5: a) Monthly, b) seasonal, and c) annual comparison of mean water balance component values for the entire Thur catchment for the years 2000 – 2019, with 1:1 correlation lines indicated.

3.5.3 Spatiotemporal recharge in the Thur catchment

Variation in the gridded water balance components

The spatial distribution of mean monthly P values over the 20 year period from 2000 to 2019 were highest in the high elevation regions to the south of the Thur catchment, and lowest in the northern reaches of the catchment (Figure 3-6a left). Monthly P values (Figure 3-6a bottom right) ranged between 1.05 and 282.15 mm/month over the 20 year period, with a monthly mean of 114.68 mm/month. Annual values (Figure 3-6a top right) show high (>1500 mm/year) P values for 2001 and 2002 (nationally recorded wet years), and low (<1250 mm/year) P values in 2003 which experienced record-breaking heatwaves throughout Europe (Casty et al., 2005; Schär et al., 2004), 2015 and 2018 which are also nationally recorded drought years (BAFU et. al., 2020). Additional dry years in the Swiss north-eastern pre-Alps were experienced during 2005 and 2011 (MeteoSwiss, 2011, 2005). From 2003 to 2009, and again in 2011, mean annual P values remained at or below the 20 year average of 1370.82 mm/year.

Low (< 40 mm/month) monthly AET_{corr} values were associated with exposed high elevation regions to the south of the Thur catchment, as well as with the lowland regions to the north where land use is more intense (refer to Figure 3-1c), while the highest AET values were associated with the mid-latitude reaches of the Thur catchment (Figure 3-6b left). Annual AET_{corr} values showed relatively little variation, with a maximum value of 543.8 mm/year for the year 2011, a minimum of 486 mm/year for 2001, and an overall mean of 513.9 mm/year for the 20 year period (Figure 3-6b top right). Monthly AET_{corr} values oscillated between ~15 and ~90 mm/month, with a mean monthly value of 60.31 mm/month (Figure 3-6b bottom right). The distributed mean monthly $Q_{q\text{-}dis}$ values were greatest in association with the valley bottoms where water accumulates, with minimum $Q_{q\text{-}dis}$ associated with the steeper slopes associated with the southern regions of the catchment (Figure 3-6c left). Over the 20 year period monthly $Q_{q\text{-}dis}$ values ranged between 1.53 and 135.1 mm/month, with a mean value of 40 mm/month (Figure 3-6c bottom right). Mean annual $Q_{q\text{-}dis}$ values were highest in 2002 (693 mm/year), which is in line with a nationally recorded wet year (BAFU et. al., 2020), while the years 2012 and 2013 also presented relatively high (>530 mm/year) $Q_{q\text{-}dis}$ values (Figure 3-6c top right). Low $Q_{q\text{-}dis}$ values were associated with the drought years of 2003, 2015, and 2018 (302, 417 and 363 mm/year respectively), with the 2005, 2009, 2014, and 2017 $Q_{q\text{-}dis}$ values also falling below the 20 year average of 480 mm/year. The input components into the water budget calculation, P, AET_{corr}, and $Q_{q\text{-}dis}$, display a spatial distribution that is strongly related to the catchment's topographic variations (refer to Figure 3-1d).

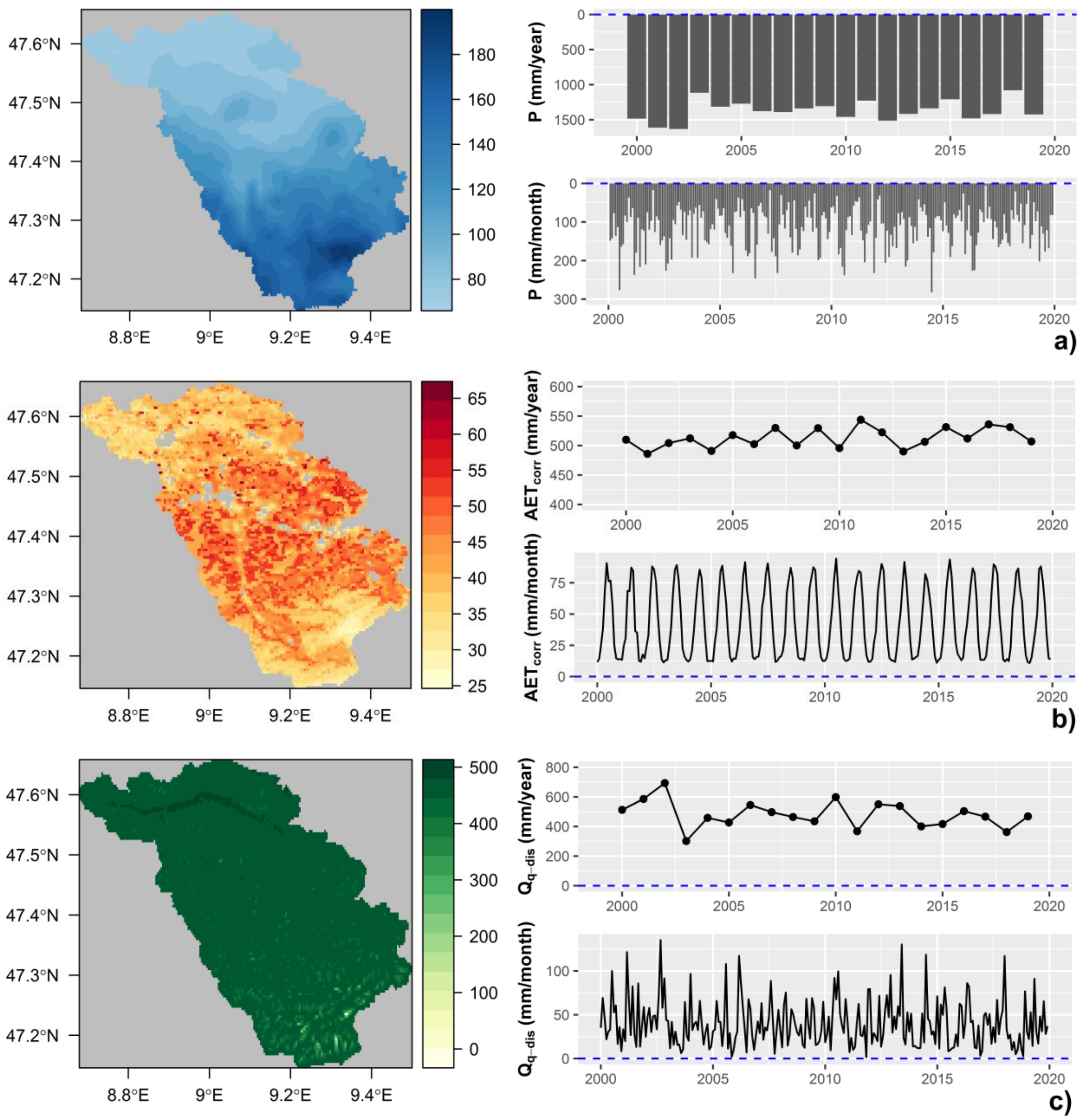


Figure 3-6: Mean spatial distribution of a) P, b) AET_{corr}, and c) $Q_{q\text{-}dis}$ in mm/month, with monthly and annual time series of P, AET_{corr}, and $Q_{q\text{-}dis}$ indicated (in mm) for the years 2000 - 2019 for the Thur catchment. Grey areas equal no data areas (urban areas or water bodies, which are not included in MOD16 ET data sets).

Spatiotemporal groundwater recharge over a 20 year period

Gridded recharge maps were generated by closing the water balance after Eq.7. The mean R values for the Thur catchment between the years 2000 – 2019 ranged from smaller values (<500 mm/year) in the central and northern regions, to large values (>1000 mm/year) in the southern regions (Figure 3-7a); this is strongly controlled by a difference in precipitation gradient between north and south. The gridded R values are a conservative spatial estimate of water available for recharge in the Thur catchment area, while the net spatial change of R values assessed using a pixel-wise linear regression is a measure of how much R (in mm) has changed per pixel over the 20 year period (Figure 3-7b). Significant long-term change in R values were calculated (Figure 3-7b). At the 95th percentile level, areas within the Thur catchment experiencing significant R value change comprised 4.4% (or 74.98 km^2) of the total area, and all significant change was negative. The significant R value changes were restricted to the lower reaches of the Thur catchment, parts of the Fr/Wae sub-catchments and the lower reaches of the Jon sub-catchment (refer to Figure 3-1a for sub-catchment locations).

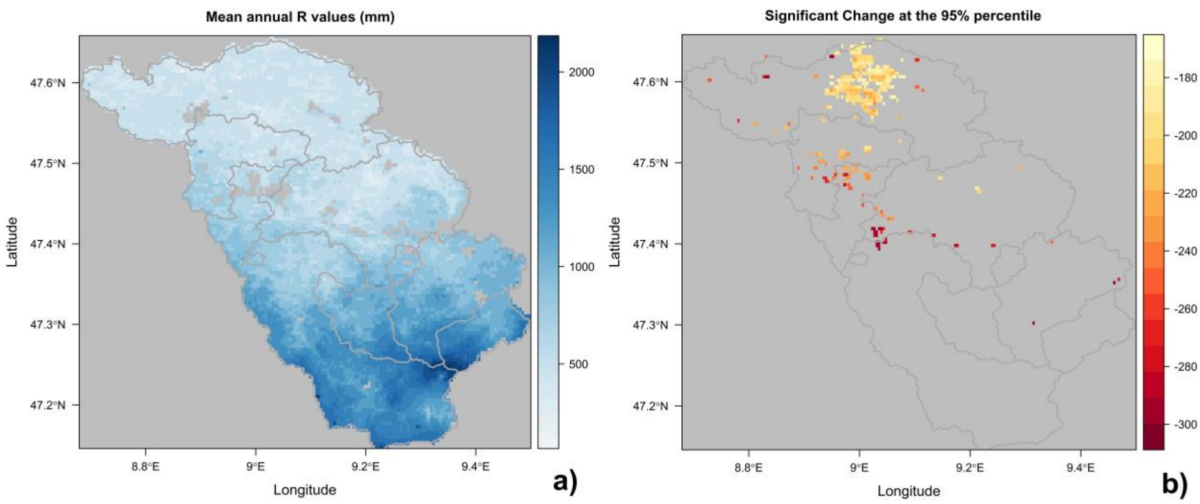


Figure 3-7: a) Mean annual R values (mm/y) for the Thur catchment over 20 years (2000 – 2019), and b) pixel-wise (500 m x 500 m) linear regression of R with significant annual change indicated for the 20 year period at the 95th percentile level.

Over the 20 year study period, the mean temporal recharge values for the entire Thur catchment displayed an average monthly (short-term) mean R value of 34.13 mm/month (Figure 3-8a), while annual (long-term) R values ranged between 208.3 and 577.8 mm/year, with a mean of 409.55 mm/year (Figure 3-8b). Seasonal (medium-term) values displayed a mean R of 121 mm/month during the winter months, 85 mm/month during spring, 93.4 mm/month during summer, and 110 mm/month during the autumn months (Figure 3-8c). It must be noted that, due to the use of a conservative baseflow separation method with respect to Q_b (refer to Section 3.4.1 and Figure S 2 of Appendix I: Supplementary Information to Chapter 3 where differences of up to 22% are indicated depending on the separation method), resulting R values are conservative, and it is likely that the study area is capable of experiencing greater recharge rates. As discussed by Immerzeel et al. (2020) and Viviroli et al. (2007), mountains can be described as the world's water towers; where precipitation and subsequent runoff and discharge potentials are high. Although monthly data suggests that over short periods the Thur catchment did on occasion experience water shortage in terms of water demand being higher than water availability, especially during the spring and early summer months, as indicated by the negative values (15% of the monthly data values were ≤ 0), over medium to long-term periods a sustained net surplus of recharge was evident in the Thur catchment over the 20 years period.

Figure 3-8a and b show short- (monthly) and long-term (annual) temporal trends in R, where surplus (blue) or deficit (red) R values are indicated with respect to monthly and annual mean values for the 20 year period. Although short-term R values can on occasion be negative, in particular during the spring of 2007, 2009 and 2018, a mean value of 34.13 mm/month suggests that on average, water availability in the Thur catchment was greater than water demand. Medium-term (seasonal) intervals show that mean seasonal R values were at their lowest during spring, while the highest mean seasonal R values occurred during the winter months (Figure 3-8c). Although over medium- and long-term intervals water demand did not exceed water availability, Figure 3-8b indicates that notable annual R deficits (values below the long-term annual mean of 409.55 mm/year) for the Thur catchment are in line with national drought years (2003, 2015, and 2018), while the year 2001 displayed high R surplus (values above long-term mean of 409.55 mm/year). Comparing the intensity of R deficit across the different national drought years, the 2003 drought is seen as having being the least extreme (307.22 mm/year) and the 2018 drought the most extreme (208.3 mm/year) in terms of R deficit values (this point is further discussed in Section 3.6). Post 2003 the annual R deficit did not recover again to above mean R values until 2012, with R values remaining below the long-term mean from 2003 up to and including 2011. Concerning soil moisture variations, Orth and Seneviratne (2012) showed that, rather than evapotranspiration or runoff, soil moisture memory effects depend on both the initial soil moisture state and the subsequent accumulation of precipitation. Concerning the increasing intensity of R deficits in the Thur catchment from 2003 to 2018, due to the above average precipitation values during 2001 and 2002 (refer to Figure 3-6a), initial soil moisture would likely have been elevated prior to 2003. The droughts of 2015 and 2018 followed a period of continued R deficit (from 2003 to 2011), during which average or below average precipitation rates were experienced. Similar findings by Van Loon and Laaha (2015) suggest that both drought duration and deficit is governed by average catchment wetness via precipitation and catchment storage capacity.

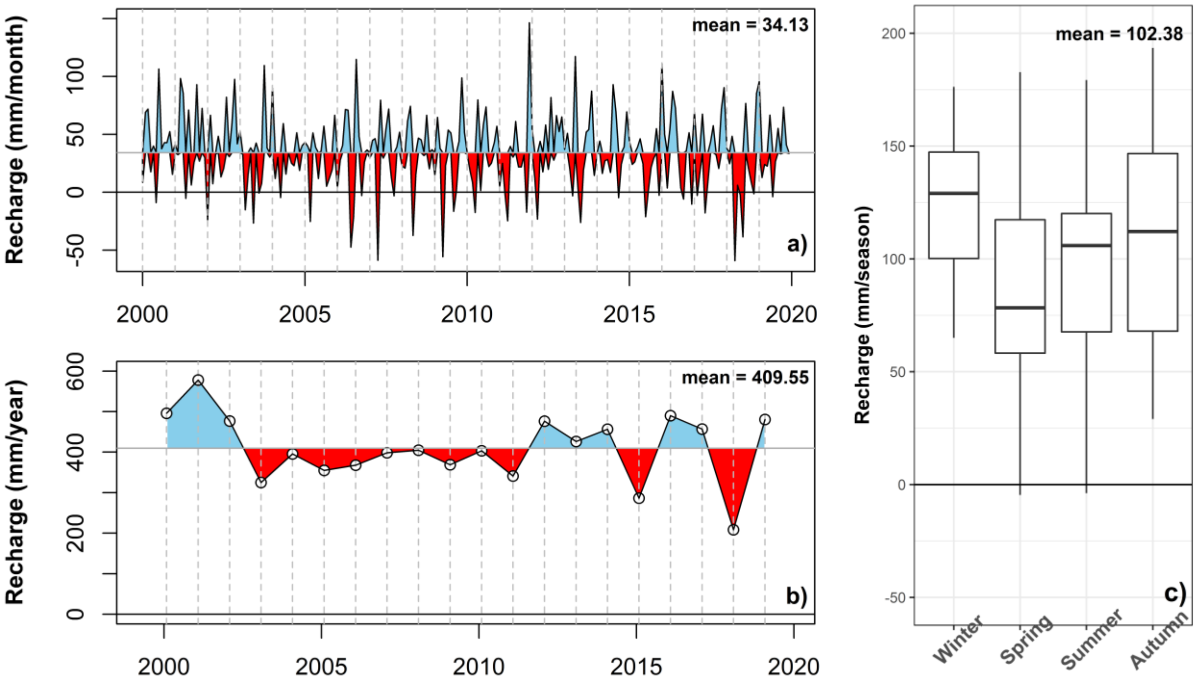


Figure 3-8: a) Mean monthly, b) annual, and c) seasonal recharge values (mm) centred on the short- medium- and long-term mean values for the years 2000 – 2019. Red values indicate recharge potential below and blue above mean values.

3.5.4 Sensitivity assessment of water balance components

Uncertainties in input components to the Thur catchment's water balance were assessed and the variance of each component compared after Eq. 8. Annual values of both P and $Q_{q\text{-}dis}$ were approximately normally distributed, while AET_{corr} was bimodal and displayed the highest degree of variance (Figure 3-9a). A stochastic perturbation was added to the variance of the individual variables P, AET_{corr}, and $Q_{q\text{-}dis}$, variables combined, via the introduction of noise which was then compared to the variance of R. Tendencies show that P, although having a lower variance than AET_{corr}, experienced the greatest spread and subsequent uncertainty in the period from 2000 to 2019 (Figure 3-9b). The spread of AET_{corr} was smaller, followed by $Q_{q\text{-}dis}$, suggesting greater certainty in these data sets, particularly in $Q_{q\text{-}dis}$. These results highlight some of the primary uncertainties in the water budget calculation.

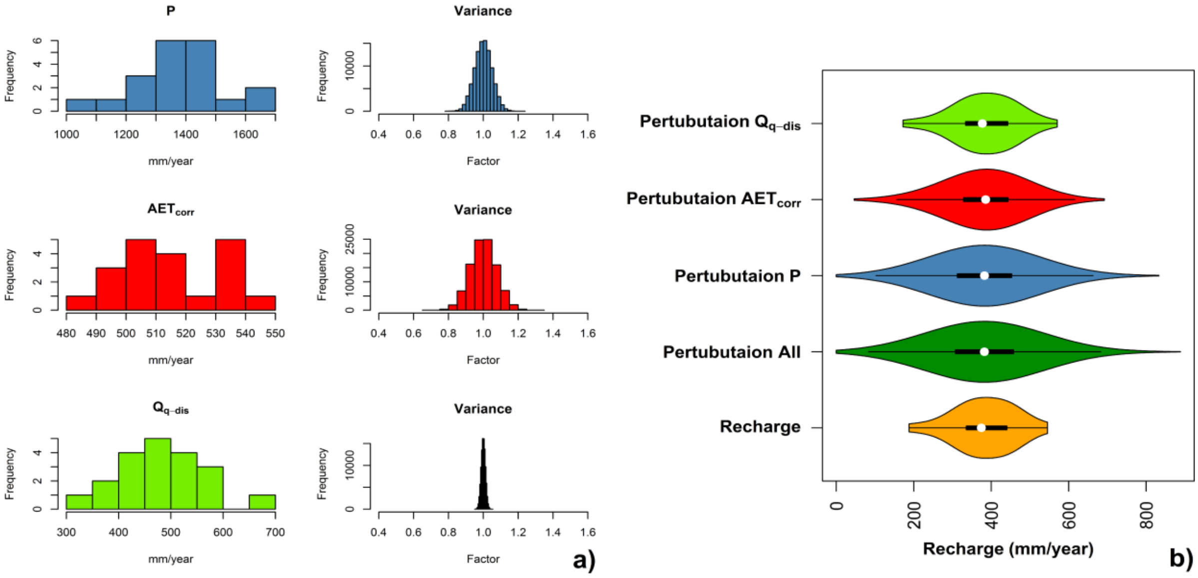


Figure 3-9: a) Distribution and variance of annual P, AET_{corr}, and $Q_{q\text{-}dis}$, values (mm) and b) perturbation of annual water budget component values (mm) compared to R values.

3.6 Discussion

This study investigated the feasibility of estimating spatiotemporal variations in groundwater recharge using a combination of satellite image products in conjunction with ground-based discharge data in a mesoscale catchment over a 20 year period. The calculation and separation of the different water balance components has the potential to be very useful for local and regional water availability assessments and long-term water resource planning, in particular for regions where the availability of direct measurements are either limited or non-existent.

3.6.1 Actual evapotranspiration

Although the MOD ET product reproduces basin scale AET response with acceptable uncertainty, when compared to expected annual values from Mu et al. (2011), Zappa et al. (2017), and Seneviratne et al. (2012) original MOD ET values for the Thur catchment were high, with mean pixel values ranging between 684.5 - 765.9 mm/year. Previous studies have shown that the MOD ET product may result in an over estimation when compared to ground-based values (Miranda et al., 2017; Ruhoff et al., 2013; Velpuri et al., 2013; Zhao and Liu, 2014). One reason that MOD ET product may have resulted in overestimated values for the Thur catchment is that the product itself lacks topographic correction (see Zhao and Liu, 2014). In addition, the scale of the MOD ET grids might be inappropriate for the size of some of the Thur's sub-catchments, in particular for the Mos and He sub-catchments. In light of both the mesoscale size of the Thur catchment, and its variable topography, a correction of the MOD

ET values was deemed necessary. However, additional ground-based ET data might have provided for more detailed ET corrections for the Thur catchment.

Inversely fitting the MOD ET data to the measured lysimeter values resulted in a good fit where the maximum monthly values are concerned (see Section 3.5.3). However, minimum monthly values showed less correlation (refer to Figure 3-2d). Concerning the correction, if more sophisticated statistical techniques were used and/or a different strategy to weight the values individually were applied, variations in the satellite data may have been better quantified. However, this could also have resulted in an overfitting of the data (Zhao et al., 2019). As the lysimeter data only represents a single point-scale measurement, this study did not seek to achieve a perfect match between MOD ET and lysimeter ET. Notwithstanding this simple approach, corrected AET values compare exceedingly well with previous AET studies conducted in the Thur catchment (Mu et al., 2011; Spreafico and Weingartner, 2005; Zappa et al., 2017). Thus, a simple single correction factor for MOD ET data was deemed suitable in scaling the AET values to within a suitable range for the Thur catchment.

3.6.2 Baseflow separation

Although a well-studied concept, baseflow remains difficult to define as demonstrated in this study (see Section 3.4.1 and Figure S 2 of Appendix I: Supplementary Information to Chapter 3) and elsewhere (Duncan, 2019; Healy and Scanlon, 2010; Nathan and McMahon, 1990). Significant errors may be introduced where baseflow is used as a primary indicator of recharge as this represents only a portion of a catchment's total drainage (Sophocleous, 2002). However, this study assumes little or no groundwater loss via inter-catchment exchange, from abstraction or via evapotranspiration. In addition, the baseflow separation method is also often only appropriate in humid and sub-humid conditions (Healy and Scanlon, 2010). At larger spatiotemporal scales Q_b characteristics can provide information on groundwater status and seasonal low flows which are integral to instream ecology (Duncan, 2019). Furthermore, Q_b has been ascribed as an integrated characteristic of a catchment's storage potential and response time (Van Loon and Laaha, 2015), and studies have equated both Q_b and baseflow-index values as being equal to recharge (e.g. Lee et al., 2006; Reitz et al., 2017). With average contributions of baseflow ranging from 31% – 57% of total streamflow, the importance of subsurface discharge is highlighted; a process which is often neglected in studies solely based on surface data (Hoffmann, 2002). In particular during the dry summers of 2003, 2015, and 2018 elevated baseflow would have made an important contribution to the Thur River and its tributaries; highlighting the importance of groundwater in maintaining aquatic ecosystems during dry periods (Moeck et al., 2020).

3.6.3 Closing the water balance

Input P values over seasonal and annual time scales correlated well with aggregated output values of AET_{corr}, Q_q, and Q_b, indicating a trend towards total closure of the Thur catchment's water balance, and supporting the assumption that over longer timescales the Thur catchment represents a steady-state system (Spreafico and Weingartner, 2005; Zappa et al., 2017). Although minor fluctuations might occur in the Thur's ΔS value as shown in Zappa et al. (2017), over longer time scales ΔS would generally be very small relative to the volumes of the other water balance components (Reitz et al., 2017). However, the lack of complete water balance closure might be attributed to both small fluctuations in ΔS, especially over shorter time intervals (e.g. monthly), and the effect of snow storage (Dal Molin et al., 2020) which was not accounted for in this study.

3.6.4 Spatiotemporal recharge

Over the 20 year period the Thur catchment experienced a total of eleven years with below-average R values (refer to Figure 3-8b), nine of which were consecutively lower than the mean. Spatially significant change assessed using a linear pixel-wise regression indicated a negative trend of R for the 20 year period; a manifestation of both the 11 years of below-average R and the long-term R deficit from 2003 – 2011. In spite of this, only 4% of the Thur catchment experienced significant change (at the 95th percentile), primarily in association with the lower reaches of the Thur catchment and in small regions of the Fr/Wae and Jon sub-catchments (Figure 3-7b). This negative trend could be further attributed to the lower average P values associated with the affected regions (refer to Figure 3-6a).

The years 2003, 2015, and 2018 were national drought years in Switzerland and the impact thereof is evident in the long-term temporal P, $Q_{q\text{-}dis}$, and R values. While fluctuations in the AET_{corr} values showed relatively little response to changes in P over the 20 year period, the limiting effect of P on R is evident from the spatiotemporal assessment, which is in line with findings of P limiting Q in the Thur catchment (Dal Molin et al., 2020). The relationship between P and ET has been shown to be one of long-term equilibrium, dependent on larger-scale climate fluctuations (e.g. El Nino), rather than the monthly, seasonal, yearly time steps investigated here (Zhang et al., 2013). Although 2003 is known as a year of record-breaking heatwave throughout Europe, compared to the 2015 and 2018 drought years the intensity of R deficits in 2003 appears to have been positively buffered by higher than average precipitation during 2001 and 2002. This suggests that the long-term R deficit behaviour in the Thur catchment is in line with findings by Orth and Seneviratne (2012) concerning soil moisture variations.

Concerning the increasing intensities of relative R deficits from the 2003, to the 2015, and finally the 2018 drought years, this study highlights the effects of hydrological wet years preceding hydrological drought years in terms of recharge deficit intensity. As such, average catchment wetness and soil moisture effects could be an important factor to consider as part of a water management strategy within the Thur catchment. Advances in remotely sensed soil moisture studies may aid in this endeavour (Dorigo et al., 2016; Nicolai-Shaw et al., 2015), and further investigation along this line is recommended for the Thur catchment.

As mentioned in Section 3.5.3, over short time intervals R values were occasionally negative. This might be as a result of a time lag in the R and $Q_{q\text{-}dis}$ values, or due to the inherrent errors in the input components (refer to Section 3.5.4). In other studies, where the sum of the AET_{corr} and $Q_{q\text{-}dis}$ values were greater than corresponding P values, a common approach has been to adjust one of the components to ensure water balance closure. For example, Reitz et al. (2017) estimated gridded annual recharge, quickflow, and ET for the contiguous U.S., but in 15% of all map pixels the sum of ET and quickflow were higher than precipitation and adjustments were made to close the water balance. The majority of these adjustments are made to the ET values, as ET is the most dificult water balance component to accurately quantify (Bhattarai et al., 2016; Hulsman et al., 2020; Reitz et al., 2017; Zhao and Liu, 2014). To draw attention to the difficulties of estimating recharge from a relatively simple water budget calculation, no attempt was made to close the balance in this study (see Section 3.5.2). As such, estimated spatiotemporal R values determined in this study serve to gauge the minmum rate at which the groundwater table should be re-supplied in the Thur catchment.

On average, when considering the total water balance of the Thur catchment and assuming negligible change in subsurface storage, recharge (R) accounted for 29%, quick flow ($Q_{q\text{-}dis}$) for 34%, and AET (AET_{corr}) for 37% of total precipitation. This is in line with modelled values for the region after Zappa et al. (2017). In light of the method uncertainties in estimating quick- and baseflow from total discharge value (a maximum difference of 22% was observed between the different methods; refer to Supplementary Figure S2), the recharge estimates for the Thur catchment may in fact, be greater (and consequently quick flow smaller). However, this potential for greater recharge, may again be negated in regions where the groundwater table intersects rooting depth. A study by von Freyberg et al. (2015), reported recharge in the Mos sub-catchment as 71% of precipitation. However, these recharge estimates were lysimeter-based, where both quick- and baseflow are infiltrated. The sum of R and $Q_{q\text{-}dis}$ values comprise 63% of precipitation in the Thur catchment, increased recharge estimates depending on the baseflow separation method used. When comparing water balance components for the different sub-catchments of the Thur catchment, the amount of R was seen to increase only slightly with higher the elevation sub-catchments (Figure 3-10a), and greater changes were observed in the proportion of decreasing evapotranspiration with respect to increasing quickflow (Figure 3-10b). Refer to Supplementary Figure S4 and Table S2 for percentage error compared to total available water in terms of P in the Thur catchment. Although not considered in detail in this study, the geological setting and lithological variances might also further control the baseflow contribution (see Dal Molin et al., 2020).

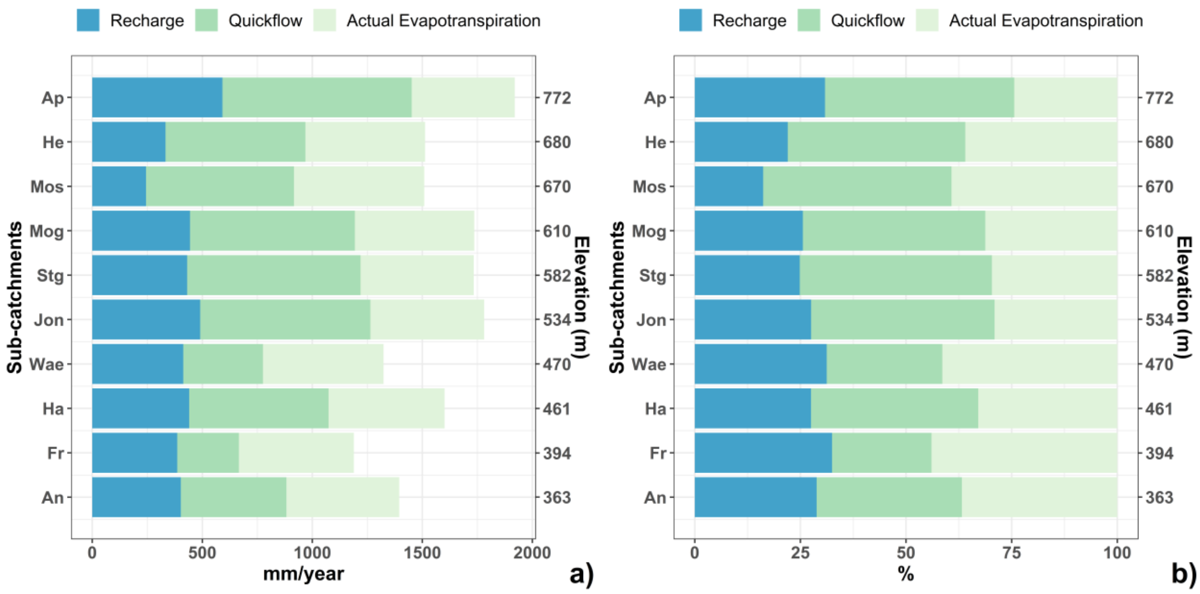


Figure 3-10: Average annual groundwater recharge, quickflow, and actual evapotranspiration in the Thur's sub-catchments as a function of a) elevation, and b) as percentage (%) of precipitation, with An representing the entire Thur catchment.

3.6.5 Limitations

Although long-term changes in subsurface storage are possible, assuming that storage change is small relative to the volumes of P, AET_{corr}, and $Q_{q\text{-}dis}$, 100% closure constraint was used for time span (20 years) of this study. Moreover, no attempt was made to describe interpixel transfer of groundwater flow. Simply the contributing factor of P entering a pixel cell to become the recharge component R, as expressed by a conservative Q_b value at the discharge station, was mapped. Understanding groundwater travel time at the gridded scale, by considering lateral and vertical connection between the pixels, could improve the spatiotemporal understanding of groundwater recharge in the Thur catchment, especially over shorter-time periods. Chemical and isotope data may provide further insight into specific recharge areas and associated groundwater ages (Healy and Scanlon, 2010).

While it is important to monitor the local effects of groundwater abstraction, the small volumes abstracted relative to P implies that current groundwater abstraction rates have little impact on the water balance of the Thur catchment as a whole, and were therefore omitted from this study. Furthermore, any groundwater abstracted is utilized locally within the Thur catchment, predominantly for the production of potable water and in parts for irrigation and industry. Abstracted water used for irrigation would flow directly back into the aquifer (minus the losses incurred via evapotranspiration), while the industrial and drinking water portions would flow back to the rivers via the wastewater treatment plants; ultimately contributing to the Thur catchment's baseflow and quickflow (Han et al., 2017).

Further discrepancies in the water budget may arise from errors or uncertainties in the calculated components (refer to Section 3.5.4), inadequate spatial and temporal accounting of these components (Coxon et al., 2015; Healy and Scanlon, 2010; Khan et al., 2018; Sun et al., 2018), or from missing or superfluous terms in the water budget calculation (e.g. Parizi et al., 2020). Although the use of satellite image products in conjunction with ground-based discharge data provides evidence of closure of the Thur catchment's water balance, comparing spatial data over time as binary plots, although a common practice, is reductionist in that a single value (e.g. mean pixel value) is meant to represent characteristics of an entire region. This is potentially reductionist, especially in catchments with variable terrain.

Terrain complexity, spatial resolution, the distribution and number of measuring stations, along with time series availability and measurement frequency can affect the quality and representativity of measurements taken (Coxon et al., 2015; Schiemann et al., 2010; Turnipseed and Sauer, 2010). For example, in spite of the MeteoSwiss product being of a high standard and in spite of having a lower variance than AET_{corr}, perturbations of P displayed the greatest component sensitivity (Figure 3-9b). Precipitation (P) was the only input into the water budget calculation, and therefore small variations or uncertainties in P strongly affect the output water balance components, including discharge and recharge. The uncertainty of AET_{corr}, although smaller, may also be affected by errors which arise as a result of terrain complexities as outlined above. Discharge values used in this study represent both high quality as well as high temporal resolution data. This is evident in the low variance and small spread of perturbed $Q_{q\text{-}dis}$ values (Figure 3-9a and b). The conservative approach used in this study to determine Q_b implies that resulting values from Eq. 7 represent minimum possible R values. In spite of the uncertainty in the values, the use of independent data sets (remotely sensed and ground-based), resulted in a good closure of the Thur catchment's long-term water balance (refer to Supplementary Figure S4 and Table S2).

Overall, the results of this study are in line with findings by Schädler and Weingartner (2002a), highlighting the effect of terrain complexity on major contributing components when calculating a water budget. Uncertainties in the MOD ET product where within range (10% – 30%) of the reported ET uncertainties and studies have shown that the PM-based MOD ET product is suitable for regions with spatially heterogeneous land cover, such as those found in the Thur catchment (Cleugh et al., 2007; Mu et al., 2011; Running et al., 2019). However, the PM-based method only applies to active vegetation, which may result in skewed values in regions where snow cover is present during the winter months (Mdaghri-Alaoui and Eugster, 2001). Due to errors relating to leaf and cloud shadowing effects, Srivastava et al. (2017) recommend a regional-scale standardization of the MOD ET product, which was done by correcting the MOD ET product by a factor of 0.71. Additionally, the spatiotemporal resolution of the MOD ET product, although suitable for characterizing processes in mesoscale catchments such as the entire Thur catchment, might be too coarse for use in small catchments such as the Mos and He sub-catchments (both of which are smaller than 17 km^2). This could further explain the uncertainty in the AET_{corr} values, as these were derived from the MOD ET product corrected to the lysimeter data collected in the Mos sub-catchment. Lastly, it must also be noted that 20 years provide a relatively small window of observation where the Thur's long-term water balance is concerned.

3.7 Conclusion

This study demonstrates that the approach of satellite image products used in conjunction with ground-based data to estimate spatiotemporal groundwater recharge has the potential to be useful both for local and regional water availability assessments, as well as long-term water resource planning. The use of remotely sensed data as presented here offers a method of determining a basin's water balance at the mesoscale through the integration and analysis of observed data, reconciled within the water budget equation.

Gridded water balance components P, AET_{corr}, and $Q_{q\text{-}dis}$ were able to adequately capture the spatiotemporal variability of groundwater recharge in the Thur catchment over a 20-year period. The pixel-wise linear regression suggests a decline in R from 2000 to 2019, in particular within the lower reaches of the Thur catchment. However, knowledge of spatiotemporal characteristics remains factor, and full comprehension of the intrinsic heterogeneities and complexities of specific basins may never be entirely possible. Temporal data of the water balance components emphasized the limiting effect of P on R, and stressed the importance of hydrological wet years preceding hydrological drought years in terms of long-term recharge deficit. In light of this, the inclusion of soil moisture data is recommended in future studies to provide additional insight into spatiotemporal groundwater recharger behaviour in the Thur catchment or other (mesoscale) catchments.

Although reductionist, a remotely sensed water budget calculation may go some way towards a holistic starting point for monitoring recharge in mesoscale catchments, especially in poorly monitored or remote catchments where the lack of ground-based observations could be augmented. For example, although the 500 m x 500 m gridded resolution used in this study was found to be a limiting factor when dealing with the Thur's smaller sub-catchments, freely available MOD ET data was corrected locally using long-term ground-based lysimeter measurements from a single site within the Thur catchment. By comparing variance with other modelled water budged terms it was shown that, although the MOD ET product tended to overestimate AET the overestimation was consistent and larger uncertainties were associated precipitation values. The use of the MOD ET data was shown to be valuable in determining AET for the mesoscaled Thur catchment, and it is believed that it is applicable to regions with relatively little or no ground-based AET measurements, remaining cognisant of potential over or under estimation.

For many catchments long-term observations are either completely missing or, where monitoring networks do exists, these are often falling into disrepair due to a lack of finances and/or upkeep (Montanari et al., 2013; Sivapalan et al., 2003). Spatiotemporal groundwater recharge estimates are useful for water resource managers who want to estimate trends in the water balance and track these changes over time. Remotely sensed data can be a useful asset in the advancement of hydrological understanding, even where gauged basins are concerned. This provides significant advantages when dealing with poorly gauged basins and establishing long-term data records for such basins in terms of their water availability (Gleason and Durand, 2020). However, even with additional methodological innovation in the field of RS, this study underscores the current need for continued, and in some places new, ground-based monitoring of hydrogeological components; the lack of which is a major limiting factor in sustainable water management where mesoscale or smaller catchment sizes are concerned.

4. Event Sampling for Groundwater Dynamics: $\delta^{18}O$ and $\delta^{2}H$ in the Mesoscale Thur Catchment

4.1 Abstract

As water consumption continues to increase, it is imperative to understand the water sources and flow controlling a catchment's surface-groundwater interaction, and its subsequent water availability. River water represent a connection between the surface and sub-surface environment, and where flow is present, provides a relatively easy sampling opportunity. Many monitoring campaigns or impact studies are restricted in terms of time and finances, resulting in only a limited number of samples being taken during a limited number of sampling campaigns, upon which potentially critical decisions are made regarding a catchment's water distribution and quantity. In this study, the Thur River in Switzerland was sampled over a period of three years, during which river sampling was conducted bi-annually on the basis of extreme events (high- and lowflow), in order to establish the usefulness of event sampling in providing insights into the water dynamics of a mesoscale catchment (~1700 km^2). Groundwater samples, collected bi-annually, along with rainwater from a secondary data source, were used to help characterize the Thur catchment's spatiotemporal water dynamics. Environmental tracers, including $\delta^{18}O$ and $\delta^{2}H$, were analysed using a clustering method along with a three end-member mixing analysis. The findings of this study suggest that event sampled surface river water are useful in establishing the spatiotemporal water source variabilities of a catchment. However, the inclusion of additional sampling sources provided a more comprehensive spatial context in identifying the source contribution of groundwater and surface water in the Thur catchment. The findings of this study indicate that high elevation (> 680 m asl.) water sources in the Thur catchment are dominated by an end-member water type characteristic of river runoff, while sites associated with the middle reaches of the Thur catchment (680 – 480 m asl.) are dominated by an end-member water characterised by groundwater, and sites located in the low elevation (< 480 m asl.) reaches of the Thur catchment are predominantly composed of an almost equal mixture of two end-members characteristic of groundwater and precipitation water types. This study highlights the reliance of water in the Thur catchment on different water sources depending on when and where in the catchment the water was sampled.

4.2 Introduction

In a world where water consumption, and the subsequent dependence on groundwater is predicted to increase, it is imperative to understand water sources and flow which control a catchment's water quantity and quality. This makes the effective monitoring of a catchment's water dynamics, in particular its surface and groundwater exchange, particularly important. However, many studies aimed at assessing current and future impacts are often restricted, both in terms of time and finances, resulting in sampling campaigns which are by necessity limited to a handful of spatial and temporal measurements, on the basis of which potentially critical decisions are made regarding a catchment's ability to maintain its current (or in some cases historic) integrity (Morrison-Saunders and Bailey, 2003). In an attempt to best capture the phenomena determining a catchment's water cycle, and in order to gain insight into the range of conditions (such as floods, droughts, freshwater availability, circulation, distribution, and quality) governing a catchment's water dynamics, sampling is subsequently often conducted in a manner, which aims to capture events (highflow or lowflow) within a catchment.

In most cases, a catchment's water input stems from precipitation (rainfall or snowfall). Subsequently, knowledge concerning rainfall patterns, distribution, and intensities form an important part of monitoring a catchment's water dynamics. However, precipitation can display a great spatiotemporal variability; the accurate measurement of which is often limited, especially in larger and topographically variable catchments (Schädler and Weingartner, 2002). Technological advancements such as remote sensing, the application of innovative sensor technology, and information and communications technology (ICT) is opening doors to more comprehensive monitoring and subsequent understanding of hydro-meteorological characteristics; vital in developing climate change resilience (Adeyewa and Nakamura, 2003; Huffman et al., 2007; The World Bank, 2013).

Groundwater recharge (R) indicates the existence of renewable groundwater resources and is therefore an important component in water sustainability studies (Döll and Fiedler, 2008; Jasechko et al., 2014; Moeck et al., 2020; Mohan et al., 2018). Groundwater recharge is defined by the rate at which water can infiltrate through the soil to a given depth to reach the saturated zone or groundwater table (Brunner et al., 2007; Xu and Beekman, 2018). However, recharge is also one of the least understood water source characteristics, largely because it varies in space and time and is difficult to measure directly (Scanlon et al., 2002). The most direct recharge observations stem from piezometer measurements in monitoring wells (Bierkens and Wada, 2019). In the case of unconfined aquifers, methods such as the water table fluctuation method (WTF) can be applied where changes in groundwater levels are measured in monitoring wells and multiplied by the system's specific yield (Sy) (Crosbie et al., 2005; Healy and Cook, 2002). Characterization and management of catchment-wide recharge is further complicated by the spatiotemporal heterogeneity of the subsurface and the number and depths of monitoring wells (Alley et al., 2002). In particular, where mesoscale catchments (typically 10 – 10^4 km^2) are concerned, determining hydrological fluxes and in particular groundwater recharge, is often hampered by a lack of data, complex hydrogeological settings, or a combination of both, making such catchments essentially "ungauged" in a hydrogeological sense (Pool et al., 2017; Rojas-Serna et al., 2016; Viviroli and Seibert, 2015).

The measure of movement of tracer substances (including both natural and artificial tracers), both in precipitation, groundwater, and surface runoff can provide insight into water source, recharge, and discharge in a catchment. However, the orders of magnitude slower movement of groundwater compared to surface water, limits the usefulness of adding artificial tracers to groundwater to understand its movement (Berghuijs and Kirchner, 2017; Cook, 2020; Gabrielli et al., 2018). Instead, environmental tracers are often measured instead (Elsner and Imfeld, 2016; Fukada et al., 2004; Hunkeler et al., 2004, 1999; Maloszewski et al., 2002; Palau et al., 2016; Schreglmann et al., 2013). These tracers are particularly useful in understanding the flow of water in larger catchments (Cook, 2020).

Isotopes, a particular category of environmental tracers, represent variants of the same chemical element which differ only in the number of neutrons (and subsequent mass) present in their nucleus. In any catchment, isotope ratios of hydrogen and oxygen, whether in the rain, surface, or groundwater, are indicators of hydrogeological processes such as surface-groundwater interactions, travel time, the dispersion of short-term pulses (e.g. flood events, or point source pollution), and a drainage basin's hydrological changes in response to climate or land use change (e.g. IAEAA, 2012; Ojiambo et al., 2001). The heavy isotopes of water (δ^2H and $\delta^{18}O$) preferentially remain in the liquid phase during evaporation and preferentially pass into the liquid phase during condensation, implying that rainfall the world over is depleted in heavy isotopes relative to seawater, especially in mountainous terrains (Rayleigh, 1896). As air masses move inland, rainfall becomes progressively lighter (Coplen et al., 1999). As the stable water isotope molecules partition into ratios of their light and heavy counterparts ($^{18}O/^{16}O$ and $^{2}H/^{1}H$) through the process of fractionation, source and migration of groundwater, along with geochemical processes occurring along the flow paths, can be inferred. These passive tracers represent a relatively affordable and easily available source of information regarding sources and mixing of sources in a watershed (Carrera et al., 2004; Cook, 2020; Markovich et al., 2019).

When different water sources (or end-members) with different isotopic or chemical compositions are mixed, quantitative information concerning mixing can be established (Cook, 2020). The stable isotope composition of groundwater reflects the integrated effects of rain compositions, modified by the influx of surface water generally enriched in heavy isotopes (δ^2H and $\delta^{18}O$), allowing for the determination of relative amounts of water from various sources via the quantification of mass-balance relationships (Coplen et al., 2000; IAEAA, 2012). Water composition will usually be distinct for rainwater, surface water, and groundwater due to physical and chemical processes, so surface- and groundwater exchange can often be detected from water chemical surveys (Meredith et al., 2009). Water in catchments can be naturally stored in lakes, vegetation, soils, and unconsolidated sediment deposits such as talus, moraines, alluvium, and rockslides, as well as in the fractures and fissures of bedrock, and in the form of snow and permafrost (Clow et al., 2003; Langston et al., 2011; Liu et al., 2004; Roy and Hayashi, 2009; Staudinger et al., 2017). Most often, soils found in high elevation catchments are rather shallow and vegetation is constrained mainly by temperature with increasing altitude (Körner, 2007). In lowland catchments, soils are generally deeper, implying more vegetation, greater evapotranspiration (Refer to Ch. 3), and more extensive aquifers and subsequent subsurface water storage (Staudinger et al., 2017).

In light of both the natural occurrence and the characteristics of environmental tracers, this study used event sampled environmental tracers $\delta^{18}O$ and $\delta^{2}H$ to determine the water dynamics, in terms of spatial and temporal surface and groundwater interaction, in the Thur catchment for the years 2017-2020. The Thur catchment is a well-studied, dynamic system (Abbaspour et al., 2007; Barnwal et al., 2017; Chittoor Viswanathan et al., 2016; Dal Molin et al., 2020; Doulatyari et al., 2017; Kurth et al., 2015; Kurth and Schirmer, 2014; Paillex et al., 2017, 2005; Schirmer et al., 2013; Schneider et al., 2011; Viviroli et al., 2009; Vogt et al., 2011), with variable topography, the Thur River being free of any major natural or artificial reservoirs, and with a mesoscale sized catchment area (~1700 km^2). Event sampled surface water samples, analysed for their isotope values, were used to explore the spatiotemporal surface- and groundwater dynamics. This study 1) compares event sampled environmental tracers $\delta^{18}O$, $\delta^{2}H$, and $Ca2^{+}$ from surface river water to groundwater and rainfall water fom the Thur catchment, 2) explores the spatiotemporal characteristics of water sources in the Thur catchment based on the concentration of environmental tracers sampled in surface water, groundwater, and rainwater using cluster analysis and end-member mixing analysis, and 3) establishes the usefulness of event sampling in providing insights in to water dynamics of a mesoscale catchment. This study simulates real world assessments, where sampling was conducted on the basis of “best possible knowledge” regarding maximum and minimum annual flow; with limited advanced knowledge concerning absolute maximum event peaks.

4.3 Study area

The Thur catchment, with an approximate catchment size of 1700 km^2, is located in the north-eastern part of Switzerland (Figure 4-1). The Pleistocene molass-sandstones, marls and conglomerates of the lower reaches of the Swiss plateau (approximately 350 m asl.), composed predominantly of marine sediments and minor basement granites, contains the Thur valley aquifer (Figure 4-2); one of the largest groundwater systems in Switzerland (Hayashi et al., 2012; Keller, 1992; Schneider et al., 2011). Here, productive groundwater occurrences are confined largely to the gravel and sand dominated fluvio-glacial deposits hosted largely within valley bottoms (dark blue; Figure 4-2), where the average depth to the groundwater table is 1.4 m. This primary aquifer, located in the lower reaches of the Thur catchment, provides up to 49% (16 million m^3/y) of the drinking water requirements to the Canton Thurgau (https://umwelt.tg.ch/), in which the majority of the aquifer is located. Minor aquifers hosted within fluvio-glacial deposits and scattered along the length of the Thur River and its tributaries (dark blue; Figure 4-2), although still productive groundwater sources, have a greater average depth to groundwater (~3.5 m) (Gurtz et al., 1999). In addition to these minor aquifers, fractured-rock (dark green; Figure 4-2) provides another source of groundwater within the Thur catchment. These mixed host rocks and minor alluvial deposits are the primary source of drinking water in the upper reaches of the Thur catchment (https://www.sg.ch; https://www.ar.ch).

The headwaters of the Thur River originate in the glacier-free, limestone-dominated, pre-alpine region of the Swiss plateau, with waters draining from the region of Mt. Säntis (2502 m asl.) in the south, past Andelfingen (362.9 m asl.), and eventually draining into the Rhine River to the north-west of the catchment. The average slope inclination in the Thur catchment is 7.9º, but varies depending on the morphological location (e.g. plateau vs. pre-alpine regions) (Melsen et al., 2016). A variability of morphological and climatic elements govern the hydrological regime of the Thur catchment. This variability in topography, precipitation, and potential evapotranspiration results in a streamflow discharge response, which can fluctuate by up to two orders of magnitude within a few hours. The warm-summer humid continent climate of the Thur catchment results in average precipitation rates which vary from 700 mm/y in the low lying areas near Andelfingen, to 2700 mm/y in the mountainous region, while evapotranspiration rates range from 400 mm/y in regions of high elevation (> 1600 m asl.), to over 1000 mm/y in association with the central region of the Thur catchment (~ 700 m asl.) (Peel et al., 2007).

The Thur River is the longest river (~ 130 km) in Switzerland free of any major natural of artificial reservoirs. In addition to the Thur River, the Thur catchment includes three major tributaries to the Thur: the Murg, the Necker and the Sitter Rivers. (Figure 4-1). The event sampled surface sites (Figure 4-1) were selected based on their longitudinal distribution along the Thur River, where possible, upstream of any major towns, and bearing in mind the prospect of having to be sampled in a single day to capture a single event. The exception to this are the Appenzell (Ap) sites (1, 2, and 3) which, although sampled both during high- and lowflow events, are located near the source of the Sitter and therefore impossible to sample on the same day as the Thur River samples. The sampled groundwater sites are located both within primary and secondary aquifers associated with the Thur River, as well as in association with some of its major tributaries (Figure 4-2).

4.4 Data and methods

In this section, data collection and analysis of event sampled river water, groundwater and rainwater collected from 36 sites, is described. These datasets were used to characterize surface-groundwater interaction in the Thur catchment, with the use of a cluster analysis, source determination, and an end-member mixing analysis (EMMA). Where data is shown in seasonal intervals, winter represents the months of December, January, and February, spring the months of March, April, and May, summer the months of June, July, and August, and autumn the months of September, October, and November. Event sampled stable isotope values from river water were used to characterize water dynamics in the Thur River.

4.4.1 Sample collection

Event sampled river water

Longitudinal profile event samples were collected bi-annually along the length of the Thur River over the period from June 2018 to January 2020, where the 2018 year was a national drought year (BAFU et. al., 2020). Eight (8) surface water (SW) samples were taken during a single event, during which either low- or highflow conditions prevailed (refer to Figure 4-1 and Table 4-1). Each of the eight Thur River sites was sampled on the same day of the flow event. An additional three (3) sites were sampled from the high elevation region of the Sitter River (a major tributary to the Thur River). At each site, samples were collected for the analysis of both stable water isotopes as well as major anion and cation concentrations (refer to Table S 3 and Table S 4 of Appendix II: Supplementary Information to Chapter 4 for geochemical data sets). The surface river water sampling intervals were based on annual high-flow-events (e.g. 534 m^3/s) during the high precipitation season (predominantly spring and autumn), and low-flow events (e.g. 1.4 m^3/s) during dry spells (predominantly summer and autumn). In addition, in 2019 snow was sampled at two sites (Table 4-1). One site (Thur11) was specifically sampled for snow, while another site (Ap1) was event sampled at a time when the sample site was still snow covered.

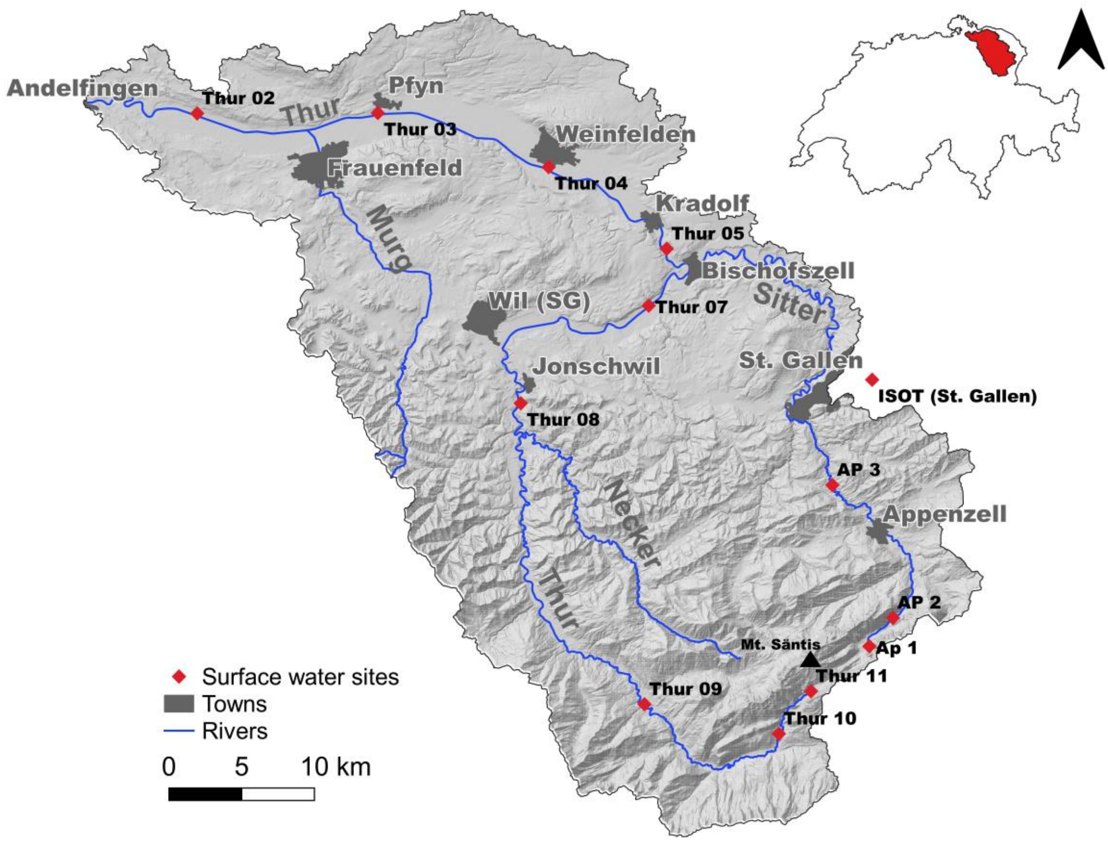


Figure 4-1: Characteristics of the Thur catchment with its major drainage lines, topography, and surface water and rainfall isotope (ISOT) sample sites indicated (DEM25 (2003), Source: Federal Office of Topography).

Groundwater

Groundwater (GW) isotope samples were taken bi-annually (courtesy of the Office for the Environment of the cantons Thurgau and St. Gallen) from 24 different wells associated primarily with the Thur River. These samples were collected via the pumping of piezometers or wells, and subsequently represent mixed groundwater samples. Additional sites sampled are located in close proximity to some of Thur River's major tributaries: the Necker, Sitter, and Murg Rivers (refer to Figure 4-2 and Table 4-1). The sampling was conducted bi-annually for each well starting from June 2017 to June 2020. Geochemical data of the groundwater sites was provided by the Cantonal authorities (Office for the Environment, cantons Thurgau and St. Gallen) for the respective groundwater sites (refer to Table S 4 in Appendix II: Supplementary Information to Chapter 4).

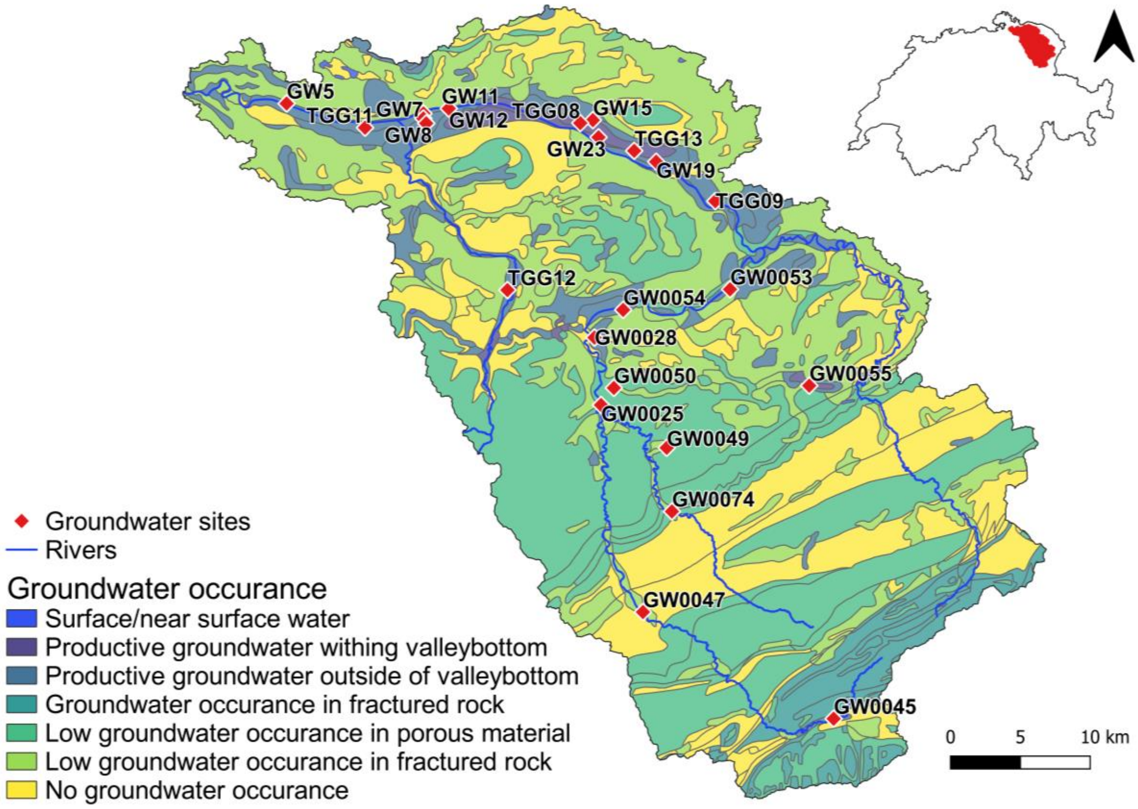


Figure 4-2: Groundwater occurrence in the Thur catchment (based on the 1:100 000 geology map) and groundwater isotope sampling sites indicated (Geokarten 500, Source: Federal Office of Topography).

Table 4-1: Sites sampled for surface and groundwater isotopes in the Thur catchment

Site ID	X	Y	Altitude	Sample Nº	Type of sample
Thur02	701179	271895	378	6	Event sample
Thur03	713595	272175	402	6	Event sample
Thur04	725414	268706	436	6	Event sample
Thur05	733640	263278	487	6	Event sample
Thur07	732481	259365	477	6	Event sample
Thur08	723819	252508	543	6	Event sample
Thur09	732730	232086	753	6	Event sample
Thur10	742009	230250	1032	6	Event sample
Ap1	748108	236359	1485	2	Event sample/Snow
Ap2	749690	238334	850	2	Event sample
Ap3	745351	247335	680	2	Event sample
GW5	700800	271925	390	6	Groundwater
GW6	710615	271410	392	5	Groundwater
GW7	710616	271054	389	5	Groundwater
GW8	710826	270712	392	4	Groundwater
GW11	712420	271800	392	11	Groundwater
GW12	712425	271800	399	6	Groundwater
GW15	722756	271176	420	7	Groundwater
GW19	727349	268305	437	6	Groundwater
GW23	723188	269965	422	6	Groundwater
TGG08	721860	270950	416	10	Groundwater
TGG09	731637	265580	449	10	Groundwater
TGG11	706453	270314	381	10	Groundwater
TGG12	716880	258950	522	8	Groundwater
TGG13	725760	269050	429	10	Groundwater
GW0025	723745	250898	560	2	Groundwater
GW0028	723180	255690	560	2	Groundwater
GW0045	740850	228880	896	2	Groundwater
GW0047	727041	236207	627	2	Groundwater
GW0049	728510	247940	630	2	Groundwater
GW0050	724640	252130	582	2	Groundwater
GW0053	732820	259317	476	2	Groundwater
GW0054	725195	257703	507	2	Groundwater
GW0055	738630	252570	645	2	Groundwater
GW0074	728974	243412	661	2	Groundwater
Thur11	744160	233206	1527	1	Snow

*Refer to Table S 3 for sampling details

Rainwater

In Switzerland, a nation-wide monitoring program measures isotopic composition of precipitation as part of a national groundwater monitoring-network NAQUA module - ISOT (FOEN, https://www.bafu.admin.ch/bafu). One ISOT monitoring station is located directly to the east of the Thur catchment near the town of St. Gallen (Table 4-2). The isotopic signature of the water sampled from the ISOT stations represents a monthly mixed sample of both rain and snow, depending on the season. Since this data is collected for the purpose of a long-term monitoring, a consistent data series of $\delta^{18}O$ and $\delta^{2}H$ isotope ratios in rainwater is available for the years 2004 – 2020 from the St. Gallen site. The long-term series of monthly rainfall data from the St. Gallen ISOT station was used to further improve the hydrogeological characterization of the Thur catchment, and to calculate the Local Meteoric Water Line (LMWL) of the Thur catchment: a long-term correlation of $\delta^{18}O$ and $\delta^{2}H$ values.

Table 4-2: Location, altitude, average $\delta^{18}O$, and meteoric water line equation of the ISOT site St. Gallen

ISOT site	X	Y	Altitude	Time period	Average $\delta^{18}O$ (‰)	LMWL Equation
St. Gallen (SG)	747940	254600	780 m	2004 - 2020	-11.4	$\delta^{2}H=8.1\ \delta^{18}O+11.4$

4.4.2 Data analysis

Laboratory analysis

Event sampled Thur River water and groundwater samples were filtered through a 0.22 µm pore sized nylon filter prior to being analysed for their $\delta^{18}O$ and $\delta^{2}H$ ratios using a cavity ring down spectroscopy (CRDS) Picarro spectrometer (L1102-I, Santa Clara, CA) at the Eawag laboratory in Zurich, and calibrated against isotope standards from the International Atomic Energy Agency. An accuracy of 0.03‰ is achieved with the CRDS, and a precision of 0.05 to 0.1‰ for $\delta^{18}O$ is possible (Walker et al., 2016). The overall analytical errors are ±0.2‰ and ±1.2‰ for $\delta^{18}O$ and $\delta^{2}H$ respectively. Isotope signatures of ^{18}O and ^{2}H are conventionally expressed as δ values, representing deviations in parts per mil (‰) from the international standard (Vienna Standard Mean Ocean Water or V-SMOW). Ratios of isotopes are expressed relative to a standard using the delta (δ) notation:

$$\boldsymbol{\delta} = \frac{\boldsymbol{R_{sample}} - \boldsymbol{R_{standard}}}{\boldsymbol{R_{standard}}} \times \mathbf{1000}\ ‰, \qquad \textbf{(9)}$$

where R refers to $^{2}H/H$ or $^{18}O/^{16}O$ ratios (^{2}H and ^{18}O are usually less abundant than H and ^{16}O).

A δ-value identical to the standard would be 0‰, while positive values indicate a greater proportion of the less abundant isotope than the standard, and negative values indicate a lower proportion of the less abundant isotope.

Because ^{2}H and ^{18}O are affected in similar ways, values of $\delta^{2}H$ and $\delta^{18}O$ are highly correlated in precipitation. The global meteoric water line (GMWL) is an empirical relationship that expresses the average correlation between $\delta^{2}H$ and $\delta^{18}O$ values in precipitation, and is given by Eq. 10 (Craig, 1961):

$$\boldsymbol{\delta^{2}\mathrm{H} = \ \delta^{18}\mathrm{O} + 10} \qquad \textbf{(10)}$$

While the GMWL from global precipitation can be expressed as $\delta^{2}H$= 8 $\delta^{18}O$+10 (Craig, 1961), a local meteoric water line (LMWL) was determined from the long-term precipitation data from the St. Gallen ISOT station using Eq. 10. Sample water collected for the determination of major ion composition was analysed within 24 hours of collection by the AuA Laboratory at Eawag, Zürich after ISO 14911 (ISO, 1999) and ISO 10304-1 (ISO, 2009) standards.

Multivariate analysis

End-members are sources that contribute to a mix of water sampled (Neill et al., 2011). It is common practice when identifying the number of end-members to be used in a mixing model, to perform a multivariate analysis such as a principal component analysis (PCA) or clustering analysis (Barthold et al., 2011; Burns et al., 2001; Markovich et al., 2019; Rahman et al., 2015). While a PCA reduces the dimensionally of the data by finding the least-squares cluster membership vector, a k-mean cluster tries to find the least-squares partition of the data (Feldman et al., 2020). Such multivariate analyses methods are generally used in order to reduce the conceptual uncertainty in the end-member selection (Hooper, 2003; Liu et al., 2008). However, rather than to determine end-members, this study conducted a multivariate analysis to help visualize the spatial characteristics of the Thur catchment's hydrogeological dynamics. Due to the small number of sites and low number of chemical variables measured, a PCA was not deemed suitable. Instead, a k-means cluster was used to help characterize the spatial variability of the conservative tracers δ^2H and δ^{18} measured in the Thur catchment. As k-means clustering is sensitive to outliers, a k-medoids or PAM (partitioning around medoids) clustering was used instead, using the mean δ^2H and δ^{18}O values from each sampled site (Kaufman and Rousseeuw, 1990). The PAM cluster analysis was performed for using the R package *factoextra* and *cluster* (retrieved from: https://cran.r-project.org/web/packages) (R Core Team, 2018).

Mixing analysis of environmental tracers

In order to identify and quantify the composition of sampled ground- and surface water in terms of their end-member composition, a mixing ratio can be estimated by means of a mass balance approach, whereby the known concentrations of tracers are used to quantify the fraction of different waters contributing to the sampled mix water (Barthold et al., 2011; Christophersen, 1990; Cook, 2020; Hounslow, 1995). This method of end-member mixing analysis (EMMA) relies on knowing the concentrations of environmental tracers, measured in the different water samples. (Barthold et al., 2011; Carrera et al., 2004; Cook and Dogramaci, 2019; Hooper et al., 1990; Jasechko, 2019). End-member concentrations represent extreme values, while the values of the remaining samples lie somewhere between the end-member data points and represent an integrated signal concerning a catchment's flow paths. All EMMA methods assume that 1) the sampled water is a mixture of source solutions, 2) the process of mixing is linear, and 3) the source solutions have extreme compositional concentrations (Barthold et al., 2011). Conservative tracers (e.g. δ^2H and δ^{18}) are used to gain information concerning water sources and transport processes, while non-conservative tracers which may undergo chemical alteration (e.g. Ca^{2+}), are often used to determine the hydrochemical conditions in the sampled mix water (Cook, 2020). As most water associated with the major aquifers located in the Thur catchment can be classified as being of a calcium carbonate origin, with Ca^{2+} and HCO_3^- making up more than 50% of the total mineralization (Hoehn and Scholtis, 2011), Ca^{2+} was selected as a representative non-conservative environmental tracer in the EMMA.

The isotopic composition of three compartments: 1) rainwater, 2) River runoff water, and 3) groundwater were measured in the Thur catchment for the years 2017 - 2020. As no geochemical data exists for the snow site Thur11, this site was omitted from the end-member mixing model. While river runoff could be a mixture of groundwater (discharging groundwater as baseflow contribution) and runoff from precipitation as well as some direct precipitation, and groundwater could be a mixture of infiltrated local rainwater and surface water, as well as inflowing groundwater, rainwater would never be a mixture of either. This makes rainwater an obvious end-member. In order to determine additional end-member sources, concentrations of geochemical variables measured at each site were evaluated using mixing diagrams (after Christophersen, 1990; Hooper et al., 1990; Liu et al., 2004). Once the end-members were determined, a three end-member mixing analysis was conducted for each groundwater and surface water site in the Thur catchment to determine the contributing proportion or fraction (*f*) of each of the three source in the measured mix water at each site. This was done using two environmental tracers (δ^{18}O and Ca^{2+}) and solving for the following mass-balance equation:

$$\boldsymbol{f1} = \frac{(\delta^{18}\mathrm{O}_{\ mix} - \delta 18\mathrm{O}_{\ s3})(\mathrm{Ca}_{s2} - \mathrm{Ca}_{s3}) - (\delta^{18}\mathrm{O}_{\ s2} - \delta 18\mathrm{O}_{\ s3})(\mathrm{Ca}_{mix} - \mathrm{Ca}_{s3})}{(\delta^{18}\mathrm{O}_{\ s1} - \delta 18\mathrm{O}_{\ s3})(\mathrm{Ca}_{\ s2} - \mathrm{Ca}_{\ s3}) - (\delta^{18}\mathrm{O}_{\ s2} - \delta 18\mathrm{O}_{\ s3})(\mathrm{Ca}_{\ s1} - \mathrm{Ca}_{\ s3})} \quad (11)$$

$$f2 = \frac{(\delta^{18}O_{mix} - \delta 18O_{s3})}{(\delta^{18}O_{s2} - \delta 18O_{s3})} - \frac{(\delta^{18}O_{s1} - \delta 18O_{s3})}{(\delta^{18}O_{s2} - \delta 18O_{s3})} f1 \quad (12)$$

$$f3 = 1 - f1 - f2, \quad (13)$$

where, f represents the fractions, and $s1, s2$ and $s3$ the different source concentrations from rainwater, groundwater and surface water end-members (Em). When using a mass balance approach to quantify surface-groundwater interactions, any alteration to water mixtures is assumed to be related to the water source (Kalbus et al., 2006).

4.4.3 Uncertainties

When defining end-members, whether by reason or through the objective analysis of the dimension of the dataset, there is generally no single solution for the chemical composition of the selected end-member (Edmonds and Edmond, 1995). Selected end-members should, as far as possible, define the range of the mixing subspace (Renner, 1995). Where the data subspace is not well defined by the selected end-members, either the tracers used during the analysis are not conservative, or the source components are not well characterized (Liu et al., 2004). As only a limited number of years and sites were sampled during this study, a comparison between the temporal and spatial variability of measured tracer values was conducted (refer to Table S 5 in Appendix II: Supplementary Information to Chapter 4). When compared to the spatial variability between the sampled sites, the temporal variation was found to be minimal. As a result, only spatial variability was assessed in the EMMA.

Mixing ratios are commonly associated with high uncertainties (Carrera et al., 2004; Hooper, 2003; Popp et al., 2019). Aside from the selection of sample sites and sampling frequencies, uncertainties concerning the conceptual three end-member mixing model used in this study include the assumption that i) end-members evolve in a linear manner, ii) that the tracers used behave conservatively (or at least that any chemical reaction is much slower than the mixing process), iii) that the end-members do not change their chemical signatures over time, iv) that tracer signals are sufficiently distinct, and v) that all end-members were correctly identified (Carrera et al., 2004; Hooper et al., 1990; Popp et al., 2019; Valder et al., 2012). Furthermore, the sampling strategy employed in this study, would only capture the fast temporal surface dynamics and spatial variations, whereby overland event water, including the travel of precipitation through the vadose zone, may not take on the groundwater chemistry (Barthold et al., 2011; Kirkby, 1988). Subsequently, where such sources dominate, they may be overrepresented.

4.5 Results

This section looks at the spatiotemporal variability of the stable isotopes sample in the Thur catchment between 2017 and 2020. The ISOT data was used to help characterise variabilities of the environmental tracers measured in the event sampled surface river water as well as the groundwater sites in context of the Thur catchment's water cycle over space and time.

4.5.1 Temporal isotope variability

Figure 4-3 illustrates the isotopic composition (in ‰ of V-SMOW) of rainwater from the ISOT station in relation to the groundwater and the event sampled river water collected from the

Thur catchment. Figure 4-3a highlights the similarity of the samples, in particularly the ISOT precipitation samples, to the GMWL. Zooming in, Figure 4-3b illustrates the range of values measured in the groundwater and event sampled high- and lowflow river water. Sixteen years of rainfall data from the St. Gallen ISOT station were used to generate the LMWL; a representative compositional line from which all of the other water samples in the Thur catchment should originate. The highflow event samples displayed a greater range in isotopic values (20‰ and 3.1‰ of δ^2H and δ^{18}O respectively) compared to the lowflow and groundwater samples: which displayed the smallest isotopic variation (16‰ and 2.5‰ of δ^2H and δ^{18}O respectively). Highflow samples also display a greater deviation from and to the left of the LMWL, with their δ^2H and particularly their δ^{18}O isotope values being depleted relative to the LMWL, suggestive of a rainout effect (Clark and Fritz, 1997). Lowflow and groundwater samples on the other hand, show a relative isotopic enrichment, particularly where δ^{18}O is concerned, and deviate to the right of the LMWL. The event sampled snow sites were plotted along with the rainfall data for the three-year sample period to illustrate the seasonal variability in the δ^{18}O isotopic composition of precipitation in the Thur catchment (Figure 4-3c). Rainfall samples were more enriched in their δ^{18}O composition during the summer months, while a strong depletion in δ^{18}O is notable during the winter months, while snow samples remained relatively depleted, even during late spring.

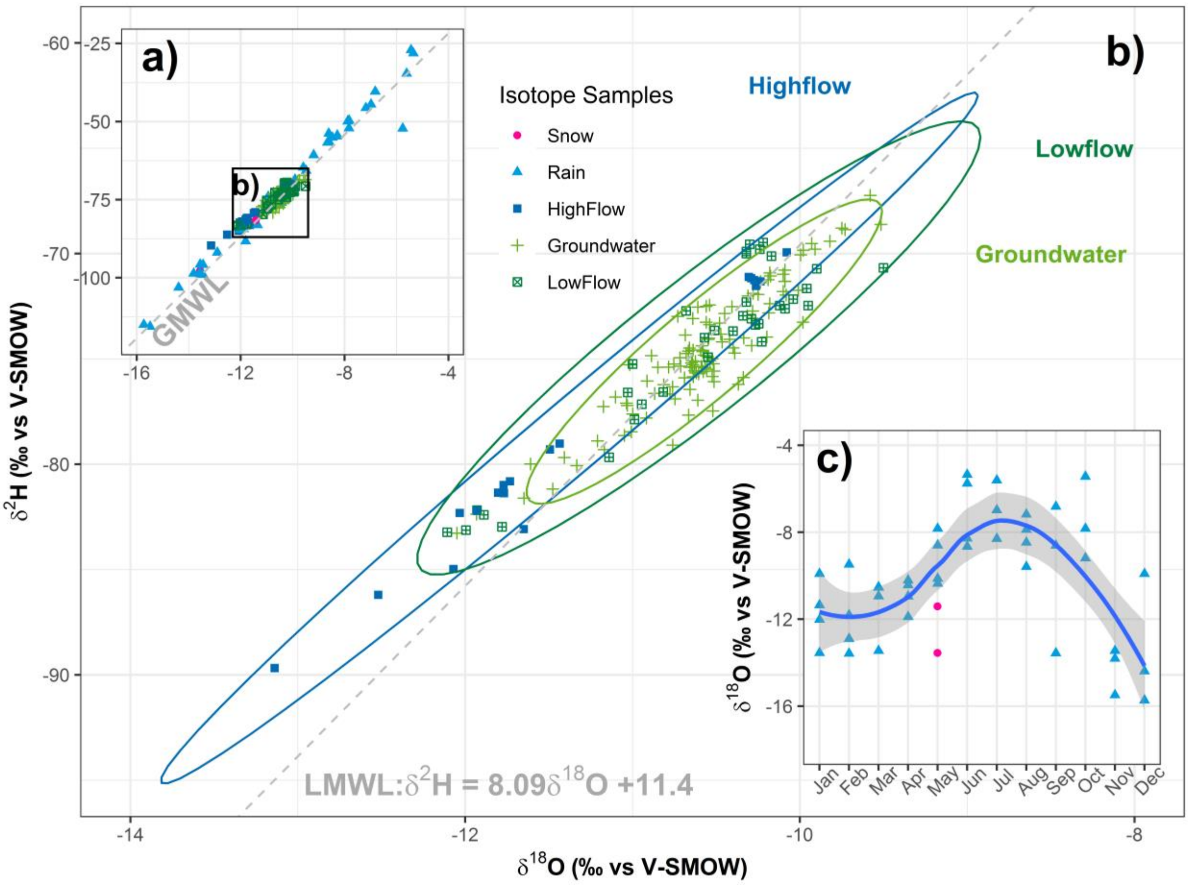


Figure 4-3: a) Stable water isotope composition of snow, rain, groundwater, and event sampled high- and lowflow samples from the Thur catchment in relation to the GMWL, b) zoomed in on groundwater (measured over the period from 2017 – 2020), and high- and lowflow samples (measured from 2018-2020) with respect to the LMWL, and c) seasonal variability in precipitation data (snow and rain).

Comparing seasonal variability in the isotopic composition of event sampled surface water from the Thur River with the isotopic values from rain and groundwater, highlights the overall seasonal variability of the different compartments, with the greatest compositional variability found in the rainfall data, followed by the surface river water, and then the groundwater samples (Figure 4-4). Mean annual $\delta^{18}O$ values varied between -10.2‰, -11.4‰, -10.6‰, and -10.6‰ for rain, highflow, lowflow, and groundwater samples respectively. Winter rainfall samples were relatively depleted (with mean $\delta^{18}O$ value of -12.2‰), with isotope values increasing during spring (-10.5‰), reaching maximum $\delta^{18}O$ values during summer (-7.5‰), and then decreasing again during autumn (-10.5‰). Event sampled highflow river samples displayed minimum mean $\delta^{18}O$ values during spring (-12‰), in line with spring snow values. This suggests that the snowmelt buffers the isotopic composition of surface water during spring.

Lowflow samples were on average more enriched in $\delta^{18}O$ values than highflow samples, with mean lowflow values of -10.6‰ and mean highflow values of -11.4‰. Although the lowflow samples, like the rain samples, were most enriched during summer, overall the surface sample $\delta^{18}O$ values displayed less variability when compared to the rainfall values. Groundwater samples show even less compositional variability. Being a compositional mix of both rainfall and runoff water, groundwater values appear comparatively buffered, with the most depleted mean $\delta^{18}O$ values found during spring (-11‰) and the most enriched values were found during autumn (-10.5‰). This indicates that the positively buffered values of the summer rainfall and surface runoff waters only reflects in the groundwater signature during autumn. This suggests a travel time requirement of two to three months for rain and surface water signatures to arrive at the groundwater. Mean $\delta^{18}O$ values of event sampled lowflow river water samples were most similar to groundwater samples during the summer months. While highflow samples were relatively depleted during spring, due to influencing snow components, lowflow surface values appeared positively buffered during winter when compared to rainfall values. This suggest a contribution from the groundwater component, which displayed enriched isotope values during autumn, supporting a minimum of two- to three-month travel time requirement from the sub-surface to surface.

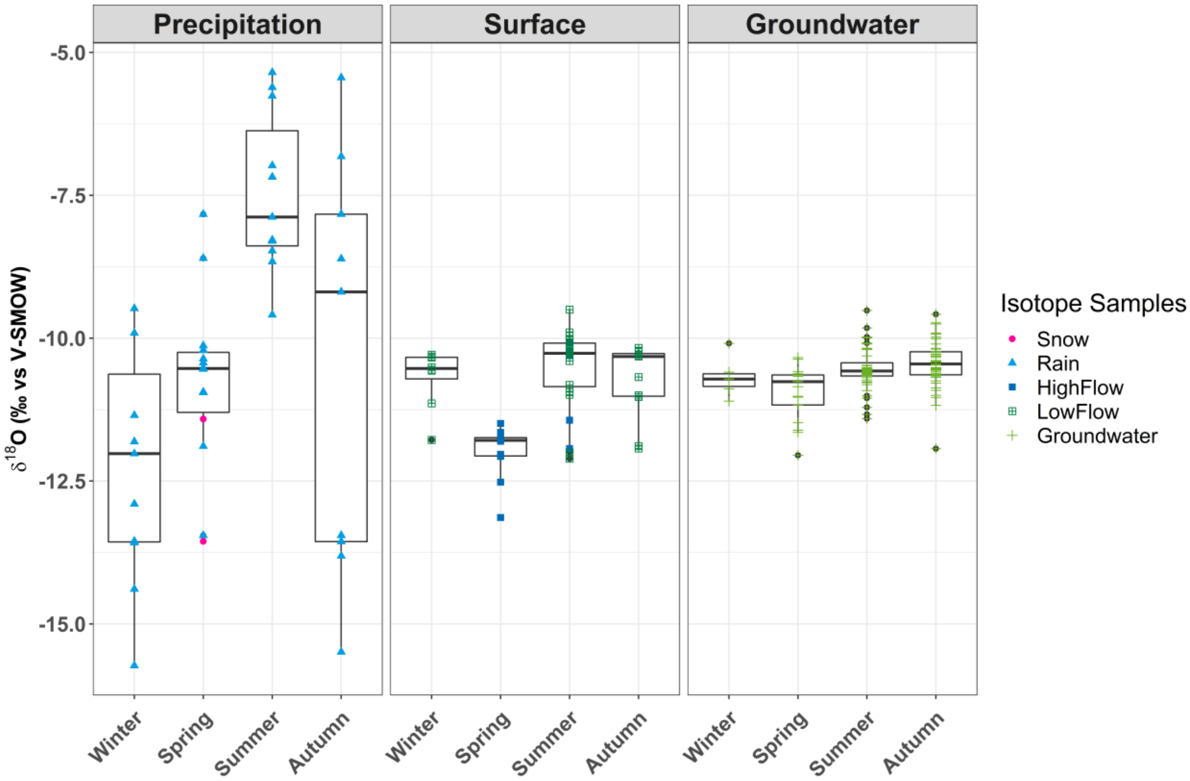


Figure 4-4: Seasonal variations of δ^{18}O isotopic signatures in precipitation, high- and low-flow event samples and groundwater samples.

4.5.2 Spatial variability of conservative tracers

Variability of isotopes

When plotting the measured water isotope variants δ^{2}H vs. δ^{18}O of the event sampled surface water, groundwater, and rainwater sites in the Thur catchment, little or no grouping was evident as the samples all more or less followed the LMWL trend (refer to Figure 4-3a). Notably, Site Ap1 displayed the most depleted, and the rainwater site ISOT the most enriched isotope values, with the remainder of the sites plotting somewhere in between. However, when applying a PAM clustering (refer to Figure S 6 in Appendix II: Supplementary Information to Chapter 4 for optimal cluster plot selection) using the mean δ^{2}H and δ^{18}O values, the sampled sites could be characterized as belonging to three separate clusters (Figure 4-5a). When plotting these clusters in terms of their values and site locations with respect to elevation, a clearer grouping was evident (Figure 4-5 b). The high-altitude sites (> 680 m asl.) located along the Sitter River and upstream of the Necker River confluence with the Thur River grouped as one cluster (Cluster 1). The sites associated with middle reaches of the Thur River (~ 680 – 480 m asl.), which includes the Necker River and the section of the Thur River between the confluences of the Necker and the Sitter Rivers, grouped as a second cluster (Cluster 2). Finally, the low elevation (< 480 m asl.) section of the Thur River, located downstream of the Necker River confluence, highlighted a third cluster (Cluster 3). Here, however, spatial overlap between Clusters 2 and 3 was evident. Elevation and steepness of slope appeared to be the primary driver behind Cluster 1, but Cluster 2 and Cluster 3 overlapped in the lower reaches of the Thur catchment, in spite of the reduced altitude of their respective sites. This suggests the presence of another contributing compositional aspect behind the water types of sites located at or directly above the confluence of the Sitter River.

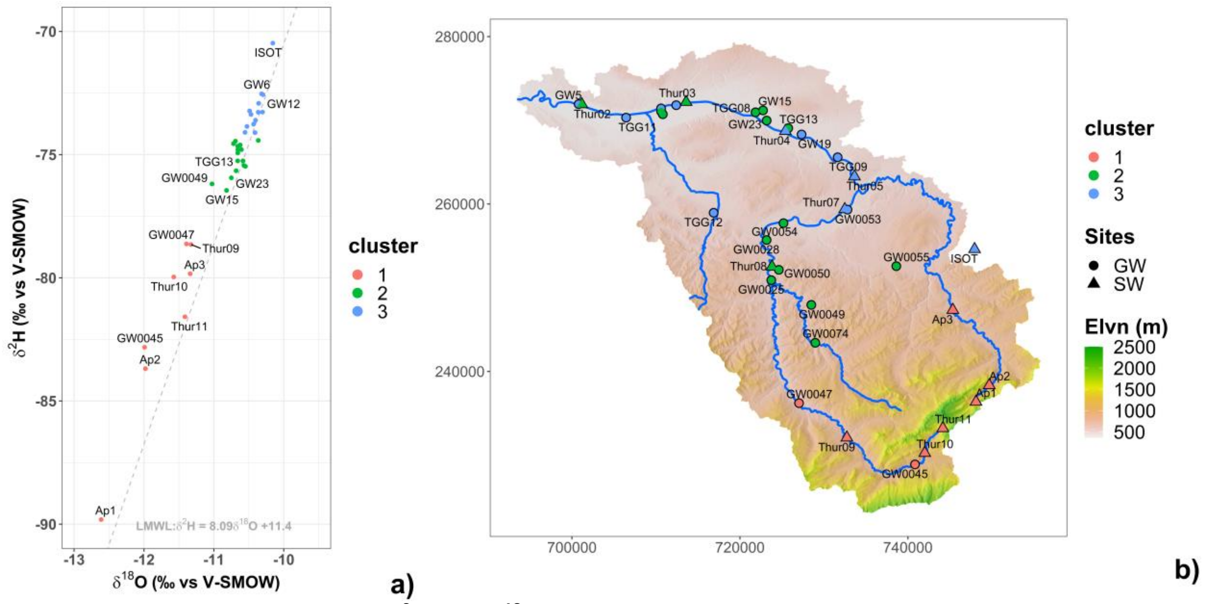


Figure 4-5: PAM clustered mean δ²H and δ¹⁸O values for the sites sampled in the Thur catchment with LMWL indicated, and b) PAM clusters plotted with respect to elevation for both the surface water (SW) and groundwater (GW) sites (DEM25 (2003), Source: Federal Office of Topography).

Looking at just the groundwater sites in more detail, Figure 4-6 indicates that the gradient of the isotopic ratios of the groundwater sites was less steep (6.2) than that of the LMWL (8.09). Values of δ²H and δ¹⁸O were more depleted for groundwater sites located at higher altitudes (> ~680 m asl.), while sites associated with the lower reaches of the Thur and the Murg Rivers were more enriched in their δ²H and δ¹⁸O values, and δ²H /δ¹⁸O radios deviating to the right of the LMWL (Figure 4-6). Surface river water in the lower elevation reaches of the Thur River would have experienced greater travel times along the course of the river. Subsequently these surface waters would experience greater degrees of evaporation, due to longer exposure to wind and air temperatures, prior to infiltrating into the sub-surface and resulting in groundwater recharge. Once infiltrated into the sub-surface, rock-water interaction is unlikely to have a significant effect on the δ¹⁸O isotope composition of the water, unless low-temperature rock interaction takes place, or gases such as CO_2 are present (Jasechko, 2019; Karolytė et al., 2017; Kloppmann et al., 2002; Rey et al., 2018), which is likely not the case here, as no significant depletion of δ¹⁸O independent of δ²H was observed. Groundwater samples from high elevation regions were comparatively depleted in their major anion and cation compositions (refer to Figure 4-7a and Table S 4 in Appendix II: Supplementary Information to Chapter 4), and their δ²H and δ¹⁸O values tended to deviate to the left of the LMWL, suggesting a contribution from highflow surface waters to the groundwater (refer to Figure 4-3b).

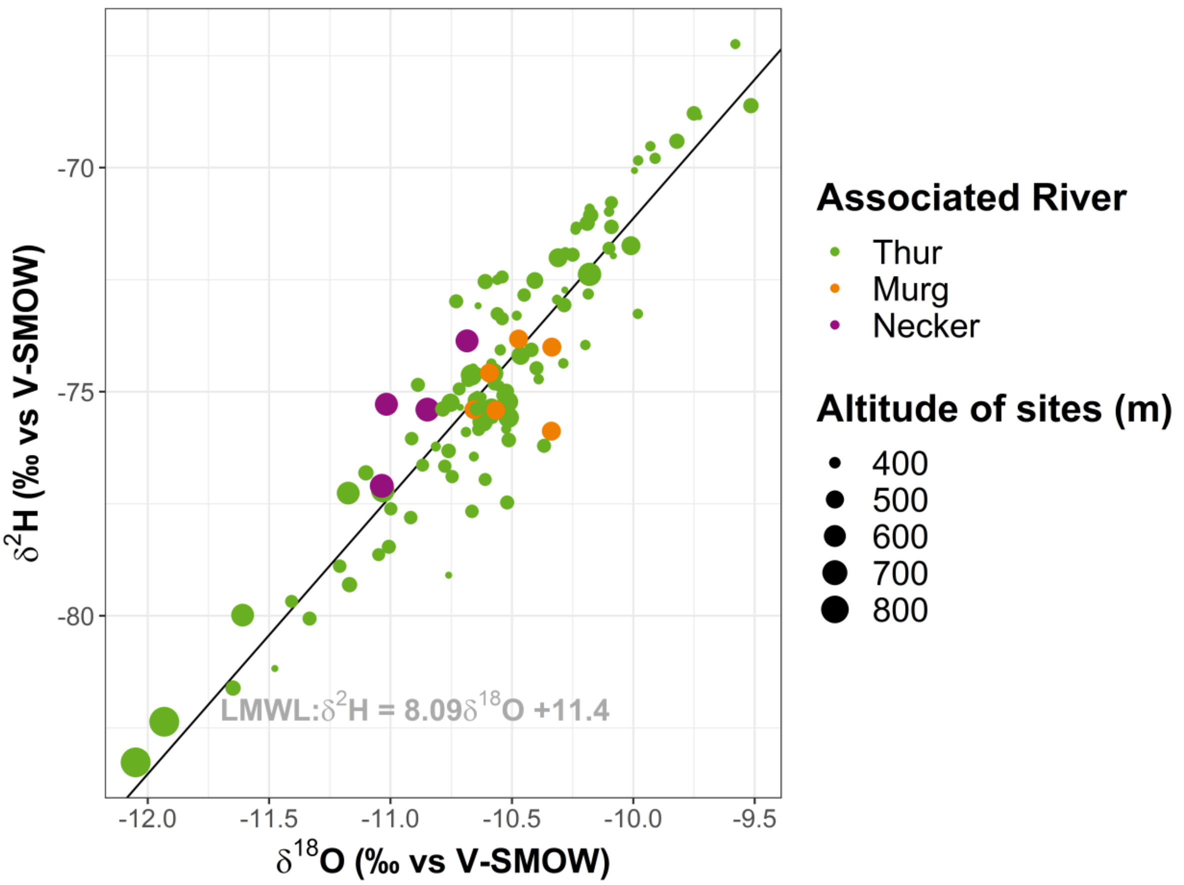


Figure 4-6: δ^2H and δ^{18}O isotopic values of groundwater samples in relation to site location and altitude.

Variability of major ions

Measured anion and cation concentrations of Mg^{2+}, Ca^{2+}, NO_3^-, and HCO_3^-, measured in sites grouped as Cluster 2 and Cluster 3 (Figure 4-7a), were compared with concentration trends measured in groundwater (GW) and surface water (SW) sites (Figure 4-7b). With the exception of Na^+, Cl^- and NO_3^- concentrations, the concentration trends of the sites grouped as Cluster 2 and Cluster 3 and tended to mirror the respective GW and SW trends. The sources of Na^+ and Cl^- are often seasonally loaded, with periods of lowflow generally having increased salt loads in comparison to periods of highflow (Hellwig et al., 2017). While NO_3^-, being a common component of fertilizer and sewage treatment plants, generally stems from anthropogenic rather than geogenic sources in the Thur catchment (Chittoor Viswanathan et al., 2016). Concentrations of Mg^{2+}, Ca^{2+}, and HCO_3^- however, can be linked to geogenic processes in the Thur catchment, with the sub-surface being of a limestone-dominated origin in the source regions of the Thur River, and of marine sediment-dominated origin in the middle and lower reaches of the Thur catchment (Hayashi et al., 2012; Keller, 1992).

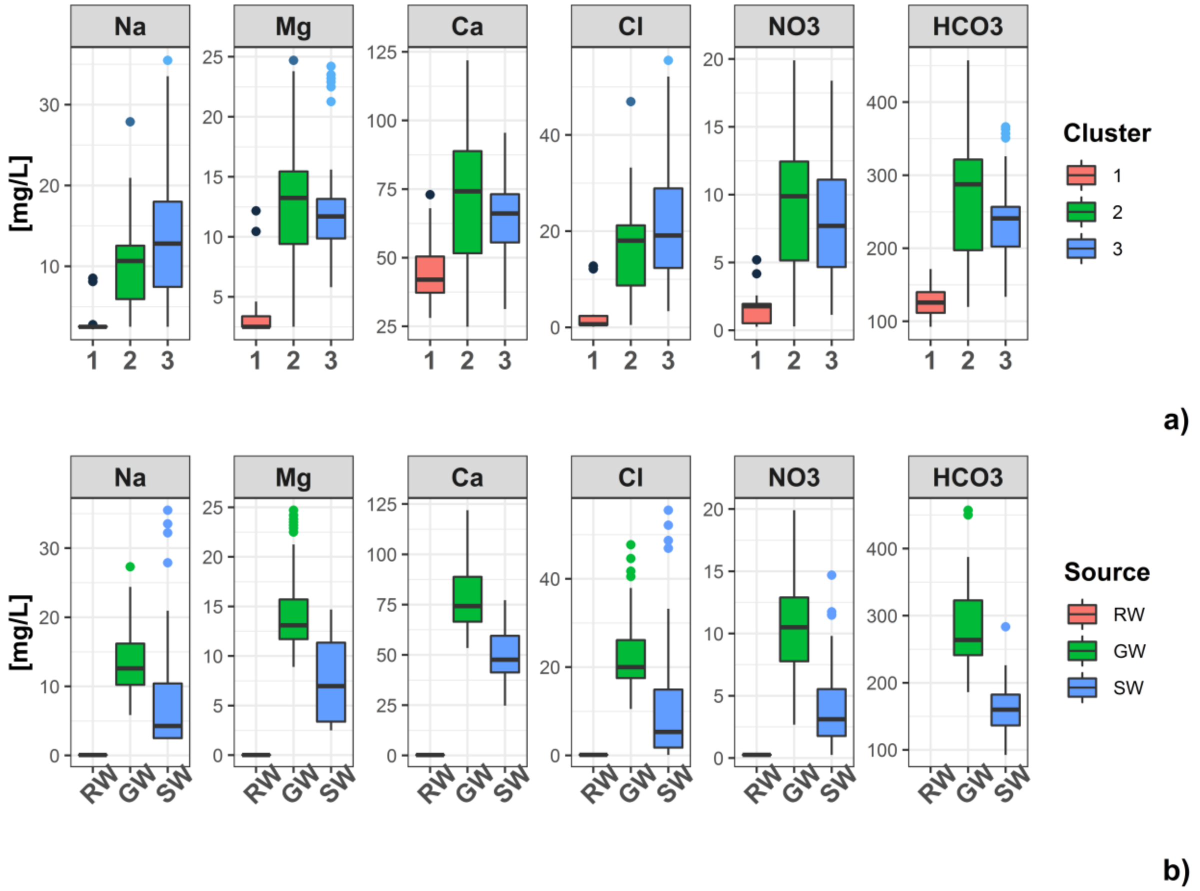


Figure 4-7: a) Plot comparing ion concentrations of the three clusters (Cluster 1, 2, and 3) derived from PAM clustering with b) concentrations measured in three different sources rainwater (RW), groundwater (GW), and surface water runoff (SW).

The sites located in the lower reaches of the Thur catchment (Figure 4-8a), where Clusters 2 and 3 were found to spatially overlap, were examined in more detail. Two sets of sites exist which both make up a series of sites located tangentially to the Thur River (Figure 4-8b). In the first series, composed entirely of groundwater wells (GW6, GW7, and GW8), Site GW6 is located closest to the Thur River (and was grouped as a Cluster 3 water type), while sites GW7 and GW8 (both of which were grouped as a Cluster 2 water type) are located increasingly further away from the Thur River. Looking at the ion concentrations measured in this first series (Figure 4-9a), GW6 displayed elevated Na^+ and Cl^- values with respect to GW7 and GW8, while GW8 and GW7 displayed elevated Mg^{2+}, Ca^{2+}, NO_3^-, and HCO_3^- concentrations (with GW8 generally displaying overall grater concentrations than GW7, with the exception of NO_3^-). The second series composed of one groundwater site (TGG13) and one surface water site (Thur04), although less defining than the first series, displayed a similar trend (Figure 4-8b). Although the measured concentrations of Na^+ and Cl^- were greater, the spread of Na^+ and Cl^- concentrations in the groundwater site (GW6) of the first series was comparable to those measured in the surface water site of the second series (Thur4). Comparably similar to the first series, the Mg^{2+}, Ca^{2+}, NO_3^-, and HCO_3^- concentrations measured in the groundwater site of the second series (TGG13) was again much greater than the concentrations measured in the surface water site Thur04 (Figure 4-9b).

In both series, a declining concertation of Mg^{2+}, Ca^{2+}, NO_3^-, and HCO_3^- was evident with increasing proximity to the Thur River, while in both series the Na^+ and Cl^- concentrations displayed a greater variability with increasing proximity to the Thur River (Figure 4-9a and b). Using these concentration trends, Clusters 2 and 3 could be further explained, with sites associated with Cluster 2 representing a definite groundwater dominated water type, and sites from Cluster 3 a surface water dominated cluster (Figure 4-7b). However, whether the sites from Cluster 3 represent a surface water types dominated by river runoff or locally fallen rainwater, remained unclear.

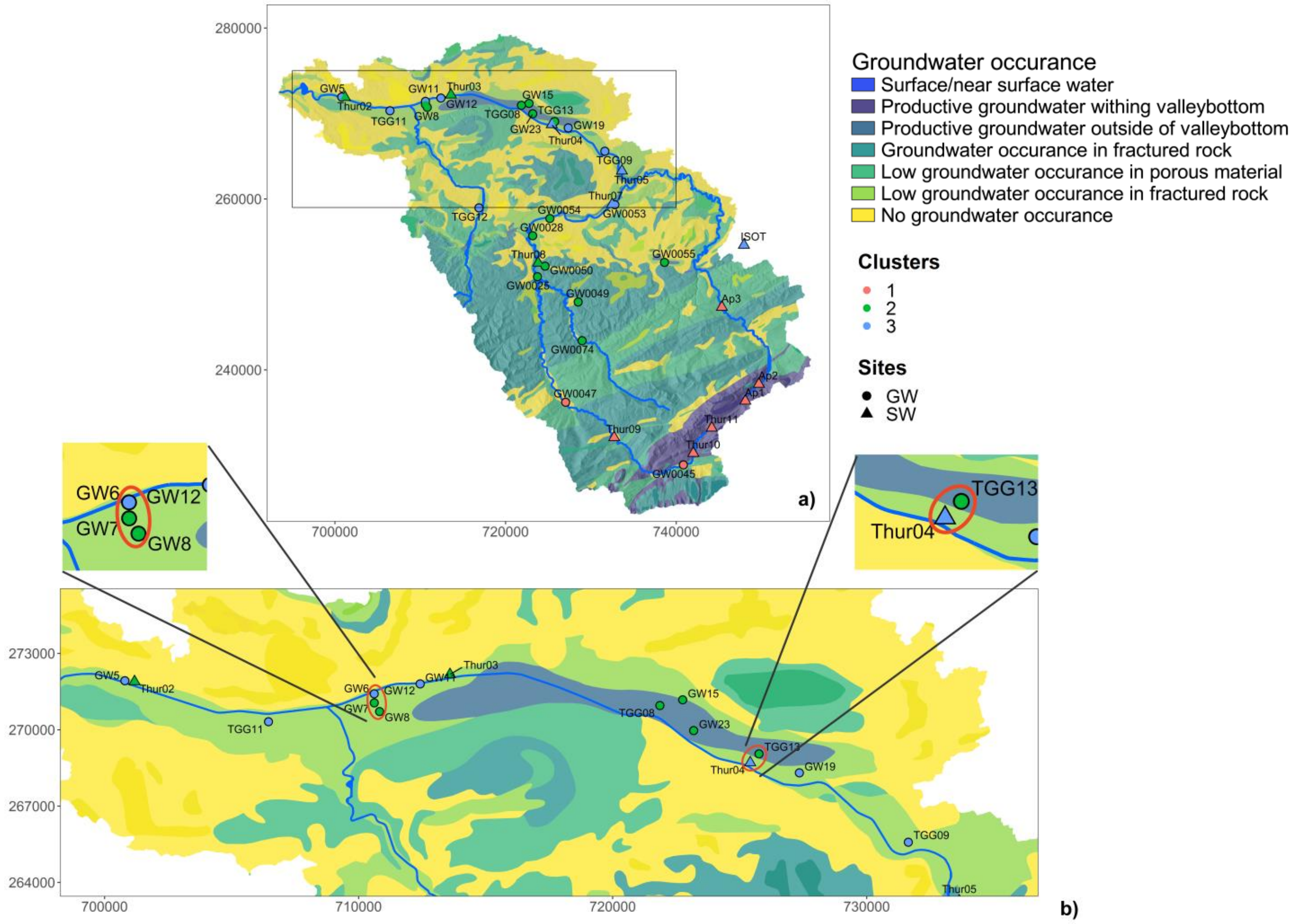
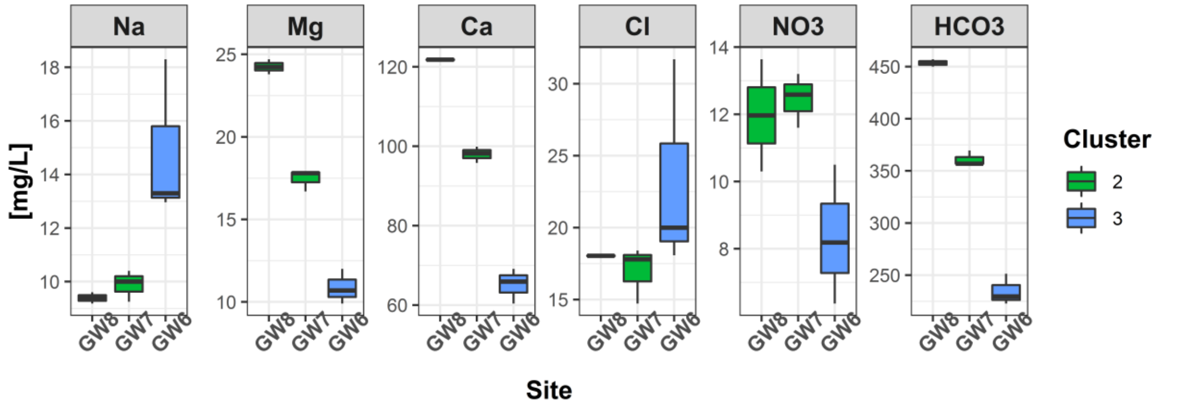


Figure 4-8: Spatial variation of PAM clustered mean isotope values in the Thur catchment from sampled surface water (SW) and groundwater (GW) sites with respect to a) geology, and b) zoomed into northern section of catchment with two series of sites indicated circled in red (Geokarten 500, Source: Federal Office of Topography).



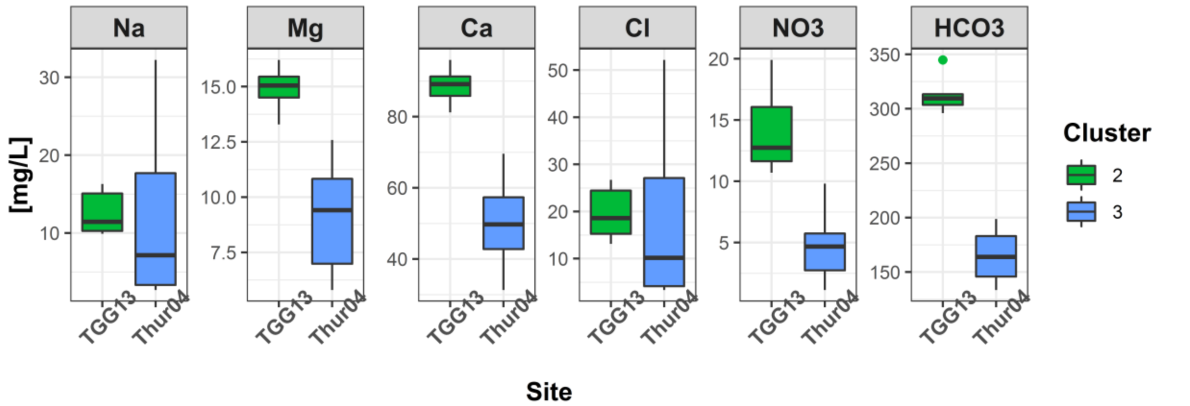


Figure 4-9: a) Comparison of groundwater site series GW8, GW7, and GW6, and b) comparison of groundwater and surface water site series TGG13.

4.5.3 Sources and mixes

In order to characterize the spatial dimensionality of the Thur catchment's hydrogeological system further, an EMMA was conducted using the event sampled river water data along with the rain and groundwater data sets. The mean values of the environmental tracer concentrations Ca^{2+} and $\delta^{18}O$ measured at each site was assessed using a mixing diagram (Figure 4-10a). Based on this, end-members (Em) were determined in such a way that they represented the majority of the dimension of the mixing subspace. The mixing subspace was defined as the triangle created by the vertices of three end-members: selected to encompass the majority of the sampled values. The three selected end-members included the Em1 associated with the precipitation values from the middle reaches of the Thur catchment (ISOT site), Em2 associated with the high altitude surface headwaters of the Thur catchment (Ap1 site), and Em3 associated with the groundwater from within close proximity of the Thur River in the lower reaches of the Thur catchment (GW8 site). Four sites in the Thur catchment (GW0045, GW0025, GW0054, and GW0053) fell outside of the mixing space as defined by the selected end-members (sites indicated with red asterisk in Figure 4-10b). In the case of these four sites, the selected end-members did not result in a satisfactory mix, with mixing errors ranging from 11.7 - 0.05% at GW0025 and GW0053 respectively.

Figure 4-10b shows the results of the three EMMA, with sampled sites arranged in order of decreasing elevation; from the most upstream location either along the Thur or the Sitter River, to the most downstream site located near Andelfingen (refer to Figure 4-1). Of the sampled mix waters, Em2 was a dominant component in the surface sites from the upper reaches of the Thur catchment (including sites Ap2, Ap3, Thur10, and Thur9), with the Em2 signature making up between 73 – 46% of the mixes measured at the Ap2 and Thur9 sites respectively, and 72% and 47% of the mixes measured in the groundwater sites GW0045 and GW0047 respectively. These sites were all grouped as Cluster 1 types by the PAM clustering process (refer to Section 4.5.2). Although all of the sampled groundwater sites were more strongly dominated by the Em3 component when compared to the surface water sites, this was particularly true for the sites located in the middle reaches of the Thur catchment (associated with Cluster 2; refer to Section 4.5.2). For these sites (including GW0074, GW0049, GW0050, GW0028, and GW0054), the Em3 component made up between 38% and 93% of the total mix water measured. Although still present, the Em2 component was much reduced in the sites located in the middle reaches of the Thur catchment (making up on average 17 % of the sampled mixtures). This strong Em3 component, evident in the sites located in the middle reaches of the Thur catchment, declines somewhat in the samples from the lower reaches of the Thur catchment (both for the sites grouped as Clusters 2 and 3), with an increase in the proportion of the Em1 component present in both the sampled surface and groundwater sites. In this lower region of the Thur catchment, the Em3 component made up between 34 – 41% and 53 – 77% in the surface and groundwater sites respectively, while the Em1 component measured in the surface sites ranged between 42% and 55% with groundwater water sites showing a slightly lower Em1 proportion of between 14 – 45%.

Looking at the proportions (%) of end-members present at each of the sampled sites (Figure 4-10b), it is evident the upper higher-altitude sites were predominantly Em2 dominated, with Em2 making up an average of 49%, Em1 35 %, and Em3 16% of the sampled mixes. The sites located in the middle reaches of the Thur catchment were dominated by the Em3 component. On average, the sampled mix water from the middle reaches of the Thur catchment were composed of 71% of the Em3, 17% of the Em2, and 12% of the Em1 component. Finally, the sites located in the lower reaches of the Thur catchment were shown to be composed predominantly of a mix of the Em3 and the Em1 component, with Em3 making up an average of 57%, Em1 an average of 31%, and Em2 and average of 9% of the sampled water. The three designated end-members are characterized by the ISOT precipitation site (Em1), the Ap 1 surface water site (Em2), and the GW8 groundwater site (Em3). This elucidates the primary fractions which make up the mixed water types sampled in the Thur catchment, with Cluster 1 being predominantly a surface river dominant water type, Cluster 2 a groundwater dominant type, and Cluster 3 a mixed groundwater and precipitation type. The almost equal mixture of Em1 and Em3 in the sampled source waters, helps to explain some of the spatial cluster overlap concerning Clusters 2 and 3 (as classified using the PAM clustering) observed in the lower reaches of the Thur catchment.

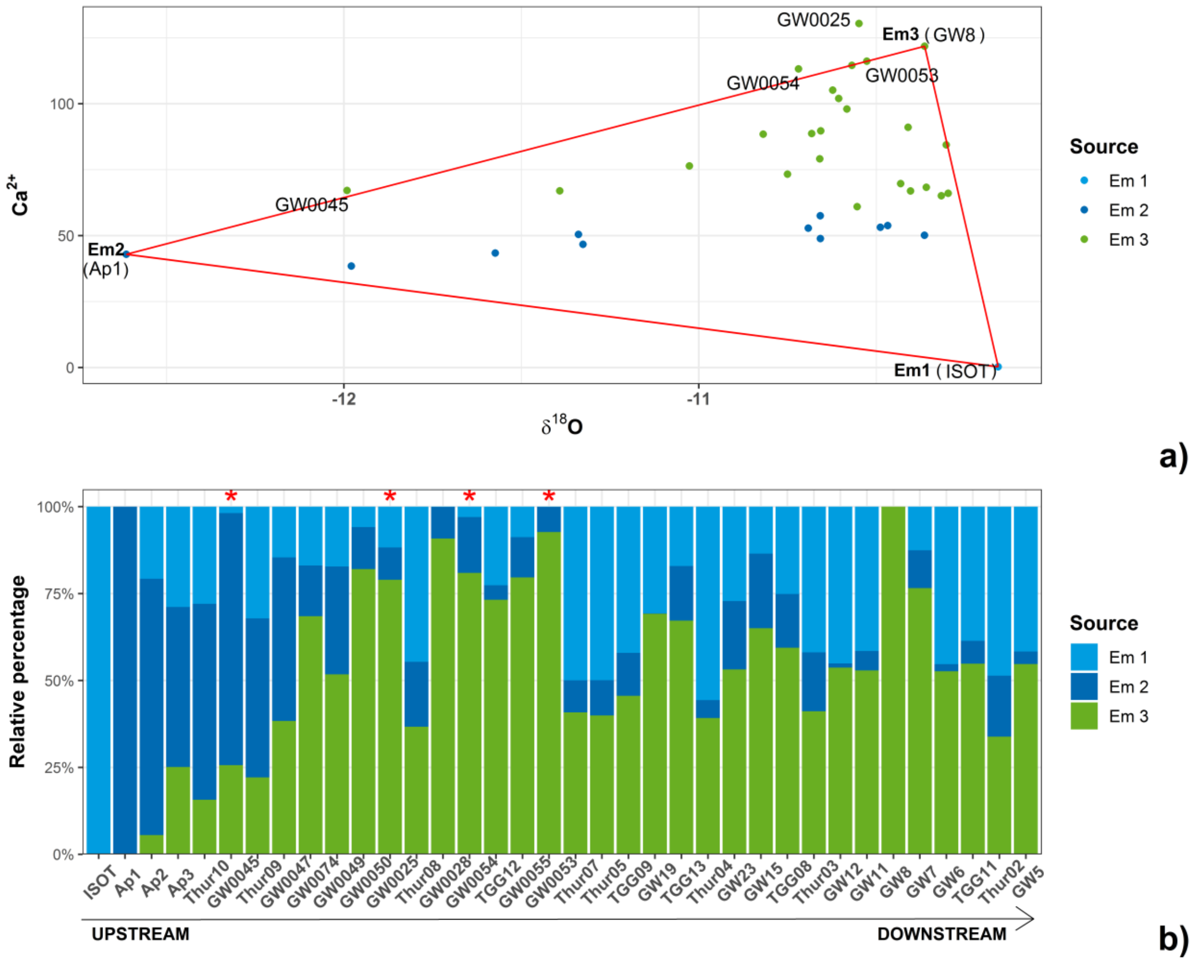


Figure 4-10: a) Mixing subspace (in red) as defined by three end-members (Em1, Em2, and Em3), and b) results of the three end-member mixing analysis showing percentage of end-members present per site. Sites marked with a red asterisk fall outside of mixing space as defined by the selected end-members.

4.5.4 Spatiotemporal variability of event sampled river water

The event sampled high- and lowflow Thur River water samples were assessed, independently of the groundwater and rainwater data, both in terms of their spatial and their temporal characteristics. The temporal characteristics of the event sampled surface water was assessed by comparing 2018 data, which was a national drought year (BAFU et. al., 2020), with data collected during 2019 (Figure 4-11). The spatial characteristics of the event sampled surface water were assessed by comparing the water isotope concentrations δ^2H and $\delta^{18}O$ measured in the event-sample surface water to the respective altitude of the sampled sites (Figure 4-12) Over the three-year sampling period, the average isotopic composition in the highflow samples ranged from -78‰ and -11.3‰ for δ^2H and $\delta^{18}O$ respectively, and between -74‰ and -10.5‰ in lowflow samples for δ^2H and $\delta^{18}O$ respectively.

The temporal characteristics of the event sampled river water were investigated by comparing available isotopic data for the 2018 drought year with the isotopic signatures from the same sites sampled during 2019. Figure 4-11 highlights a relative compositional similarity between the high- and lowflow samples during the hydrological drought year 2018. During 2019 however, the lowflow samples were relatively more enriched, while the highflow samples were relatively depleted in their δ^2H and $\delta^{18}O$ isotope values. The spread of isotopic values from event sampled surface waters from the Thur River shows that the samples collected during

2018 had a smaller variability in their isotopic signatures, with all of the measured values ranging between -83‰ and -70‰ for δ^2H, and between -12.1‰ and -10‰ for $\delta^{18}O$. For the 2019 event sampling year, a greater variability in the stable water isotope concentration was evident, with values ranging from -90‰ to -70‰ and from-13.1‰ to -9.5‰ for δ^2H and $\delta^{18}O$ respectively. When compared to the location of the sites with respect to their altitudes, this indicates a reduced surface runoff component present during 2018 (also shown in Figure 4-12). The overall isotopic enrichment seen in the 2018 samples, in particularly the higher-altitude samples, further suggests a predominance of a water source that has undergone greater degrees of enrichment prevailing in 2018. Although this enriched water source could stem from the dwindling river water, the fact that even the high-altitude sites were enriched points towards a potential groundwater source contributing a significant proportion of water sampled in the Thur River during times of drought. Although sample availability made a comparison between 2018 and 2019 possible, insufficient samples were available to do an additional high- and lowflow comparison for 2020.

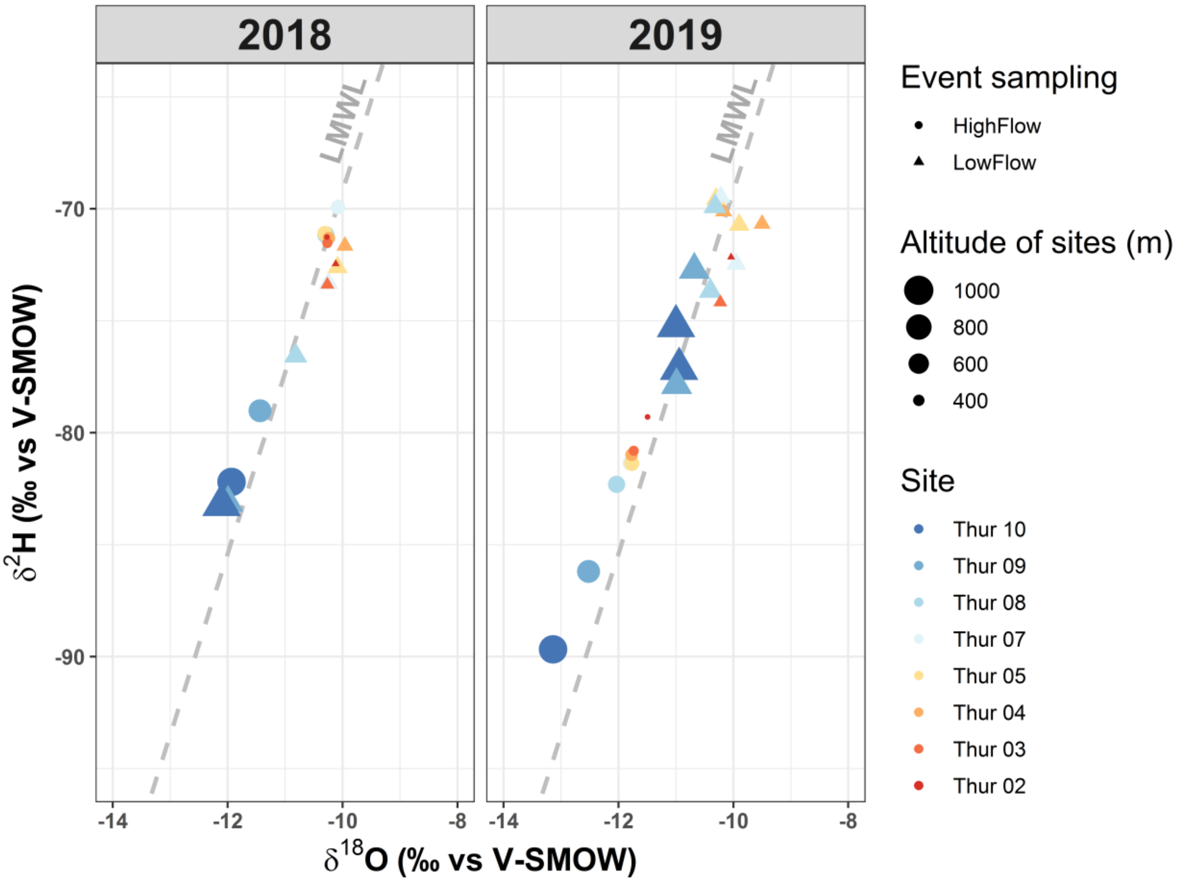


Figure 4-11: Spread of isotope values from event sampled surface waters from the Thur River comparing drought year samples (2018) with normal year (2019) samples (LMWL indicated).

Spatially, the isotopic variability in the event sampled river water showed a greater compositional depletion in the high-altitude highflow samples (located at or above 680 m asl.) relative to the high-altitude lowflow samples (Figure 4-12). Lowflow samples, particularly the low-altitude lowflow samples, showed a greater tendency for plotting towards the right of the LMWL, suggesting that these samples had undergone greater degrees of evaporation. Looking at the distribution of isotope concentrations of the event sampled surface waters from the Thur River, the compositional predominance of relatively depleted signatures during highflow sampling would indicate a source dominated by surface water (SW) runoff; this water being relatively depleted in the heavier δ^2H and $\delta^{18}O$ isotopes. Lowflow samples on the other hand show a predominance for water that is relatively enriched in δ^2H and $\delta^{18}O$ concentrations; the source of which could be attributed to groundwater (GW).

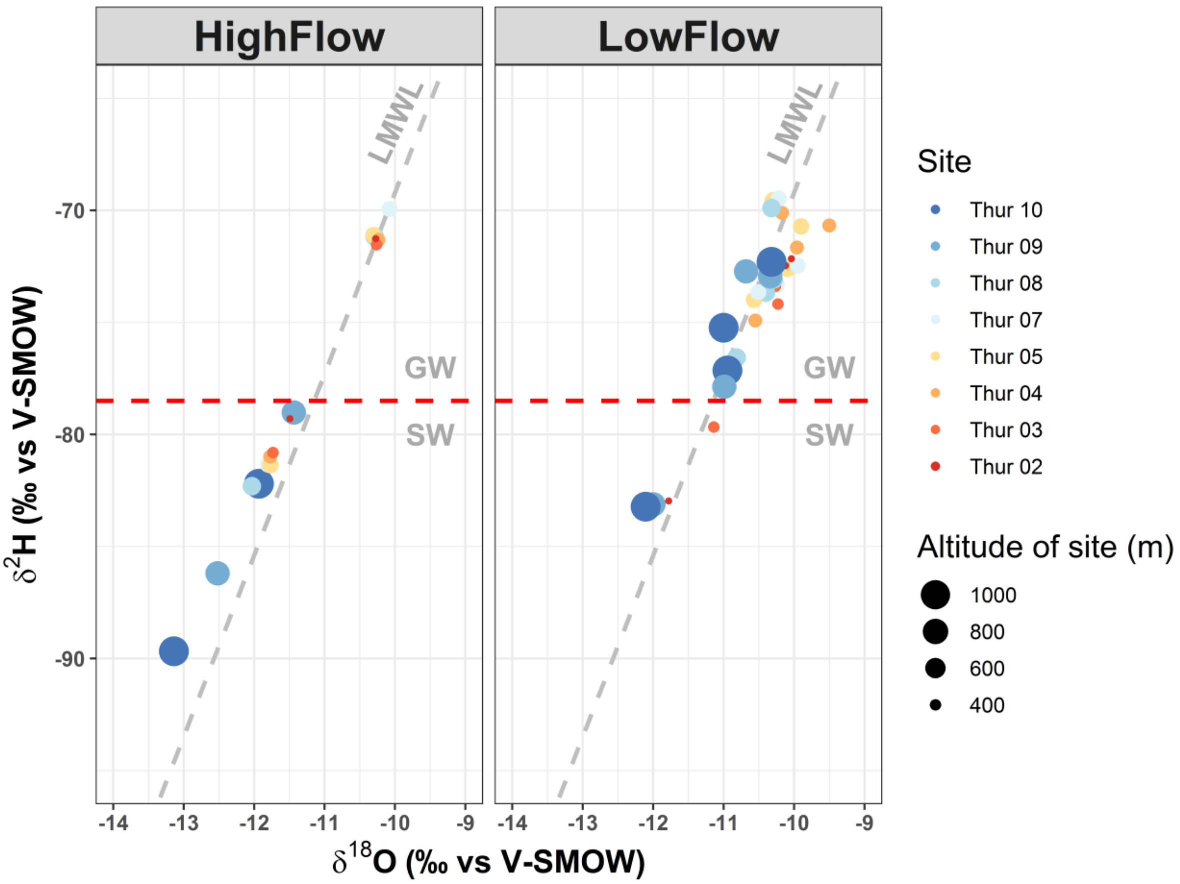


Figure 4-12: Distribution of isotopic composition of event sampled surface water from the Thur River compositionally showing a predominance of surface water (SW) runoff during highflow, and a predominance groundwater (GW) during lowflow (LMWL indicated).

4.6 Discussion

As river water represent a connection between surface and sub-surface processes, the Thur River was sampled for its water isotope and geochemical composition during highflow and a lowflow events for the years 2018 to 2020. In addition, groundwater sites associated with the Thur River, as well as some of its major tributaries were sampled bi-annually over the period from June 2017 to June 2020. Rainfall isotope data from an ISOT site was used to support the analysis of the Thur catchment's spatiotemporal hydrogeology. This section discusses the results from the analysed data in terms of the spatial and temporal characteristics of the Thur catchment. It also reviews the adequacy of using event sampled river water to characterize a catchment's surface-groundwater exchange, along with providing potential improvements to future event sampling.

4.6.1 Temporal surface-groundwater dynamics

The average water isotope values of rainfall and groundwater samples in the Thur catchment from 2017 - 2020 fell within expected regional values (Jasechko, 2019). Comparing the isotopic characteristics of the surface river water and groundwater samples measured in the Thur catchment, a strong similarity to the isotopic composition of rainwater (whose values in turn are similar to that of the GMWL) was observed (Figure 4-3a). Local isotope composition of precipitation has been shown to exert a first-order control on the isotopic composition of local groundwater the world over (Jasechko, 2019), with the importance of rainwater for groundwater recharge in the Thur catchment having been demonstrated in Chapter 3.

Deviations in the surface river water and groundwater values from the LMWL occur as a result of fractionation: processes that alter the stable ^{2}H and ^{18}O compositions post rain-out (Jasechko, 2019). A deviation to the right of the LMWL due to enriched $\delta^{18}O$ values was evident primarily in the lowflow event samples and some of the groundwater samples. This enriched deviation from the LMWL is commonly attributed to partial evaporation along $\delta^{2}H/\delta^{18}O$ ratios with slopes of ~3 to ~6 (Jasechko, 2019). A deviation away from and to the left of the LMWL was evident particularly in the highflow river samples and the high-altitude groundwater samples. This depletion of $\delta^{2}H$ and particularly $\delta^{18}O$ is most likely as a result of amount effect during heavy rainfall events (Clark and Fritz, 1997). This rainout effect signature would then be transported to the subsurface, subsequently resulting in the groundwater (in particular the high-altitude samples) carrying a highflow signature.

A seasonal variability of the rainwater samples was evident, with higher $\delta^{2}H$ and $\delta^{18}O$ values measured during the warmer summer months (June, July, and August), and lower values measured during the colder winter months (December, January, and February). This is typical of rainfall signatures associated with regions outside of the tropics (Jasechko, 2019). Snow samples taken during late spring indicated a relatively depleted isotopic composition. During spring months (Mar, Apr, and May), snowmelt appears to dampen the highflow isotope values from sampled Thur River water. Although only two snow samples were collected, and only during spring, their values highlighted the importance of snowmelt to the highflow sample characteristics during the spring months. Groundwater isotope values were comparatively buffered throughout the year. This would be because of mixing (refer to Section 4.5.3), with groundwater in the Thur catchment being composed primarily of a mixture of varying proportions of locally infiltrated rainwater and surface water. Isotopically enriched groundwater values measured during autumn, suggests a travel time requirement of at least three months for the more enriched rain and surface water signatures to arrive at the groundwater (in line with the study by Hoehn and Scholtis, 2011). During the winter months (Dec, Jan, and Feb), the enriched surface water values relative to the rainfall values, suggests a contribution from the groundwater component (the values of which were enriched during the autumn months) to the river water. This process of groundwater discharge to surface water also appears to encompass a travel time requirement of approximately three months.

4.6.2 Spatial surface-groundwater dynamics

A multivariate analysis, using a k-means PAM cluster of the mean isotope values from each site, helped identify the spatial distribution of the water types in the Thur catchment. Three clusters where identified: 1) a runoff surface water type (Cluster 1), 2) a sub-surface groundwater component type derived from geological interaction (Cluster 2), and 3) a groundwater and precipitation mix type (Cluster 3). Although these clusters are representative of the water types in the Thur catchment, the overlap observed of Clusters 2 and 3 in the lower reaches of the Thur catchment could not be explained purely based on site location and altitude. An evaluation of the major anion and cation concentrations in the water samples, along with an EMMA, helped to explain the spatial overlap of Clusters 2 and 3 (refer to Section 4.5.2).

The use of both a k-means PAM clustering of the water isotope values, along with knowledge concerning the ionic concentrations of the water samples, enabled a clearer characterisation of catchment processes driving the water types in the Thur catchment. Catchment characteristics and processes include 1) elevation and associated steepness of slope, which affects temperature, rainout, and runoff rates, 2) geology, which based on water chemistry, affects the infiltration, storage and exfiltration of groundwater as well as groundwater travel time, and 3) surface related processes such as land use that affects both evapotranspiration rates as well as water chemistry. These characteristics and processes result in the spatial distribution of the three clusters identified in the Thur catchment. Expanding on the overlapping water types in the lower reaches of the Thur catchment (as described by Clusters 2 and 3), in places where surface water sites fell into Cluster 2, it is postulated that groundwater exfiltration can be expected. This goes some way to describing the groundwater flow in the Thur valley aquifer, as well as identifying the importance of runoff to groundwater recharge in the high-elevation, and rainwater to groundwater recharge in the lower elevation reaches of the Thur catchment. However, in order to determine the proportion of contributing source waters to the mix waters sampled throughout the Thur catchment, the three EMMA was necessary.

Although the Thur catchment represents a dynamic and heterogeneous system, three dominant hydrogeological processes, associated with three different regions, were identified in the Thur catchment, including direct rainfall infiltration, infiltration of surface river water to groundwater, and groundwater exfiltration to the river, or a combination of these. The selection of end-member sources included a precipitation type (Em1), a surface water type (Em2), and a groundwater type (Em3). However, four sites (GW0045, GW0025, GW0054, and GW0053) fell outside of the defined mixing space, suggesting an incomplete mix at these sites. This is most likely due to an incomplete source component characterization, with additional potential end-members present in the Thur catchment. Assuming that alteration in the mix water can only result from source water mixing (Kalbus et al., 2006), additional sources such as soil water, and water associated with different geological regions of the Thur catchment could be a factor. For example, the possible flow path from the karstic regions could not be assessed in every detail necessary to limit uncertainties. More data and detail investigations would be required to provide further insight. In addition, groundwater retention time, infiltration processes and surface water travel time, which was not considered here, are factors which will lead to the alteration of the geochemical composition of a catchments various water sources (Hounslow, 1995).

Aside from the four sites whose mixes were not adequately described, the remaining 89% of the sites sampled in the Thur catchment could be adequately characterized using the selected end-members. Overall, the sites associated with the high elevation reaches of the Thur catchment were dominated by surface water runoff, with Em2 making up as much as 72% and 47% of the sampled groundwater sites (Cluster 1). The sites associated with the middle reaches of the Thur catchment (Cluster 2), showed a high prevalence for groundwater with the Em3 component contributing up to 92%, of sampled groundwater site mixes, and up to

37% of the sampled surface site mixes. Direct infiltration of precipitation appears to be an important component of the groundwater sites associated with the lower reaches of the Thur catchment, where the Em1 component made up a maximum of 27% in the Cluster 2 type groundwater sites, and as much as 54% in the Cluster 3 type groundwater sites. However, as mentioned in Section 4.4.3, an overrepresentation of the surface water is possible, as only events (high- and lowflow) were sampled. Furthermore, in the lower region of the Thur catchment, where Clusters 2 and 3 were seen to overlap, some of the sampled surface waters (e.g. Thur03 and Thur04) displaying a dominance of the Em3 fraction could be enriched via groundwater exfiltration. When looking at the source components contributing to these two sites, 41% of Thur03 and 34% of Thur04 was described by of the Em3 fraction. The small fraction of Em2 in the lower reaches of the Thur catchment could also signal a reduced (or almost negligible) influence of this high-altitude end-member in the sampled waters from the lower reaches of the Thur catchment. Additionally, as a result of its passage through the vadose zone, the directly infiltrated precipitation would increase its Ca^{2+} concentration (refer to Section 4.4.3). Subsequently, an overestimation of the proportion of directly infiltrated precipitation in the southern regions of the Thur catchment, is possible.

In spite of the cluster analysis not having been used to determine the individual end-members, the classification was deemed useful in determining spatial changes and variability in the Thur catchment's water types. When combined with knowledge concerning the major ion concentrations and the results from the EMMA, water sources and mixes could be characterized. A surface water type signature (EM2) characterized sites associated with Cluster 1, where topography and steepness of slope are the primary drivers.. While in the lower reaches of the Thur catchment, where topography was no longer the distinguishing factor between the water types, Clusters 2 and 3 were found to spatially overlap. The use of water chemistry, in particular the knowledge concerning the isotopic and major anion and cation concentrations, along with results from the EMMA, provided additional information regarding the sources and processes active in the lower reaches of the Thur catchment. Sites associated with Cluster 2 were classified as being a groundwater-dominated, and Cluster 3 as a mix of groundwater and rainwater-dominated water type.

Although the use of isotope data from only one station has been shown to oversimplify catchment processes where large catchments are concerned (IAEAA, 2012), this study showed that the sampling of a handful of sites can provide valuable insight into catchment characteristics and processes. The use of event sampled surface water samples alone was able to provide insight into the processes characterizing the water distribution in the Thur catchment, especially where drought periods are concerned. However, the inclusion of groundwater and rainwater data enabled a more complete analysis of the Thur catchment. The use of an EMMA provided greater clarity concerning the compositional proportion of sources present in each of the waters sampled in the Thur catchment, along with the spatial variability of this composition.

4.6.3 The value of event-sampled water

The event sampled surface river water characteristics provided insight into the Thur catchment's entire water dynamics. The compositional distribution of isotope values measured in the event sampled surface water from the Thur River displayed a compositional predominance for surface water (SW) runoff water during highflow events, and a predominance for groundwater (GW) during lowflow events (Figure 4-12). The significant contribution of groundwater to alpine streamflow, especially during winter low flows, is a commonly accepted concept (Arnoux et al., 2020). During the 2018 drought year both high- and lowflow values displayed a smaller compositional spread, plotting more closely together, while during 2019, highflow and lowflow values plotted as two separate groups, with highflow samples showing more enriched and lowflow samples more depleted isotope concentrations. As only lowflow samples were available from the 2020 year, an additional annual comparison of high- and lowflows with the 2018 and 2019 year was not possible. In spite of this, based purely on sample composition, location, altitude, and timing of sampling, the two event sampled years were able to capture influences of groundwater contributions and spatial variations. This suggests that sampling the extreme events of a river's surface flow provides valuable insight into the hydrogeological characteristics of a catchment. As the dependence on groundwater as a water source increases, the importance of mapping recharge sources will become ever more important (Jasechko, 2019; Wada and Bierkens, 2014). It has been shown that isotopic data can help determine recharge sources, but this might be further improved upon by including chemical data from pollution potentials such as irrigation and liquid waste return flows (e.g. Burri et al., 2019; Chittoor Viswanathan et al., 2016), in order to monitor both groundwater quantity and quality more effectively.

4.6.4 Limitations and outlook

It is not uncommon to use a combination of tracers in order to characterize catchment processes. Environmental tracers provide information concerning water sources or transport processes (Cook, 2020). However, in order to identify the hydrogeological dimensions of a large catchment, the size and the composition of the tracer set are crucial (Barthold et al., 2011). Subsequently, the small number of tracers used in this study may be insufficient in explaining the source contributions to surface and groundwater mixes in the Thur catchment. The use of a larger tracer set could provide more robust estimates (Barthold et al., 2011; Popp et al., 2019). Furthermore, an investigation into the source trends rather than their specific proportions (in terms of percentage) within the mixed samples could provide additional insight into the spatial variability of water sources in the Thur catchment. Additionally, the identification of end-members, and subsequent fraction contribution to the sampled mixture, per sub-catchment rather than for the entire Thur catchment could provide a clearer picture regarding the evolution of waters along various flow paths. This could help reduce potential artefacts introduced as a result of assumptions concerning the conservative behaviour of tracers, as each set of sub-catchments would represent a more specific climatic condition, altitude, and geology (e.g. Guan et al., 2009; Petrella and Celico, 2013). The spatial connectivity of the system and whether a lateral or vertical exchange of ground- and surface water sources is being investigated needs to be carefully considered and described, perhaps with the use of a hydrogeological model. Furthermore, an EMMA of the different water types (e.g. surface water vs. groundwater) in isolation prior to a combined evaluation may help characterize the contributing sources, and subsequently the physical processes governing the evolution of water sources in the different regions of the Thur catchment, in more detail.

Where Em1 and Em2 are concerned, a question arises concerning representativeness of these end-members for the entire Thur catchment. Seeing as Em1 is characterized by a single precipitation site, and Em2 by a surface water site located in the high altitude limestone-dominated region of the Thur catchment, selecting these as end-member sources to describe the mixing proportions of water sampled from surface and groundwater sites located throughout the study area, might be an over-simplification of the geochemical processes and the groundwater flow paths involved in the evolution of water types in the Thur catchment. Furthermore, in light of the manner in which groundwater samples were collected, samples would represent a composite mixture of water ranging from recently infiltrated surface river water and rainwater, to older water from further down, which has undergone greater geochemical alteration as a result of longer subsurface residence time. Localized sampling might help elucidate the contributing fraction of precipitation to surface water in the lower reaches of the Thur catchment further. However, the alteration of conservative tracer concentrations, such as δ^2H and $\delta^{18}O$, once infiltrated into the subsurface is not common (Jasechko et al., 2016), and non-conservative tracer concentrations are always very low in any precipitation data. However, altitude gradient does affect isotopic composition (Cook, 2020), therefore, the use of the single precipitation site (ISOT) may result in a poor mix-water characterization, especially where the high-altitude sites are concerned. Subsequently, considering the size and homogenous nature of the Thur catchment, rather than additional sample collection, it might be advisable to divide the catchment into sub-catchments or regions based on geology and altitude when conducting an EMMA. Furthermore, additional tracers, such as EC, pH, or additional hydrochemical species in the EMMA could reduce uncertainties where source waters are concerned (Barthold et al., 2011; Popp et al., 2019).

Overall, the addition of geochemical data assisted in characterizing the Thur's spatial water dynamics. The inclusion of further chemical data, such as measurements of micropollutants could help establish current groundwater quality concerns, and help establish future monitoring and protection schemes in the Thur catchment. The inclusion of soil moisture samples, along with a study of groundwater retention time, might help to further establish the sources of the sites that were not well described by the EMMA in this study. While the measurement of additional environmental tracers might aid in identifying additional sub-surface processes (Barthold et al., 2011; Popp et al., 2021). Furthermore, an extension of the classical end-member mixing model as conducted by Popp et al. (2019), in which systematic biases due to unobserved end-members were accounted for by incorporating tracer-related observational errors using an observation Bayesian mixing model, allowed for the identification of a residual end-member. The use of such an approach could help identify possible unknown end-members in the Thur catchment.

4.7 Conclusion

An improved conceptual understanding of the spatiotemporal water source characteristics in the Thur catchment was made possible through the analysis of environmental tracers from event sampled surface river water, investigated in combination with groundwater and rainwater data, and sampled over the entire catchment over a period of three years. Findings from this study highlight the variability of source waters throughout the Thur catchment, and emphasise the importance of rainwater for groundwater recharge. Although temporal variations in concentrations of stable tracers were shown to be negligible in comparison to the spatial variations, knowledge concerning groundwater travel time was gleaned from looking at the stable water isotope concentrations from four different sources (rain, snow, river and groundwater) on a seasonal basis. Knowing that the travel time requirement for groundwater recharge is approximately three months, this being the case also for subsequent discharge of groundwater to the Thur River, may prove to be important were water quantity and quality management is concerned. Coupled with the spatial knowledge derived from the combination of the cluster analysis and the EMMA, water sources and subsequent mixes of waters sampled in the Thur catchment where characterized, with three dominant water types identified, and mix waters defined by region. Although additional water sources, such as soil or pore water, might also be influential in determining the water types sampled in the Thur catchment. However, this study demonstrated that the sampling of a handful of event sampled sites can provide insight into a catchment's spatiotemporal processes. Event sampled water isotope values offer a relatively inexpensive window into the surface-groundwater characteristics of a mesoscale catchment. The additional knowledge concerning stable tracer characteristics from groundwater and rainfall water aided in the spatiotemporal characterization of the Thur catchment's water types and sources, especially where spatial characteristics are concerned. As the dependence on groundwater as a water source increases, it is anticipated that greater emphasis will be placed on the importance of mapping recharge sources in an attempt to monitor and protect a catchment's water quantity and quality.

5. Concluding Remarks

This dissertation presented relevant insights into various threats and challenges facing sustainable groundwater management across different scales. Major treats to groundwater quality were reviewed globally and consolidated, and pertinent case studies highlighting historic and current anthropogenic contaminants were presented (Chapter 2). Some of the more recent case studies indicated an increasing number of qualitative threats stemming from efforts attempting to increase groundwater quantity. This speaks to a potentially larger issue concerning groundwater availability. However, the “hidden” nature of groundwater makes it difficult to monitor or measure and subsequently to protect, especially in remote or ungauged catchments (common in developing countries). Chapter 3 of this dissertation addressed this topic by employing readily available remotely sensed data and open source tools to estimate the spatiotemporal recharge of the humid mesoscale Thur catchment in Switzerland in a manner potentially transferrable to other catchments. As a final study, and following on from the endeavours in Chapter 3 in keeping methods transferable to other catchments, the potential to characterize the spatiotemporal variability of river and groundwater source components in the Thur catchment, using a handful of river water samples collected during high- and lowflow events, was explored (Chapter 4). The following section briefly recaps the overall findings presented in Chapters 2, 3, and 4, and discusses their limitations and uncertainties. In light of these findings, suggestions concerning future research directions, both in the context of global groundwater and where the Thur catchment is concerned, are presented. Chapter 5 concludes with a personal note on perspectives gained over the duration of this research project concerning the outlook of groundwater management under anthropogenic conditions.

5.1 Synopsis of findings

Chapter 2 framed the contaminant threats of inorganic and organic products to global groundwater quality, both in terms of the products themselves, as well as their interaction with the hydrogeological system. The review demonstrated that, in spite of the extensive research that has been conducted within the various fields relating to contaminant hydrogeology, persistent uncertainties remain where sustainable groundwater quality is concerned. Many of these uncertainties arise as a result of the spatiotemporal variability of the hydrogeological system and the complex manner in which contaminants interact with the environment (e.g. chlorinated organic compounds in karstic systems and long-term mining impacts investigated in Sections 2.6.2 and 2.6.3). Additional uncertainties and subsequent threats to groundwater quality arise due to a lack of available data concerning the application and consumption of contaminating products, as well as our all too often myopic evaluation of groundwater in terms of its prospects as a sustainable and renewable resource.

In light of the spatiotemporal variability of hydrogeological processes intrinsic to most groundwater sources, in addition to the lack of ground-based data availability common in many regions, determining groundwater recharge at a scale applicable to water resource management can present a major challenge. Chapter 3 demonstrated the effectiveness of using readily available RS evapotranspiration data and open source tools in estimating the spatiotemporal variability of groundwater recharge of a mesoscale catchment. Using a parsimonious water balance approach, the gridded water balance components used to estimate recharge resulted in a good closure of the Thur catchment's long-term water balance, despite missing water balance terms such as soil moisture conditions, snow cover and snowmelt conditions, and detailed groundwater abstraction rates. Estimated recharge rates were in line with values from other recharge studies conducted in the Thur catchment. Furthermore, the results from Chapter 3 were able to highlight the impact of temporal variabilities in the water balance components, such as the negative effect of successive drought years, and the buffering effect of exceptionally wet years, on groundwater recharge in the Thur catchment. Spatial maps of groundwater recharge from Chapter 3 indicated a greater recharge potential in association with the high elevation reaches of the Thur catchment (in line with elevated precipitation values in this region). However, due to limited soil depths in these high elevation pre-alpine areas, associated with steep and erosive slopes, effective storage of groundwater is likely very limited, and any infiltrated water would rapidly travel further downstream within the shallow sub-surface of valley bottoms. Concerning corrections to the evapotranspiration product in Chapter 3, although resultant mean values were in line with expected values, the use of a single ground-based site to correct the MODIS evapotranspiration product, although exceedingly valuable, might be inadequate where a mesoscale catchment with a high degree of topographic variation is concerned. Furthermore, as no interpixel exchange was considered, the gridded discharge components as used in Chapter 3 could be carrying groundwater values recharged under historical conditions, potentially leading to temporally incorrect spatiotemporal recharge estimates.

Having a handful of water samples further improved the understanding of processes driving the spatiotemporal variance observed in Chapter 3. Findings in Chapter 4 described three (3) major water source regions within Thur catchment. An almost equal mixture of rainwater and groundwater was found to be the source component of the surface and groundwater sites associated with the Cluster 3 region located in the low elevation (< 480 m asl.) reaches of the Thur catchment: an area associated with one of the largest groundwater systems in Switzerland. Groundwater signatures were found to be a predominant source component in water samples associated with the Cluster 2 located in the middle elevation reaches of the Thur catchment (680 – 480 m asl.). Furthermore, the groundwater source associated with Cluster 2 was also shown to be a dominant factor in many of the downstream groundwater and surface water mixes. While water associated with Cluster 1, sampled from high elevation regions (> 680 m asl.) of the Thur catchment was shown to be composed predominantly of surface runoff with contributions from heavy rainfall events.

Overall, this research project analysed and compiled information concerning anthropogenic threats to groundwater quality at the global scale. At the mesoscale, the effectiveness of readily available data sets and open source tools in estimating groundwater recharge in the Thur catchment was demonstrated. While the analysis of environmental tracers, analysed from a handful of sites sampled along the length of the Thur River, refined the characterization of the surface-groundwater dynamics of the Thur catchment.

5.2 Future studies

In light of persistent uncertainties concerning the application and consumption of known and emerging contaminants, a global need for early warning systems, capable of anticipating risks associated with compounds, along with a centralized and easily accessible information system concerning product distribution, composition, and intended use, was identified in Chapter 2.

In addition, the undervaluation of groundwater as a sustainable resource, whether because of political indifference, social stigma, or disregard for ecosystem services, was found to be a persistent issue where sustainable groundwater governance is concerned. Chapter 2 proposed improved collaboration and understanding between the different groundwater-dependent sectors and bodies of groundwater governance, as a means of facilitating a more holistic approach to groundwater management. However, reality is one of system-complexity, and perhaps as a follow up to the literature review presented in Chapter 2, a good starting point would be the consolidation of tested and proven methods. This could be in the form of a literature review, or perhaps a public database or website, but it should include a list of existing databases and repositories (or lack thereof) relating to product application and historic contaminant occurrence, along with a couple of exemplary case studies addressing issues concerning adaptive catchment-wide groundwater management strategies and effective communication of the inherent value of groundwater to stakeholders.

In order for the spatiotemporal recharge estimate method from the Thur catchment to be useful to water managers as a first step in the assessment of local and regional water availabilities, experimental tests in other mesoscaled catchments using the same or similar set of gridded water balance components and tools, are essential. These test cases should include catchments located within both similar and very different climatic and topographic conditions as those found in the Thur catchment, in order to test for spatial variability in the gridded water balance components. Further studies could help evaluate the relative value of additional water balance components, such as soil moisture or snow accumulation components. The incorporation of additional variables into the water budget calculation described in Chapter 3 (Eq. 7), could reduce some of the uncertainties associated with the recharge estimate. Although Chapter 3 demonstrated that the approach of using satellite image products in conjunction with ground-based data resulted in realistic groundwater recharge estimates in the Thur catchment, it also emphasised the importance of continued ground-based monitoring. For example, although evapotranspiration data was readily available, a correction with ground-based data was necessary in order for MODIS values to be in agreement with expected values from the same or similar regions. Furthermore, information concerning volumes of water discharged, essential in closing the water balance, was taken from operational gauging stations located in the Thur catchment.

In Chapter 4, three regions dominated by different water sources were identified in the Thur catchment. The region associated with the Cluster 2-type water is located in the middle elevation region of the Thur catchment and downstream of the high recharge potential areas mapped in Chapter 3. With little or no sub-surface storage associated with the high elevation reaches, it could be reasoned that the middle elevation region of the Thur catchment would be the primary recipient of the available recharge water mapped in Chapter 3. Building on Chapter 4, an expansion to the classical EMMA, using an observation Bayesian mixing model, could identify potential residual end-members and help establish surface-groundwater exchange in more detail, and perhaps even provide information concerning groundwater flow paths. A complementary approach could be the use of a physically based model. Establishing lateral and vertical interpixel transfer of groundwater with the aid of a physically based model, could provide clearer information concerning groundwater flow paths in the Thur catchment; potentially providing a clearer understanding of the occurrence of Cluster 2 type water sources in the Cluster 3 region. In addition, the inclusion of interpixel coupling could address issues concerning surface-groundwater lag-times between estimated recharge and measured discharge values.

Findings from Chapter 4 showed that even if monitoring sites are spatially sparse, it was the temporal consistency of ground-based measurements which was important in characterizing surface-groundwater dynamics. In order to improve on this, a few fixed auto samplers, installed to sample Thur River water (with an event targeted sampling interval) at locations representative of the three water types identified in Chapter 4, would provide further insight concerning water sources, event fluxes, and water distribution in the Thur catchment. In addition to their conservative tracer content (δ^2H and $\delta^{18}O$), these water samples could also be analysed for their contaminant content (e.g. agricultural content such as nitrate or phosphate to account for the higher altitude regions, and emerging contaminants potentially associated with the more urbanized lower elevation region of the Thur catchment). When coupled with groundwater quantity components, either via a physical model or through the simple use of spatial and temporal maps, a more holistic view concerning the contaminant sources, pathways, and potential threats to the groundwater quality and quantity in the Thur catchment can be established.

5.3 Personal perspectives

Considering the extent to which groundwater is utilized both as a source of drinking water as well as in agricultural and industrial related processes, coupled with the increasing demand for freshwater as the global population continues to grow, it is vital that we start to view groundwater as a valuable resource. Furthermore, if groundwater is adequately monitored, protected, and recharged it has the potential to be an infinitely renewable resource, both in terms of its quality and its quantity. In a world where data is becoming increasingly easy to access, perhaps it is time to start effectively addressing the issues concerning data consolidation and exchange in a manner which will address issues concerning the consumption and utilization of groundwater, as well as the sale and application of potential contaminants. This, along with remotely sensed data, capable of monitoring globally changing hydrological processes and land use conditions, could help establish early warning systems concerning threats to both groundwater quality and quantity.

To date, a large number of hydrogeological studies have been conducted within the Thur catchment, covering a range of topics including the investigation of natural hydrogeological processes, water management, and societal perceptions concerning water management practices. Moreover, due to both established and progressive management strategies, extensive and long-term surface and groundwater quality and quantity data exists for the Thur catchment. Additionally, ongoing restoration and rewilding efforts of the Thur River make it an exemplary study site concerning questions with regard to groundwater recharge. In light of the historic and modern day anthropogenic issues threatening global groundwater resources, the Thur catchment has the potential to be a study site capable of providing examples and solutions, both innovative and applicable. Whilst it is important that research is central in addressing resource requirements where groundwater is concerned, it is through the transdisciplinary and transboundary bridging, from scientific findings and innovations to transformative applications and behaviour in management and stakeholders, that groundwater can become a truly sustainable resource.

References

Abbaspour, K.C., Yang, J., Maximov, I., Siber, R., Bogner, K., Mieleitner, J., Zobrist, J., Srinivasan, R., 2007. Modelling hydrology and water quality in the pre-alpine/alpine Thur watershed using SWAT. J. Hydrol. 333, 413–430. https://doi.org/10.1016/j.jhydrol.2006.09.014

Adeyewa, Z.D., Nakamura, K., 2003. Validation of TRMM Radar Rainfall Data over Major Climatic Regions in Africa. J. Appl. Meteorol. 42, 331–347. https://doi.org/10.1175/1520-0450(2003)042<0331:VOTRRD>2.0.CO;2

Aeschbach-Hertig, W., Gleeson, T., 2012. Regional strategies for the accelerating global problem of groundwater depletion. Nat. Geosci. 5, 853–861. https://doi.org/10.1038/ngeo1617

Al-fares, W., Bakalowicz, M., Guérin, R., Dukhan, M., 2002. Analysis of the karst aquifer structure of the Lamalou area (Hérault, France) with ground penetrating radar. J. Appl. Geophys. 51, 97–106.

Alley, W.M., Healy, R.W., LaBaugh, J.W., Reilly, T.E., 2002. Flow and Storage in Groundwater Systems. Science (80-.). 296, 1985–1990. https://doi.org/10.1126/science.1067123

Anderson, M.C., Kustas, W.P., Norman, J.M., 2007. Upscaling Flux Observations from Local to Continental Scales Using Thermal Remote Sensing. Agron. J. 99, 240–254. https://doi.org/10.2134/agronj2005.0096S

Anderson, M.C., Kustas, W.P., Norman, J.M., Hain, C.R., Mecikalski, J.R., Schultz, L., González-Dugo, M.P., Cammalleri, C., D’Urso, G., Pimstein, A., Gao, F., 2011. Mapping daily evapotranspiration at field to continental scales using geostationary and polar orbiting satellite imagery. Hydrol. Earth Syst. Sci. 15, 223–239. https://doi.org/10.5194/hess-15-223-2011

Anderson, M.G., Burt, T.P., Speight, J.G., 1978. The role of topography in controlling throughflow generation. Earth Surf. Process. 3, 187–195. https://doi.org/10.1002/esp.3290030402

Andreo, B., Goldscheider, N., Vadillo, I., Vías, J.M., Neukum, C., Sinreich, M., Jiménez, P., Brechenmacher, J., Carrasco, F., Hötzl, H., 2006. Karst groundwater protection: First application of a Pan-European Approach to vulnerability, hazard and risk mapping in the Sierra de Líbar (Southern Spain). Sci. Total Environ. 357, 54–73.

Antrop, M., 2004. Landscape change and the urbanization process in Europe. Landsc. Urban Plan. 67, 9–26. https://doi.org/10.1016/S0169-2046(03)00026-4

Appleyard, S., 1995. The Impact Of Urban Development On Recharge And Groundwater Quality In A Coastal Aquifer Near Perth, Western Australia. Hydrogeol. J. https://doi.org/10.1007/s100400050072

Arias-Estévez, M., López-Periago, E., Martínez-Carballo, E., Simal-Gándara, J., Mejuto, J.C., García-Río, L., 2008. The mobility and degradation of pesticides in soils and the pollution of groundwater resources. Agric. Ecosyst. Environ. 123, 247–260. https://doi.org/10.1016/j.agee.2007.07.011

Armanios, D.E., Fisher, J.B., 2014. Measuring water availability with limited ground data: Assessing the feasibility of an entirely remote-sensing-based hydrologic budget of the Rufiji Basin, Tanzania, using TRMM, GRACE, MODIS, SRB, and AIRS. Hydrol. Process. 28, 853–867. https://doi.org/10.1002/hyp.9611

Arnoux, M., Halloran, L.J.S., Berdat, E., Hunkeler, D., 2020. Characterizing seasonal groundwater storage in alpine catchments using time-lapse gravimetry, water stable isotopes and water balance methods. Hydrol. Process. 34, 4319–4333. https://doi.org/10.1002/hyp.13884

Ashton, P.J., 2010. The demise of the Nile crocodile (Crocodylus niloticus) as a keystone species for aquatic ecosystem conservation in South Africa: The case of the Olifants River. Aquat. Conserv. Mar. Freshw. Ecosyst. 20, 489–493.

https://doi.org/10.1002/aqc.1132
Baba, A., Ayyildiz, O., 2006. Urban Groundwater Pollution in Turkey. A national Review of Urban Groundwater Quality Issues. Urban Groundw. Manag. Sustain. 93–110. https://doi.org/10.1007/1-4020-5175-1_7
BAFU et. al., 2020. Klimawandel in der Schweiz. Idikatoren zu Ursachen, Auswirkungen, Massnahmen. Bern.
Baillieux, A., Moeck, C., Perrochet, P., Hunkeler, D., 2015. Assessing groundwater quality trends in pumping wells using spatially varying transfer functions. Hydrogeol. J. 23, 1449–1463. https://doi.org/10.1007/s10040-015-1279-5
Baker, R.S., Nielsen, S.G., Heron, G., Ploug, N., 2016. How effective is thermal remediation of DNAPL source zones in reducing groundwater concentrations? Groundw. Monit. Remediat. 36, 38–53.
Baldocchi, D.D., 2003. Assessing the eddy covariance technique for evaluating carbon dioxide exchange rates of ecosystems: Past, present and future. Glob. Chang. Biol. 9, 479–492. https://doi.org/10.1046/j.1365-2486.2003.00629.x
Ballesteros, D., Malard, A., Jeannin, P.-Y., Jiménez-Sánchez, M., García-Sansegundo, J., Meléndez-Asensio, M., Sendra, G., 2015. KARSYS hydrogeological 3D modeling of alpine karst aquifers developed in geologically complex areas: Picos de Europa National Park (Spain). Environ. Earth Sci. 74, 7699–7714. https://doi.org/10.1007/s12665-015-4712-0
Banaszkiewicz, T., 2010. Evolution of Pesticide Use, in: Skibniewska, K.A. (Ed.), Contemporary Problems of Management and Environmental Protection V. Influence of the Pesticide Dump on the Environment. Department of Land Reclamation and Environmental Management, University of Warmia and Mazury, pp. 7–18.
Banzhaf, S., Nödler, K., Licha, T., Krein, A., Scheytt, T., 2012. Redox-sensitivity and mobility of selected pharmaceutical compounds in a low flow column experiment. Sci. Total Environ. 438, 113–121. https://doi.org/10.1016/j.scitotenv.2012.08.041
Baran, N., Lepiller, M., Mouvet, C., 2008. Agricultural diffuse pollution in a chalk aquifer (Trois Fontaines, France): Influence of pesticide properties and hydrodynamic constraints. J. Hydrol. 358, 56–69. https://doi.org/10.1016/j.jhydrol.2008.05.031
Barlow, J.R.B., Kingsbury, J.A., Coupe, R.H., 2012. Changes in Shallow Groundwater Quality Beneath Recently Urbanized Areas in the Memphis, Tennessee Area. J. Am. Water Resour. Assoc. 48, 336–354. https://doi.org/10.1111/j.1752-1688.2011.00616.x
Barnes, K.K., Kolpin, D.W., Furlong, E.T., Meyer, M.T., Zaugg, S.D., Barber, L.B., 2008. A national reconnaissance for pharmaceuticals and other organic wastewater contaminants in the United States - II) Untreated drinking water sources. Sci. Total Environ. 402, 201–216. https://doi.org/10.1016/j.scitotenv.2008.02.021
Barnwal, R.P., Bharti, S., Misra, S., Obaidat, M.S., 2017. UCGNet: wireless sensor network-based active aquifer contamination monitoring and control system for underground coal gasification. Int. J. Commun. Syst. 30, 1–10. https://doi.org/10.1002/dac.2852
Barrett, M.H., Hiscock, K.M., Pedley, S., Lerner, D.N., Tellam, J.H., French, M.J., 1999. Marker species for identifying urban groundwater recharge sources: A review and case study in Nottingham, UK. Water Res. 33, 3083–3097. https://doi.org/10.1016/S0043-1354(99)00021-4
Barron, O. V., Barr, A.D., Donn, M.J., 2013. Effect of urbanisation on the water balance of a catchment with shallow groundwater. J. Hydrol. 485, 162–176. https://doi.org/10.1016/j.jhydrol.2012.04.027
Bartelt-Hunt, S., Snow, D.D., Damon-Powell, T., Miesbach, D., 2011. Occurrence of steroid hormones and antibiotics in shallow groundwater impacted by livestock waste control facilities. J. Contam. Hydrol. 123, 94–103. https://doi.org/10.1016/j.jconhyd.2010.12.010
Barthold, F.K., Tyralla, C., Schneider, K., Vaché, K.B., Frede, H.-G., Breuer, L., 2011. How many tracers do we need for end member mixing analysis (EMMA)? A sensitivity analysis. Water Resour. Res. 47, 1–14. https://doi.org/10.1029/2011WR010604
Bastiaanssen, W.G.M., Pelgrum, H., Wang, J., Ma, Y., Moreno, J.F., Roerink, G.J., Van Der Wal, T., 1998. A remote sensing surface energy balance algorithm for land (SEBAL). 2.

Validation. J. Hydrol. 212–213, 213–229. https://doi.org/10.1016/S0022-1694(98)00254-6
Batt, A.L., Snow, D.D., Aga, D.S., 2006. Occurrence of sulfonamide antimicrobials in private water wells in Washington County, Idaho, USA. Chemosphere 64, 1963–1971. https://doi.org/10.1016/j.chemosphere.2006.01.029
Baumann, M., 2009. Ein neues Grundwassermodell für das Thurtal (Mitteilungen der Thurgauischen Naturforschenden Gesellschaft 63). Frauenfeld.
Bauser, G., Franssen, H.J.H., Kaiser, H.P., Kuhlmann, U., Stauffer, F., Kinzelbach, W., 2010. Real-time management of an Urban groundwater well field threatened by pollution. Environ. Sci. Technol. 44, 6802–6807. https://doi.org/10.1021/es100648j
Bay, S., Jones, B.H., Schiff, K., Washburn, L., 2003. Water quality impacts of stormwater discharges to Santa Monica Bay. Mar. Environ. Res. 56, 205–223. https://doi.org/10.1016/S0141-1136(02)00331-8
Becker, A., Nemec, J., 1987. Macroscale hydrologic models in support to climate research. Influ. Clim. Chang. Clim. Var. Hydrol. Regime Water Resour. 431–446.
Becker, M.W., 2006. Potential for Satellite Remote Sensing of Ground Water. Ground Water 44, 306–318. https://doi.org/10.1111/j.1745-6584.2005.00123.x
Begert, M., Seiz, G., Foppa, N., Schlegel, T., Appenzeller, C., Müller, G., 2007. Die Überführung der klimatologischen Referenzstationen der Schweiz in das Swiss National Basic Climatological Network (Swiss NBCN). Arbeitsbericht MeteoSchweiz 43.
Benettin, P., Van Der Velde, Y., Van Der Zee, S.E.A.T.M., Rinaldo, A., Botter, G., 2013. Chloride circulation in a lowland catchment and the formulation of transport by travel time distributions. Water Resour. Res. https://doi.org/10.1002/wrcr.20309
Berghuijs, W.R., Hartmann, A., Woods, R.A., 2016. Streamflow sensitivity to water storage changes across Europe. Geophys. Res. Lett. 43, 1980–1987. https://doi.org/10.1002/2016GL067927
Berghuijs, W.R., Kirchner, J.W., 2017. The relationship between contrasting ages of groundwater and streamflow. Geophys. Res. Lett. 44, 8925–8935. https://doi.org/10.1002/2017GL074962
Beven, K., 2001. On hypothesis testing in hydrology. Hydrol. Process. 15, 1655–1657. https://doi.org/10.1002/hyp.436
Beven, K., Binley, A., 1992. The future of distributed models: Model calibration and uncertainty prediction. Hydrol. Process. 6, 279–298. https://doi.org/10.1002/hyp.3360060305
Beven, K.J., Kirkby, M.J., 1979a. A physically based, variable contributing area model of basin hydrology / Un modèle à base physique de zone d'appel variable de l'hydrologie du bassin versant. Hydrol. Sci. Bull. 24, 43–69. https://doi.org/10.1080/02626667909491834
Beven, K.J., Kirkby, M.J., 1979b. A physically based, variable contributing area model of basin hydrology / Un modèle à base physique de zone d'appel variable de l'hydrologie du bassin versant. Hydrol. Sci. Bull. 24, 43–69. https://doi.org/10.1080/02626667909491834
Bhanja, S.N., Mukherjee, A., Saha, D., Velicogna, I., Famiglietti, J.S., 2016. Validation of GRACE based groundwater storage anomaly using in-situ groundwater level measurements in India. J. Hydrol. 543, 729–738. https://doi.org/10.1016/j.jhydrol.2016.10.042
Bhaskar, A.S., Beesley, L., Burns, M.J., Fletcher, T.D., Hamel, P., Oldham, C.E., Roy, A.H., 2016. Will it rise or will it fall? Managing the complex effects of urbanization on base flow. Freshw. Sci. 35, 293–310. https://doi.org/10.1086/685084
Bhatt, P., Kumar, M.S., Mudliar, S., Chakrabarti, T., 2007. Biodegradation of chlorinated compounds—a review. Crit. Rev. Environ. Sci. Technol. 37, 165–198.
Bhattarai, N., Shaw, S.B., Quackenbush, L.J., Im, J., Niraula, R., 2016. Evaluating five remote sensing based single-source surface energy balance models for estimating daily evapotranspiration in a humid subtropical climate. Int. J. Appl. Earth Obs. Geoinf. 49, 75–86. https://doi.org/10.1016/j.jag.2016.01.010

Biello, D., 2012. Gigaloposes: Urban Land Area May Triple by 2030. Sci. Am.
Bierkens, M.F.P., Wada, Y., 2019. Non-renewable groundwater use and groundwater depletion : a review. Environ. Res. Lett. 14, 63002. https://doi.org/10.1088/1748-9326/ab1a5f
Bjerg, P.L., Rugge, K., Pedersen, J.K., Christensen, T.H., 1995. Distribution of Redox-Sensitive Groundwater Quality Parameters Downgradient of a Landfill (Grindsted, Denmark). Environ. Sci. Technol. 29, 1387–1394. https://doi.org/10.1021/es00005a035
Blanchoud, H., Moreau-Guigon, E., Farrugia, F., Chevreuil, M., Mouchel, J.M., 2007. Contribution by urban and agricultural pesticide uses to water contamination at the scale of the Marne watershed. Sci. Total Environ. 375, 168–179. https://doi.org/10.1016/j.scitotenv.2006.12.009
Blume, T., Zehe, E., Bronstert, A., 2007. Rainfall-runoff response, event-based runoff coefficients and hydrograph separation. Hydrol. Sci. J. 52, 843–862. https://doi.org/10.1623/hysj.52.5.843
Böhlke, J.K., Denver, J.M., 1995. Combined Use of Groundwater Dating, Chemical, and Isotopic Analyses to Resolve the History and Fate of Nitrate Contamination in Two Agricultural Watersheds, Atlantic Coastal Plain, Maryland. Water Resour. Res. 31, 2319–2339. https://doi.org/10.1029/95WR01584
Bonell, M., Gilmour, D.A., 1978. The development of overland flow in a tropical rainforest catchment. J. Hydrol. 39, 365–382. https://doi.org/10.1016/0022-1694(78)90012-4
Bonilla Valverde, J.P., Stefan, C., Palma Nava, A., Bernardo da Silva, E., Pivaral Vivar, H.L., 2018. Inventory of managed aquifer recharge schemes in Latin America and the Caribbean. Sustain. Water Resour. Manag. 4, 163–178. https://doi.org/10.1007/s40899-018-0231-y
Booth, D.B., Roy, A.H., Smith, B., Capps, K., 2016. Global perspectives on the urban stream syndrome. J. Freshw. Sci. 35, 412–420. https://doi.org/10.1086/684940.
Bormann, H., Diekkrüger, B., 2003. Possibilities and limitations of regional hydrological models applied within an environmental change study in Benin (West Africa). Phys. Chem. Earth, Parts A/B/C 28, 1323–1332. https://doi.org/10.1016/j.pce.2003.09.008
Botkin, D.B., Keller, E.A., 2011. Environmental Science: Earth as a Living Planet 8th Ed., Journal of Environment Quality. John Wiley & Sons, Inc. https://doi.org/10.2134/jeq1995.00472425002400050040x
Botter, G., Bertuzzo, E., Rinaldo, A., 2011. Catchment residence and travel time distributions: The master equation. Geophys. Res. Lett. https://doi.org/10.1029/2011GL047666
Bottoni, P., Caroli, S., Caracciolo, A.B., 2010. Pharmaceuticals as priority water contaminants. Toxicol. Environ. Chem. 92, 549–565. https://doi.org/10.1080/02772241003614320
Boxall, A.B.A., Kolpin, D.W., Halling-Sørensen, B., Tolls, J., 2003. Peer Reviewed: Are Veterinary Medicines Causing Environmental Risks? Environ. Sci. Technol. 37, 286A-294A. https://doi.org/10.1021/es032519b
Boxall, B., Fogg, L., Blackwell, P., Kay, P., Pemberton, E.J., Croxford, A., 2002. Review of Veterinary medicines in the environment. Rev. Environ. Contam. Toxicol. 180, 1–91. https://doi.org/10.1007/0-387-21729-0_1
Braune, E., Xu, Y., 2008. Groundwater management issues in Southern Africa - An IWRM perspective. Water SA 34, 699–706.
Brotzge, J.A., Crawford, K.C., 2003. Examination of the surface energy budget: A comparison of eddy correlation and bowen ratio measurement systems. J. Hydrometeorol. 4, 160–178. https://doi.org/10.1175/1525-7541(2003)4<160:EOTSEB>2.0.CO;2
Brown, A.E., Zhang, L., McMahon, T.A., Western, A.W., Vertessy, R.A., 2005. A review of paired catchment studies for determining changes in water yield resulting from alterations in vegetation. J. Hydrol. 310, 28–61. https://doi.org/10.1016/j.jhydrol.2004.12.010
Brunner, P., Hendricks Franssen, H.J., Kgotlhang, L., Bauer-Gottwein, P., Kinzelbach, W.,

2007. How can remote sensing contribute in groundwater modeling? Hydrogeol. J. 15, 5–18. https://doi.org/10.1007/s10040-006-0127-z
Brunner, P., Simmons, C.T., 2012. HydroGeoSphere: A Fully Integrated, Physically Based Hydrological Model. Ground Water. https://doi.org/10.1111/j.1745-6584.2011.00882.x
Bu, Q., Wang, B., Huang, J., Deng, S., Yu, G., 2013. Pharmaceuticals and personal care products in the aquatic environment in China: A review. J. Hazard. Mater. 262, 189–211. https://doi.org/10.1016/j.jhazmat.2013.08.040
Burns, D.A., McDonnell, J.J., Hooper, R.P., Peters, N.E., Freer, J.E., Kendall, C., Beven, K., 2001. Quantifying contributions to storm runoff through end-member mixing analysis and hydrologic measurements at the Panola Mountain Research Watershed (Georgia, USA). Hydrol. Process. 15, 1903–1924. https://doi.org/10.1002/hyp.246
Burri, N.M., Weatherl, R., Moeck, C., Schirmer, M., 2019. A review of threats to groundwater quality in the anthropocene. Sci. Total Environ. 684, 136–154. https://doi.org/10.1016/j.scitotenv.2019.05.236
Capel, P.D., Spexet, A.H., Larson, S.J., 1999. Occurrence and behavior of the herbicide Prometon in the hydrologic system. Environ. Sci. Technol. 33, 674–680. https://doi.org/10.1021/es9807340
Carrera, J., Vázquez-Suñé, E., Castillo, O., Sánchez-Vila, X., 2004. A methodology to compute mixing ratios with uncertain end-members. Water Resour. Res. 40, 1–11. https://doi.org/10.1029/2003WR002263
Carvalho, I.T., Santos, L., 2016. Antibiotics in the aquatic environments: A review of the European scenario. Environ. Int. 94, 736–757. https://doi.org/10.1016/j.envint.2016.06.025
Casty, C., Wanner, H., Luterbacher, J., Esper, J., Böhm, R., 2005. Temperature and precipitation variability in the European Alps since 1500. Int. J. Climatol. 25, 1855–1880. https://doi.org/10.1002/joc.1216
Chalikakis, K., Plagnes, V., Guerin, R., Valois, R., Bosch, F.P., 2011. Contribution of geophysical methods to karst-system exploration: an overview. Hydrogeol. J. 19, 1169.
Chapman, S.W., Parker, B.L., 2005. Plume persistence due to aquitard back diffusion following dense nonaqueous phase liquid source removal or isolation. Water Resour. Res. 41.
Chen, J.L., Wilson, C.R., Tapley, B.D., Scanlon, B., Güntner, A., 2016. Long-term groundwater storage change in Victoria, Australia from satellite gravity and in situ observations. Glob. Planet. Change 139, 56–65. https://doi.org/10.1016/j.gloplacha.2016.01.002
Chittoor Viswanathan, V., Jiang, Y., Berg, M., Hunkeler, D., Schirmer, M., 2016. An integrated spatial snap-shot monitoring method for identifying seasonal changes and spatial changes in surface water quality. J. Hydrol. 539, 567–576. https://doi.org/10.1016/j.jhydrol.2016.05.017
Christoffels, E., Brunsch, A., Wunderlich-Pfeiffer, J., Mertens, F.M., 2016. Monitoring micropollutants in the Swist river basin. Water Sci. Technol. 74, 2280–2296. https://doi.org/10.2166/wst.2016.392
Christophersen, N., 1990. Modeling Streamwater Chemistry as a Mixture of Soil Water End-Members - A Step Towards Second Generation Acidification Models 1694. https://doi.org/10.1016/0022-1694(90)90130-P
Clark, I.D., Fritz, P., 1997. Environmental Isotopes in Hydrogeology. CRC Press, Taylor & Francis Group, London, New York.
Clements, T., Denolle, M.A., 2018. Tracking Groundwater Levels Using the Ambient Seismic Field. Geophys. Res. Lett. 45, 6459–6465. https://doi.org/10.1029/2018GL077706
Cleugh, H.A., Leuning, R., Mu, Q., Running, S.W., 2007. Regional evaporation estimates from flux tower and MODIS satellite data. Remote Sens. Environ. 106, 285–304. https://doi.org/10.1016/j.rse.2006.07.007
Clow, D.W., Schrott, L., Webb, R., Campbell, D.H., Torizzo, A., Dornblaser, M., 2003. Ground Water Occurrence and Contributions to Streamflow in an Alpine Catchment, Colorado Front Range. Ground Water 41, 937–950. https://doi.org/10.1111/j.1745-

6584.2003.tb02436.x
Conant, J.B., Cherry, J.A., Gillham, R.W., 2004. A PCE groundwater plume discharging to a river: influence of the streambed and near-river zone on contaminant distributions. J. Contam. Hydrol. 73, 249–279.
Condon, L.E., Maxwell, R.M., 2019. Simulating the sensitivity of evapotranspiration and streamflow to large-scale groundwater depletion. Sci. Adv. 5. https://doi.org/10.1126/sciadv.aav4574
Conrad, O., Bechtel, B., Bock, M., Dietrich, H., Fischer, E., Gerlitz, L., Wehberg, J., Wichmann, V., Böhner, J., 2015. System for Automated Geoscientific Analyses (SAGA) v. 2.1.4. Geosci. Model Dev. 8, 1991–2007. https://doi.org/10.5194/gmd-8-1991-2015
Cook, P., 2020. Introduction to istopes and environmental tracers as incicators of groundwater flow, The Groundwater Project. Ontario, Canada.
Cook, P.G., Dogramaci, S., 2019. Estimating Recharge From Recirculated Groundwater With Dissolved Gases: An End-Member Mixing Analysis. Water Resour. Res. 55, 5468–5486. https://doi.org/10.1029/2019WR025012
Coplen, T.B., Herczeg, A.L., Barnes, C., 2000. Isotope Engineering—Using Stable Isotopes of the Water Molecule to Solve Practical Problems, in: Cook, P.G., Herczeg, A.L. (Eds.), Environmental Tracers in Subsurface Hydrology. Springer US, Boston, MA, pp. 79–110. https://doi.org/10.1007/978-1-4615-4557-6_3
Coxon, G., Freer, J., Westerberg, I.K., Wagener, T., Woods, R., Smith, P.J., 2015. A novel framework for discharge uncertainty quantification applied to 500 UK gauging stations. Water Resour. Res. 51, 5531–5546. https://doi.org/10.1002/2014WR016532
Craig, H., 1961. Isotopic variations in meteoric waters. Science (80-.). 133, 1702–1703. https://doi.org/10.1126/science.133.3465.1702
Creutzfeldt, B., Troch, P.A., Güntner, A., Ferré, T.P.A., Graeff, T., Merz, B., 2014. Storage-discharge relationships at different catchment scales based on local high-precision gravimetry. Hydrol. Process. 28, 1465–1475. https://doi.org/10.1002/hyp.9689
Crosbie, R.S., Binning, P., Kalma, J.D., 2005. A time series approach to inferring groundwater recharge using the water table fluctuation method. Water Resour. Res. 41, 1–9. https://doi.org/10.1029/2004WR003077
Crosbie, R.S., Davies, P., Harrington, N., Lamontagne, S., 2015. Ground truthing groundwater-recharge estimates derived from remotely sensed evapotranspiration: a case in South Australia. Hydrogeol. J. 23, 335–350. https://doi.org/10.1007/s10040-014-1200-7
Cui, Y., Chen, X., Gao, J., Yan, B., Tang, G., Hong, Y., 2018. Global water cycle and remote sensing big data: overview, challenge, and opportunities. Big Earth Data 2, 282–297. https://doi.org/10.1080/20964471.2018.1548052
Custodio, E., 2005. Intensive Use of Groundwater and Sustainability. Ground Water 43. https://doi.org/10.1201/9781439833629.ch11
Dages, C., Voltz, M., Bsaibes, A., Prévot, L., Huttel, O., Louchart, X., Garnier, F., Negro, S., 2009. Estimating the role of a ditch network in groundwater recharge in a Mediterranean catchment using a water balance approach. J. Hydrol. 375, 498–512. https://doi.org/10.1016/j.jhydrol.2009.07.002
Dal Molin, M., Schirmer, M., Zappa, M., Fenicia, F., 2020. Understanding dominant controls on streamflow spatial variability to set up a semi-distributed hydrological model: The case study of the Thur catchment. Hydrol. Earth Syst. Sci. 24, 1319–1345. https://doi.org/10.5194/hess-24-1319-2020
Datry, T., Bonada, N., Boulton, A., 2017. Intermittent Rivers and Ephemeral Streams: Ecology and Management, Intermittent Rivers and Ephemeral Streams: Ecology and Management.
de Graaf, I.E.M., van Beek, R.L.P.H., Gleeson, T., Moosdorf, N., Schmitz, O., Sutanudjaja, E.H., Bierkens, M.F.P., 2017. A global-scale two-layer transient groundwater model: Development and application to groundwater depletion. Adv. Water Resour. 102, 53–67. https://doi.org/10.1016/j.advwatres.2017.01.011
De Jong, R., Verbesselt, J., Schaepman, M.E., De Bruin, S., 2011. Detection of breakpoints

in Global NDVI time series. 34th Int. Symp. Remote Sens. Environ. - GEOSS Era Towar. Oper. Environ. Monit.
de Lavenne, A., Andréassian, V., Thirel, G., Ramos, M.H., Perrin, C., 2019. A Regularization Approach to Improve the Sequential Calibration of a Semidistributed Hydrological Model. Water Resour. Res. 55, 8821–8839. https://doi.org/10.1029/2018WR024266
Decrem, M., Spiess, E., Richner, W., Herzog, F., 2007. Impact of Swiss agricultural policies on nitrate leaching from arable land. Agron. Sustain. Dev. 27, 243–253. https://doi.org/10.1051/agro:2007012
Dhakate, R., Singh, V.S., 2008. Heavy metal contamination in groundwater due to mining activities in Sukinda valley, Orissa -A case study. J. Geogr. Reg. Plan. 1, 58–67.
Dhungel, R., Fiedler, F., 2016. Water balance to recharge calculation: Implications for watershed management using systems dynamics approach. Hydrology 3. https://doi.org/10.3390/hydrology3010013
Diamond, M.L., Hodge, E., 2007. Urban contaminant dynamics: from source to effect. Environ. Sci. Technol. 41, 3796–3805. https://doi.org/10.1021/es072542n
Díaz-Cruz, M.S., Barceló, D., 2008. Trace organic chemicals contamination in ground water recharge. Chemosphere 72, 333–342. https://doi.org/10.1016/j.chemosphere.2008.02.031
Dillon, P., 2005. Future management of aquifer recharge. Hydrogeol. J. 13, 313–316. https://doi.org/10.1007/s10040-004-0413-6
Dillon, P., Pavelic, P., Declan, P., Ward, J., Beringen, H., 2009. Managed aquifer recharge: An Introduction.
Döll, P., Fiedler, K., 2008. Global-scale modeling of groundwater recharge. Hydrol. Earth Syst. Sci. 12, 863–885. https://doi.org/10.5194/hess-12-863-2008
Dorigo, W., Wagner, W., Albergel, C., Albrecht, F., Balsamo, G., Brocca, L., Chung, D., Ertl, M., Forkel, M., Gruber, A., Haas, E., Hamer, P., Hirschi, M., Ikonen, J., de Jeu, R., Kidd, R., Lahoz, W., 2016. ESA CCI Soil Moisture for improved Earth system understanding: state-of-the art and future directions. Remote Sens. Environ. Submitt. https://doi.org/10.1016/j.rse.2017.07.001
Doulatyari, B., Betterle, A., Radny, D., Celegon, E.A., Fanton, P., Schirmer, M., Botter, G., 2017. Patterns of streamflow regimes along the river network: The case of the Thur river. Environ. Model. Softw. 93, 42–58. https://doi.org/10.1016/j.envsoft.2017.03.002
Drebenstedt, C., Singhal, R., 2014. Mine Planning and Equipment Selection. https://doi.org/10.1007/978-3-319-02678-7
Dulio, V., van Bavel, B., Brorström-Lundén, E., Harmsen, J., Hollender, J., Schlabach, M., Slobodnik, J., Thomas, K., Koschorreck, J., 2018. Emerging pollutants in the EU: 10 years of NORMAN in support of environmental policies and regulations. Environ. Sci. Eur. 30. https://doi.org/10.1186/s12302-018-0135-3
Duncan, H.P., 2019. Baseflow separation – A practical approach. J. Hydrol. 575, 308–313. https://doi.org/10.1016/j.jhydrol.2019.05.040
Dunne, T., Black, R.D., 1970. Partial areea contributions to storm runff in a small New England watershed. Water Resour. Res. 6, 1296–1311.
Durand, J.F., 2012. The impact of gold mining on the Witwatersrand on the rivers and karst system of Gauteng and North West Province, South Africa. J. African Earth Sci. 68, 24–43. https://doi.org/10.1016/j.jafrearsci.2012.03.013
Durand, J.F., Meeuvis, J., Fourie, M., 2010. The threat of mine effluent to the UNESCO status of the Cradle of Humankind World Heritage Site. J. Transdiscipl. Res. South. Africa 6, 73–92.
Eckhardt, K., 2005. How to construct recursive digital filters for baseflow separation. Hydrol. Process. 19, 507–515. https://doi.org/10.1002/hyp.5675
Edmonds, H.N., Edmond, J.M., 1995. A three-component mixing model for ridge-crest hydrothermal fluids. Earth Planet. Sci. Lett. 134, 53–67. https://doi.org/10.1016/0012-821X(95)00115-S
El-Salam, M.M.A., Abu-Zuid, G.I., 2015. Impact of landfill leachate on the groundwater quality: A case study in Egypt. J. Adv. Res. 6, 579–586.

El Khalil, H., El Hamiani, O., Bitton, G., Ouazzani, N., Boularbah, A., 2008. Heavy metal contamination from mining sites in South Morocco: Monitoring metal content and toxicity of soil runoff and groundwater. Environ. Monit. Assess. 136, 147–160. https://doi.org/10.1007/s10661-007-9671-9

Ellis, P.A., Rivett, M.O., 2007. Assessing the impact of VOC-contaminated groundwater on surface water at the city scale. J. Contam. Hydrol. 91, 107–127.

Elsner, M., Imfeld, G., 2016. Compound-specific isotope analysis (CSIA) of micropollutants in the environment - current developments and future challenges. Curr. Opin. Biotechnol. 41, 60–72. https://doi.org/10.1016/j.copbio.2016.04.014

Enzien, M. V., Picardal, F., Hazen, T.C., Arnold, R.G., Fliermans, C.B., 1994. Reductive dechlorination of trichloroethylene and tetrachloroethylene under aerobic conditions in a sediment column. Appl. Environ. Microbiol. 60, 2200–2204.

EU-Ground Water Directive, 2006. Directive 2006/118/EC of the European parliament and of the council. Off. J. Eur. Union 2006. https://doi.org/2004R0726 - v.7 of 05.06.2013

European Commission, 2008. Groundwater Protection in Europe. The New Groundwater Directive-Consolidating the EU Regulatory Framework. https://doi.org/10.2779/84304

Famiglietti, J.S., 2014. The global groundwater crisis. Nat. Clim. Chang. 4, 945–948. https://doi.org/10.1038/nclimate2425

FAO, 2018. World Fertiliser Trends and Outlook to 2018.

FAO, 2009. Global agriculture towards 2050. High Lev. Expert Forum-How to Feed world 2050 1–4. https://doi.org/http://www.fao.org/fileadmin/templates/wsfs/docs/Issues_papers/HLEF2050_Global_Agriculture.pdf

Faye, S.C., Faye, S., Wohnlich, S., Gaye, C.B., 2004. An assessment of the risk associated with urban development in the Thiaroye area (Senegal). Environ. Geol. 45, 312–322. https://doi.org/10.1007/s00254-003-0887-x

Feldman, D., Schmidt, M., Sohler, C., 2020. Turning Big Data Into Tiny Data: Constant-Size Coresets for k-Means, PCA, and Projective Clustering. SIAM J. Comput. 49, 601–657. https://doi.org/10.1137/18M1209854

Fendeková, M., Fendek, M., 2012. Groundwater drought in the nitra river basin - Identification and classification. J. Hydrol. Hydromechanics 60, 185–193. https://doi.org/10.2478/v10098-012-0016-1

Fenicia, F., Wrede, S., Kavetski, D., Pfister, L., Hoffmann, L., Savenije, H.H.G., Mcdonnell, J.J., 2010. Assessing the impact of mixing assumptions on the estimation of streamwater mean residence time 1741, 1730–1741. https://doi.org/10.1002/hyp.7595

Fennell, D.E., Gossett, J.M., 1998. Modeling the production of and competition for hydrogen in a dechlorinating culture. Environ. Sci. Technol. 32, 2450–2460. https://doi.org/10.1021/es980136l

Fent, K., Weston, A.A., Caminada, D., 2006. Ecotoxicology of human pharmaceuticals. Aquat. Toxicol. 76, 122–159. https://doi.org/10.1016/j.aquatox.2005.09.009

Ferguson, C.R., Sheffield, J., Wood, E.F., Gao, H., 2010. Quantifying uncertainty in a remote sensing-based estimate of evapotranspiration over continental USA. Int. J. Remote Sens. 31, 3821–3865. https://doi.org/10.1080/01431161.2010.483490

Fetter, C.W., Boving, T., Kreamer, D., 2017. Contaminant Hydrogeology, 3rd ed. Waveland Press.

Field, M.S., 2018. Investigating and Remediating Contaminated Karst Aquifers, in: Karst Groundwater Contamination and Public Health. Springer, pp. 101–115.

Fischer, D., Charles, E.G., Baehr, A.L., 2003. Effects of Stormwater Infiltration on Quality of Groundwater Beneath Retention and Detention Basins. J. Environ. Eng. 129, 464–471. https://doi.org/10.1061/(ASCE)0733-9372(2003)129:5(464)

Fishel, F., 1997. Pesticides and the Environment. Agric. Guid. (University Missouri-Columbia).

Ford, D., Williams, P.D., 2013. Karst hydrogeology and geomorphology. John Wiley & Sons.

FQPA, 1996. Food Quality Protection Act of. Congr. Regist. 1489–1538. https://doi.org/10.1002/047126363X.agr085

Franz, K.J., Butcher, P., Ajami, N.K., 2010. Addressing snow model uncertainty for hydrologic prediction. Adv. Water Resour. https://doi.org/10.1016/j.advwatres.2010.05.004
Fredrick, K.C., Becker, M.W., Matott, L.S., Daw, A., Bandilla, K., Flewelling, D.M., 2007. Development of a numerical groundwater flow model using SRTM elevations. Hydrogeol. J. 15, 171–181. https://doi.org/10.1007/s10040-006-0115-3
Freitas, J.G., Rivett, M.O., Roche, R.S., Durrant, M., Walker, C., Tellam, J.H., 2015. Heterogeneous hyporheic zone dechlorination of a TCE groundwater plume discharging to an urban river reach. Sci. Total Environ. 505, 236–252.
Friedler, E., 2001. Water reuse - An integral part of water resources management: Israel as a case study. Water Policy 3, 29–39. https://doi.org/10.1016/S1366-7017(01)00003-4
Fukada, T., Hiscock, K.M., Dennis, P.F., 2004. A dual-isotope approach to the nitrogen hydrochemistry of an urban aquifer. Appl. Geochemistry 19, 709–719. https://doi.org/10.1016/j.apgeochem.2003.11.001
Gabrielli, C.P., Morgenstern, U., Stewart, M.K., McDonnell, J.J., 2018. Contrasting Groundwater and Streamflow Ages at the Maimai Watershed. Water Resour. Res. 54, 3937–3957. https://doi.org/10.1029/2017WR021825
Gallegos, T.J., Varela, B.A., Haines, S.S., Engle, M.A., 2015. Hyraulic fracturing water use varibility in the United States and potential environmental implications. Water Resour. Res. 5839–5845. https://doi.org/10.1002/2015WR017278.Received
García-Galán, M.J., Garrido, T., Fraile, J., Ginebreda, A., Díaz-Cruz, M.S., Barceló, D., 2010. Simultaneous occurrence of nitrates and sulfonamide antibiotics in two ground water bodies of Catalonia (Spain). J. Hydrol. 383, 93–101. https://doi.org/10.1016/j.jhydrol.2009.06.042
Gavrilescu, M., Demnerová, K., Aamand, J., Agathos, S., Fava, F., 2015. Emerging pollutants in the environment: Present and future challenges in biomonitoring, ecological risks and bioremediation. N. Biotechnol. 32, 147–156. https://doi.org/10.1016/j.nbt.2014.01.001
Ghasemizadeh, R., Hellweger, F., Butscher, C., Padilla, I., Vesper, D., Field, M., Alshawabkeh, A., 2012. Review: Groundwater flow and transport modeling of karst aquifers, with particular reference to the North Coast Limestone aquifer system of Puerto Rico. Hydrogeol. J. 20, 1441–1461. https://doi.org/10.1007/s10040-012-0897-4
Gleason, C.J., Durand, M.T., 2020. Remote Sensing of River Discharge: A Review and a Framing for the Discipline. Remote Sens. 12, 1107. https://doi.org/10.3390/rs12071107
Gleason, C.J., Wada, Y., Wang, J., 2018. A Hybrid of Optical Remote Sensing and Hydrological Modeling Improves Water Balance Estimation. J. Adv. Model. Earth Syst. 10, 2–17. https://doi.org/10.1002/2017MS000986
Gning, A.A., Orban, P., Gesels, J., Ngom, F.D., Dassargues, A., Malou, R., Brouyère, S., 2017. Factors controlling the evolution of groundwater dynamics and chemistry in the Senegal River Delta. J. Hydrol. Reg. Stud. 10, 133–144. https://doi.org/10.1016/j.ejrh.2017.01.005
Gonçalves, C.M., Da Silva, J.C.G.E., Alpendurada, M.F., 2007. Evaluation of the pesticide contamination of groundwater sampled over two years from a vulnerable zone in Portugal. J. Agric. Food Chem. 55, 6227–6235. https://doi.org/10.1021/jf063663u
Göppert, N., Goldscheider, N., 2008. Solute and colloid transport in karst conduits under low-and high-flow conditions. Groundwater 46, 61–68.
Gordalla, B.C., Ewers, U., Frimmel, F.H., 2013. Hydraulic fracturing: A toxicological threat for groundwater and drinking-water? Environ. Earth Sci. 70, 3875–3893. https://doi.org/10.1007/s12665-013-2672-9
Graf, T., Therrien, R., 2007. Variable-density groundwater flow and solute transport in irregular 2D fracture networks. Adv. Water Resour. 30, 455–468. https://doi.org/10.1016/j.advwatres.2006.05.003
Green, C.T., Fisher, L.H., Bekins, B.A., 2008. Nitrogen Fluxes through Unsaturated Zones in Five Agricultural Settings across the United States. J. Environ. Qual. 37, 1073. https://doi.org/10.2134/jeq2007.0010

Grimmeisen, F., Zemann, M., Goeppert, N., Goldscheider, N., 2016. Weekly variations of discharge and groundwater quality caused by intermittent water supply in an urbanized karst catchment. J. Hydrol. 537, 157–170. https://doi.org/10.1016/j.jhydrol.2016.03.045
Groffman, P.M., Boulware, N.J., Zipperer, W.C., Pouyat, R. V., Band, L.E., Colosimo, M.F., 2002. Soil nitrogen cycle processes in urban riparian zones. Environ. Sci. Technol. 36, 4547–4552. https://doi.org/10.1021/es020649z
Groffman, P.M., Law, N.L., Belt, K.T., Band, L.E., Fisher, G.T., 2004. Nitrogen fluxes and retention in urban watershed ecosystems. Ecosystems 7, 393–403. https://doi.org/10.1007/s10021-003-0039-x
Guan, H., Simmons, C.T., Love, A.J., 2009. Orographic controls on rain water isotope distribution in the Mount Lofty Ranges of South Australia. J. Hydrol. 374, 255–264. https://doi.org/10.1016/j.jhydrol.2009.06.018
Gurdak, J.J., 2017. Climate-induced pumping. Nat. Geosci. 10, 71–71. https://doi.org/10.1038/ngeo2885
Gurdak, J.J., Hanson, R.T., McMahon, P.B., Bruce, B.W., McCray, J.E., Thyne, G.D., Reedy, R.C., 2007. Climate Variability Controls on Unsaturated Water and Chemical Movement, High Plains Aquifer, USA. Vadose Zo. J. https://doi.org/10.2136/vzj2006.0087
Gurtz, J., Baltensweiler, A., Lang, H., 1999. Spatially distributed hydrotope-based modelling of evapotranspiration and runoff in mountainous basins. Hydrol. Process. 13, 2751–2768. https://doi.org/10.1002/(SICI)1099-1085(19991215)13:17<2751::AID-HYP897>3.0.CO;2-O
Gutierrez, A., Baran, N., 2009. Long-term transfer of diffuse pollution at catchment scale: Respective roles of soil, and the unsaturated and saturated zones (Brévilles, France). J. Hydrol. 369, 381–391. https://doi.org/10.1016/j.jhydrol.2009.02.050
Haase, D., 2009. Effects of urbanisation on the water balance - A long-term trajectory. Environ. Impact Assess. Rev. 29, 211–219. https://doi.org/10.1016/j.eiar.2009.01.002
Hakoun, V., Orban, P., Dassargues, A., Brouyère, S., 2017. Factors controlling spatial and temporal patterns of multiple pesticide compounds in groundwater (Hesbaye chalk aquifer, Belgium). Environ. Pollut. 223, 185–199. https://doi.org/10.1016/j.envpol.2017.01.012
Hall, F.R., 1968. Base-Flow Recessions-A Review. Water Resour. Res. 4, 973–983. https://doi.org/10.1029/WR004i005p00973
Han, D., Currell, M.J., Cao, G., Hall, B., 2017. Alterations to groundwater recharge due to anthropogenic landscape change. J. Hydrol. 554, 545–557. https://doi.org/10.1016/j.jhydrol.2017.09.018
Han, D., Tong, X., Currell, M.J., Cao, G., Jin, M., Tong, C., 2014. Evaluation of the impact of an uncontrolled landfill on surrounding groundwater quality, Zhoukou, China. J. Geochemical Explor. 136, 24–39.
Harmancioglu, N., Ozkul, S., Fistikoglu, O., Geerders, P., 2003. Integrated technologies for environmental monitoring and information production.
Hatch, C.E., Fisher, A.T., Revenaugh, J.S., Constantz, J., Ruehl, C., 2006. Quantifying surface water-groundwater interactions using time series analysis of streambed thermal records: Method development. Water Resour. Res. 42, 1–14. https://doi.org/10.1029/2005WR004787
Hayashi, M., Vogt, T., Mächler, L., Schirmer, M., 2012. Diurnal fluctuations of electrical conductivity in a pre-alpine river: Effects of photosynthesis and groundwater exchange. J. Hydrol. 450–451, 93–104. https://doi.org/10.1016/j.jhydrol.2012.05.020
Healy, R.W., Cook, P.G., 2002. Using groundwater levels to estimate recharge. Hydrogeol. J. 10, 91–109. https://doi.org/10.1007/s10040-001-0178-0
Healy, R.W., Scanlon, B.R., 2010. Estimating Groundwater Recharge. https://doi.org/10.1017/cbo9780511780745
Healy, R.W., Winter, T.C., LaBaugh, J.W., Franke, O.L., 2007. Water budgets: Foundations for effective water- resources and environmental management: U.S. Geological Survey Circular 1308, 90 p. Ars Comb. 95, 65–70.

Hebig, K.H., Groza, L.G., Sabourin, M.J., Scheytt, T.J., Ptacek, C.J., 2017. Transport behavior of the pharmaceutical compounds carbamazepine, sulfamethoxazole, gemfibrozil, ibuprofen, and naproxen, and the lifestyle drug caffeine, in saturated laboratory columns. Sci. Total Environ. 590–591, 708–719. https://doi.org/10.1016/j.scitotenv.2017.03.031
Hellwig, J., Stahl, K., 2018. An assessment of trends and potential future changes in groundwater-baseflow drought based on catchment response times. Hydrol. Earth Syst. Sci. 22, 6209–6224. https://doi.org/10.5194/hess-22-6209-2018
Hellwig, J., Stahl, K., Lange, J., 2017. Patterns in the linkage of water quantity and quality during low-flows. Hydrol. Process. 31, 4195–4205. https://doi.org/10.1002/hyp.11354
Hendricks Franssen, H.J., Kaiser, H.P., Kuhlmann, U., Bauser, G., Stauffer, F., Mller, R., Kinzelbach, W., 2011. Operational real-time modeling with ensemble Kalman filter of variably saturated subsurface flow including stream-aquifer interaction and parameter updating. Water Resour. Res. 47. https://doi.org/10.1029/2010WR009480
Hensen, B., Lange, J., Jackisch, N., Zieger, F., Olsson, O., Kümmerer, K., 2018. Entry of biocides and their transformation products into groundwater via urban stormwater in fi ltration systems. Water Res. 144, 413–423. https://doi.org/10.1016/j.watres.2018.07.046
Henton, P., 1981. The problem of water table rebound after mining activity. Stud. Environ. Sci. 17.
Hering, J.G., Hoehn, E., Klinke, A., Maurer, M., Peter, A., Reichert, P., Robinson, C., Schirmer, K., Schirmer, M., Stamm, C., Wehrli, B., 2012. Moving targets, long-lived infrastructure, and increasing needs for integration and adaptation in water management: An illustration from Switzerland. Environ. Sci. Technol. 46, 112–118. https://doi.org/10.1021/es202189s
Hiemstra, P., Kolpa, R.J., Van Eekhout, J.M.J.M., Van Kessel, T.A.L., Adamse, E.D., Van Paassen, J.A.M., 2003. “Natural” recharge of groundwater: Bank infiltration in the Netherlands. J. Water Supply Res. Technol. - AQUA 52, 37–47.
Hillebrand, O., Nödler, K., Geyer, T., Licha, T., 2014. Investigating the dynamics of two herbicides at a karst spring in Germany: Consequences for sustainable raw water management. Sci. Total Environ. 482, 193–200.
Hirschi, M., Michel, D., Lehner, I., Seneviratne, S.I., 2017. A site-level comparison of lysimeter and eddy covariance flux measurements of evapotranspiration. Hydrol. Earth Syst. Sci. 21, 1809–1825. https://doi.org/10.5194/hess-21-1809-2017
Hiscock, K.M., Grischek, T., 2002. Attenuation of groundwater pollution by bank filtration. J. Hydrol. 266, 139–144. https://doi.org/10.1016/S0022-1694(02)00158-0
Hobbs, P., Oelofse, S.H.H., Rascher, J., 2008. Management of Environmental Impacts from Coal Mining in the Upper Olifants River Catchment as a Function of Age and Scale. Int. J. Water Resour. Dev. 24, 417–431. https://doi.org/10.1080/07900620802127366
Hoehn, E., Scholtis, A., 2011. Exchange between a river and groundwater, assessed with hydrochemical data. Hydrol. Earth Syst. Sci. 15, 983–988. https://doi.org/10.5194/hess-15-983-2011
Hoffmann, J., 2002. The future of satellite remote sensing in hydrogeology. J. Hydrogeol. 247–250. https://doi.org/10.1007/s10040-004-0409-2
Hong, S., Hendrickx, J.M.H., Borchers, B., 2009. Up-scaling of SEBAL derived evapotranspiration maps from Landsat (30m) to MODIS (250m) scale. J. Hydrol. 370, 122–138. https://doi.org/10.1016/j.jhydrol.2009.03.002
Hong, Y., Adler, R.F., Hossain, F., Curtis, S., Huffman, G.J., 2007. A first approach to global runoff simulation using satellite rainfall estimation. Water Resour. Res. 43. https://doi.org/10.1029/2006WR005739
Hooper, R.P., 2003. Diagnostic tools for mixing models of stream water chemistry. Water Resour. Res. 39, 1–13. https://doi.org/10.1029/2002WR001528
Hooper, R.P., Christophersen, N., Peters, N.E., 1990. Modelling streamwater chemistry as a mixture of soilwater end-members - An application to the Panola Mountain catchment, Georgia, U.S.A. J. Hydrol. 116, 321–343. https://doi.org/10.1016/0022-1694(90)90131-

G
Horsburgh, J.S., Spackman Jones, A., Stevens, D.K., Tarboton, D.G., Mesner, N.O., 2010. A sensor network for high frequency estimation of water quality constituent fluxes using surrogates. Environ. Model. Softw. 25, 1031–1044. https://doi.org/10.1016/j.envsoft.2009.10.012
Horsburgh, J.S., Tarboton, D.G., Maidment, D.R., Zaslavsky, I., 2011. Components of an environmental observatory information system. Comput. Geosci. 37, 207–218. https://doi.org/10.1016/j.cageo.2010.07.003
Horton, R.E., 1933. The Role of infiltration in the hydrologic cycle. Trans. Am. Geophys. Union 14, 446. https://doi.org/10.1029/TR014i001p00446
Horvat, A.J.M., Babić, S., Pavlović, D.M., Ašperger, D., Pelko, S., Kaštelan-Macan, M., Petrović, M., Mance, A.D., 2012. Analysis, occurrence and fate of anthelmintics and their transformation products in the environment. TrAC - Trends Anal. Chem. 31, 61–84. https://doi.org/10.1016/j.trac.2011.06.023
Hounslow, A.W., 1995. Water quality data: Analysis and interpretation, Water Quality Data: Analysis and Interpretation. Taylor & Francis, London, New York. https://doi.org/10.1201/9780203734117
Howard, K.W.F., 2015. Sustainable cities and the groundwater governance challenge. Environ. Earth Sci. 73, 2543–2554. https://doi.org/10.1007/s12665-014-3370-y
Howard, K.W.F., 2002. Urban Groundwater Issues - an Introduction. Curr. Probl. Hydrogeol. Urban Agglom. Ind. Centres 1–15.
Howard, P.H., Muir, D.C.G., 2013. Identifying new persistent and bioaccumulative organics among chemicals in commerce. III: Byproducts, impurities, and transformation products. Environ. Sci. Technol. 47, 5259–5266. https://doi.org/10.1021/es4004075
Hrachowitz, M., Savenije, H., Bogaard, T.A., Tetzlaff, D., Soulsby, C., 2013a. What can flux tracking teach us about water age distribution patterns and their temporal dynamics? Hydrol. Earth Syst. Sci. 17, 533–564. https://doi.org/10.5194/hess-17-533-2013
Hrachowitz, M., Savenije, H.H.G., Blöschl, G., McDonnell, J.J., Sivapalan, M., Pomeroy, J.W., Arheimer, B., Blume, T., Clark, M.P., Ehret, U., Fenicia, F., Freer, J.E., Gelfan, A., Gupta, H.V., Hughes, D.A., Hut, R.W., Montanari, A., Pande, S., Tetzlaff, D., Troch, P.A., Uhlenbrook, S., Wagener, T., Winsemius, H.C., Woods, R.A., Zehe, E., Cudennec, C., 2013b. A decade of Predictions in Ungauged Basins (PUB)—a review. Hydrol. Sci. J. 58, 1198–1255. https://doi.org/10.1080/02626667.2013.803183
Huffman, G.J., Bolvin, D.T., Nelkin, E.J., Wolff, D.B., Adler, R.F., Gu, G., Hong, Y., Bowman, K.P., Stocker, E.F., 2007. The TRMM Multisatellite Precipitation Analysis (TMPA): Quasi-Global, Multiyear, Combined-Sensor Precipitation Estimates at Fine Scales. J. Hydrometeorol. 8, 38–55. https://doi.org/10.1175/JHM560.1
Hulsman, P., Savenije, H.H.G., Hrachowitz, M., 2020. Learning from satellite observations : increased understanding of catchment processes through stepwise model improvement.
Hunkeler, D., Aravena, R., Butler, B.J., 1999. Monitoring Microbial Dechlorination of Tetrachloroethene (PCE) in Groundwater Using Compound-Specific Stable Carbon Isotope Ratios: Microcosm and Field Studies. Environ. Sci. Technol. 33, 2733–2738. https://doi.org/10.1021/es981282u
Hunkeler, D., Chollet, N., Pittet, X., Aravena, R., Cherry, J.A., Parker, B.L., 2004. Effect of source variability and transport processes on carbon isotope ratios of TCE and PCE in two sandy aquifers. J. Contam. Hydrol. 74, 265–282.
IAEAA, 2012. Monitoring isotopes in rivers : Creation of the global network of isotopes in rivers (GNIR) Results of a. Vienna.
ICOLD, 1996. Guide To Tailings Dams and Impoundments. Paris, France,.
Immerzeel, W.W., Lutz, A.F., Andrade, M., Bahl, A., Biemans, H., Bolch, T., Hyde, S., Brumby, S., Davies, B.J., Elmore, A.C., Emmer, A., Feng, M., Fernández, A., Haritashya, U., Kargel, J.S., Koppes, M., Kraaijenbrink, P.D.A., Kulkarni, A. V., Mayewski, P.A., Nepal, S., Pacheco, P., Painter, T.H., Pellicciotti, F., Rajaram, H., Rupper, S., Sinisalo, A., Shrestha, A.B., Viviroli, D., Wada, Y., Xiao, C., Yao, T., Baillie,

J.E.M., 2020. Importance and vulnerability of the world's water towers. Nature 577, 364–369. https://doi.org/10.1038/s41586-019-1822-y
Institute of Hydrology, 1980. Low Flow Studies Report. Crowmarsh Gifford Wallingford, Oxon.
Irmak, A., G., R., Kjaersgaard, J., Huntington, J., Kamble, B., Trezza, R., Ratcliffe, I., 2012. Operational Remote Sensing of ET and Challenges, in: Irmak, A. (Ed.), Evapotranspiration - Remote Sensing and Modeling. InTech, p. 13. https://doi.org/10.5772/25174
ISO, 2009. Water quality - Determination of dissolved anions by liquid chromatography of ions - Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate. 10304–1:2009.
ISO, 1999. Water quality - Determination of dissolved Li^+, Na^+, NH_4^+, K^+, Mn^{2+}, Ca^{2+}, Mg^{2+}, Sr^{2+} and Ba^{2+} using ion chromatography - Method for water and waste water. 14911:1999.
Jasechko, S., 2019. Global Isotope Hydrogeology—Review. Rev. Geophys. 57, 835–965. https://doi.org/10.1029/2018RG000627
Jasechko, S., Birks, S.J., Gleeson, T., Wada, Y., Fawcett, P.J., Sharp, Z.D., McDonnell, J.J., Welker, J.M., 2014. The pronounced seasonality of global groundwater recharge. Water Resour. Res. 50, 8845–8867. https://doi.org/10.1002/2014WR015809
Jasechko, S., Kirchner, J.W., Welker, J.M., McDonnell, J.J., 2016. Substantial proportion of global streamflow less than three months old. Nat. Geosci. 9, 126–129. https://doi.org/10.1038/ngeo2636
Jekel, M., Dott, W., Bergmann, A., Dünnbier, U., Gnirß, R., Haist-Gulde, B., Hamscher, G., Letzel, M., Licha, T., Lyko, S., Miehe, U., Sacher, F., Scheurer, M., Schmidt, C.K., Reemtsma, T., Ruhl, A.S., 2015. Selection of organic process and source indicator substances for the anthropogenically influenced water cycle. Chemosphere 125, 155–167. https://doi.org/10.1016/j.chemosphere.2014.12.025
Jones, M., 2010. The Groundwater Hydrology of the Okavango Basin, FAO (2010) Internal Report. OKACOM 1–83.
K'oreje, K.O., Vergeynst, L., Ombaka, D., De Wispelaere, P., Okoth, M., Van Langenhove, H., Demeestere, K., 2016. Occurrence patterns of pharmaceutical residues in wastewater, surface water and groundwater of Nairobi and Kisumu city, Kenya. Chemosphere 149, 238–244. https://doi.org/10.1016/j.chemosphere.2016.01.095
Kaczala, F., Blum, S.E., 2016. The Occurrence of Veterunary Pharmaceuticals in the Environment: A Review. Curr. Anal. Chem. 12, 169–182.
Kalbus, E., Reinstorf, F., Schirmer, M., 2006. Measuring methods for groundwater - surface water interactions: a review. Hydrol. Earth Syst. Sci. 10, 873–887. https://doi.org/10.5194/hess-10-873-2006
Kalma, J.D., McVicar, T.R., McCabe, M.F., 2008. Estimating land surface evaporation: A review of methods using remotely sensed surface temperature data. Surv. Geophys. 29, 421–469. https://doi.org/10.1007/s10712-008-9037-z
Kanton Thurgau Amt für Umwelt et. al., 2008. Grundwassermodell Thurtal (Band 63).
Karn, S.K., Harada, H., 2001. Surface water pollution in three urban territories of Nepal, India, and Bangladesh. Environ. Manage. 28, 483–496. https://doi.org/10.1007/s002670010238
Karolytė, R., Johnson, G., Serno, S., Gilfillan, S.M.V., 2017. The Influence of Water-rock Reactions and O Isotope Exchange with CO2 on Water Stable Isotope Composition of CO2 Springs in SE Australia. Energy Procedia 114, 3832–3839. https://doi.org/10.1016/j.egypro.2017.03.1515
Karthikeyan, K.G., Meyer, M.T., 2006. Occurrence of antibiotics in wastewater treatment facilities in Wisconsin, USA. Sci. Total Environ. 361, 196–207. https://doi.org/10.1016/j.scitotenv.2005.06.030
Kaufman, L., Rousseeuw, P.J., 1990. Partitioning Around Medoids (Program PAM), in: Finding Groups in Data: An Introduction to Cluster Analysis. John Wiley & Sons, Inc., pp. 68–125. https://doi.org/10.1002/9780470316801

Kaufmann, G., 2016. Modelling karst aquifer evolution in fractured, porous rocks. J. Hydrol. 543, 796–807.
Keller, B., 1992. Hydrogeologie des schweizerischen Molasse-Beckens: Aktueller Wissensstand und weiterfuhrende Betrachtungen. Eclogae Geol. Helv. 85, 611–652.
Khan, M.R., Koneshloo, M., Knappett, P.S.K., Ahmed, K.M., Bostick, B.C., Mailloux, B.J., Mozumder, R.H., Zahid, A., Harvey, C.F., Van Geen, A., Michael, H.A., 2016. Megacity pumping and preferential flow threaten groundwater quality. Nat. Commun. 7, 1–8. https://doi.org/10.1038/ncomms12833
Khan, M.S., Liaqat, U.W., Baik, J., Choi, M., 2018. Stand-alone uncertainty characterization of GLEAM, GLDAS and MOD16 evapotranspiration products using an extended triple collocation approach. Agric. For. Meteorol. 252, 256–268. https://doi.org/10.1016/j.agrformet.2018.01.022
Kim, K.R., Owens, G., Kwon, S.I., So, K.H., Lee, D.B., Ok, Y.S., 2011. Occurrence and environmental fate of veterinary antibiotics in the terrestrial environment. Water. Air. Soil Pollut. 214, 163–174. https://doi.org/10.1007/s11270-010-0412-2
Kirchner, J.W., 2009. Catchments as simple dynamical systems: Catchment characterization, rainfall-runoff modeling, and doing hydrology backward. Water Resour. Res. 45, 1–34. https://doi.org/10.1029/2008WR006912
Kirkby, M., 1988. Hillslope runoff processes and models. J. Hydrol. 100, 315–339. https://doi.org/10.1016/0022-1694(88)90190-4
Kirkby, M.J., 1969. Infiltration, throughflow, and overland flow, in: Water, Earth, and Man; a Synthesis of Hydrology, Geomorphology, and Socio-Economic Geography. pp. 215–227.
Kirkby, M.J., Chorley, R.J., 1967. Throughflow, overland flow and erosion. Int. Assoc. Sci. Hydrol. Bull. 12, 5–21. https://doi.org/10.1080/02626666709493533
Klammler, H., Hatfield, K., Newman, M.A., Cho, J., Annable, M.D., Parker, B.L., Cherry, J.A., Perminova, I., 2016. A new device for characterizing fracture networks and measuring groundwater and contaminant fluxes in fractured rock aquifers. Water Resour. Res. 52, 5400–5420. https://doi.org/10.1002/2015wr018389
Kloppmann, W., Girard, J.-P., Négrel, P., 2002. Exotic stable isotope compositions of saline waters and brines from the crystalline basement. Chem. Geol. 184, 49–70. https://doi.org/10.1016/S0009-2541(01)00352-7
Knüppe, K., 2011. The challenges facing sustainable and adaptive groundwater management in South Africa. Water SA 37, 67–79. https://doi.org/10.4314/wsa.v37i1.64110
Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B., Buxton, H.T., 2002. Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999-2000: A national reconnaissance. Environ. Sci. Technol. 36, 1202–1211. https://doi.org/10.1021/es011055j
Körner, C., 2007. The use of 'altitude' in ecological research. Trends Ecol. Evol. 22, 569–574. https://doi.org/10.1016/j.tree.2007.09.006
Kueper, B.H., McWhorter, D.B., 1991. The behavior of dense, nonaqueous phase liquids in fractured clay and rock. Groundwater 29, 716–728.
Kunz, M., Schindler-Wildhaber, Y., Dietzel, A., Wittmer, I., Leib, V., 2016. Zustand der Schweizer Fliessgewässer. Ergebnisse der Nationalen Beobachtung Oberflächengewässerqualität (NAWA) 2011–2014. BAFU. Umwelt-Zustand 1620, 87.
Kurth, A.M., Schirmer, M., 2014. Thirty years of river restoration in Switzerland: Implemented measures and lessons learned. Environ. Earth Sci. 72, 2065–2079. https://doi.org/10.1007/s12665-014-3115-y
Kurth, A.M., Weber, C., Schirmer, M., 2015. How effective is river restoration in re-establishing groundwater–surface water interactions? – A case study. Hydrol. Earth Syst. Sci. 19, 2663–2672. https://doi.org/10.5194/hess-19-2663-2015
Küster, A., Adler, N., 2014. Pharmaceuticals in the environment: Scientific evidence of risks and its regulation. Philos. Trans. R. Soc. B Biol. Sci. 369. https://doi.org/10.1098/rstb.2013.0587

Landgrebe, D., 1997. The evolution of Landsat data analysis. Photogramm. Eng. Remote Sensing 63, 859–867.
Laner, D., Crest, M., Scharff, H., Morris, J.W.F., Barlaz, M.A., 2012. A review of approaches for the long-term management of municipal solid waste landfills. Waste Manag. 32, 498–512. https://doi.org/10.1016/j.wasman.2011.11.010
Langston, G., Bentley, L.R., Hayashi, M., McClymont, A., Pidlisecky, A., 2011. Internal structure and hydrological functions of an alpine proglacial moraine. Hydrol. Process. 25, 2967–2982. https://doi.org/10.1002/hyp.8144
Lapworth, D.J., Baran, N., Stuart, M.E., Ward, R.S., 2012. Emerging organic contaminants in groundwater: A review of sources, fate and occurrence. Environ. Pollut. 163, 287–303. https://doi.org/10.1016/j.envpol.2011.12.034
Lapworth, D.J., Krishan, G., MacDonald, A.M., Rao, M.S., 2017. Groundwater quality in the alluvial aquifer system of northwest India: New evidence of the extent of anthropogenic and geogenic contamination. Sci. Total Environ. 599–600, 1433–1444. https://doi.org/10.1016/j.scitotenv.2017.04.223
Ledford, S.H., Lautz, L.K., Stella, J.C., 2016. Hydrogeologic Processes Impacting Storage, Fate, and Transport of Chloride from Road Salt in Urban Riparian Aquifers. Environ. Sci. Technol. 50, 4979–4988. https://doi.org/10.1021/acs.est.6b00402
Lee, C.H., Chen, W.P., Lee, R.H., 2006. Estimation of groundwater recharge using water balance coupled with base-flow-record estimation and stable-base-flow analysis. Environ. Geol. 51, 73–82. https://doi.org/10.1007/s00254-006-0305-2
Lee, J., Bang, K.., 2000. Characterization of urban stormwater runoff. Water Res. 34, 1773–1780. https://doi.org/10.1016/S0043-1354(99)00325-5
Lerner, D.N., Kueper, B.H., Wealthall, G.P., Smith, J.W.N., Leharne, S.A., 2003. An illustrated handbook of DNAPL transport and fate in the subsurface.
Lesser, L.E., Mora, A., Moreau, C., Mahlknecht, J., Hernández-Antonio, A., Ramírez, A.I., Barrios-Piña, H., 2018. Survey of 218 organic contaminants in groundwater derived from the world's largest untreated wastewater irrigation system: Mezquital Valley, Mexico. Chemosphere 198, 510–521. https://doi.org/10.1016/j.chemosphere.2018.01.154
Levison, J.K., Novakowski, K.S., 2012. Rapid transport from the surface to wells in fractured rock: A unique infiltration tracer experiment. J. Contam. Hydrol. https://doi.org/10.1016/j.jconhyd.2012.01.001
Lim, K.J., Engel, B.A., Tang, Z., Choi, J., 2005. Automated Web GIS based hydrograph analysis tool, WHAT. J. Am. Water Resour. Assoc. 1397, 1407–1416.
Lindsey, M.E., Meyer, M., Thurman, E.M., 2001. Analysis of trace levels of sulfonamide and tetracycline antimicrobials in groundwater and surface water using solid-phase extraction and liquid chromatography/mass spectrometry. Anal. Chem. 73, 4640–4646. https://doi.org/10.1021/ac010514w
Liu, F., Bales, R.C., Conklin, M.H., Conrad, M.E., 2008. Streamflow generation from snowmelt in semi-arid, seasonally snow-covered, forested catchments, Valles Caldera, New Mexico. Water Resour. Res. 44, 1–13. https://doi.org/10.1029/2007WR006728
Liu, F., Williams, M.W., Caine, N., 2004. Source waters and flow paths in an alpine catchment, Colorado Front Range, United States. Water Resour. Res. 40, 1–16. https://doi.org/10.1029/2004WR003076
Longe, E.O., Balogun, M.R., 2010. Groundwater quality assessment near a municipal landfill, Lagos, Nigeria. Res. J. Appl. Sci. Eng. Technol. 2, 39–44.
Loop, C.M., White, W.B., 2001. A conceptual model for DNAPL transport in karst ground water basins. Groundwater 39, 119–127.
Loos, R., Locoro, G., Comero, S., Contini, S., Schwesig, D., Werres, F., Balsaa, P., Gans, O., Weiss, S., Blaha, L., Bolchi, M., Gawlik, B.M., 2010. Pan-European survey on the occurrence of selected polar organic persistent pollutants in ground water. Water Res. 44, 4115–4126. https://doi.org/10.1016/j.watres.2010.05.032
López-Serna, R., Jurado, A., Vázquez-Suñé, E., Carrera, J., Petrović, M., Barceló, D., 2013. Occurrence of 95 pharmaceuticals and transformation products in urban groundwaters

underlying the metropolis of Barcelona, Spain. Environ. Pollut. 174, 305–315. https://doi.org/10.1016/j.envpol.2012.11.022
Lovett, G.M., Burns, D. a, Driscoll, C.T., Jenkins, J.C., Mitchell, M.J., Rustad, L., Shanley, J.B., Likens, G.E., Haeuber, R., 2007. Who needs environmental monitoring ? In a nutshell : Ecol. Soc. Am. 5, 253–260.
Luo, X., Liang, X., Lin, J.-S., 2016. Plant transpiration and groundwater dynamics in water-limited climates: Impacts of hydraulic redistribution. Water Resour. Res. 52, 4416–4437. https://doi.org/10.1002/2015WR017316
Mackay, D.M., Roberts, P. V, Cherry, J.A., 1985. Transport of organic contaminants in groundwater. Environ. Sci. Technol. 19, 384–392.
Mallin, M.A., Johnson, V.L., Ensign, S.H., 2009. Comparative impacts of stormwater runoff on water quality of an urban, a suburban, and a rural stream. Environ. Monit. Assess. 159, 475–491. https://doi.org/10.1007/s10661-008-0644-4
Maloszewski, P., Stichler, W., Zuber, A., Rank, D., 2002. Identifying the flow systems in a karstic-fissured-porous aquifer, the Schneealpe, Austria, by modelling of environmental 18O and 3H isotopes. J. Hydrol. 256, 48–59.
Manamsa, K., Crane, E., Stuart, M., Talbot, J., Lapworth, D., Hart, A., 2016. A national-scale assessment of micro-organic contaminants in groundwater of England and Wales. Sci. Total Environ. 568, 712–726. https://doi.org/10.1016/j.scitotenv.2016.03.017
Markovich, K.H., Dahlke, H.E., Arumí, J.L., Maxwell, R.M., Fogg, G.E., 2019. Bayesian hydrograph separation in a minimally gauged alpine volcanic watershed in central Chile. J. Hydrol. 575, 1288–1300. https://doi.org/10.1016/j.jhydrol.2019.06.014
Marsalek, J., Jiménez-Cisneros, B., Karamouz, M., Malmquist, P.-A., Goldenfum, J., Chocat, B., 2007. Urban Water Cycle Processes and Interactions, 1st ed. London. https://doi.org/10.15713/ins.mmj.3
Martinec, J., 1975. Subsurface flow from snowmelt traced by tritium. Water Resour. Res. 11, 496–498. https://doi.org/10.1029/WR011i003p00496
Mateo-Sagasta, J., Marjani, S., Turral, H., Burke, J., 2017. Water pollution from agriculture: a global review. FAO IWMI 35.
Matteucci, F., Ercole, C., Del Gallo, M., 2015. A study of chlorinated solvent contamination of the aquifers of an industrial area in central Italy: A possibility of bioremediation. Front. Microbiol. 6, 1–10. https://doi.org/10.3389/fmicb.2015.00924
McCarthy, T.S., 2011. The impact of acid mine drainage in South Africa. S. Afr. J. Sci. 107, 1–7. https://doi.org/10.4102/sajs.v107i5/6.712
McDonnell, J.J., 2017. Beyond the water balance. Nat. Geosci. 10, 396. https://doi.org/10.1038/ngeo2964
McDonnell, J.J., Sivapalan, M., Vache, K., Dunn, S., Grant, G., Haggerty, R., Hinz, C., Hooper, R., Kirchner, J., Roderick, M.L., Selker, J., Weiler, M., 2007. Moving beyond heterogeneity and process complexity: A new vision for watershed hydrology. Water Resour. Res. 43, 1–6. https://doi.org/10.1029/2006WR005467
McIntosh, J.C., 2012. Impacts of urbanization on groundwater recharge and water quality in semi-arid basins. Groundw. Model. Manag. under Uncertain. 61–64.
McMahon, P.B., Dennehy, K.F., Bruce, B.W., Böhlke, J.K., Michel, R.L., Gurdak, J.J., Hurlbut, D.B., 2006. Storage and transit time of chemicals in thick unsaturated zones under rangeland and irrigated cropland, High Plains, United States. Water Resour. Res. 42. https://doi.org/10.1029/2005WR004417
Mdaghri-Alaoui, A., Eugster, W., 2001. Field determination of the water balance of the Areuse River delta, Switzerland. Hydrol. Sci. J. 46, 747–760. https://doi.org/10.1080/02626660109492868
Meeks, J., Moeck, C., Brunner, P., Hunkeler, D., 2017. Infiltration under snow cover: Modeling approaches and predictive uncertainty. J. Hydrol. 546, 16–27. https://doi.org/10.1016/j.jhydrol.2016.12.042
Melsen, L., Teuling, A., Torfs, P., Zappa, M., Mizukami, N., Clark, M., Uijlenhoet, R., 2016. Representation of spatial and temporal variability in large-domain hydrological models: case study for a mesoscale pre-Alpine basin. Hydrol. Earth Syst. Sci. 20, 2207–2226.

https://doi.org/10.5194/hess-20-2207-2016
Meredith, K.T., Hollins, S.E., Hughes, C.E., Cendón, D.I., Hankin, S., Stone, D.J.M., 2009. Temporal variation in stable isotopes (18O and 2H) and major ion concentrations within the Darling River between Bourke and Wilcannia due to variable flows, saline groundwater influx and evaporation. J. Hydrol. 378, 313–324. https://doi.org/10.1016/j.jhydrol.2009.09.036
MeteoSwiss, 2016. Documentation of MeteoSwiss Grid-Data Products: Monthly and Yearly Mean Precipiatation, Federal Office of Meteorology and Climatology (FDHA). https://doi.org/OFEV2014
MeteoSwiss, 2013. Documentation of MeteoSwiss Grid-Data Products - Monthly and Yearly Precipitation : RhiresM and RhiresY 4. https://doi.org/OFEV2014
MeteoSwiss, 2011. Klimabulletin Jahr 2011 Swiss Federal Office of Meteorology and Climatology. Bern.
MeteoSwiss, 2005. 2005 Jahresbericht Swiss Federal Office of Meteorology and Climatology. Bern.
Meyer, J.L., Paul, M.J., Taulbee, W.K., 2005. Stream ecosystem function in urbanizing landscapes. J. North Am. Benthol. Soc. 24, 602–612. https://doi.org/10.1899/04-021.1
Milly, P.C.D., 1994. Climate, interseasonal storage of soil water, and the annual water balance. Adv. Water Resour. 17, 19–24. https://doi.org/10.1016/0309-1708(94)90020-5
Minnig, M., Moeck, C., Radny, D., Schirmer, M., 2018. Impact of urbanization on groundwater recharge rates in Dübendorf, Switzerland. J. Hydrol. 563, 1135–1146. https://doi.org/10.1016/j.jhydrol.2017.09.058
Miranda, R.D.Q., Galvíncio, J.D., Moura, M.S.B. De, Jones, C.A., Srinivasan, R., 2017. Reliability of MODIS Evapotranspiration Products for Heterogeneous Dry Forest: A Study Case of Caatinga. Adv. Meteorol. 2017, 1–14. https://doi.org/10.1155/2017/9314801
Mitchell, V.G., 2006. Applying integrated urban water management concepts: A review of Australian experience. Environ. Manage. 37, 589–605. https://doi.org/10.1007/s00267-004-0252-1
Moeck, C., Affolter, A., Radny, D., Dressmann, H., Auckenthaler, A., Huggenberger, P., Schirmer, M., 2017a. Improved water resource management for a highly complex environment using three-dimensional groundwater modelling. Hydrogeol. J. https://doi.org/10.1007/s10040-017-1640-y
Moeck, C., Grech-Cumbo, N., Podgorski, J., Bretzler, A., Gurdak, J.J., Berg, M., Schirmer, M., 2020. A global-scale dataset of direct natural groundwater recharge rates: A review of variables, processes and relationships. Sci. Total Environ. 717, 137042. https://doi.org/10.1016/j.scitotenv.2020.137042
Moeck, C., Radny, D., Borer, P., Rothardt, J., Auckenthaler, A., Berg, M., Schirmer, M., 2016. Multicomponent statistical analysis to identify flow and transport processes in a highly-complex environment. J. Hydrol. 542, 437–449.
Moeck, C., Radny, D., Popp, A., Brennwald, M., Stoll, S., Auckenthaler, A., Berg, M., Schirmer, M., 2017b. Characterization of a managed aquifer recharge system using multiple tracers. Sci. Total Environ. 609, 701–714. https://doi.org/10.1016/j.scitotenv.2017.07.211
Moeck, C., von Freyberg, J., Schirmer, M., 2018. Groundwater recharge predictions in contrasted climate: The effect of model complexity and calibration period on recharge rates. Environ. Model. Softw. 103, 74–89. https://doi.org/10.1016/j.envsoft.2018.02.005
Mohan, C., Western, A.W., Wei, Y., Saft, M., 2018. Predicting groundwater recharge for varying land cover and climate conditions-a global meta-study. Hydrol. Earth Syst. Sci. 22, 2689–2703. https://doi.org/10.5194/hess-22-2689-2018
Molin, M.D., Schirmer, M., Zappa, M., Fenicia, F., 2020. Understanding dominant controls on streamflow spatial variability to set up a semi-distributed hydrological model : the case study of the Thur catchment 1319–1345.
Montanari, A., Young, G., Savenije, H.H.G., Hughes, D., Wagener, T., Ren, L.L., Koutsoyiannis, D., Cudennec, C., Toth, E., Grimaldi, S., Blöschl, G., Sivapalan, M.,

Beven, K., Gupta, H., Hipsey, M., Schaefli, B., Arheimer, B., Boegh, E., Schymanski, S.J., Di Baldassarre, G., Yu, B., Hubert, P., Huang, Y., Schumann, A., Post, D. a., Srinivasan, V., Harman, C., Thompson, S., Rogger, M., Viglione, A., McMillan, H., Characklis, G., Pang, Z., Belyaev, V., 2013. “Panta Rhei—Everything Flows”: Change in hydrology and society—The IAHS Scientific Decade 2013–2022. Hydrol. Sci. J. 58, 1256–1275. https://doi.org/10.1080/02626667.2013.809088
Monteith, J.L., 1965. Evaporation and environment. Symp. Soc. Exp. Biol. https://doi.org/10.1613/jair.301
Montgomery, J.L., Harmon, T., Haas, C.N., Hooper, R., Clesceri, N.L., Grahm, W., Kaiser, W., Sanderson, A., Minsker, B., Schnoor, J., Brezonik, P., 2007. The WATERS Network: An Integrated Environmental Observatory Network for Water Research. Environ. Sci. Technol. 41, 6642–6647. https://doi.org/10.1021/es072618f
Morrison-Saunders, A., Bailey, J., 2003. Practitioner Perspectives on the Role of Science in Environmental Impact Assessment. Environ. Manage. 31, 683–695. https://doi.org/10.1007/s00267-003-2709-z
Moschet, C., Wittmer, I., Simovic, J., Junghans, M., Piazzoli, A., Singer, H., Stamm, C., Leu, C., Hollender, J., 2014. How a complete pesticide screening changes the assessment of surface water quality. Environ. Sci. Technol. 48, 5423–5432. https://doi.org/10.1021/es500371t
Mu, Q., Zhao, M., Running, S.W., 2011. Improvements to a MODIS global terrestrial evapotranspiration algorithm. Remote Sens. Environ. 115, 1781–1800. https://doi.org/10.1016/j.rse.2011.02.019
Munz, N.A., Burdon, F.J., de Zwart, D., Junghans, M., Melo, L., Reyes, M., Schï¿½nenberger, U., Singer, H.P., Spycher, B., Hollender, J., Stamm, C., 2017. Pesticides drive risk of micropollutants in wastewater-impacted streams during low flow conditions. Water Res. 110, 366–377. https://doi.org/10.1016/j.watres.2016.11.001
Musgrove, M., Opsahl, S.P., Mahler, B.J., Herrington, C., Sample, T.L., Banta, J.R., 2016. Source, variability, and transformation of nitrate in a regional karst aquifer: Edwards aquifer, central Texas. Sci. Total Environ. 568, 457–469. https://doi.org/10.1016/j.scitotenv.2016.05.201
Musingafi, M.C.C., Tom, T., 2014. Fresh Water Sources Pollution : A Human Related Threat To Fresh Water Security in South Africa. J. Public policy Gov. 1, 72–81.
Musolff, A., Leschik, S., Reinstorf, F., Strauch, G., Schirmer, M., 2010. Micropollutant loads in the urban water cycle. Environ. Sci. Technol. 44, 4877–4883. https://doi.org/10.1021/es903823a
Mutiyar, P.K., Mittal, A.K., 2013. Occurrences and fate of an antibiotic amoxicillin in extended aeration-based sewage treatment plant in Delhi, India: a case study of emerging pollutant. Desalin. Water Treat. 51, 6158–6164. https://doi.org/10.1080/19443994.2013.770199
Mutzner, L., Staufer, P., Ort, C., 2016. Model-based screening for critical wet-weather discharges related to micropollutants from urban areas. Water Res. 104, 547–557. https://doi.org/10.1016/j.watres.2016.08.003
Naicker, K., Cukrowska, E., Mccarthy, T.S., 2003. Acid mine drainage arising from gold mining activity in Johannesburg , South Africa and environs. Environ. Pollut. 122, 29–40.
Nathan, R.J., McMahon, T.A., 1990. Evaluation of automated techniques for base flow and recession analyses. Water Resour. Res. 26, 1465–1473. https://doi.org/10.1029/WR026i007p01465
Neill, C., Chaves, J.E., Biggs, T., Deegan, L.A., Elsenbeer, H., Figueiredo, R.O., Germer, S., Johnson, M.S., Lehmann, J., Markewitz, D., Piccolo, M.C., 2011. Runoff sources and land cover change in the Amazon: an end-member mixing analysis from small watersheds. Biogeochemistry 105, 7–18. https://doi.org/10.1007/s10533-011-9597-8
Nicolai-Shaw, N., Hirschi, M., Mittelbach, H., Seneviratne, S.I., 2015. Spatial representativeness of soil moisture using in situ, remote sensing, and land reanalysis data. J. Geophys. Res. Atmos. 120, 9955–9964. https://doi.org/10.1002/2015JD023305

Nishida, K., Nemani, R.R., Running, S.W., Glassy, J.M., 2003. An operational remote sensing algorithm of land surface evaporation. J. Geophys. Res. D Atmos. 108. https://doi.org/10.1029/2002jd002062
O'Driscoll, M.A., DeWalle, D.R., McGuire, K.J., Gburek, W.J., 2005. Seasonal 18O variations and groundwater recharge for three landscape types in central Pennsylvania, USA. J. Hydrol. 303, 108–124. https://doi.org/10.1016/j.jhydrol.2004.08.020
Ojiambo, B.S., Poreda, R.J., Lyons, W.B., 2001. Ground Water/Surface Water Interactions in Lake Naivasha, Kenya, Using δ18O, δD, and 3H/3He Age-Dating. Ground Water 39, 526–533. https://doi.org/10.1111/j.1745-6584.2001.tb02341.x
Oki, T., Kanae, S., 2006. Global hydrological cycles and world water resources. Science (80- .). 313, 1068–1072. https://doi.org/10.1126/science.1128845
Okumu-Okot, J., 2012. Solid Waste Management in African Cities – East Africa. Waste Manag. - An Integr. Vis. 19. https://doi.org/10.5772/50241
Orth, R., Seneviratne, S.I., 2015. Introduction of a simple-model-based land surface dataset for Europe. Environ. Res. Lett. 10. https://doi.org/10.1088/1748-9326/10/4/044012
Orth, R., Seneviratne, S.I., 2012. Analysis of soil moisture memory from observations in Europe. J. Geophys. Res. Atmos. 117, 1–19. https://doi.org/10.1029/2011JD017366
Paillex, A., Logar, I., Schirmer, M., Schuwirth, N., Siber, R., Yang, H., Reichert, P., 2005. Rewidening and rewilding the Thur river (Switzerland). REFORM 1–5.
Paillex, A., Schuwirth, N., Lorenz, A.W., Januschke, K., Peter, A., Reichert, P., 2017. Integrating and extending ecological river assessment: Concept and test with two restoration projects. Ecol. Indic. 72, 131–141. https://doi.org/10.1016/j.ecolind.2016.07.048
Palau, J., Jamin, P., Badin, A., Vanhecke, N., Haerens, B., Brouyère, S., Hunkeler, D., 2016. Use of dual carbon-chlorine isotope analysis to assess the degradation pathways of 1,1,1-trichloroethane in groundwater. Water Res. 92, 235–243. https://doi.org/10.1016/j.watres.2016.01.057
Panasiuk, O., Hedström, A., Marsalek, J., Ashley, R.M., Viklander, M., 2015. Contamination of stormwater by wastewater: A review of detection methods. J. Environ. Manage. 152, 241–250. https://doi.org/10.1016/j.jenvman.2015.01.050
Parizi, E., Hosseini, S.M., Ashtiani, B.A., Simmons, C.T., 2020. Normalized difference vegetation index as the dominant predicting factor of groundwater recharge in phreatic aquifers : case studies across Iran. Sci. Rep. 1–19. https://doi.org/10.1038/s41598-020-74561-4
Park, S.-S., Kim, S.-O., Yun, S.-T., Chae, G.-T., Yu, S.-Y., Kim, S., Kim, Y., 2005. Effects of land use on the spatial distribution of trace metals and volatile organic compounds in urban groundwater, Seoul, Korea. Environ. Geol. 48, 1116–1131. https://doi.org/10.1007/s00254-005-0053-8
Parker, J.C., Park, E., 2004. Modeling field-scale dense nonaqueous phase liquid dissolution kinetics in heterogeneous aquifers. Water Resour. Res. 40.
Pavelsky, T.M., 2014. Using width-based rating curves from spatially discontinuous satellite imagery to monitor river discharge. Hydrol. Process. 28, 3035–3040. https://doi.org/10.1002/hyp.10157
Peel, M.C., Finlayson, B.L., McMahon, T.A., 2007. Updated world map of the Köppen-Geiger climate classification. Hydrol. Earth Syst. Sci. 11, 1633–1644. https://doi.org/10.5194/hess-11-1633-2007
Pekel, J.F., Cottam, A., Gorelick, N., Belward, A.S., 2016. High-resolution mapping of global surface water and its long-term changes. Nature 540, 418–422. https://doi.org/10.1038/nature20584
Peng, X., Ou, W., Wang, C., Wang, Z., Huang, Q., Jin, J., Tan, J., 2014. Occurrence and ecological potential of pharmaceuticals and personal care products in groundwater and reservoirs in the vicinity of municipal landfills in China. Sci. Total Environ. 490, 889–898. https://doi.org/10.1016/j.scitotenv.2014.05.068
Petrella, E., Celico, F., 2013. Mixing of water in a carbonate aquifer, southern Italy, analysed through stable isotope investigations. Int. J. Speleol. 42, 25–33.

https://doi.org/10.5038/1827-806X.42.1.4
Picardal, F., Arnold, R.G., Huey, B.B., 1995. Effects of electron donor and acceptor conditions on reductive dehalogenation of tetrachloromethane by Shewanella putrefaciens 200. Appl. Environ. Microbiol. 61, 8–12. https://doi.org/10.1016/j.visres.2004.12.003
Pitt, R., Clark, S., Field, R., 1999. Groundwater contamination potential from stormwater infiltration practices. Urban Water 1, 217–236. https://doi.org/10.1016/S1462-0758(99)00014-X
Pool, S., Viviroli, D., Seibert, J., 2017. Prediction of hydrographs and flow-duration curves in almost ungauged catchments: Which runoff measurements are most informative for model calibration? J. Hydrol. 554, 613–622. https://doi.org/10.1016/j.jhydrol.2017.09.037
Popp, A.L., Pardo-Álvarez, Á., Schilling, O.S., Scheidegger, A., Musy, S., Peel, M., Brunner, P., Purtschert, R., Hunkeler, D., Kipfer, R., 2021. A Framework for Untangling Transient Groundwater Mixing and Travel Times. Water Resour. Res. 57, 1–16. https://doi.org/10.1029/2020WR028362
Popp, A.L., Scheidegger, A., Moeck, C., Brennwald, M.S., Kipfer, R., 2019. Integrating Bayesian Groundwater Mixing Modeling With On-Site Helium Analysis to Identify Unknown Water Sources. Water Resour. Res. 55, 10602–10615. https://doi.org/10.1029/2019WR025677
Quinn, J., Geiger, C., Clausen, C., Brooks, K., Coon, C., O'Hara, S., Krug, T., Major, D., Yoon, W.-S., Gavaskar, A., 2005. Field demonstration of DNAPL dehalogenation using emulsified zero-valent iron. Environ. Sci. Technol. 39, 1309–1318.
R Core Team, 2018. A Language and Environment for Statistical Computing.
Rahman, K., Besacier-Monbertrand, A.-L., Castella, E., Lods-Crozet, B., Ilg, C., Beguin, O., 2015. Quantification of the daily dynamics of streamflow components in a small alpine watershed in Switzerland using end member mixing analysis. Environ. Earth Sci. 74, 4927–4937. https://doi.org/10.1007/s12665-015-4505-5
Rajib, A., Evenson, G.R., Golden, H.E., Lane, C.R., 2018. Hydrologic model predictability improves with spatially explicit calibration using remotely sensed evapotranspiration and biophysical parameters. J. Hydrol. 567, 668–683. https://doi.org/10.1016/j.jhydrol.2018.10.024
Rana, G., Katerji, N., 2000. Measurement and estimation of actual evapotranspiration in the field under Mediterranean climate: A review. Eur. J. Agron. 13, 125–153. https://doi.org/10.1016/S1161-0301(00)00070-8
Randall, G.W., Mulla, D.J., 2001. Nitrate Nitrogen in Surface Waters as Influenced by Climatic Conditions and Agricultural Practices. J. Environ. Qual. https://doi.org/10.2134/jeq2001.302337x
Rayleigh, Lord, 1896. L. Theoretical considerations respecting the separation of gases by diffusion and similar processes. London, Edinburgh, Dublin Philos. Mag. J. Sci. 42, 493–498. https://doi.org/10.1080/14786449608620944
Reh, R., Licha, T., Nödler, K., Geyer, T., Sauter, M., 2015. Evaluation and application of organic micro-pollutants (OMPs) as indicators in karst system characterization. Environ. Sci. Pollut. Res. 22, 4631–4643.
Rehman, M.S.U., Rashid, N., Ashfaq, M., Saif, A., Ahmad, N., Han, J.I., 2015. Global risk of pharmaceutical contamination from highly populated developing countries. Chemosphere 138, 1045–1055. https://doi.org/10.1016/j.chemosphere.2013.02.036
Reinstorf, F., Strauch, G., Schirmer, K., Gläser, H.-R., Möder, M., Wennrich, R., Osenbrück, K., Schirmer, M., 2008. Mass fluxes and spatial trends of xenobiotics in the waters of the city of Halle, Germany. Environ. Pollut. 152, 452–460. https://doi.org/10.1016/j.envpol.2007.05.033
Reisinger, A.J., Groffman, P.M., Rosi-Marshall, E.J., 2016. Nitrogen-cycling process rates across urban ecosystems. FEMS Microbiol. Ecol. 92, 1–11. https://doi.org/10.1093/femsec-fiw198
Reitz, M., Sanford, W.E., Senay, G.B., Cazenas, J., 2017. Annual Estimates of Recharge,

Quick-Flow Runoff, and Evapotranspiration for the Contiguous U.S. Using Empirical Regression Equations. JAWRA J. Am. Water Resour. Assoc. 53, 961–983. https://doi.org/10.1111/1752-1688.12546
Renner, R.M., 1995. The construction of extreme compositions. Math. Geol. 27, 485–497. https://doi.org/10.1007/BF02084423
Rey, N., Rosa, E., Cloutier, V., Lefebvre, R., 2018. Using water stable isotopes for tracing surface and groundwater flow systems in the Barlow-Ojibway Clay Belt, Quebec, Canada. Can. Water Resour. J. / Rev. Can. des ressources hydriques 43, 173–194. https://doi.org/10.1080/07011784.2017.1403960
Rickwood, C.J., Carr, G.M., 2009. Development and sensitivity analysis of a global drinking water quality index. Environ. Monit. Assess. 156, 73–90. https://doi.org/10.1007/s10661-008-0464-6
Rivett, M.O., Shepherd, K.A., Keeys, L.L., Brennan, A.E., 2005. Chlorinated solvents in the Birmingham aquifer, UK: 1986–2001. Q. J. Eng. Geol. Hydrogeol. 38, 337–350.
Robert, T., Caterina, D., Deceuster, J., Kaufmann, O., Nguyen, F., 2012. A salt tracer test monitored with surface ERT to detect preferential flow and transport paths in fractured/karstified limestones. Geophysics 77, B55–B67.
Rodríguez-Huerta, E., Rosas-Casals, M., Hernández-Terrones, L.M., 2020. A water balance model to estimate climate change impact on groundwater recharge in Yucatan Peninsula, Mexico. Hydrol. Sci. J. https://doi.org/10.1080/02626667.2019.1702989
Rodriguez-Iturbe, I., Porporato, A., Rldolfi, L., Isham, V., Cox, D.R., 1999. Probabilistic modelling of water balance at a point: The role of climate, soil and vegetation. Proc. R. Soc. A Math. Phys. Eng. Sci. 455, 3789–3805. https://doi.org/10.1098/rspa.1999.0477
Rojas-Serna, C., Lebecherel, L., Perrin, C., Andréassian, V., Oudin, L., 2016. How should a rainfall-runoff model be parameterized in an almost ungauged catchment? A methodology tested on 609 catchments. Water Resour. Res. 52, 4765–4784. https://doi.org/10.1002/2015WR018549
Rösner, U., 1998. Effects of historical mining activities on surface water and groundwater - An example from northwest Arizona. Environ. Geol. 33, 224–230. https://doi.org/10.1007/s002540050241
Rössler, O., Kotlarski, S., Fischer, A.M., Keller, D., Liniger, M., Weingartner, R., 2019. Evaluating the added value of the new Swiss climate scenarios for hydrology : An example from the Thur catchment. Clim. Serv. 13, 1–13. https://doi.org/10.1016/j.cliser.2019.01.001
Rost, S., Gerten, D., Heyder, U., 2008. Human alterations of the terrestrial water cycle through land management. Adv. Geosci. 18, 43–50. https://doi.org/10.5194/adgeo-18-43-2008
Roy, J.W., Hayashi, M., 2009. Multiple, distinct groundwater flow systems of a single moraine–talus feature in an alpine watershed. J. Hydrol. 373, 139–150. https://doi.org/10.1016/j.jhydrol.2009.04.018
Ruhoff, A.L., Paz, A.R., Aragao, L.E.O.C., Mu, Q., Malhi, Y., Collischonn, W., Rocha, H.R., Running, S.W., 2013. Assessment of the MODIS global evapotranspiration algorithm using eddy covariance measurements and hydrological modelling in the Rio Grande basin. Hydrol. Sci. J. 58, 1658–1676. https://doi.org/10.1080/02626667.2013.837578
Running, S.W., Justice, C.O., Salomonson, V., Hall, D., Barker, J., Kaufmann, Y.J., Strahler, A.H., Heute, A.R., Muller, J.-P., Vanderbilt, V., Wan, Z.M., Teillet, P., Carneggie, D., 1994. Terrestrial remote sensing science and algorithms planned for EOS/MODIS. Int. J. Remote Sens. 15, 3587–3620. https://doi.org/10.1080/01431169408954346
Running, S.W., Mu, Q., Zhao, M., Moreno, A., 2019. MOD16A3GF MODIS/Terra Net Evapotranspiration Gap-Filled Yearly L4 Global 500 m SIN Grid V006. NASA EOSDIS L. Process. DAAC 1–37. https://doi.org/10.5067/MODIS/MOD16A3GF.006
Ruth, C.E., Michel, D., Hirschi, M., Seneviratne, S.I., 2018. Comparative Study of a Long-Established Large Weighing Lysimeter and a State-of-the-Art Mini-lysimeter. Vadose Zo. J. 17, 170026. https://doi.org/10.2136/vzj2017.01.0026
Sacher, F., Lange, F.T., Brauch, H.J., Blankenhorn, I., 2001. Pharmaceuticals in

groundwaters: Analytical methods and results of a monitoring program in Baden-Württemberg, Germany. J. Chromatogr. A 938, 199–210. https://doi.org/10.1016/S0021-9673(01)01266-3
San-Sebastián-Sauto, J., Fernández-Escalante, E., Calero-Gil, R., Carvalho, T., Rodríguez-Escales, P., 2018. Characterization and benchmarking of seven managed aquifer recharge systems in south-western Europe. Sustain. Water Resour. Manag. 4, 193–215. https://doi.org/10.1007/s40899-018-0232-x
Scanlon, B.R., Healy, R.W., Cook, P.G., 2002. Choosing appropriate technique for quantifying groundwater recharge. Hydrogeol. J. 10, 18–39. https://doi.org/10.1007/s10040-0010176-2
Scanlon, B.R., Reedy, R.C., Stonestrom, D.A., Prudic, D.E., Dennehy, K.F., 2005. Impact of land use and land cover change on groundwater recharge and quality in the southwestern US. Glob. Chang. Biol. 11, 1577–1593. https://doi.org/10.1111/j.1365-2486.2005.01026.x
Schädler, B., Weingartner, R., 2002. Components of the Natural Water Balance 1961–1990, in: FOWG: Hydrological Atlas of Switzerland (Plate 6.3). Bern.
Schär, C., Vidale, P.L., Lüthi, D., Frei, C., Häberli, C., Liniger, M.A., Appenzeller, C., 2004. The role of increasing temperature variability in European summer heatwaves. Nature 427, 332–336. https://doi.org/10.1038/nature02300
Scheytt, T., Mersmann, P., Lindstädt, R., Heberer, T., 2005. Determination of sorption coefficients of pharmaceutically active substances carbamazepine, diclofenac, and ibuprofen, in sandy sediments. Chemosphere 60, 245–253. https://doi.org/10.1016/j.chemosphere.2004.12.042
Schiemann, R., Liniger, M.A., Frei, C., 2010. Reduced space optimal interpolation of daily rain gauge precipitation in Switzerland. J. Geophys. Res. Atmos. 115, 1–18. https://doi.org/10.1029/2009JD013047
Schirmer, M., Leschik, S., Musolff, A., 2013. Current research in urban hydrogeology - A review. Adv. Water Resour. 51, 280–291. https://doi.org/10.1016/j.advwatres.2012.06.015
Schirmer, M., Luster, J., Linde, N., Perona, P., Mitchell, E.A.D., Barry, D.A., Hollender, J., Cirpka, O.A., Schneider, P., Vogt, T., Radny, D., Durisch-Kaiser, E., 2014. Morphological, hydrological, biogeochemical and ecological changes and challenges in river restoration – the Thur River case study. Hydrol. Earth Syst. Sci. 18, 2449–2462. https://doi.org/10.5194/hess-18-2449-2014
Schmucki, E., Marty, C., Fierz, C., Lehning, M., 2014. Evaluation of modelled snow depth and snow water equivalent at three contrasting sites in Switzerland using SNOWPACK simulations driven by different meteorological data input. Cold Reg. Sci. Technol. https://doi.org/10.1016/j.coldregions.2013.12.004
Schnarr, M., Truax, C., Farquhar, G., Hood, E., Gonullu, T., Stickney, B., 1998. Laboratory and controlled field experiments using potassium permanganate to remediate trichloroethylene and perchloroethylene DNAPLs in porous media. J. Contam. Hydrol. https://doi.org/10.1016/S0169-7722(97)00012-0
Schneider, P., Vogt, T., Schirmer, M., Doetsch, J., Linde, N., Pasquale, N., Perona, P., Cirpka, O.A., 2011. Towards improved instrumentation for assessing river-groundwater interactions in a restored river corridor. Hydrol. Earth Syst. Sci. 15, 2531–2549. https://doi.org/10.5194/hess-15-2531-2011
Schrader, F., Durner, W., Fank, J., Gebler, S., Pütz, T., Hannes, M., Wollschläger, U., 2013. Estimating Precipitation and Actual Evapotranspiration from Precision Lysimeter Measurements. Procedia Environ. Sci. 19, 543–552. https://doi.org/10.1016/j.proenv.2013.06.061
Schreglmann, K., Hoeche, M., Steinbeiss, S., Reinnicke, S., Elsner, M., 2013. Carbon and nitrogen isotope analysis of atrazine and desethylatrazine at sub-microgram per liter concentrations in groundwater. Anal. Bioanal. Chem. 405, 2857–2867. https://doi.org/10.1007/s00216-012-6616-0
Schwartz, F.W., Smith, L., Crowe, A.S., 1983. A Stochastic-Analysis of Macroscopic

Dispersion in Fractured Media. Water Resour. Res. 19, 1253–1265. https://doi.org/DOI 10.1029/WR019i005p01253
Schwartz, M.O., Kgomanyane, J., 2008. Modelling natural attenuation of heavy-metal groundwater contamination in the Selebi-Phikwe mining area, Botswana. Environ. Geol. 54, 819–830. https://doi.org/10.1007/s00254-007-0865-9
Scott, R., 1995. Flooding of Central and Grand Rand Gold Mines: an investigation into controls over the inflow rate, water quality and the predicted impacts of flooded mines. Water Res. Commision, WRC Rep. No. 486/1/95 1–238.
Seibert, J., McGlynn, B.L., 2007. A new triangular multiple flow direction algorithm for computing upslope areas from gridded digital elevation models. Water Resour. Res. 43. https://doi.org/10.1029/2006WR005128
Seneviratne, S.I., Lehner, I., Gurtz, J., Teuling, A.J., Lang, H., Moser, U., Grebner, D., Menzel, L., Schroff, K., Vitvar, T., Zappa, M., 2012. Swiss prealpine Rietholzbach research catchment and lysimeter: 32 year time series and 2003 drought event. Water Resour. Res. 48, 1–20. https://doi.org/10.1029/2011WR011749
Shapiro, A.M., Brenneis, R.J., 2018. Variability of organic carbon content and the retention and release of trichloroethene in the rock matrix of a mudstone aquifer. J. Contam. Hydrol. 217, 32–42.
Shareef, A., Page, D., Vanderzalm, J., Williams, M., Gupta, V.V.S.R., Dillon, P., Kookana, R., 2014. Biodegradation of Simazine and Diuron Herbicides under Aerobic and Anoxic Conditions Relevant to Managed Aquifer Recharge of Storm Water. Clean - Soil, Air, Water 42, 745–752. https://doi.org/10.1002/clen.201300092
Sharma, S.K., Kennedy, M.D., 2017. Soil aquifer treatment for wastewater treatment and reuse. Int. Biodeterior. Biodegrad. 119, 671–677. https://doi.org/10.1016/j.ibiod.2016.09.013
Sheffield, J., Wood, E.F., Pan, M., Beck, H., Coccia, G., Serrat-Capdevila, A., Verbist, K., 2018. Satellite Remote Sensing for Water Resources Management - Potential for Supporting Sustainable Development in Data Poor Regions. Water Resour. Res. 9724–9758. https://doi.org/10.1029/2017WR022437
Sinclair, C.J., Boxall, A.B.A., 2003. Assessing the ecotoxicity of pesticide transformation products. Environ. Sci. Technol. 37, 4617–4625. https://doi.org/10.1021/es030038m
Singh, S., Kumar, V., Chauhan, A., Datta, S., Wani, A.B., Singh, N., Singh, J., 2018. Toxicity, degradation and analysis of the herbicide atrazine. Environ. Chem. Lett. 16, 211–237. https://doi.org/10.1007/s10311-017-0665-8
Sivapalan, M., Takeuchi, K., Franks, S.W., Gupta, V.K., Karambiri, H., Lakshmi, V., Liang, X., McDonnell, J.J., Mendiondo, E.M., O'connell, P.E., OKI, T., Pomery, J.W., Schertzer, D., Uhlenbrook, S., Zehe, E., 2003. IAHS Decade on Predictions in Ungauged Basins (PUB), 2003–2012: Shaping an exciting future for the hydrological sciences. Hydrol. Sci. J. 48, 857–880. https://doi.org/10.1623/hysj.48.6.857.51421
Soga, K., Page, J.W.E., Illangasekare, T.H., 2004. A review of NAPL source zone remediation efficiency and the mass flux approach. J. Hazard. Mater. 110, 13–27. https://doi.org/10.1016/j.jhazmat.2004.02.034
Sood, A., Smakhtin, V., 2015. Global hydrological models: a review. Hydrol. Sci. J. 60, 549–565. https://doi.org/10.1080/02626667.2014.950580
Sophocleous, M., 2002. Interactions between groundwater and surface water: The state of the science. Hydrogeol. J. 10, 52–67. https://doi.org/10.1007/s10040-001-0170-8
Sorensen, J.P.R., Lapworth, D.J., Nkhuwa, D.C.W., Stuart, M.E., Gooddy, D.C., Bell, R.A., Chirwa, M., Kabika, J., Liemisa, M., Chibesa, M., Pedley, S., 2015. Emerging contaminants in urban groundwater sources in Africa. Water Res. 72, 51–63. https://doi.org/10.1016/j.watres.2014.08.002
Spalding, R.F., Exner, M.E., 1993. Occurrence of Nitrate in Groundwater—A Review. J. Environ. Qual. 22, 392. https://doi.org/10.2134/jeq1993.00472425002200030002x
Spiliotopoulos, M., Holden, N.M., Loukas, A., 2017. Mapping evapotranspiration coefficients in a temperate maritime climate using the metric model and landsat TM. Water (Switzerland) 9. https://doi.org/10.3390/w9010023

Spreafico, M., Weingartner, R., 2005. The Hydrology of Switzerland - Selected aspects and results. Bern. https://doi.org/PNR61

Sridhar, V., Billah, M.M., Hildreth, J.W., 2014. Coupled Surface and Groundwater Hydrological Modeling in a Changing Climate. Groundwater. https://doi.org/10.1111/GWAT.12610

Srivastava, A., Sahoo, B., Raghuwanshi, N.S., Singh, R., 2017. Evaluation of variable-Infiltration capacity model and MODIS-Terra satellite-derived grid-scale evapotranspiration estimates in a river basin with tropical monsoon-type climatology. J. Irrig. Drain. Eng. 143. https://doi.org/10.1061/(ASCE)IR.1943-4774.0001199

Staudinger, M., Stoelzle, M., Cochand, F., Seibert, J., Weiler, M., Hunkeler, D., 2019. Your work is my boundary condition!: Challenges and approaches for a closer collaboration between hydrologists and hydrogeologists. J. Hydrol. 571, 235–243. https://doi.org/10.1016/j.jhydrol.2019.01.058

Staudinger, M., Stoelzle, M., Seeger, S., Seibert, J., Weiler, M., Stahl, K., 2017. Catchment water storage variation with elevation. Hydrol. Process. 31, 2000–2015. https://doi.org/10.1002/hyp.11158

Stefan, C., Ansems, N., 2017. Web-based global inventory of managed aquifer recharge applications. Sustain. Water Resour. Manag. 4, 153–162. https://doi.org/10.1007/s40899-017-0212-6

Stepien, D.K., Regnery, J., Merz, C., Püttmann, W., 2013. Behavior of organophosphates and hydrophilic ethers during bank filtration and their potential application as organic tracers. A field study from the Oderbruch, Germany. Sci. Total Environ. 458–460, 150–159. https://doi.org/10.1016/j.scitotenv.2013.04.020

Strauch, G., Moeder, M., Wennrich, R., Osenbrueck, K., Glaeser, H.-R., Schladitz, T., Mueller, C., Schirmer, K., Reinstorf, F., Schirmer, M., 2008. Indicators for assessing anthropogenic impact on urban surface and groundwater. J. Soils Sediments 8, 23–33. https://doi.org/10.1065/jss2007.06.234

Stroo, H.F., Unger, M., Ward, C.H., Kavanaugh, M.C., Vogel, C., Leeson, A., Marqusee, J.A., Smith, B.P., 2003. Peer Reviewed: Remediating Chlorinated Solvent Source Zones. Environ. Sci. Technol. 37, 224A-230A. https://doi.org/10.1021/es032488k

Stuart, M.E., Manamsa, K., Talbot, J.C., Crane, E.J., 2011. Emerging contaminants in groundwater. Br. Geol. Surv. Open Rep. OR/11/013, 111. https://doi.org/10.1089/109287503768335887

Sun, Q., Li, Y., Li, M., Ashfaq, M., Lv, M., Wang, H., Hu, A., Yu, C.P., 2016. PPCPs in Jiulong River estuary (China): Spatiotemporal distributions, fate, and their use as chemical markers of wastewater. Chemosphere 150, 596–604. https://doi.org/10.1016/j.chemosphere.2016.02.036

Sun, Q., Miao, C., Duan, Q., Ashouri, H., Sorooshian, S., Hsu, K.L., 2018. A Review of Global Precipitation Data Sets: Data Sources, Estimation, and Intercomparisons. Rev. Geophys. 56, 79–107. https://doi.org/10.1002/2017RG000574

Sutcliffe, J. V., Agrawal, R.P., Tucker, J.M., 1981. The water balance of the Betwa basin, India / Le bilan hydrologique du bassin versant de Betwa en Inde. Hydrol. Sci. Bull. 26, 149–158. https://doi.org/10.1080/02626668109490872

Taffahi, H., Bensouda, N., Alj, Y.S., 2013. Automated groundwater monitoring using telemetry. Proc. - Int. Conf. Intell. Syst. Model. Simulation, ISMS 596–600. https://doi.org/10.1109/ISMS.2013.50

Tang, C., Chen, J., Shindo, S., Sakura, Y., Zhang, W., Shen, Y., 2004. Assessment of groundwater contamination by nitrates associated with wastewater irrigation: A case study in Shijiazhuang region, China. Hydrol. Process. 18, 2303–2312. https://doi.org/10.1002/hyp.5531

Tang, Q., Gao, H., Yeh, P., Oki, T., Su, F., Lettenmaier, D.P., 2010. Dynamics of Terrestrial Water Storage Change from Satellite and Surface Observations and Modeling. J. Hydrometeorol. 11, 156–170. https://doi.org/10.1175/2009JHM1152.1

Tarboron, G., 1997. A new method for the determination of flow directions and upslope areas in grid digital elevation models. Water Resour. Res. 33, 309–319.

Taylor, R., 2014. When wells run dry. Nature 516, 179–180. https://doi.org/10.1038/516179a
Teijon, G., Candela, L., Tamoh, K., Molina-díaz, A., Fernández-alba, A.R., 2010. Occurrence of emerging contaminants , priority substances (2008 / 105 / CE) and heavy metals in treated wastewater and groundwater at Depurbaix facility (Barcelona , Spain). Sci. Total Environ. 408, 3584–3595. https://doi.org/10.1016/j.scitotenv.2010.04.041
Teuten, E.L., Saquing, J.M., Knappe, D.R.U., Barlaz, M.A., Jonsson, S., Bjorn, A., Rowland, S.J., Thompson, R.C., Galloway, T.S., Yamashita, R., Ochi, D., Watanuki, Y., Moore, C., Viet, P.H., Tana, T.S., Prudente, M., Boonyatumanond, R., Zakaria, M.P., Akkhavong, K., Ogata, Y., Hirai, H., Iwasa, S., Mizukawa, K., Hagino, Y., Imamura, A., Saha, M., Takada, H., 2009. Transport and release of chemicals from plastics to the environment and to wildlife. Philos. Trans. R. Soc. B Biol. Sci. 364, 2027–2045. https://doi.org/10.1098/rstb.2008.0284
The European Parlament and the Council of the European Union, 2000. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. Off. J. Eur. Parliam. L327, 1–82. https://doi.org/10.1039/ap9842100196
The World Bank, 2013. Turn Down the Heat: Climate Extremes, Regional Impacts, and the Case for Resilience. A Report of the World Bank by the Potsdam Institute for Climate Impact Research and Climate Analytics, The World Bank. Creative Commons Attribution—NonCommercial–NoDerivatives3.0 Unported license (CC BY-NC-ND 3.0), Washington DC.
Tilahun, K., Merkel, B.J., 2009. Estimation of groundwater recharge using a GIS-based distributed water balance model in Dire Dawa, Ethiopia. Hydrogeol. J. 17, 1443–1457. https://doi.org/10.1007/s10040-009-0455-x
Tucker, R.F., Viljoen, R.P., Viljoen, M.J., 2016. A Review of the Witwatersrand Basin - The World's Greatest Goldfield. J. Int. Geosience 39, 105. https://doi.org/10.18814/epiiugs/2016/v39i2/95771
Tufenkji, N., Ryan, J.N., Elimelech, M., 2002. The Promise of Bank Filtration. Environ. Sci. Technol. 36, 422A-428A. https://doi.org/10.1021/es022441j
Turnipseed, D.P., Sauer, V.B., 2010. Discharge measurements at gaging stations:U.S. Geological Survey Techniques and Methods book 3, chap. A8.
Tutu, H., McCarthy, T.S., Cukrowska, E., 2008. The chemical characteristics of acid mine drainage with particular reference to sources, distribution and remediation: The Witwatersrand Basin, South Africa as a case study. Appl. Geochemistry 23, 3666–3684. https://doi.org/10.1016/j.apgeochem.2008.09.002
Tweed, S.O., Leblanc, M., Webb, J.A., Lubczynski, M.W., 2007. Remote sensing and GIS for mapping groundwater recharge and discharge areas in salinity prone catchments, southeastern Australia. Hydrogeol. J. 15, 75–96. https://doi.org/10.1007/s10040-006-0129-x
UNDP United Nations Development programme, 2018. Sustainable Development Goal 6 Targets & Indicators [WWW Document]. URL http://www.undp.org/content/undp/en/home/sustainable-development-goals/goal-6-clean-water-and-sanitation/targets/
United Nations, 2007. World Urbanization Prospects The 2007 Revision Highlights. Desa ESA/P/WP/2, 883. https://doi.org/10.2307/2808041
United States Geological Survey, 2018. MODFLOW 6 – Description of Input and Output 200.
Valder, J.F., Long, A.J., Davis, A.D., Kenner, S.J., 2012. Multivariate statistical approach to estimate mixing proportions for unknown end members. J. Hydrol. 460–461, 65–76. https://doi.org/10.1016/j.jhydrol.2012.06.037
Van Liew, M.W., 2004. Impact of flood retarding structures on simulated streamflow for various sized watersheds under varying climatic conditions. IAHS-AISH Publ. 33–40.
Van Loon, A.F., Laaha, G., 2015. Hydrological drought severity explained by climate and catchment characteristics. J. Hydrol. 526, 3–14. https://doi.org/10.1016/j.jhydrol.2014.10.059
Velpuri, N.M., Senay, G.B., Singh, R.K., Bohms, S., Verdin, J.P., 2013. A comprehensive

evaluation of two MODIS evapotranspiration products over the conterminous United States: Using point and gridded FLUXNET and water balance ET. Remote Sens. Environ. 139, 35–49. https://doi.org/10.1016/j.rse.2013.07.013
Venter, Z.S., Cramer, M.D., Hawkins, H.-J., 2018. Drivers of woody plant encroachment over Africa. Nat. Commun. 9, 2272. https://doi.org/10.1038/s41467-018-04616-8
Verhoest, N., Hudson, J., Hoeben, R., De Troch, F., 2003. Monitoring and modelling catchment water quantity and quality. 8th Conf. Eur. Netw. Exp. Represent. Basins Ghent (Belgium), 27 – 29 Sept. 2000 2003, 1–111.
Viviroli, D., Dürr, H.H., Messerli, B., Meybeck, M., Weingartner, R., 2007. Mountains of the world, water towers for humanity: Typology, mapping, and global significance. Water Resour. Res. 43, 1–13. https://doi.org/10.1029/2006WR005653
Viviroli, D., Seibert, J., 2015. Can a regionalized model parameterisation be improved with a limited number of runoff measurements? J. Hydrol. 529, 49–61. https://doi.org/10.1016/j.jhydrol.2015.07.009
Viviroli, D., Zappa, M., Schwanbeck, J., Gurtz, J., Weingartner, R., 2009. Continuous simulation for flood estimation in ungauged mesoscale catchments of Switzerland – Part I: Modelling framework and calibration results. J. Hydrol. 377, 191–207. https://doi.org/10.1016/j.jhydrol.2009.08.023
Vogt, T., Hoehn Dr., E., Schneider Dr., P., Cirpka Dr., O.A., 2009. Untersuchung der flusswasserinfiltration in voralpinen schottern mittels zeitreihenanalyse. Grundwasser 14, 179–194. https://doi.org/10.1007/s00767-009-0108-y
Vogt, T., Schirmer, M., Cirpka, O. a., 2011. Heat transport of diurnal temperature oscillations upon river-water infiltration investigated by fiber-optic high-resolution temperature profiling. Hydrol. Earth Syst. Sci. Discuss. 8, 6257–6289. https://doi.org/10.5194/hessd-8-6257-2011
Voisin, J., Cournoyer, B., Vienney, A., Mermillod-Blondin, F., 2018. Aquifer recharge with stormwater runoff in urban areas: Influence of vadose zone thickness on nutrient and bacterial transfers from the surface of infiltration basins to groundwater. Sci. Total Environ. 637–638, 1496–1507. https://doi.org/10.1016/j.scitotenv.2018.05.094
Von Der Heyden, C.J., New, M.G., 2004. Groundwater pollution on the Zambian Copperbelt: Deciphering the source and the risk. Sci. Total Environ. 327, 17–30. https://doi.org/10.1016/j.scitotenv.2003.08.028
von Freyberg, J., Moeck, C., Schirmer, M., 2015. Estimation of groundwater recharge and drought severity with varying model complexity. J. Hydrol. 527, 844–857. https://doi.org/10.1016/j.jhydrol.2015.05.025
Vörösmarty, C.J., Green, P., Salisbury, J., Lammers, R.B., 2000. Global Water Resources: Vulnerability from Climate Change and Population Growth. Science (80-.). 289, 284–288. https://doi.org/10.1126/science.289.5477.284
Vulliet, E., Cren-Olivé, C., 2011. Screening of pharmaceuticals and hormones at the regional scale, in surface and groundwaters intended to human consumption. Environ. Pollut. 159, 2929–2934. https://doi.org/10.1016/j.envpol.2011.04.033
Wada, Y., Bierkens, M.F.P., 2014. Sustainability of global water use: past reconstruction and future projections. Environ. Res. Lett. 9, 104003. https://doi.org/10.1088/1748-9326/9/10/104003
Wada, Y., de Graaf, I.E.M., van Beek, L.P.H., 2016. High-resolution modeling of human and climate impacts on global water resources. J. Adv. Model. Earth Syst. 8, 735–763. https://doi.org/10.1002/2015MS000618
Wada, Y., Van Beek, L.P.H., Van Kempen, C.M., Reckman, J.W.T.M., Vasak, S., Bierkens, M.F.P., 2010. Global depletion of groundwater resources. Geophys. Res. Lett. 37, 1–5. https://doi.org/10.1029/2010GL044571
Wagener, T., Montanari, A., 2011. Convergence of approaches toward reducing uncertainty in predictions in ungauged basins. Water Resour. Res. 47, 1–8. https://doi.org/10.1029/2010WR009469
Wakida, F.T., Lerner, D.N., 2005. Non-agricultural sources of groundwater nitrate: A review and case study. Water Res. 39, 3–16. https://doi.org/10.1016/j.watres.2004.07.026

Walker, S.A., Azetsu-Scott, K., Normandeau, C., Kelley, D.E., Friedrich, R., Newton, R., Schlosser, P., Mckay, J.L., Abdi, W., Kerrigan, E., Craig, S.E., Wallace, D.W.R., 2016. Oxygen isotope measurements of seawater (H218O/H216O): A comparison of cavity ring-down spectroscopy (CRDS) and isotope ratio mass spectrometry (IRMS). Limnol. Oceanogr. Methods 14, 31–38. https://doi.org/10.1002/lom3.10067

Walsh, C., Fletcher, T., Bos, D., Imberger, S., 2015. Restoring a stream through retention of urban stormwater runoff : a catchment scale experiment in a social – ecological system. Freshw. Sci. 34, 1161–1168. https://doi.org/10.1086/682422.

Walsh, C.J., Roy, A.H., Feminella, J.W., Cottingham, P.D., Peter, M., Ii, R.P.M., Ii, R.A.P.M.O., 2005. The urban stream syndrome : current knowledge and the search for a cure The urban stream syndrome : current knowledge and 24, 706–723. https://doi.org/10.1899/04-028.1

Wang, L., Liu, H., 2006. An efficient method for identifying and filling surface depressions in digital elevation models for hydrologic analysis and modelling. Int. J. Geogr. Inf. Sci. 20, 193–213. https://doi.org/10.1080/13658810500433453

Wang, L., von Freyberg, J., van Meerveld, I., Seibert, J., Kirchner, J.W., 2019. What is the best time to take stream isotope samples for event-based model calibration? J. Hydrol. 577, 123950. https://doi.org/10.1016/j.jhydrol.2019.123950

Wang, X., Xie, H., 2018. A review on applications of remote sensing and geographic information systems (GIS) in water resources and flood risk management. Water (Switzerland) 10, 1–11. https://doi.org/10.3390/w10050608

Wang, Z., Zhang, X.H., Huang, Y., Wang, H., 2015. Comprehensive evaluation of pharmaceuticals and personal care products (PPCPs) in typical highly urbanized regions across China. Environ. Pollut. 204, 223–232. https://doi.org/10.1016/j.envpol.2015.04.021

WFD-CIS, 2016. Guidance Document No 34: Water balances, Common Implementation Strategy for the WFD - Guidance Documents. https://doi.org/10.2779/352735

Whipkey, R.Z., 1965. Subsurface stormflow from forested slopes. Int. Assoc. Sci. Hydrol. Bull. 10, 74–85. https://doi.org/10.1080/02626666509493392

Winsemius, H.C., Savenije, H.H.G., Bastiaanssen, W.G.M., 2008. Constraining model parameters on remotely sensed evaporation: justification for distribution in ungauged basins? Hydrol. Earth Syst. Sci. 12, 1403–1413. https://doi.org/10.5194/hessd-5-2293-2008

Winter, T.C., Rosenberry, D.O., 1995. The interaction of ground water with prairie pothole wetlands in the Cottonwood Lake area, east-central North Dakota, 1979–1990. Wetlands 15, 193–211. https://doi.org/10.1007/BF03160700

Wittmer, I.K., Bader, H.P., Scheidegger, R., Singer, H., Lück, A., Hanke, I., Carlsson, C., Stamm, C., 2010. Significance of urban and agricultural land use for biocide and pesticide dynamics in surface waters. Water Res. 44, 2850–2862. https://doi.org/10.1016/j.watres.2010.01.030

Wittmer, I.K., Scheidegger, R., Bader, H.P., Singer, H., Stamm, C., 2011. Loss rates of urban biocides can exceed those of agricultural pesticides. Sci. Total Environ. 409, 920–932. https://doi.org/10.1016/j.scitotenv.2010.11.031

Wolock, D.M., 2003. Estimated mean annual natural ground-water recharge in the conterminous United States [WWW Document]. U.S. Geol. Surv. Open-File Rep. 03–311.

World Bank, 2018. World Bank Annual Report 2018. Washington, DC. https://doi.org/10.1596/978- 1-4648-1296-5

Wu, Y., Hunkeler, D., 2013. Hyporheic exchange in a karst conduit and sediment system – A laboratory analog study. J. Hydrol. 501, 125–132. https://doi.org/10.1016/j.jhydrol.2013.07.040

WWAP, 2017. The United Nations World Water Development Report 2017. Wastewater: The Untapped Resource. Paris.

WWAP, 2013. UN - Water Annual Report 2013, United Nations. Paris. https://doi.org/10.2307/3395557

Xu, C.Y., Chen, D., 2005. Comparison of seven models for estimation of evapotranspiration and groundwater recharge using lysimeter measurement data in Germany. Hydrol. Process. 19, 3717–3734. https://doi.org/10.1002/hyp.5853

Xu, Y., Beekman, H.E., 2018. Review: Groundwater recharge estimation in arid and semi-arid southern Africa. Hydrogeol. J. 27, 929–943. https://doi.org/10.1007/s10040-018-1898-8

Xu, Z., Massei, N., Padilla, I., Hartmann, A., Hu, B., 2018. Correction to: Characterization, modeling, and remediation of karst in a changing environment (Environmental Earth Sciences, (2018), 77, 12, (476), 10.1007/s12665-018-7660-7). Environ. Earth Sci. 77, 1–6. https://doi.org/10.1007/s12665-018-7733-7

Yu, X., Ghasemizadeh, R., Padilla, I., Irizarry, C., Kaeli, D., Alshawabkeh, A., 2015. Spatiotemporal changes of CVOC concentrations in karst aquifers: Analysis of three decades of data from Puerto Rico. Sci. Total Environ. 511, 1–10. https://doi.org/10.1016/j.scitotenv.2014.12.031

Yuan, Q., Snow, D.D., Bartelt-Hunt, S.L., 2013. Potential water quality impacts originating from land burial of cattle carcasses. Sci. Total Environ. 456–457, 246–253. https://doi.org/10.1016/j.scitotenv.2013.03.083

Zappa, M., Liechti, K., Deller, M., Barben, M., Wasser-, K., 2017. Wasserhaushalt der Schweiz 2.0 203–212.

Zappa, M., Pos, F., Strasser, U., Warmerdam, P., Gurtz, J., 2003. Seasonal water balance of an Alpine Catchment as Evaluated by different methods for spatially distributed snowmelt modelling. Nord. Hydrol. https://doi.org/10.2166/nh.2003.0003

Zhang, J., Ding, Z., Yuan, W., Zuo, Q., 2013. Research on the relationship between rainfall and reference crop evapotranspiration with multi-time scales. Paddy Water Environ. 11, 473–482. https://doi.org/10.1007/s10333-012-0338-y

Zhang, K., Kimball, J.S., Running, S.W., 2016. A review of remote sensing based actual evapotranspiration estimation. Wiley Interdiscip. Rev. Water 3, 834–853. https://doi.org/10.1002/wat2.1168

Zhang, Y.Q., Chiew, F.H.S., Zhang, L., Leuning, R., Cleugh, H.A., 2008. Estimating catchment evaporation and runoff using MODIS leaf area index and the Penman-Monteith equation. Water Resour. Res. 44, 1–15. https://doi.org/10.1029/2007WR006563

Zhang, Y.Q., Viney, N.R., Chiew, F.H.S., Van Dijk, A.I.J.M., Liu, Y.Y., 2011. Improving hydrological and vegetation modelling using regional model calibration schemes together with remote sensing data 12–16.

Zhao, K., Wulder, M.A., Hu, T., Bright, R., Wu, Q., Qin, H., Li, Y., Toman, E., Mallick, B., Zhang, X., Brown, M., 2019. Detecting change-point, trend, and seasonality in satellite time series data to track abrupt changes and nonlinear dynamics: A Bayesian ensemble algorithm. Remote Sens. Environ. 232, 111181. https://doi.org/10.1016/j.rse.2019.04.034

Zhao, X., Liu, Y., 2014. Relative Contribution of the Topographic Influence on the Triangle Approach for Evapotranspiration Estimation over Mountainous Areas. Adv. Meteorol. 2014, 1–16. https://doi.org/10.1155/2014/584040

Zomlot, Z., Verbeiren, B., Huysmans, M., Batelaan, O., 2015. Spatial distribution of groundwater recharge and base flow: Assessment of controlling factors. J. Hydrol. Reg. Stud. 4, 349–368. https://doi.org/10.1016/j.ejrh.2015.07.005

Web References

Contributed R Packages. Accessed 02.04.2021, 10:15 https://cran.r-project.org/web/packages

FAO. FAOSTAT. Land Use Classification. Latest update: 09/01/2019. Accessed: 24/04/2019 http://www.fao.org/3/y4252e/y4252e06.htm.

FOEN. Unweltindikator-Trinkwasserverbrauch. Accessed 07.03.2021. https://www.bfs.admin.ch/bfs/de/home/statistiken/raum-umwelt/umweltindikatoren/alle-

indikatoren/nutzung-natuerliche-ressourcen/trinkwasserverbrauch.html
FOEN. ISOT module. Accessed: 14.11.2020. https://www.bafu.admin.ch/bafu/en/home/topics/water/info-specialists/state-of-waterbodies/state-of-groundwater/naqua-national-groundwater-monitoring/isot-module.html
Office for the Environment, Canton St. Gallen. Accessed 15.04.2021, 11:49. https://www.sg.ch/umwelt-natur/wasser/grundwasser---quellen-/grundwassernutzung/trinkwassernutzung.html
Office for the Environment, Thurgau. Accessed 11.08.2020, 14:30. https://umwelt.tg.ch/wasser/wassernutzungen/zahlen-und-fakten.html/2158,
Web-based Hydrograph Analysis Tool. Accessed 28.11.2020. https://engineering.purdue.edu/mapserve/WHAT/
WHO & UNICEF. 2017. World File. Accessed 14/01/2019. https://washdata.org/data/household#!/

Appendix I: Supplementary Information to Chapter 3

Proportion of baseflow (Q_b) to total streamflow (Q)

In order to predict the three months (October - December of 2019) of missing discharge data from the Halden discharge station, a linear regression model was used: m = lm(Q ~ DateTime, data = Halden).

Table S 1: Average seasonal ratio of baseflow (Q_b) to total stream flow (Q) for the Thur catchment (An) and its sub-catchments for the 20-year period, in increasing order of elevation

Sub-catchment	Winter	Spring	Summer	Autumn	Elevation (m) at discharge station
Andelfingen (An)	0.49	0.53	0.42	0.44	363
Frauenfeld (Fr)	0.54	0.57	0.53	0.56	394
Halden (Ha)	0.46	0.50	0.39	0.42	461
Waengi (Wae)	0.53	0.54	0.52	0.55	470
Jonschwil (Jon)	0.42	0.49	0.39	0.38	534
St. Gallen (Stg)	0.41	0.43	0.32	0.36	582
Mogelsberg (Mog)	0.42	0.41	0.31	0.37	610
Mosnang (Mos)	0.39	0.39	0.34	0.37	670
Herisau (He)	0.49	0.47	0.39	0.47	680
Appenzell (Ap)	0.44	0.47	0.36	0.37	772

A ratio of Q_b to total stream flow (Q) was determined after the Institute of Hydrology (1980).

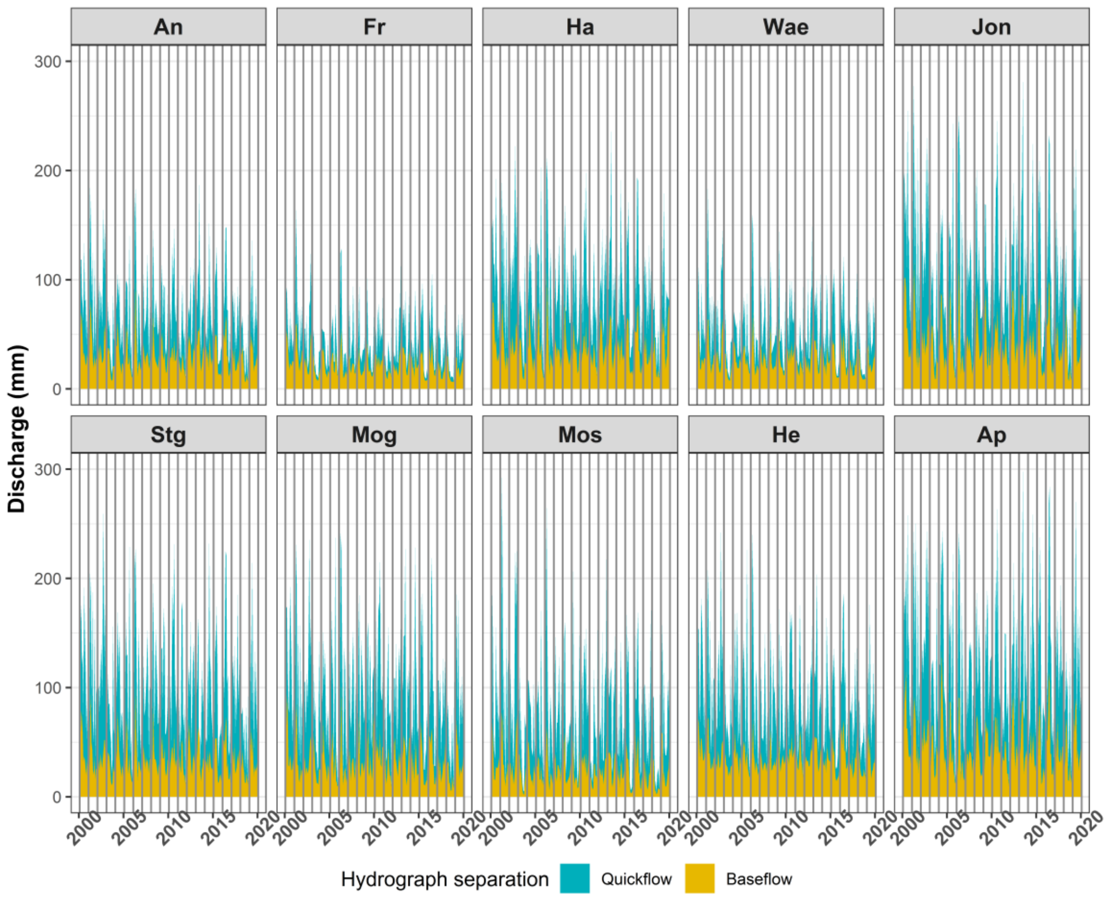


Figure S 1: Proportion of baseflow (Q_b) to quickflow (Q_q) for the Thur catchment (An) and its sub-catchments listed from left to right in increasing order of elevation.

Baseflow separation method comparison

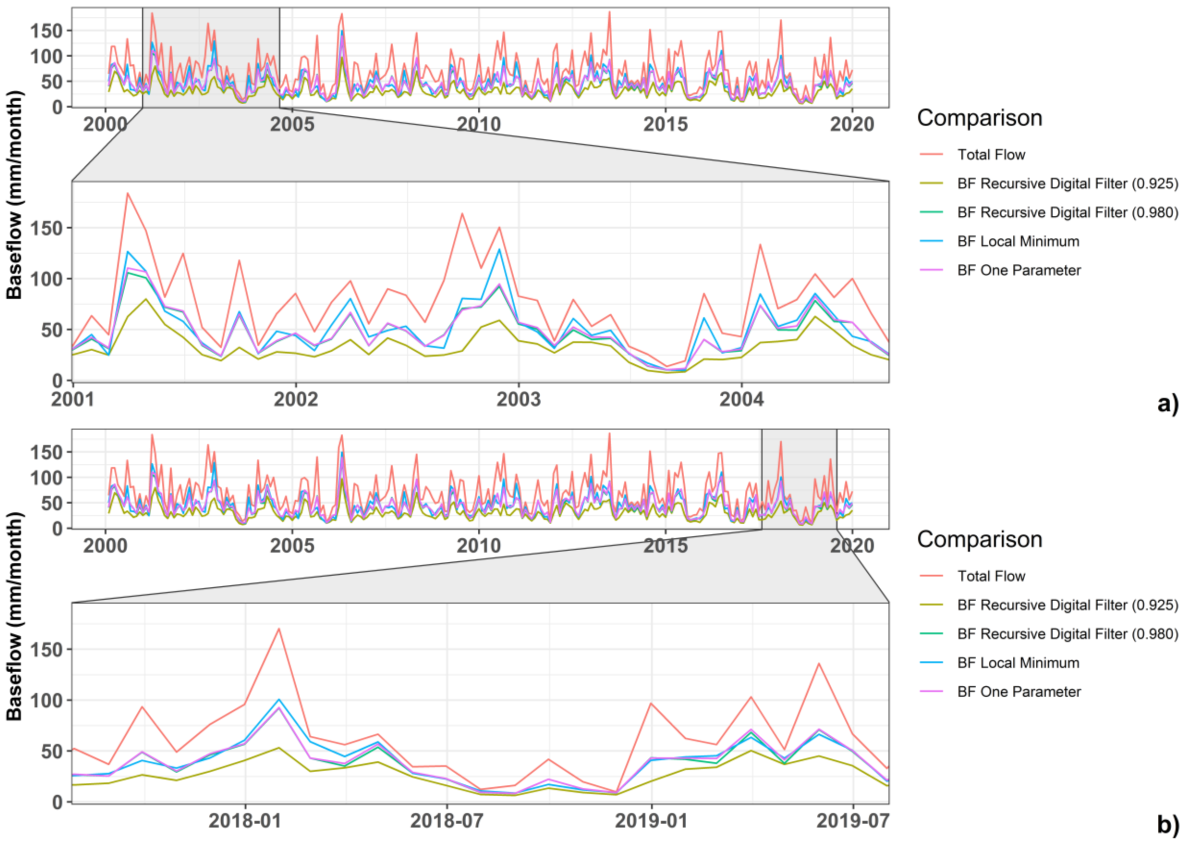


Figure S 2: Comparison of baseflow (BF) separation in the Thur River determined using the recursive digital filter set to 0.925 from the EcoHydRology package, and recursive digital filter set to 0.980, local minimum, and one parameter from the WHAT Tool (https://engineering.purdue.edu/mapserve/WHAT/) enlarged for a) wet years 2001 - 2002, followed by drought in 2003, and b) drought of 2018.

Gridded quickflow weigh ranking method comparison

A comparison of gridded discharge values based on a topographically-based top-down flow accumulation (FA) algorithm generated using SAGA GIS (Conrad et al., 2015) was conducted using the normalized FA (blue) versus the inverted (after the study of de Lavenne et al., 2019) normalized FA (red) as a weighting factor (Figure S 3).

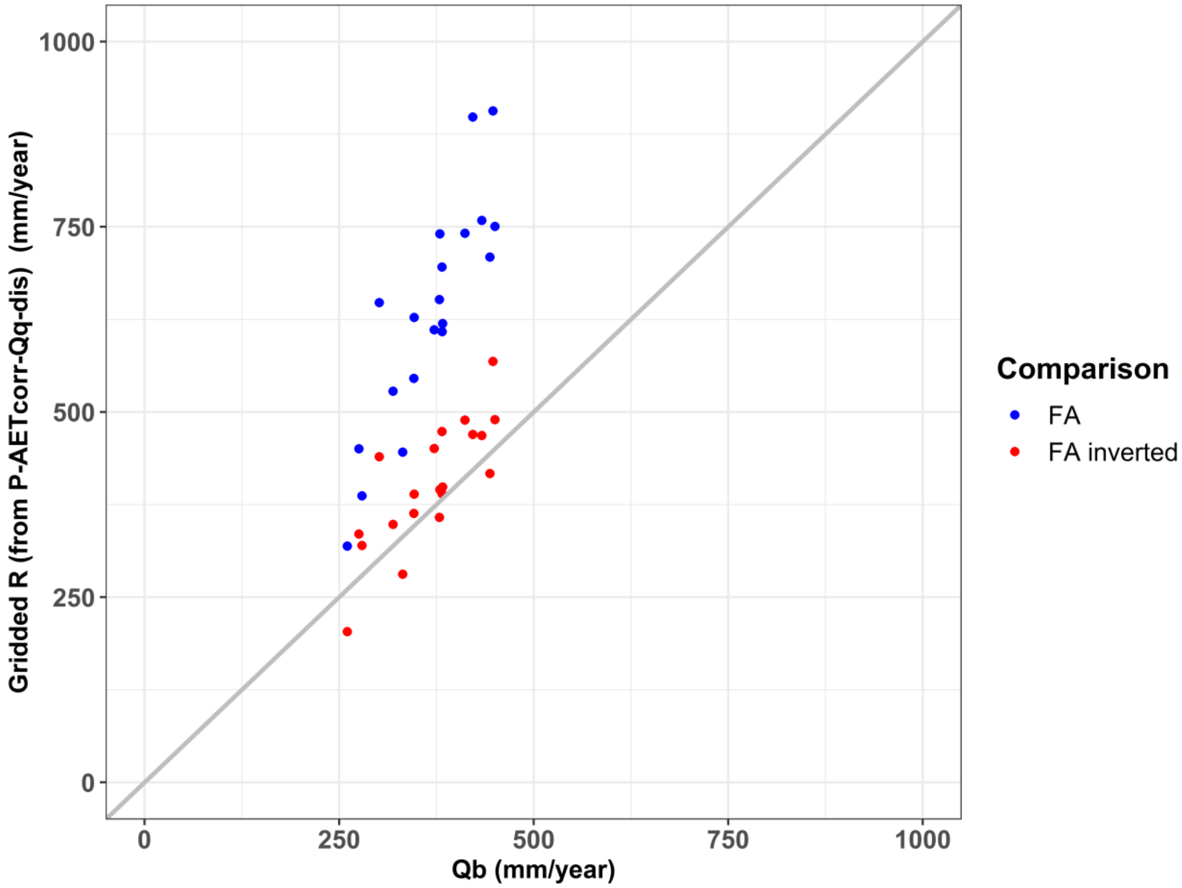


Figure S 3: Comparison of gridded discharge values weighted based on a normalized topographically based flow accumulation (FA) and an inverted normalized FA algorithm.

Water budget closure in the Thur catchment

When compared to total P values, the total water budget (sum of AET_{corr}, $Q_{q\text{-}dis}$ and R) of the Thur catchment and its sub-catchments all display a slight overestimation (Figure S 4), with total error ranging from 0.88% in the low elevation Fr sub-catchment, to 3.13% in the high elevation sub-catchment Ap (Figure S 4).

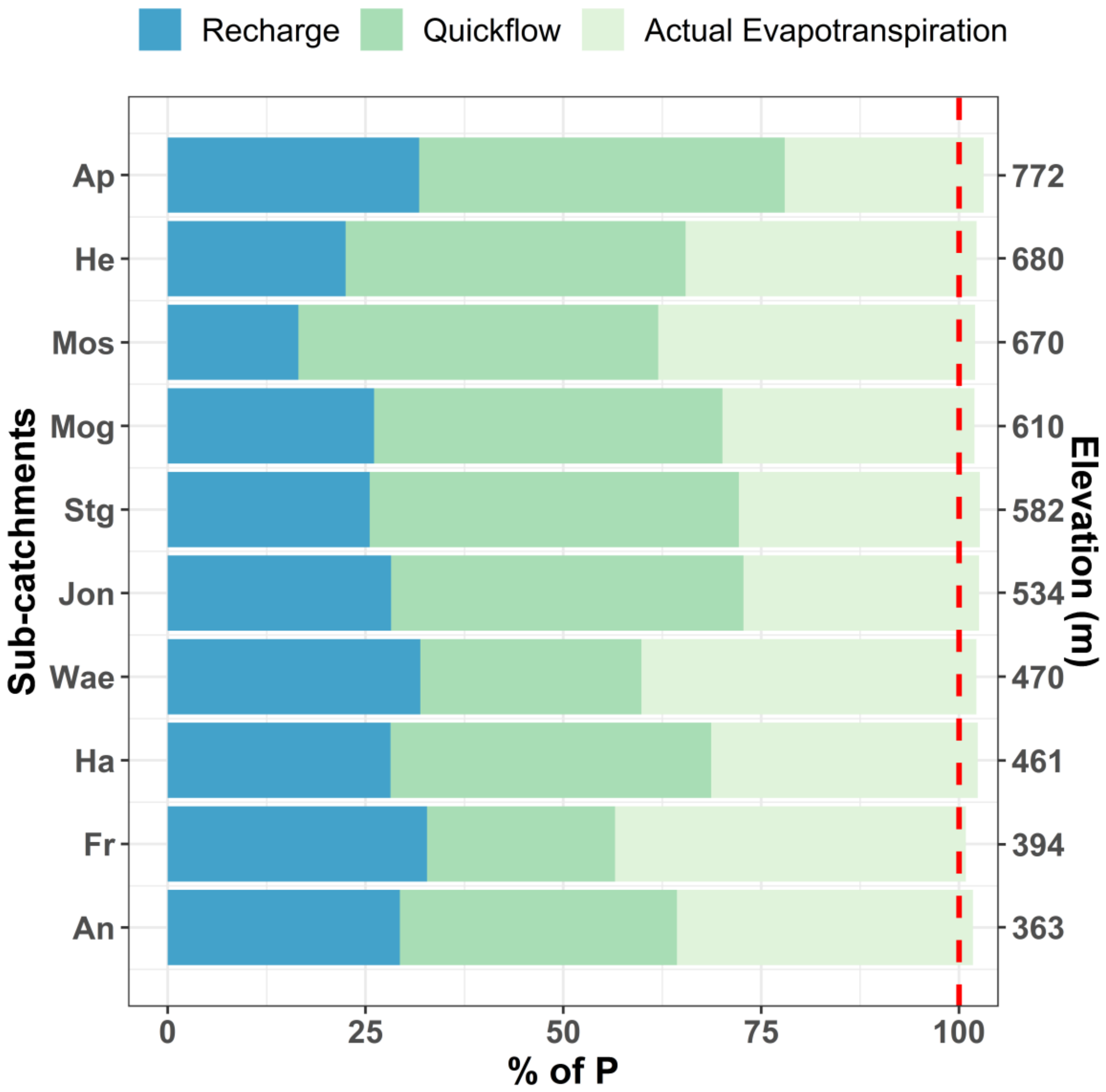


Figure S 4: Average annual groundwater recharge (R), quickflow ($Q_{q\text{-}dis}$), and actual evapotranspiration (AET_{corr}) in the Thur's sub-catchments as percentage (%) of precipitation (P), with An representing the entire Thur catchment.

Table S 2: Mean values of AET_{corr}, $Q_{q\text{-}dis}$, Q_b, and R as a percentage of mean P for the Thur (An) and its sub-catchments

Sub-catchments	Mean AET_{corr}	Mean $Q_{q\text{-}dis}$	Mean Q_b	Mean R	Mean P	AET_{corr} as % P	$Q_{q\text{-}dis}$ as % P	Q_b as % P	R as % P	% of total error
An	512.91	479.79	367.40	402.28	1370.82	37.42	35.00	26.80	29.35	1.77
Ap	468.25	860.11	520.58	591.68	1861.75	25.15	46.20	27.96	31.78	3.13
Fr	522.74	280.06	277.39	386.12	1178.53	44.36	23.76	23.54	32.76	0.88
Ha	527.02	633.62	428.60	440.25	1563.81	33.70	40.52	27.41	28.15	2.37
He	544.02	635.76	425.23	332.71	1479.65	36.77	42.97	28.74	22.49	2.23
Jon	517.08	773.50	489.30	490.33	1736.84	29.77	44.53	28.17	28.23	2.53
Mog	542.51	749.25	386.17	444.01	1702.37	31.87	44.01	22.68	26.08	1.96
Mos	591.84	672.26	322.07	244.33	1478.43	40.03	45.47	21.78	16.53	2.03
Stg	514.61	788.02	405.53	431.10	1689.10	30.47	46.65	24.01	25.52	2.64
Wae	548.13	361.99	332.24	413.54	1295.23	42.32	27.95	25.65	31.93	2.2

Appendix II: Supplementary Information to Chapter 4

Environmental tracer data

Table S 3: δ^2H and $\delta^{18}O$ values for the snow, groundwater, and event sampled surface water sites from the Thur catchment for the years 2017-2020

Date	Month	Site	Temp	Altitude	Source	δ^2H	$\delta^{18}O$	d-excess	Location	Sample type
26.02.2019	2	TGG08		416	Groundwater	-75	-10.7	10.8	Thur	Groundwater
26.02.2019	2	TGG09	8.4	449	Groundwater	-77	-11.1	12.0	Thur	Groundwater
26.02.2019	2	TGG11	9.7	381	Groundwater	-75	-10.7	10.4	Thur	Groundwater
26.02.2019	2	TGG12	11.1	522	Groundwater	-75	-10.6	10.2	Murg	Groundwater
26.02.2019	2	TGG13	11.7	429	Groundwater	-75	-10.9	12.3	Thur	Groundwater
29.04.2019	4	GW0025		560	Groundwater	-75	-10.6	9.3	Thur	Groundwater
29.04.2019	4	GW0049		630	Groundwater	-75	-11.0	12.9	Necker	Groundwater
29.04.2019	4	GW0050		582	Groundwater	-75	-10.7	10.7	Thur	Groundwater
12.11.2018	4	GW0074		661	Groundwater	-77	-11.0	11.2	Necker	Groundwater
06.05.2019	5	GW0028		560	Groundwater	-76	-10.6	9.3	Thur	Groundwater
16.05.2019	5	GW0045		896	Groundwater	-83	-12.1	13.1	Thur	Groundwater
16.05.2019	5	GW0047		627	Groundwater	-80	-11.6	12.9	Thur	Groundwater
08.05.2019	5	GW0053		476	Groundwater	-75	-10.7	10.0	Thur	Groundwater
15.05.2019	5	GW0054		507	Groundwater	-75	-10.8	10.8	Thur	Groundwater
21.05.2019	5	GW0055		645	Groundwater	-77	-11.0	11.0	Sitter	Groundwater
28.05.2018	5	TGG09	10.2	449	Groundwater	-82	-11.7	11.6	Thur	Groundwater
13.05.2019	5	TGG09	8.7	449	Groundwater	-79	-11.2	10.1	Thur	Groundwater
29.05.2018	5	TGG11	9.8	381	Groundwater	-81	-11.5	10.6	Thur	Groundwater
14.05.2019	5	TGG11	9.2	381	Groundwater	-79	-10.8	7.0	Thur	Groundwater
15.05.2019	5	TGG12	11.2	522	Groundwater	-76	-10.3	6.8	Murg	Groundwater
30.05.2018	5	TGG13	11.2	429	Groundwater	-75	-10.6	9.8	Thur	Groundwater
15.05.2019	5	TGG13	11.5	429	Groundwater	-76	-10.4	6.7	Thur	Groundwater
23.06.2020	6	GW11	15.3	392	Groundwater	-73	-10.6	12.0	Thur	Groundwater
30.10.2019	6	GW11	16.5	392	Groundwater	-73	-10.0	6.6	Thur	Groundwater
26.06.2019	6	GW12		399	Groundwater	-73	-10.2	8.7	Thur	Groundwater
22.06.2020	6	GW15	13.1	420	Groundwater	-73	-10.5	10.9	Thur	Groundwater
22.06.2020	6	GW19	11.7	437	Groundwater	-71	-10.1	9.4	Thur	Groundwater
03.06.2019	6	GW23		422	Groundwater	-78	-10.7	7.7	Thur	Groundwater
22.06.2020	6	GW23	11.5	422	Groundwater	-73	-10.6	11.2	Thur	Groundwater

23.06.2020	6	GW5	14.1	390	Groundwater	-74	-10.7	10.8	Thur	Groundwater
23.06.2020	6	GW6	14.6	392	Groundwater	-71	-10.1	9.8	Thur	Groundwater
23.06.2020	6	GW7	12.4	389	Groundwater	-73	-10.5	10.6	Thur	Groundwater
23.06.2020	6	GW8	12	392	Groundwater	-75	-10.6	10.0	Thur	Groundwater
03.06.2019	6	TGG08		416	Groundwater	-76	-10.6	9.3	Thur	Groundwater
08.06.2020	6	TGG09		449	Groundwater	-73	-10.6	12.3	Thur	Groundwater
09.06.2020	6	TGG11	10.7	381	Groundwater	-73	-10.6	12.1	Thur	Groundwater
10.06.2020	6	TGG12	11.3	522	Groundwater	-72	-10.3	10.5	Murg	Groundwater
10.06.2020	6	TGG13	11.7	429	Groundwater	-73	-10.7	12.8	Thur	Groundwater
11.07.2018	7	GW11	17.9	392	Groundwater	-75	-10.6	10.5	Thur	Groundwater
11.07.2017	7	GW11	16.97	392	Groundwater	-76	-10.6	9.0	Thur	Groundwater
11.07.2017	7	GW12	16.37	399	Groundwater	-75	-10.6	9.0	Thur	Groundwater
11.07.2018	7	GW12	18.2	399	Groundwater	-74	-10.6	10.3	Thur	Groundwater
11.07.2018	7	GW15	12.3	420	Groundwater	-79	-11.2	10.8	Thur	Groundwater
11.07.2017	7	GW15	11.84	420	Groundwater	-77	-10.8	9.6	Thur	Groundwater
11.07.2019	7	GW15	11.4	420	Groundwater	-75	-10.6	9.4	Thur	Groundwater
11.07.2018	7	GW19	11.6	437	Groundwater	-76	-10.8	9.8	Thur	Groundwater
10.07.2017	7	GW19	11.02	437	Groundwater	-76	-10.5	8.0	Thur	Groundwater
11.07.2017	7	GW23	7.43	422	Groundwater	-78	-10.9	9.5	Thur	Groundwater
09.07.2018	7	GW5	17.2	390	Groundwater	-76	-10.8	10.3	Thur	Groundwater
10.07.2017	7	GW5	14.49	390	Groundwater	-76	-10.6	9.1	Thur	Groundwater
11.07.2017	7	GW6	18.47	392	Groundwater	-76	-10.7	9.6	Thur	Groundwater
09.07.2018	7	GW6	17.7	392	Groundwater	-74	-10.6	10.3	Thur	Groundwater
09.07.2018	7	GW7	11.5	389	Groundwater	-75	-10.6	9.9	Thur	Groundwater
10.07.2017	7	GW7	11.74	389	Groundwater	-76	-10.5	8.4	Thur	Groundwater
10.07.2017	7	GW8	11.54	392	Groundwater	-74	-10.2	7.6	Thur	Groundwater
06.07.2020	7	TGG08		416	Groundwater	-72	-10.5	11.9	Thur	Groundwater
30.08.2018	8	TGG08		416	Groundwater	-80	-11.4	11.6	Thur	Groundwater
28.08.2017	8	TGG08		416	Groundwater	-79	-11.1	9.8	Thur	Groundwater
28.08.2017	8	TGG09		449	Groundwater	-71	-10.2	10.3	Thur	Groundwater
28.08.2018	8	TGG09	19.2	449	Groundwater	-69	-9.8	9.2	Thur	Groundwater
20.08.2019	8	TGG09	16.7	449	Groundwater	-69	-9.5	7.5	Thur	Groundwater
28.08.2017	8	TGG11		381	Groundwater	-71	-10.1	9.4	Thur	Groundwater
29.08.2018	8	TGG11	16.2	381	Groundwater	-72	-10.1	8.7	Thur	Groundwater
20.08.2019	8	TGG11	14.4	381	Groundwater	-70	-10.0	9.9	Thur	Groundwater
28.08.2018	8	TGG12	11.6	522	Groundwater	-75	-10.7	9.9	Murg	Groundwater
28.08.2017	8	TGG12		522	Groundwater	-75	-10.6	9.1	Murg	Groundwater

20.08.2019	8	TGG12	11.6	522	Groundwater	-74	-10.5	10.0	Murg	Groundwater
28.08.2018	8	TGG13	16.5	429	Groundwater	-80	-11.3	10.6	Thur	Groundwater
28.08.2017	8	TGG13		429	Groundwater	-78	-11.0	9.6	Thur	Groundwater
21.08.2019	8	TGG13		429	Groundwater	-77	-10.5	6.7	Thur	Groundwater
02.09.2019	9	TGG08		416	Groundwater	-77	-10.6	8.0	Thur	Groundwater
30.10.2018	10	GW11	15.7	392	Groundwater	-75	-10.6	10.1	Thur	Groundwater
31.10.2017	10	GW11	12.57	392	Groundwater	-71	-10.2	10.5	Thur	Groundwater
26.06.2019	10	GW11	13	392	Groundwater	-70	-10.0	10.0	Thur	Groundwater
30.10.2018	10	GW12	15.3	399	Groundwater	-75	-10.6	9.6	Thur	Groundwater
31.10.2017	10	GW12	12.44	399	Groundwater	-71	-10.2	10.6	Thur	Groundwater
30.10.2019	10	GW12	12.9	399	Groundwater	-70	-9.9	9.5	Murg	Groundwater
30.10.2018	10	GW15	12	420	Groundwater	-78	-11.0	10.4	Thur	Groundwater
30.10.2017	10	GW15	11.37	420	Groundwater	-77	-10.8	9.1	Thur	Groundwater
30.10.2019	10	GW15	12.3	420	Groundwater	-75	-10.6	9.9	Thur	Groundwater
30.10.2018	10	GW19	13.3	437	Groundwater	-74	-10.4	9.3	Thur	Groundwater
30.10.2017	10	GW19	11.96	437	Groundwater	-73	-10.3	9.2	Thur	Groundwater
30.10.2019	10	GW19	12.5	437	Groundwater	-69	-9.8	9.2	Thur	Groundwater
29.10.2018	10	GW23	12.3	422	Groundwater	-76	-10.9	11.3	Thur	Groundwater
30.10.2017	10	GW23	11.31	422	Groundwater	-75	-10.5	9.2	Thur	Groundwater
30.10.2019	10	GW23	12.2	422	Groundwater	-73	-10.5	10.8	Thur	Groundwater
30.10.2017	10	GW5	14.09	390	Groundwater	-73	-10.3	9.6	Thur	Groundwater
31.10.2018	10	GW5	17.4	390	Groundwater	-71	-10.2	10.5	Thur	Groundwater
29.10.2019	10	GW5	15.2	390	Groundwater	-67	-9.6	9.4	Thur	Groundwater
31.10.2017	10	GW6	13.16	392	Groundwater	-72	-10.3	10.4	Thur	Groundwater
29.10.2019	10	GW6	13.4	392	Groundwater	-70	-9.9	9.9	Thur	Groundwater
31.10.2017	10	GW7	13.85	389	Groundwater	-76	-10.7	8.8	Thur	Groundwater
29.10.2019	10	GW7	12.8	389	Groundwater	-76	-10.6	9.5	Thur	Groundwater
29.10.2019	10	GW8	12	392	Groundwater	-75	-10.4	8.4	Thur	Groundwater
31.10.2017	10	GW8	12.5	392	Groundwater	-74	-10.3	7.9	Thur	Groundwater
30.10.2018	10	TGG08		416	Groundwater	-77	-10.9	10.3	Thur	Groundwater
01.10.2017	10	TGG08		416	Groundwater	-75	-10.6	9.8	Thur	Groundwater
02.10.2017	10	TGG09		449	Groundwater	-75	-10.5	9.2	Thur	Groundwater
03.10.2017	10	TGG11		381	Groundwater	-73	-10.3	9.5	Thur	Groundwater
04.10.2017	10	TGG13		429	Groundwater	-74	-10.4	8.7	Thur	Groundwater
08.11.2018	11	GW0025		560	Groundwater	-76	-10.5	8.5	Thur	Groundwater
05.11.2018	11	GW0028		560	Groundwater	-75	-10.5	8.9	Thur	Groundwater
15.11.2018	11	GW0045		896	Groundwater	-82	-11.9	13.1	Thur	Groundwater

15.11.2018	11	GW0047		626.8	Groundwater	-77	-11.2	12.1	Thur	Groundwater
12.11.2018	11	GW0049		630	Groundwater	-74	-10.7	11.6	Necker	Groundwater
08.11.2018	11	GW0050		582	Groundwater	-75	-10.6	10.0	Thur	Groundwater
05.11.2018	11	GW0053		476	Groundwater	-73	-10.4	10.7	Thur	Groundwater
12.11.2018	11	GW0054		507	Groundwater	-74	-10.5	9.5	Thur	Groundwater
14.11.2018	11	GW0055		645	Groundwater	-72	-10.2	9.1	Sitter	Groundwater
29.04.2019	11	GW0074		661	Groundwater	-75	-10.9	11.4	Necker	Groundwater
04.11.2019	11	TGG08		416	Groundwater	-72	-10.1	9.0	Thur	Groundwater
26.11.2018	11	TGG09	14.1	449	Groundwater	-75	-10.8	10.9	Thur	Groundwater
27.11.2019	11	TGG09	13.1	449	Groundwater	-71	-10.2	10.3	Thur	Groundwater
27.11.2018	11	TGG11	15.6	381	Groundwater	-74	-10.5	10.3	Thur	Groundwater
27.11.2019	11	TGG11	14.5	381	Groundwater	-69	-9.7	9.0	Thur	Groundwater
28.11.2018	11	TGG12	11.4	522	Groundwater	-74	-10.3	8.7	Murg	Groundwater
27.11.2019	11	TGG12	11.6	522	Groundwater	-72	-10.0	8.3	Murg	Groundwater
26.11.2018	11	TGG13	11.5	429	Groundwater	-75	-10.7	10.7	Thur	Groundwater
27.11.2019	11	TGG13	11.8	429	Groundwater	-72	-10.3	10.1	Thur	Groundwater
02.12.2019	12	TGG08		416	Groundwater	-71	-10.1	10.0	Thur	Groundwater
22.05.2019	5	Thur_02	10	378	Surface	-79	-11.5	12.6	Thur	HighFlow
22.05.2019	5	Thur_03	9.5	402	Surface	-81	-11.7	13.0	Thur	HighFlow
22.05.2019	5	Thur_04	9.8	436	Surface	-81	-11.8	13.2	Thur	HighFlow
22.05.2019	5	Thur_05	9.2	487	Surface	-81	-11.8	12.8	Thur	HighFlow
22.05.2019	5	Thur_07	8.7	477	Surface	-81	-11.8	13.1	Thur	HighFlow
22.05.2019	5	Thur_08	8.2	543	Surface	-82	-12.0	13.9	Thur	HighFlow
22.05.2019	5	Thur_09	6.8	753	Surface	-86	-12.5	14.0	Thur	HighFlow
22.05.2019	5	Thur_10	5.6	1032	Surface	-90	-13.1	15.4	Thur	HighFlow
13.06.2018	6	Thur_02	14.4	378	Surface	-71	-10.3	10.9	Thur	HighFlow
13.06.2018	6	Thur_03	14.5	402	Surface	-72	-10.3	10.6	Thur	HighFlow
13.06.2018	6	Thur_04	13.9	436	Surface	-71	-10.2	10.6	Thur	HighFlow
13.06.2018	6	Thur_05	13.7	487	Surface	-71	-10.3	11.3	Thur	HighFlow
13.06.2018	6	Thur_07	13.8	477	Surface	-70	-10.1	10.7	Thur	HighFlow
13.06.2018	6	Thur_08	12.5	543	Surface	-71	-10.3	11.2	Thur	HighFlow
13.06.2018	6	Thur_09	11.5	753	Surface	-79	-11.4	12.5	Thur	HighFlow
13.06.2018	6	Thur_10	7.3	1032	Surface	-82	-11.9	13.2	Thur	HighFlow
06.02.2020	2	Thur_02		378	Surface	-83	-11.8	11.3	Thur	LowFlow
06.02.2020	2	Thur_03		402	Surface	-80	-11.1	9.5	Thur	LowFlow
06.02.2020	2	Thur_04		436	Surface	-75	-10.6	9.5	Thur	LowFlow
06.02.2020	2	Thur_05		487	Surface	-74	-10.6	10.6	Thur	LowFlow

06.02.2020	2	Thur_07		477	Surface	-74	-10.5	10.4	Thur	LowFlow
06.02.2020	2	Thur_08		543	Surface	-73	-10.3	9.2	Thur	LowFlow
06.02.2020	2	Thur_09		753	Surface	-73	-10.3	9.8	Thur	LowFlow
06.02.2020	2	Thur_10		1032	Surface	-72	-10.3	10.3	Thur	LowFlow
31.07.2018	7	Thur_02	28.9	378	Surface	-72	-10.1	8.5	Thur	LowFlow
22.07.2019	7	Thur_02	26	378	Surface	-72	-10.0	8.2	Thur	LowFlow
31.07.2018	7	Thur_03	24.5	402	Surface	-73	-10.3	8.7	Thur	LowFlow
22.07.2019	7	Thur_03	20.8	402	Surface	-74	-10.2	7.6	Thur	LowFlow
31.07.2018	7	Thur_04	27.8	436	Surface	-72	-10.0	8.0	Thur	LowFlow
22.07.2019	7	Thur_04	25.8	436	Surface	-71	-9.5	5.3	Thur	LowFlow
31.07.2018	7	Thur_05	27.1	487	Surface	-73	-10.1	8.1	Thur	LowFlow
22.07.2019	7	Thur_05	23.6	487	Surface	-71	-9.9	8.5	Thur	LowFlow
31.07.2018	7	Thur_07	27.6	477	Surface	-73	-10.3	8.6	Thur	LowFlow
22.07.2019	7	Thur_07	21.4	477	Surface	-72	-10.0	7.1	Thur	LowFlow
31.07.2018	7	Thur_08	22.6	543	Surface	-77	-10.8	10.0	Thur	LowFlow
22.07.2019	7	Thur_08	19.5	543	Surface	-74	-10.4	9.5	Thur	LowFlow
31.07.2018	7	Thur_09	16.7	753	Surface	-83	-12.0	12.8	Thur	LowFlow
22.07.2019	7	Thur_09	11.1	753	Surface	-78	-11.0	10.0	Thur	LowFlow
31.07.2018	7	Thur_10	10.8	1032	Surface	-83	-12.1	13.6	Thur	LowFlow
22.07.2019	7	Thur_10	8	1032	Surface	-77	-11.0	10.4	Thur	LowFlow
14.11.2019	11	Thur_02		378	Surface	-70	-10.2	12.2	Thur	LowFlow
14.11.2019	11	Thur_03		402	Surface	-70	-10.3	12.5	Thur	LowFlow
14.11.2019	11	Thur_04		436	Surface	-70	-10.2	11.2	Thur	LowFlow
14.11.2019	11	Thur_05		487	Surface	-70	-10.3	12.8	Thur	LowFlow
14.11.2019	11	Thur_07		477	Surface	-69	-10.2	12.3	Thur	LowFlow
14.11.2019	11	Thur_08		543	Surface	-70	-10.3	12.7	Thur	LowFlow
14.11.2019	11	Thur_09		753	Surface	-73	-10.7	12.7	Thur	LowFlow
14.11.2019	11	Thur_10		1032	Surface	-75	-11.0	12.8	Thur	LowFlow
25.05.2019	5	AP-1		1485	Precipitation	-98	-13.6	10.7	Sitter	Snow
25.05.2019	5	Thur_11		1527	Precipitation	-82	-11.4	9.7	Sitter	Snow
19.10.2018	10	AP-1	4.8	1485	Surface	-82	-11.9	13.3	Sitter	LowFlow
19.10.2018	10	AP-2	8.9	850	Surface	-82	-11.9	12.7	Sitter	LowFlow
26.05.2019	5	AP-2		850	Surface	-85	-12.1	11.6	Sitter	HighFlow
19.10.2018	10	AP-3	9.8	680	Surface	-77	-11.0	11.6	Sitter	LowFlow
26.05.2019	5	AP-3		680	Surface	-83	-11.7	10.1	Sitter	HighFlow

Table S 4: Mean major anion and cation concentrations for the groundwater, and event sampled surface water sites sampled in the Thur catchment for the years 2017 - 2020

Site	Source	Na	Mg	Ca	K	Cl	NO3	SO4	HCO3	CO3
Ap1	Surface	2.5	2.5	42.92	1.00	0.50	0.25	5.00	139.48	NA
Ap2	Surface	2.5	2.5	38.45	1.00	0.50	1.77	5.00	123.25	NA
Ap3	Surface	2.58	4.61	50.43	1.00	2.61	4.16	5.00	171.64	NA
GW0025	Groundwater	4.59	21.53	130.43	NA	10.57	19.28	6.59	NA	NA
GW0028	Groundwater	5.23	22.37	114.54	NA	8.02	19.69	9.34	NA	NA
GW0045	Groundwater	5.41	1.71	67.12	NA	8.46	3.53	4.46	NA	NA
GW0047	Groundwater	2.751	9.04	66.95	NA	3.25	4.61	4.80	NA	NA
GW0049	Groundwater	5.711	18.56	76.41	NA	9.82	8.07	4.43	NA	NA
GW0050	Groundwater	3.116	28.99	105.13	NA	8.35	10.12	7.14	NA	NA
GW0053	Groundwater	8.21	18.56	116.15	NA	13.25	16.80	10.79	NA	NA
GW0054	Groundwater	5.98	20.99	113.20	NA	11.04	20.55	11.56	NA	NA
GW0055	Groundwater	16.96	15.351	102.00	NA	34.90	11.27	9.06	NA	NA
GW0074	Groundwater	3.07	17.84	89.73	NA	3.61	9.58	3.60	NA	NA
GW11	Groundwater	16.19	11.37	66.92	3.02	26.68	8.93	9.20	238.64	117.74
GW12	Groundwater	16.77	11.36	66.05	3.03	27.34	8.95	9.95	233.22	112.35
GW15	Groundwater	12.26	15.81	88.46	2.33	20.77	14.02	10.92	335.46	214.56
GW19	Groundwater	18.57	14.14	84.41	2.96	25.29	11.55	10.26	312.05	191.14
GW23	Groundwater	12.72	12.80	73.29	2.21	22.38	9.24	8.11	264.86	191.40
GW5	Groundwater	14.65	12.18	68.32	3.30	25.58	5.07	10.25	248.80	127.90
GW6	Groundwater	14.85	10.87	65.12	2.99	23.26	8.35	8.97	234.59	113.70
GW7	Groundwater	9.883	17.46	97.97	2.08	16.97	12.46	11.76	361.14	240.22
GW8	Groundwater	9.39	24.25	121.80	2.84	18.04	11.97	24.85	453.55	332.57
ISOT	Rain	0.08	0.023	0.26	0.03	0.13	0.27	0.27	NA	NA
TGG08	Groundwater	12.39	13.10	79.09	2.18	21.21	11.04	8.74	291.74	171.10
TGG09	Groundwater	15.20	10.34	60.95	2.83	22.94	9.42	9.00	219.77	98.93
TGG11	Groundwater	16.45	12.87	69.70	3.16	28.03	9.31	10.98	251.11	130.27
TGG12	Groundwater	6.41	22.93	91.05	2.17	11.59	13.26	7.55	357.48	236.62
TGG13	Groundwater	12.54	14.92	88.68	2.10	19.59	14.09	10.36	312.69	191.82
Thur02	Surface	12.16	9.45	48.87	2.84	18.72	6.18	8.85	174.30	56.50
Thur03	Surface	8.93	9.29	57.51	2.41	14.09	5.67	7.70	206.24	86.51
Thur04	Surface	12.08	9.11	50.12	2.53	18.46	4.75	7.52	165.01	47.30
Thur05	Surface	12.19	9.48	53.13	2.69	17.61	5.55	7.63	170.15	52.20

Thur07	Surface	12.13	9.97	53.80	2.30	18.31	5.76	7.22	176.67	58.77
Thur08	Surface	4.55	8.38	52.84	1.45	5.53	3.05	5.25	175.50	55.87
Thur09	Surface	3.50	4.31	46.67	1.35	3.44	2.23	5.51	139.33	20.01
Thur10	Surface	3.48	3.92	43.37	1.16	2.37	0.88	5.13	102.98	NA

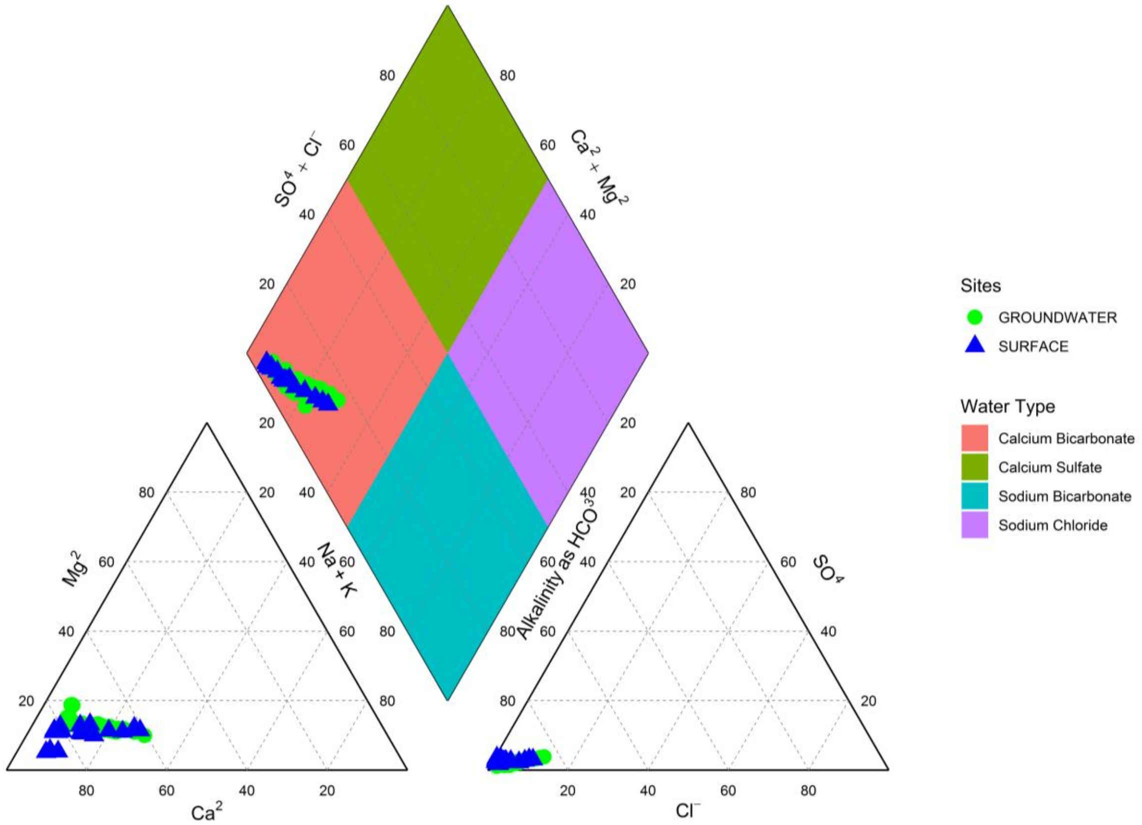


Figure S 5: The Piper plot shows the distribution of major anions and cations measured in groundwater and surface water. The water type can be derived from the hydrochemical composition. The surface water samples from the high elevation reaches plotted in the far left corners. The samples plotting further right originated from the lower elevation reaches of the river.

Table S 5: Spatial vs. temporal variation (standard deviation) of variables measured at each site in the Thur catchment

	Mg	Ca	Cl	NO3	SO4	HCO_3	CO_3	delta.2H	delta.18O
Spatial sd.	6.76	33.77	13.39	5.28	4.90	79.94	77.64	10.84	1.36
Temporal sd.	1.82	7.55	8.18	2.55	1.87	19.28	24.00	3.38	0.46

*sd. = standard deviation

PAM Clustering

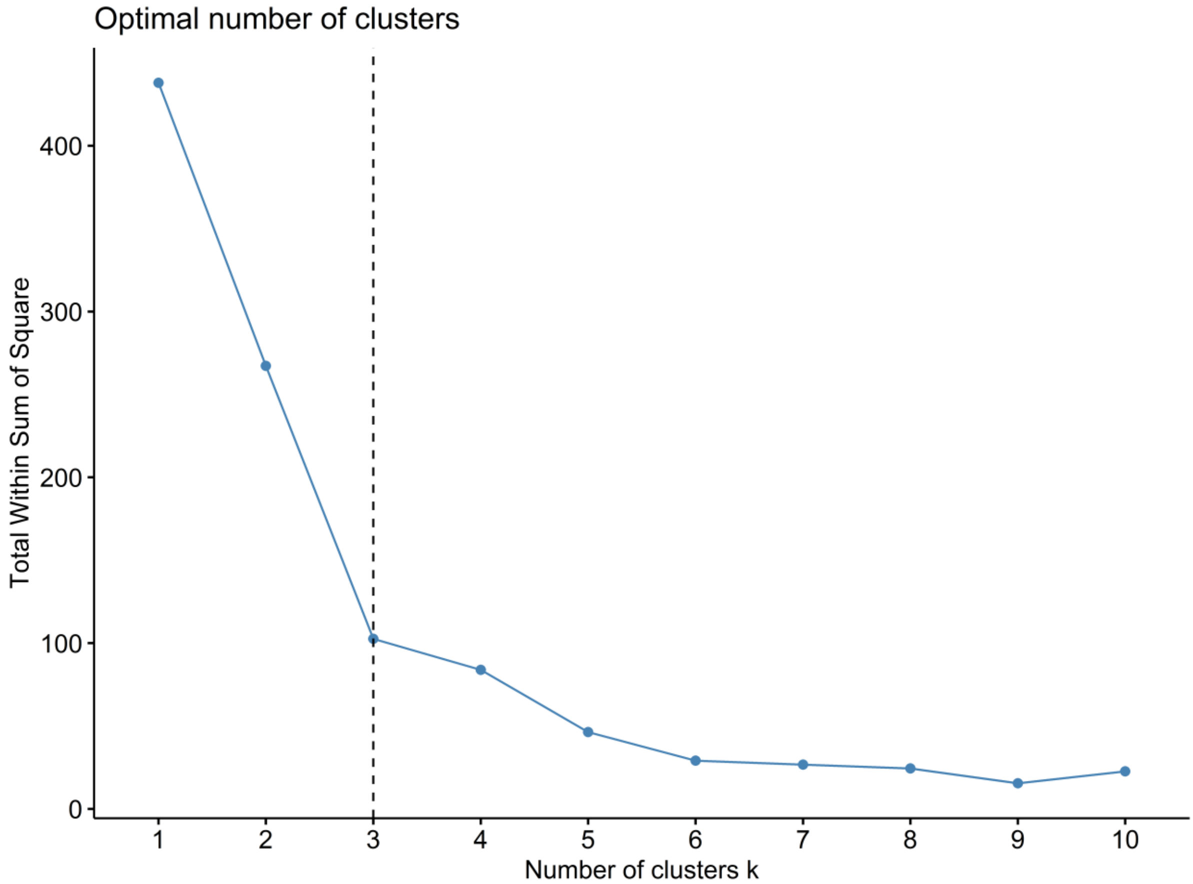


Figure S 6: Optimal cluster selection for PAM clustering using total within sum of squares (wss).