Stormwater treatment during infiltration and its effect on shallow urban groundwater quality in the Cape Flats Aquifer: field study and soil-column experiments

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Abstract

In 2019 the City of Cape Town published a Water Strategy following a 3-year drought during which time the city nearly ran out of potable water. The Strategy includes among its five commitments a commitment to diversify water supply sources and a commitment to become a water sensitive city. Stormwater harvesting and recharge of the Cape Flats Aquifer are steps toward both commitments. This study formed part of a larger transdisciplinary research project where a stormwater detention pond in Mitchell's Plain, Cape Town was retrofitted with an infiltration swale and used as a study site. The aims of the study were to evaluate the potential for stormwater treatment during infiltration through the soil, and to investigate whether stormwater infiltration could result in deterioration of groundwater quality in the underlying Cape Flats Aquifer. Research was conducted in the field by monitoring stormwater and groundwater quality at the study site, and in the laboratory using large-scale soil column experiments.

During the field study stormwater contaminants were detected at concentrations typical of an urban residential catchment with mean values of dissolved ammonium (0.35 mg/L), dissolved nitrate (0.7 mg/L) dissolved phosphorous (0.16 mg/L), dissolved aluminium (36 µg/L), dissolved zinc (81 µg/L), and total organic carbon (25 mg/L). Groundwater at the study site was shallow ranging from 2.4 to 3.7 m below ground level of the catchment and 0.1 to 1.4 m below the infiltration swale, although it remained below 0.5 m below the swale for most of the study period. Background groundwater at the study site was high in nitrate (mean 15.2 mg/L), low in total organic carbon (mean 2.7 mg/L) and low in dissolved oxygen (mean 1.4 mg/L) while the stormwater had a mean dissolved oxygen concentration of 7.4 mg/L. The field study showed that the infiltration processes resulted in an overall mean reduction in the concentrations of dissolved contaminants ammonium, phosphorus, aluminium, zinc, and total organic carbon, by 92%, 92%, 83%, 91%, and 84% respectively after accounting for dilution effects. The infiltration process also resulted in consumption of 54% of the stormwater dissolved oxygen and 37% of the groundwater nitrate after accounting for dilution effects. Furthermore, the mean groundwater nitrate concentration in the background groundwater was significantly higher ($p<0.001$) than nitrate concentrations in all other wells. This suggested that the organic carbon input from the stormwater and soil profile stimulated microbial activity which led to the consumption of the available oxygen and groundwater denitrification. Some localised and time restrained mobilisation of iron and manganese was found, however significant increase from background contaminant concentrations was found in groundwater at the study site. In addition, stormwater outflow from the study site had lower concentrations of inorganic nutrients (N and P), organic carbon and most metals compared to the incoming stormwater.

Column experiments were conducted using synthetic stormwater with concentrations of dissolved contaminants typical of a residential area, and five times higher concentrations to represent poorer stormwater quality which may be encountered in other parts of the Cape Flats. Results showed that 0.5 m of soil was able to effectively retain P, Zn, Pb, Ni, Cr and Cu during infiltration of synthetic stormwater. Removal of total nitrogen was driven by denitrification and improved in the saturated zone. Denitrification during infiltration was improved by the addition of organic carbon to the synthetic stormwater, however this also resulted in slightly higher concentrations of geogenic contaminants arsenic (13.6 vs 6.9 µg/L), iron (843 vs 657 µg/L), and manganese (21.4 vs 18.5 µg/L) in the column effluent. The concentrations used did not significantly influence the effluent concentrations of soil adsorbable contaminants (P, Zn, Pb, Ni, Cr and Cu) after infiltration through the soil or the concentration to total nitrogen in the saturated zone.

Based on this research enhanced infiltration of stormwater from relatively small (neighbourhood scale) formal residential catchments such as the one in this study is unlikely to pose a significant threat to groundwater quality, therefore this should be encouraged. Stormwater with higher contaminant concentrations may also be suitable for infiltration, however further research is required to determine the concentration limits and determining factors for suitability of a particular site.

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Acronyms and abbreviations

(hydr)oxide	Oxide, hydroxide or mixed oxide-hydroxide
AAR	Anthropogenic aquifer recharge
amsl	Above mean sea level
AWSS	Atlantis Water Supply Scheme
BDOC	Biodegradable dissolved organic carbon
BGI	Blue-green infrastructure
bgl	Below ground level
BSM	Bioretention soil media
CEC	Cation exchange capacity
CFA	Cape Flats Aquifer
CoCT	City of Cape Town
Danida	Danish International Development Agency
DO	Dissolved oxygen
DOC	Dissolved organic carbon
DWA	Department of Water Affairs
DWAF	Department of Water Affairs and Forestry
DWAF	Department of Water Affairs and Forestry
DWS	Department of Water and Sanitation
EC	Electrical conductivity
EMT	Element Materials Technology (laboratory)
EPHC	Environment Protection and Heritage Council (Australia)
GW	Groundwater
HDPE	High-density polyethene
MAR	Managed aquifer recharge
MDL	Method detection limit
MWD	Monitoring well depth
NAT	Natural aquifer treatment
NHMRC	National Health and Medical Research Council (Australia)
NRMMC	Natural Resource Management Ministerial Council (Australia)
ORP	Oxidation-reduction potential
PaWS	Pathways to water resilient South African cities
Redox	Oxidation-reduction
SAT	Soil aquifer treatment
SAWS	South African Weather Service
SAWS	South African Weather Services
SSW	synthetic stormwater
SuDS	Sustainable drainage systems
SW	Stormwater
TEA	Terminal electron acceptor
TIC	Total inorganic carbon
TKN	Total Kjeldahl nitrogen (ammonium and organic nitrogen)
TMGA	Table Mountain Group Aquifer
TN	Total nitrogen
TOC	Total organic carbon
TON	Total oxidised nitrogen (sum of nitrate and nitrite)
TP	Total phosphorus
UCT	University of Cape Town
USEPA	United States Environmental Protection Agency
VZT	Vadose zone thickness
WSC	Water sensitive city
WSUD	Water sensitive urban design

1 Introduction

1.1 Background and context

The City of Cape Town (CoCT) in South Africa receives the bulk of water for its potable water supply from six main surface water dams located outside of the city. A significant drought was experienced during the period from 2015 to 2017 which nearly resulted in the taps running dry. This so called "Day Zero" was avoided by demand management through water restrictions and tariff hikes; still, the drought highlighted the drawback of relying solely on surface water sources. In 2019 the CoCT developed their Water Strategy (City of Cape Town [CoCT], 2019) in response to the need for a water resources management approach that considers urban water resilience. Commitment number three of the five commitments made in CoCT's Water Strategy is to provide 'sufficient, reliable water from diverse sources' which includes the development of groundwater resources and water reuse. Commitment number five is to become a 'water sensitive city' by 2040 (CoCT, 2019) and this includes "*optimal use of stormwater and urban waterways for the purposes of flood control, aquifer recharge, water reuse and recreation*" (CoCT, 2019). Becoming a water sensitive city (WSC) involves the use and implementation of Water Sensitive Urban Design (WSUD) to better manage the urban water cycle, reduce pollution of urban waterways, improve biodiversity, and provide amenities to residents. WSUD has been described as "*a new paradigm in urban water management*" (Armitage *et al.*, 2014) and in the South African context must include consideration of issues such as equity as well as environmental and water resources.

Urban drainage, as a field, has developed in recent decades from simply a flood risk mitigation practice toward a more holistic water cycle management approach (Fletcher *et al.*, 2015). Within this field, many different and overlapping terms and practices have emerged, one of which is WSUD which aligns with the broad principles of a WSC; however, the former is the process while the latter is the destination or goal (Fletcher *et al.*, 2015). More recently the term blue-green infrastructure (BGI) has emerged. BGI integrates nature and urban water management, encompasses multiple benefits from reducing the heat island effect to enhancing biodiversity, and includes the co-creation of green spaces in a continuous learning and feedback process (Brears, 2023). While BGI can reduce runoff and improve stormwater quality, implementing aquifer recharge through stormwater infiltration as part of BGI is an opportunity for the CoCT to move toward becoming a WSC.

Stormwater harvesting has been investigated as an alternative water resource in the CoCT (Fisher-Jeffes, 2015) and storage in the Cape Flats Aquifer (CFA) has been found to be more suitable than storage as surface water (Okedi, 2016) due to reduced evaporation and availability of space. Managed aquifer recharge (MAR) is the intentional and managed recharge of groundwater for storage and later use (Maliva, 2020). The CFA is a shallow, unconfined, sandy, and major aquifer that could support MAR through infiltration (Okedi, 2016), but is also highly susceptible to anthropogenic contamination with a large range of potentially contaminating overlying activities such as industry, agriculture, waste disposal sites and wastewater treatment works. There are approximately 300 stormwater ponds overlying the CFA, the majority of which are detention ponds (explained below) which could be converted to infiltration basins for MAR, provided the stormwater quality, local aquifer capacity and soil conditions are appropriate. In Cape Town, the quality of stormwater runoff is, in places, very poor owing to the lack of adequate sanitation services in informal settlements, leaking or misconnected sewer pipes, illegal discharges and other non-point source pollution. A recent report on the quality of inland water bodies in Cape Town highlights phosphorus enrichment as being of key concern, while also highlighting the issue that inadequate sanitation in informal areas is a key driver of nutrient enrichment in the city's water bodies (Day *et al.*, 2020).

Stormwater detention ponds are flood control devices which receive and retain stormwater during large rainfall events and then allow the stormwater to drain back into the stormwater system through an outlet which is usually lower than the inlet. Therefore, detention ponds are normally dry and while not designed specifically to infiltrate stormwater, infiltration can occur while the pond is flooded, especially where soil conditions are conducive. Retrofitting of these detention ponds to enhance stormwater infiltration offers an opportunity for dispersed stormwater harvesting and groundwater recharge, however there are concerns that the groundwater quality may be negatively impacted by either the direct transfer of contaminants and/or because of altered geochemical conditions.

Sources of urban stormwater contaminants may be divided into four broad (and interconnected) categories namely atmospheric deposition, drainage surfaces, anthropogenic activities, and urban drainage systems (Müller *et al*., 2020). Land use may be the most important factor in altering runoff quality (Goonetilleke *et al.*, 2005) and clearly land use locally impacts the drainage surfaces, anthropogenic activities, and urban drainage systems; however, contaminants resulting from atmospheric deposition may have originated outside of the local urban catchment (Müller *et al.*, 2020). Conventional stormwater contaminants include total suspended solids (TSS), nutrients (nitrogen and phosphorous) in various forms, trace metals (cadmium, chromium, copper, lead, nickel, and zinc), and oxygen consuming substances measured as chemical oxygen demand (COD), biological oxygen demand (BOD) or total organic carbon (TOC) (Müller *et al*., 2020). Other contaminants such as petroleum hydrocarbons including polyaromatic hydrocarbons (PAHs) and trace organic compounds such as pesticides, pharmaceutical, personal care products, and other synthetic chemicals are increasingly being studied.

As the CoCT expands its use of groundwater from the CFA as a water resource it is also required to conduct MAR to avoid seawater intrusion and sustain water levels for environmental purposes. To ensure this, an injection scheme is being implemented, using highly treated wastewater which will be pumped into the aquifer through deep boreholes; further water quality improvement is expected before abstraction and treatment for potable supply (CoCT, 2023). Using stormwater to recharge the CFA through dispersed retrofitted detention ponds may offer dual benefits - substantial additional recharge which could form part of the aquifer management strategy and reduce the volume of highly treated wastewater required, as well as a reduction in the load of nutrients entering urban surface water bodies. Research investigating the impact of stormwater infiltration practices on groundwater quality (see literature review) indicates that changes to groundwater chemistry and microbiology do occur; however, the net effect on water quality is dependent on local conditions. The current research investigates the treatment of conventional stormwater contaminants during infiltration through the soil and their impact on shallow groundwater quality at a pilot study site in a low-income formal residential suburb in Mitchell's Plain.

1.2 The broader research project

This research forms part of a broader Danish International Development Agency (Danida) funded project called "Pathways to Water Resilient South African Cities" (PaWS) which seeks to generate knowledge on the physical and institutional integration of decentralised nature-based solutions into the urban water cycle to support and accelerate a transition toward water resilience in South African cities. A mono-functional detention pond in Mitchell's Plain, Cape Town has been selected as a transdisciplinary research site (the study site) where physical interventions and social engagement has been undertaken to understand how it can be transformed into a multi-functional blue-green space (Mclachlan *et al.*, 2023). Initially stormwater harvesting and MAR were the primary focus of this project which was conceived during the drought, but the focus has shifted toward other functions as the potential of these multifunctional spaces is being realised. Fell (2022) adopted a 'zoomed-out' approach and developed a GIS-based multi-criteria analysis tool for the identification of suitable sites for BGI implementation as part of a WSC transition for the CoCT. During this work around 300 stormwater ponds were identified as overlying the CFA.

The detention pond used in this study has a surface area of 9950 m^2 and receives runoff from a 170 600 m^2 catchment that comprises a formal low-income residential area. The physical intervention at the site, designed by Craig Tinashe Tanyanyiwa ('Tanyanyiwa'), is an infiltration swale which runs along a contour in front of the two stormwater inlets and contains the incoming runoff, slowing it down and preventing the flow of water directly to the outlet channel as was the case previously (Tanyanyiwa, 2023). The infiltration swale was constructed in 2021 by local residents and overseen by Tanyanyiwa. Stone riprap was used at the inlets to slow the water and catch sediment and riprap litter traps were constructed in the trench. Below the swale, vegetation has been allowed to grow and in the lowest portion of the pond is a wetland area that lies adjacent to the outlet channel (Figure 4-6 in section 4.2.2). Tanyanyiwa and the researcher worked together in the field and collaborated on the soil column experiment setup and design (Chapter 5).

1.3 Problem statement

Retrofitting stormwater ponds through the use of low-cost, low-tech methods may offer substantial stormwater harvesting potential via infiltration and storage in the CFA along with numerous other benefits. However, the ability of the soils to retain and transform chemical contaminants is unknown. The shallow depth to groundwater (<1.5 m in places) allows for a limited infiltration depth before infiltrating water reaches the groundwater table, therefore processes in the upper portion of the aquifer also need to be considered.

1.4 Aims of the research

The two overarching aims of this project were: i) to evaluate the potential for stormwater treatment during infiltration through relatively small depths of unsaturated soil, and ii) to investigate whether stormwater infiltration could contribute to deteriorating groundwater quality in the Cape Flats Aquifer.

1.5 Research questions

The research questions are divided into those considered as part of the field study and those from the column experiment.

Field Study:

1) How does the hydrological functioning of the retrofitted detention basin (study site) during the wet season (high water table) and dry season (lower water table) influence the water quality?
2) During infiltration of natural stormwater though the soil at the study site, is contaminant concentration reduced, and if so, by how much?
3) What geochemical changes occur in the shallow portion of the aquifer below the stormwater infiltration site?

Column Experiment:

4) Can the soil from the study site retain chromium, copper, nickel, lead, zinc, and phosphate during infiltration of synthetic stormwater through an unsaturated media depth of 0.5 m, 1.0 m, and 1.5 m?
5) To what extent does the presence of dissolved organic carbon (acetate and glycine) in synthetic stormwater affect denitrification during infiltration though unsaturated soil and during storage in saturated soil?
6) To what extent do the synthetic stormwater contaminant concentrations (low *vs.* five times higher) and media properties (soil *vs.* sand) influence effluent contaminant concentrations?
7) Is there a risk of mobilising naturally occurring geogenic metal contaminants (iron, manganese, and arsenic) from the soil and does the presence of organic carbon in the synthetic stormwater increase this risk?

1.6 Dissertation layout

This dissertation consists of seven chapters followed by references and appendices. Below is an overview of the content of each chapter:

Chapter 1 consists of an introduction to the research topic and its context in a developing world city and how it fits into the broader research project. The research problem is defined; aims are laid out and the key research questions are presented.

Chapter 2 consists of a review of relevant literature. It starts with an overview of water management in Cape Town, discusses anthropogenic aquifer recharge, and how managed aquifer recharge and stormwater infiltration work, and reviews the role of soils in water treatment.

Chapter 3 describes the research approach and objectives of the study.

Chapter 4 presents the field study site and water quality monitoring and discusses what was found in terms of the hydrological and water quality functioning of this retrofitted detention pond.

Chapter 5 describes the laboratory column experiment in which synthetic stormwater was infiltrated through large scale columns and discusses the results of the experiment.

Chapter 6 is discussion of the implications of results from the field study and column experiments, and what these mean for a water sensitive city transition in Cape Town.

Chapter 7 states the conclusions and recommendations.

2 Literature review

The literature review presented here is divided into three sections. The first part presents an overview of water management in Cape Town, touching on some water quality findings and concerns in the Cape Flats area specifically, and the second part gives an overview of the concept of aquifer recharge. The third and largest section looks at soil-based water treatment by examining literature on bioretention soil media, the impacts of stormwater infiltration on groundwater quality and natural aquifer treatment processes.

2.1 Water management in Cape Town

The City of Cape Town experienced a severe drought from 2015 to 2018 culminating in extreme water restrictions and an imminent threat of "Day Zero", the predicted day on which the taps would be turned off and residents would need to queue for water rations. Rains in April 2018 brought relief and "Day Zero" was avoided; however, the fragility of the water supply system in the CoCT was brought directly into the spotlight.

In 2019 the CoCT published its Water Strategy which includes five commitments, as shown in Table 2-1. Commitment number three concerns the implementation of the New Water Programme which is committed to deliver 300 million litres of additional water per day and an additional 250 million litres per day as adaptive capacity (CoCT, 2019). Currently CoCT's potable supply is derived almost exclusively from surface water sources with most of the storage dams located outside of the city catchment area. According to the city's Water Strategy (CoCT, 2019), in 2018, 96% of water resources were derived from surface water and 4% from groundwater. However, by 2040 the target portion derived from surface water is planned to decrease to 75% with the remainder split between water reuse, groundwater, and desalination.

Table 2-1: *The City of Cape Town's five commitments laid out in the Water Strategy* (CoCT, 2019).

No.	Headline	Commitment
1	Safe access to water and sanitation	• Provide safe access to water and sanitation to all residents. • Work with communities in informal settlements to improve the daily experience of access to water and sanitation, with an emphasis on building trust and increasing safety.
2	Water wise	• Promote water conservation behaviour through pricing, by-laws and supporting active citizenship. • Effectively manage water network to reduce losses.
3	Sufficient, reliable water from diverse sources	• Develop new diverse water supplies including groundwater, water re-use and desalination. • Build affordable new capacity of 300 million litres per day in ten years through the New Water Programme.
4	Shared benefit from regional water resources	• Collaborate with urban and agricultural water users and other spheres of government. • Optimise the social, economic, and ecological benefits of regional water resources.
5	A water sensitive city	• Diverse water resources and diversified infrastructure. • Optimal use of stormwater and urban waterways for flood control, aquifer recharge and recreation based on sound ecological principles. • Fit-for purpose water use, centralised and decentralised distribution.

Groundwater sources within the city include three major aquifers: the Table Mountain Group Aquifer (TMGA), the Atlantis Aquifer, and the Cape Flats Aquifer (CFA). The TMGA is a large, fractured rock aquifer adjacent to the east and west coasts of South Africa in the Eastern and Western Cape provinces where it is already utilised for domestic, industrial, and agricultural use (Duah & Xu, 2013). As part of the New Water Program in Cape Town, the TMGA is being further developed for water abstraction by the city, with the Steenbras wellfield located adjacent to Steenbras dam being developed first (CoCT, 2023). Groundwater abstraction from the Atlantis Aquifer has been ongoing for more than four decades (Bugan *et al.*, 2016) as part of a MAR water recycling scheme. Treated domestic wastewater and stormwater runoff are used to recharge the aquifer via infiltration basins upgradient of the abstraction well field. The CFA is currently being used as a decentralised, non-potable supply, largely for irrigation in the Philippi Horticultural Area, but also by other private users. The CoCT's plan is to start abstraction of water from the CFA for potable water supply and to implement MAR via injection boreholes using highly treated wastewater to form a buffer zone of higher quality water around the abstraction wellfields (CoCT, 2023).

Becoming a WSC (commitment number five, [CoCT, 2019]) requires the implementation of water sensitive urban design (WSUD) principles and sustainable drainage system (SuDS) technologies in a contextually suitable way. WSUD aims to use sustainability principles to improve urban water cycle management (Hatt, Fletcher & Deletic, 2008) and while being a WSC may be the destination, WSUD is the process (Fletcher *et al.*, 2015). SuDS are specific technologies and concepts that focus on urban stormwater management but may integrate with urban water cycle management (Fletcher *et al.*, 2015). SuDS include components such as pervious pavements, constructed wetlands and bioretention practices. Bioretention facilities are low-lying and often vegetated; they receive stormwater and allow it to filter through soil-based media before water is directed back to the stormwater system or allowed to recharge the groundwater. Stormwater detention basins are flood control structures which temporarily store stormwater and while some may infiltrate before the rest drains back into the stormwater network (Armitage *et al.*, 2013), they are not primarily designed for aquifer recharge. Infiltration of stormwater below detention basins, bioretention facilities and other SuDS may constitute unmanaged groundwater recharge, or, if there is planned reuse of the groundwater and water quality considerations, they may be considered MAR.

The Management of Stormwater Impacts Policy (CoCT, 2009) was developed to minimise the detrimental effects of urban stormwater on the environment, communities and livelihoods. The objectives of this policy are to reduce flooding and improve water quality by adopting WSUD principles and implementing SuDS. Guidelines for SuDS (Armitage *et al*., 2013) and WSUD (Armitage *et al*., 2014) have been developed for the South African context and the unique challenges faced by developing countries. In a country, and a city that is still struggling to provide basic water and sanitation services to some of its residents the vision of a WSC can encourage continuous improvement and consideration of alternative urban water management approaches (Fisher-Jeffes *et al*., 2017).

Atkins, Flügel & Hugman (2021) conducted a systematic quantification of the CoCT's urban water cycle under pre-drought scenarios and after implementation of the CoCT's New Water Programme (CoCT, 2018). Evaluation of the hydrological flows showed that current runoff is higher and groundwater recharge is lower than pre-urbanised annual flows (Atkins, Flügel & Hugman, 2021); clearly groundwater recharge using stormwater runoff would bring the urban water cycle closer to pre-urbanised conditions. The main limitations here are localised flooding risk and potential threats to groundwater quality; however, infiltration of stormwater (MAR) close to source can reduce downstream surface flooding (Mauck, 2017). SuDS technologies can be implemented to improve stormwater quality (Armitage *et al.*, 2013), and infiltration and storage in the CFA may offer further water quality improvements.

2.1.1 Water quality suitability

Surface and groundwater quality monitoring is currently undertaken by CoCT and appointed consultants. Surface water bodies are sampled and monitored for a range of parameters and reported as part of the inland water quality report (Day *et al.*, 2020) while groundwater consultants, Umvoto Africa, monitor CFA groundwater and overlying surface water as part of the New Water Programme (CoCT, 2021). Chemical contaminants which threaten surface water bodies are different to those which threaten groundwater quality. Day *et al.* (2020) emphasise the rise in phosphate concentrations as being a particularly worrying issue for surface water bodies because this nutrient drives the development of eutrophic and hypertrophic conditions and increases the risk of harmful algal blooms. The concern around phosphate in surface water systems is reflected in the Management of Urban Stormwater Impacts Policy (CoCT, 2009) which specifies pollutant removal targets for only two parameters, suspended solids (-80%) and total phosphorus (-45%).

Screening of groundwater analysis results as part of the New Water Programme was done against the South African National Standard for drinking water (SANS:241-1) (South African Bureau of Standards [SABS], 2015) and water treatment guidelines provided by the water treatment engineers for operation of the treatment plant for abstracted water (CoCT, 2021). Key chemical water quality concerns noted in the groundwater included elevated electrical conductivity (EC) together with high sodium and chloride concentrations below the Philippi Horticultural Area, elevated Total Organic Carbon (TOC) in some areas, elevated arsenic, nitrate, ammonium, and phosphate near the Mitchell's Plain wastewater treatment works, and other occasional exceedances. The contamination plume around Mitchell's Plain WWTW which emanates from an old sludge pond will be contained by injection of a treated wastewater buffer (CoCT, 2023).

Natural groundwater quality varies widely and therefore concentration limits for specific species in groundwater or in MAR systems would be difficult to determine. Whether being used for potable supply or for other decentralised direct uses such as agriculture and industry, the abstracted water quality should be suitable for the intended use. Similarly, the quality of water in surface water bodies should be of adequate quality to maintain the ecological health of the rivers and lakes. In 1996 the Department of Water Affairs and Forestry published the South African Water Quality Guidelines as a primary source of information for the determination of water quality requirements. These guidelines consist of eight volumes, each specific to an intended water use. A comparison of the guideline values for relevant chemical parameters for industrial water use (Department of Environmental Affairs and Forestry [DEAF], 1996a), agricultural water use: irrigation (DEAF, 1996b), aquatic ecosystems (DEAF, 1996c) and SANS:241-1 limits are shown in Table 2-2. Where multiple values are available in the documents the most conservative values are shown, but variations apply based on, for example: soil type, plant species, industrial processes, and ecosystem sensitivity.

Table 2-2: *Water quality limit and guideline values, South Africa.*

Parameter	**SANS:241-1 (Potable)**	**Aquatic ecosystems**	**Agricultural Use: Irrigation**	**Industrial Use**
pH	5 – 9.7*	<5% variation	6.5 – 8.4	7 - 8
EC (mS/m)	170		40	15
TDS (mg/L)	1200	<15% variation		100
TSS (mg/L)		<10% variation	50	3
Turbidity (NTU)	1*, 5*			
Nutrients and carbon (mg/L)				
Total ammonia as N	1.5			
Un-ionised ammonia as N		0.007		
Nitrite	0.9			
Nitrate	11			
Total inorganic N		0.5	5	
Total organic carbon	10			
Chemical oxygen demand				10
Inorganic phosphorus		0.005@, <15% from baseline		
Trace contaminants (µg/L)				
Zinc	5 000	2	1 000	
Lead	10	0.5#	200	
Nickel	70		200	
Chromium	50	7	100	
Copper	2 000	0.8#	200	
Arsenic	10	10	100	
Iron	2000, 300*	<10% variation	5 000	100
Manganese	400, 100*	180	20	50
Aluminium	300*	10+	5 000	

Note: * = aesthetic or operational risk. @ = oligotrophic conditions. # = for water with medium hardness. + = for pH>6.5

Water quality suitability should be incorporated into urban water cycle management to minimise risk to the environment, human health, agricultural crops, and economic activity. Potable water does not require lower concentrations of all chemical parameters than what is ideal for aquatic ecosystems, irrigation, or even industrial processes. The vision for a water sensitive city includes the use of fit-for-purpose water resources (CoCT, 2019), and water quality considerations are a critical part of this.

2.2 Anthropogenic aquifer recharge

Anthropogenic aquifer recharge (AAR) refers to all aquifer recharge that occurs owing to human activity, managed or unmanaged, intentional or unintentional (Maliva, 2020). Unintentional recharge may result from, for example, leaking water pipes or land use change - although the latter may be an intentional removal of vegetation to increase groundwater recharge. Unmanaged recharge may result from activities with a primary disposal function such as septic tanks or stormwater infiltration technologies. Stormwater infiltration may be considered managed aquifer recharge (MAR) if it has aquifer recharge as a primary function (Maliva, 2020). The term MAR implies effective management of both quantity and quality of recharged groundwater (Dillon *et al.*, 2018). The practice of infiltrating stormwater and other water (for example discharge from septic tanks) is centuries old and is often done without explicit consideration of the groundwater quality (Dillon *et al.*, 2018). MAR is often used as a tool to improve the quality of either the recharge water or the groundwater or both (Natural Resource Management Ministerial Council (NRMMC), Environment Protection and Heritage Council (EPHC) & National Health and Medical Research Council (NHMRC), 2009). The management of water quality is highly dependent on the context of the recharge system, identified risks, and intended use of recovered water (NRMMC, EPHC, and NHMRC, 2009). When the natural attenuation of contaminants during infiltration and groundwater flow is intentionally used for water quality improvement, it is referred to as natural aquifer treatment (NAT).

There are many techniques available for MAR which include (but are not limited to) injection through a well, pumping near a riverbank to induce infiltration of river water, and numerous infiltration systems. The design and management of MAR systems requires an understanding of hydrogeological principles and local hydrogeological conditions. A confined aquifer is located below a confining layer of rock or sediment, while an unconfined aquifer is bounded on top by the water table and is sometimes referred to as a water table aquifer. In unconfined aquifers the groundwater flow direction will be from a higher water table elevation to a lower water table elevation; this can be determined by measurement of groundwater depth in groundwater monitoring wells and may be influenced by localised infiltration. Groundwater flow velocity is controlled by aquifer properties such as hydraulic conductivity, porosity and dispersivity (Maliva, 2020). The ability of an aquifer to transmit water is called transmissivity (Maliva, 2020) and is an important factor in MAR because if transmissivity is low then recharge will be slow.

Infiltration devices such as basins, trenches, or swales rely on a suitable infiltration rate and lateral flow away from the infiltration area to reduce mounding (Maliva, 2020). Mounding occurs below an infiltration basin (Figure 2-1) and can be calculated from infiltration rate, aquifer transmissivity and porosity as well as the recharge basin size (NRMMC, EPHC, and NHMRC, 2009). Mounds may reach the bottom of the infiltration device at times and then subside between infiltration events.

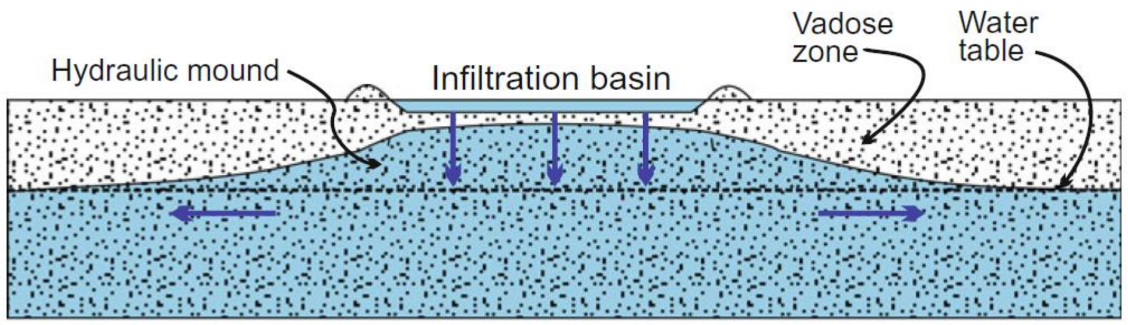

Figure 2-1: *Conceptual cross-section of mounding below an infiltration basin (Maliva, 2020).*

Mounding may be undesirable in cases where the unsaturated soil thickness is required for contaminant attenuation, or where groundwater may impact underground infrastructure. On the other hand, the development of a water table wetland habitat may be of ecological and water quality benefit.

2.3 Soil-based water treatment

Soil is made up of inorganic minerals and precipitates, water, solutes, gases, microorganisms, and organic material, all constantly interacting with each other. Soils naturally filter water through physical, chemical, and biological processes, and this ability of soils has been utilised for centuries in applications such as septic tanks and wastewater disposal. In the field of sustainable drainage systems soil is at the centre of many technologies designed to improve stormwater quality, and specific mixtures of bioretention soil media (BSM) have been utilised in bioretention and filtration systems. At stormwater infiltration sites the infiltration of stormwater through a thickness of unsaturated soil (the vadose zone) is a water filtration step where physical, chemical, and biological processes remove contaminants from the infiltrating water. Natural aquifer treatment (NAT) is the intentional use of an aquifer for contaminant attenuation during infiltration and transfer and includes the wastewater treatment technology known as soil aquifer treatment (SAT) (Maliva, 2020).

2.3.1 Soil as bioretention media

Bioretention systems which may be referred to as biofiltration systems or bioretention areas are typically landscaped depressions such as swales or basins which are vegetated and designed to remove contaminants during retention of stormwater (Hatt, Fletcher & Deletić, 2007; Hsieh, Davis & Needelman, 2007a; Armitage *et al.*, 2013; Paus *et al.*, 2014; Takaijudin *et al.*, 2015). The term biofiltration, however, is much broader than the field of stormwater management and is used in other water treatment fields to refer to any porous media filter colonised by microbial communities (Hammes *et al.*, 2011). Bioretention systems may be constructed by removing the native soil and replacing it with bioretention media (Paus *et al.*, 2014) which is typically a combination of sand, soil, compost or mulch, and other amendments (Hsieh, Davis & Needelman, 2007a). Bioretention media is sometimes called bioretention soil media (BSM), filter media, engineered soil media, or simply media, but essentially it is soil to which various amendments may have been added to improve aspects of water treatment and hydraulic properties.

Soil is often classified according to it textural class, an important physical property which is based on the fractions of sand (fine, medium, and course), silt and clay in the soil. Soil structure is formed in situ and is usually partially or fully destroyed when soil is removed or disturbed. Other important properties of soils for contaminant removal are the specific minerals present, cation exchange capacity (CEC), organic matter content, water holding capacity, and infiltration rate. Sandy loam is often used as biofiltration media (Davis *et al.*, 2001, 2006; Bratieres *et al.*, 2008; Hatt, Fletcher & Deletic, 2009; Li & Davis, 2009; Brown & Hunt, 2011) as it is the recommended soil texture type by design guidelines for biofilters (Hatt, Fletcher & Deletić, 2007). Other recommendations include loamy sand (Washington State Department of Ecology Program Water Quality, 2019), well graded sand (Woods-Ballard *et al.*, 2007), and sandy loam, loamy sand or loam for planting, layered over coarse sand (Maryland Department of the Environment (MDE), 2009). The specifications aim to meet hydraulic requirements (sufficient infiltration rates) and provide sufficient water retention time in the soil for contaminant removal. In the following sections, the soil chemistry of contaminants of interest is summarised (using the book *Soil Chemistry* by Strawn, Bohn & O'Connor (2020) as the primary reference), and bioretention literature is reviewed to gain insight on media properties, configurations, amendments, and design strategies which influence treatment performance.

Nitrogen

In soils, nitrogen is available to plants and microorganisms in two main dissolved inorganic forms; i.e. ammonium (NH_4^+), and nitrate (NO_3^-) (Strawn, Bohn & O'Connor, 2020, 73). Ammonium is the reduced form (electron donor) and may be oxidised to nitrite (NO_2^-), which in turn may be oxidised to nitrate by biologically mediated reactions involving the *Nitrosomonas* and *Nitrobacter* species respectively (Hsieh, Davis & Needelman, 2007b). This process is called nitrification and occurs in oxic environments where oxygen is reduced to water as shown in Equation 1.

$$NH_4^+ + O_2 \rightarrow NO_3^- + H_2O + H^+$$

Equation 1

Nitrate + nitrite may be referred to as total oxidised nitrogen (TON). Denitrification occurs under anoxic conditions (when NO_3^- becomes the favoured terminal electron receptor (TEA) in the absence of oxygen) and results in the transformation of nitrate to gaseous nitrogen species as shown in Equation 2 (Hsieh, Davis & Needelman, 2007b). This process requires a carbon source and electron donor (Kim, Seagren & Davis, 2003).

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \uparrow \rightarrow N_2O \uparrow \rightarrow N_2 \uparrow$$

Equation 2

Nitrogen is also present as part of organic molecules such as amino acids (which make up proteins) which are present in soils as part of the organic matter (Strawn, Bohn & O'Connor, 2020) and in stormwater. Table 2-3 shows the forms of analysable nitrogen species and groups in water samples.

Table 2-3: *Analysable nitrogen species and groups.*

	Gaseous	**TON**	**Ammoniacal N**	**Organic N**
Individual	NO, N_2O, NH_3, and N_2	NO_3^- and NO_2^-	NH_3 and NH_4^+	Many organic molecules containing N
Total Inorganic N (TIN)		Sum of NO_3^-, NO_2^-, and NH_4^+		
Total Kjeldahl N (TKN)			Sum of ammoniacal N and organic N	
Total bound N (TN_b)	Sum of all gas, mineral and organic N except N_2			

Assimilation of available nitrogen by plants and microorganisms converts the inorganic nitrogen into organic nitrogen which essentially immobilises the nitrogen. Ammonification is the process by which organic nitrogen is transformed to ammonium by organisms and becomes available again in the soil solution. Ion exchange in soils is the outer sphere electrostatic adsorption of hydrated ions on soil surfaces with an opposite charge. The cation exchange capacity (CEC) (the concentration of negatively charged clay mineral surfaces) of a soil is usually much higher than the anion exchange capacity which is variable and pH dependent (Strawn, Bohn & O'Connor, 2020). Ion exchange slows the movement of ions through soil during infiltration, thus the anions nitrate and nitrite are more mobile than the cation ammonium and more easily leached from soil. Under some conditions (for example high pH) ammonia volatilisation can occur. Thus, the predominant ways in which inorganic nitrogen may be removed from infiltrating stormwater in bioretention systems are: i) ammonium cation exchange, ii) ammonia volatilisation, iii) assimilation by plants and organisms, and iv) denitrification. A schematic of nitrogen species transformation in soils is shown in Figure 2-2.

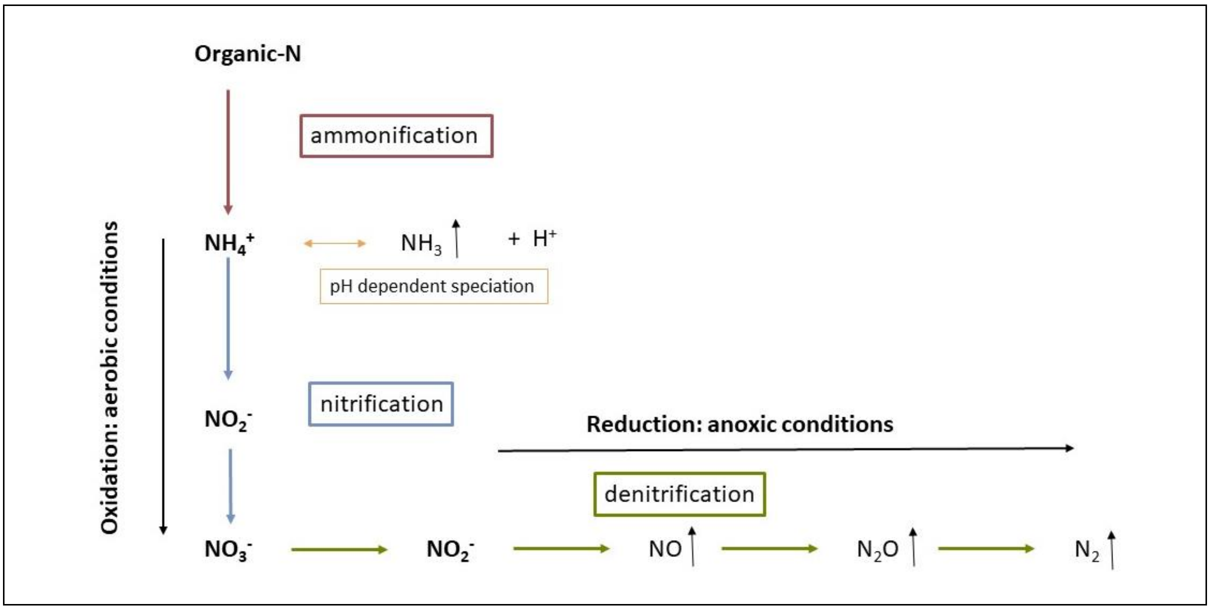

Figure 2-2: *Schematic of nitrogen species transformation in soils (excluding assimilation).*

Hatt, Fletcher & Deletić (2007) tested sandy loam and sandy loam + various inorganic (vermiculite, perlite) and organic (mulch, compost, charcoal) amendment combinations in an experiment aimed at understanding the influence of wetting and drying cycles. They reported no difference for any of the amendments compared to sandy loam only and significant nitrate leaching from the soil was found. Higher effluent nitrate concentrations were found following a dry period, suggesting that nitrification occurred during the dry period followed by washing out of nitrate with the next infiltration event. Nitrate leaching from soil has been found in other studies, especially when nutrient rich compost mulch was added to the media (Davis *et al.*, 2001; Hsieh, Davis & Needelman, 2007b; Bratieres *et al.*, 2008; Hatt, Fletcher & Deletic, 2008; Barrett, Limouzin & Lawler, 2013; Hamedani *et al.*, 2021; Kranz *et al.*, 2022).

Design strategies that promote denitrification such as creating a saturated zone (Kim, Seagren & Davis, 2003) or media layering to increase moisture retention (Hsieh, Davis & Needelman, 2007b) and the use of vegetation (Bratieres *et al.*, 2008) have been shown to improve nitrate removal. A higher cation exchange capacity (higher content of clay and organic matter) was shown to improve ammonium removal (Hsieh, Davis & Needelman, 2007b). Cation exchange is a reversible process and may slow the movement of ammonium through the media. This allows time for nitrification to occur, which improves ammonium removal but not total nitrogen removal. Leaching of inorganic nitrogen from nitrogen rich soil and compost may decrease over time as the most mobile fraction is removed (Kranz *et al.*, 2022).

The role of soil in nitrogen removal is not dependent on sorption capacity of the soil, although retardation of ammonium by cation exchange may be part of the process. By slowing the stormwater infiltration, soil can provide the environment for microbial processes to take place. Nitrification should be followed by denitrification, which requires labile organic carbon and sufficient retention time to prevent nitrate leaching. Plant growth may assist in immobilising inorganic nitrogen; however, decaying plant matter can subsequently release nitrogen (and organic carbon) back into the soil solution, and if a net removal of nitrogen from the soil system is desired, denitrification should be promoted.

Phosphate

Phosphorus exists in nature as the anion phosphate (PO_4^{3-}), which may be part of or adsorbed on a solid mineral, part of an organic compound or in solution in a protonated form (HPO_4^{2-} or $H_2PO_4^-$) (Strawn, Bohn & O'Connor, 2020). Analysis of phosphate in water samples usually detects soluble reactive phosphate (SRP), and thorough sample digestion is required to determine total phosphate or total phosphorus (TP). Phosphate is a poorly soluble anion which, in soil, is readily adsorbed on mineral surfaces (such as iron and aluminium (hydr)oxides) or precipitated with the cations Fe^{3+}, Al^{3+}, Ca^{2+}, and Mg^{2+} (Strawn, Bohn & O'Connor, 2020). Most soils have a substantial long-term capacity to adsorb phosphate though multi-stage processes including outer-sphere, inner-sphere adsorption and mineral precipitation (Strawn, Bohn & O'Connor, 2020) which bonds phosphate more strongly over time. Soil pH plays an important role in the adsorption of phosphate because it affects both the variable change on the mineral surface (more positive at lower pH) and the protonation of phosphate; however, because phosphate forms inner-sphere bonds (direct bond with mineral surface functional group) it can be adsorbed on minerals with negative surface charge (Strawn, Bohn & O'Connor, 2020).

Despite a strong theoretical basis for phosphate adsorption by soils, studies on bioretention media have had variable results with some authors reporting export of P from media (Dietz & Clausen, 2006; Hunt *et al.*, 2006; Hatt, Fletcher & Deletic, 2008) and others reporting P retention (Davis, 2007; Li & Davis, 2009; Barrett, Limouzin & Lawler, 2013). Hatt, Fletcher & Deletic (2008) found consistent leaching of soluble phosphate from sandy loam soil in column experiments, and reported TP build up in soil near the top of the column, which suggests that effluent phosphate concentration was leaching from the soil rather than an inability of the soil to adsorb incoming phosphate. Phosphate leaching from organic soil-media amendments (e.g. compost or mulch) has been widely reported (Bratieres *et al.*, 2008; Paus *et al.*, 2014; Hamedani *et al.*, 2021; Kranz *et al.*, 2022). Sandy loam soil has also resulted in phosphate retention during infiltration (Kranz *et al.*, 2022).

Water treatment residual from Al-based coagulants (Al-WTR) has been studied as an amendment to BSM to improve phosphate removal. Better phosphate removal was found where more Al-WTR (up to 10%) was used (O'Neill & Davis, 2012a), and in a long term column study, 88.5% of the applied mass of P was adsorbed by the media (O'Neill & Davis, 2012b). A more recent study compared various BSM amendments for their P removal efficiency and found that Al-WTR was the best amendment for this purpose, compared to the other amendments (zeolites, fly ash, and medical stone) studied (Zhang *et al.*, 2018). Small additions of iron fillings (2-5%) to sand have been shown to achieve substantial phosphate retention (Erickson, Gulliver & Weiss, 2012), and Hamedani *et al.* (2021) also reported that an iron amended version of biofiltration media mix improved phosphate retention. The coal combustion product, fly ash, has been shown to add significant phosphate adsorption capacity when used as 5% amendment to sand in bioretention systems (Zhang *et al.*, 2008).

O'Neill & Davis (2012a) proposed and demonstrated the use of the oxalate ratio (OR) as a simple metric for the prediction of phosphate adsorption in BSM. OR is a ratio of the concentration of oxalate extractable iron and aluminium to concentration of oxalate extractable phosphorus in the media. The oxalate extraction is designed to dissolve amorphous iron and aluminium oxides which have high phosphate adsorption capacity but is not strong enough to dissolve crystalline minerals which may have high amounts of iron and aluminium without the high adsorption capacity. OR is therefore the ratio of the capacity for phosphate adsorption to the already utilised adsorption capacity, and a value < 10 has a high risk of phosphate leaching.

In a bioretention column experiment Barrett, Limouzin & Lawler, (2013) found, unexpectedly, that the presence of a small (150 mm) saturated zone in their columns improved dissolved P removal. This was attributed to the precipitation of calcium hydroxyapatite [$Ca_5(PO4)_3(OH)$] where the longer residence time of PO_4^{3-} in the saturated zone was necessary for the reaction to occur. Hsieh, Davis & Needelman (2007a) used different media layering in a column experiment and found that when a lower hydraulic conductivity layer is at the bottom (creating a longer residence time in the soil) phosphate adsorption is improved. Certain plants may improve the retention of phosphate in stormwater biofiltration systems (Milandri *et al.*, 2012); however, this may not be exclusively owing to plant uptake but rather, to other changes that plants impart on the soil in the root zone (Lucas & Greenway, 2008).

Metal contaminants

Cadmium, chromium, copper, lead, nickel, and zinc can be considered ‘conventional’ stormwater contaminants and have been extensively studied (Müller *et al.*, 2020). The first row transition metals chromium, copper, nickel and zinc are plant and/or animal micronutrients while cadmium and lead are toxic elements, yet all can be considered contaminants if present at elevated concentrations in soil and water (Strawn, Bohn & O’Connor, 2020). Apart from chromium, these metals are present in soil as divalent cations and are more soluble/mobile at lower pH. Immobilisation of these metals can occur via adsorption on cation exchange sites, oxide minerals, and soil organic matter (SOM) or by precipitation. Many natural organic molecules are polydentate ligands which can chelate (form multiple bonds with) these metals thereby increasing their solubility. Chromium is most commonly present as Cr(III) which is insoluble, but may also be present as the chromate anion (CrO_4^{2-}), which like phosphate is a poorly soluble anion and forms inner-sphere bonds on iron and aluminium oxides. Chromate is more soluble at higher pH (Strawn, Bohn & O’Connor, 2020).

Removal of metals by bioretention soil media has often been successful, with very good removal efficiencies reported by many researchers (Davis *et al.*, 2003; Hatt, Fletcher & Deletic, 2008, 2009; Li & Davis, 2009; Paus *et al.*, 2014; Li *et al.*, 2018; Hamedani *et al.*, 2021; Kranz *et al.*, 2022). Higher compost fraction has resulted in better metal retention (Paus *et al.*, 2014). However, other studies have shown leaching of copper (Hamedani *et al.*, 2021) and chromium (Kranz *et al.*, 2022) from organic matter added to bioretention media. Kranz *et al.* (2022) measured the distribution coefficient K_d for the six conventional metal contaminants mentioned above for sandy loam soil mixed with 0, 20, 50 and 100% compost and found that while other metals had higher K_d (i.e. better adsorption) for higher compost fractions, the K_d for chromium decreased with increasing compost. However, using the same compost fractions in column leaching experiments using synthetic stormwater, the authors found that all metals exhibited an initial flush, but chromium, copper, nickel, and zinc had a second flush (highest for the 100% compost) after four pore volumes - possibly owing to chelation by organic molecules released by the compost.

2.3.2 Stormwater infiltration to groundwater

Numerous studies have shown changes in the groundwater biogeochemistry below stormwater infiltration basins as compared to background reference groundwater (Appleyard, 1993; Fischer, Charles & Baehr, 2003; Datry, Malard & Gibert, 2004; Zubair *et al.*, 2010; Foulquier *et al.*, 2010, 2011; O’Reilly *et al.*, 2012; O’Reilly, Chang & Wanielista, 2012; Mermillod-Blondin *et al.*, 2015; Voisin *et al.*, 2018; Lebon *et al.*, 2021).

Metals are well retained by soils (Salo, Harrison & Archibald, 1986) and when detected in groundwater beneath infiltration basins are usually below drinking water guideline levels (Appleyard, 1993; Datry, Malard & Gibert, 2004). In a monsoon climate Zubair *et al.* (2010) found that cadmium and copper concentrations were higher in groundwater below detention basins during post-monsoon sampling as compared to pre-monsoon and background groundwater, indicating that direct transfer of these contaminants from stormwater to groundwater did occur. On the other hand, the post-monsoon samples from below the basins showed lower than background groundwater concentrations of iron, lead and zinc (Zubair *et al.*, 2010). Lead build up in basin sediments has also been noted (Appleyard, 1993).

The dilution of groundwater contaminants by infiltrating stormwater has been found for some metals (Zubair *et al.*, 2010), some pesticides and chlorinated solvents (Fischer, Charles & Baehr, 2003), and nitrate (Lebon *et al.*, 2021). The dilution effect is often noted with regard to salinity and/or chloride concentration (Appleyard, 1993), and both or either of these parameters are used as tracers to determine the proportions of infiltrated stormwater in a sampling well below an infiltration site (Datry, Malard & Gibert, 2004; Foulquier *et al.*, 2010, 2011; O'Reilly, Chang & Wanielista, 2012; Mermillod-Blondin *et al.*, 2015; Voisin *et al.*, 2020; Lebon *et al.*, 2021) because chloride concentrations are typically much lower in stormwater than in groundwater. However, in areas with high snowfall where salt is used to de-ice roads, no change or an increase in chloride concentration can result (Fischer, Charles & Baehr, 2003).

Fischer, Charles & Baehr (2003) found a significantly ($p=0.01$) lower dissolved oxygen (DO) concentration in groundwater below stormwater detention basins as compared to background groundwater. Since then, many, but not all, studies have found a similar trend, and the difference seems to depend on the depth to groundwater, the soil structure and texture (and infiltration rate), the amount of biodegradable dissolved organic carbon (BDOC) and oxygen available in the infiltrating water and soil, and the temperature of the system. Datry, Malard & Gibert (2004) studied a stormwater infiltration system in Lyon, France which contained a 2 m thick cobble layer that had accumulated organic sediments from the stormwater. They found increased dissolved organic carbon (DOC) concentration in the shallow groundwater, presumably transported from the cobble layer, and a lower DO concentration than what could be accounted for from mixing, indicating biological consumption of the DOC and DO. The temperature of infiltrating water affected whether the final DO concentration in groundwater below the basin increased or decreased, with cold rains resulting in oxygenation (although not as much as would be predicted by mixing). Zubair *et al.* (2010) found significantly lower DO concentration below detention basins in the pre-monsoon season as compared to background and post-monsoon season; this was an indication that stormwater infiltration replenished the groundwater oxygen, but also added a carbon load which lead to oxygen depleted conditions over time. Foulquier *et al.* (2010) argue that simple mixing as opposed to biological uptake at the water table region of an aquifer may account for the changes in DOC and DO concentrations. They argue that biological uptake of BDOC and DO consumption take place during infiltration and that DO-poor infiltrated water then mixes with the groundwater. This distinction may be significant in that if BDOC is consumed during infiltration then it is not supplying a labile carbon source to groundwater ecosystems.

In the saturated and unsaturated subsurface, DO is the first terminal electron acceptor (TEA) used in biologically mediated terminal electron-accepting processes (Chapelle *et al.*, 1995). Organic carbon, whether dissolved in the infiltrating stormwater or present as part of the soil/sediment, stimulates microbial metabolism resulting in a sequence of TEA utilisation which leads to the sequential reduction of DO, nitrate, manganese(IV), iron(III), sulphate, and finally carbon dioxide (Chapelle *et al.*, 1995; O'Reilly *et al.*, 2012). Stormwater infiltration often leads to an increase in DOC in the groundwater below the infiltration site; what is not clear is the portion of DOC originating from stormwater *vs.* that which is mobilised from the topsoil and root zone of plants. This likely depends on the plant types and organic matter mass in and on the soil. The action of concentrated infiltration through the soil, even if there was no DOC in the infiltrating water, may be enough to increase the DOC concentration in the groundwater below. DOC is a bulk measurement and does not account for the composition of the organic compounds, or the biodegradability. Mermillod-Blondin *et al.* (2015) found that the proportion of DOC that was BDOC decreased during infiltration. The amount of BDOC reaching the saturated zone, plus that available or mobilised in the saturated zone, will determine the extent of consumption of TEA. If sufficient BDOC is present, DO will be consumed to a sufficient extent that NO_3^-, if present, will be used as a TEA resulting in denitrification. This is a favourable outcome with regard to water quality as nitrate is a widespread groundwater contaminant (Huno *et al.*, 2018). Therefore, increased DOC in the groundwater can have both positive and negative effects on the groundwater quality.

Researchers in France have also studied the effect of stormwater infiltration on the structure and activities of groundwater biofilms (Lebon *et al.*, 2021). They found that the biomass and structure of biofilms in impacted groundwater were greater during both rainy and dry periods and that the activity of biofilms was increased during rainy periods, indicating a rapid response of the biofilm to infiltration inputs (Lebon *et al.*, 2021).

It is evident that the infiltration of urban stormwater has effects on groundwater below infiltration and detention/retention basins in several different ways. Direct transfer of specific contaminants has been found in some cases, while in others dilution of specific contaminants in background groundwater has been observed. An increase in organic carbon has been found in most cases and the changes in microbial composition, mass, and activity have been studied. Decreases in DO, and in some cases nitrate, and an increase in dissolved iron have been found. A recent study (Lebon *et al.*, 2023) found that the vadose zone (unsaturated zone above the groundwater) characteristics, namely vadose zone thickness (VZT) and water transit time influence the concentrations of nutrients supplied by stormwater (DOC and phosphate) to groundwater, while the flux of stormwater to groundwater resulted in NO_3^- dilution and changes in microbial activity. The variables which appear to influence the effect on groundwater quality are VZT, soil texture and organic matter content in the stormwater and basin sediments, concentrations of contaminants and composition of infiltrating water and groundwater.

This literature indicates that infiltration of stormwater to groundwater can lead to the direct transfer of contaminants from the stormwater to the groundwater but can also result in dilution of pre-existing groundwater contaminants. The transfer of contaminants from stormwater to groundwater may be limited by vadose zone properties such as thickness and permeability (which influences the water transit time). The transfer of organic carbon, especially BDOC from stormwater/basin sediments to groundwater influences the biogeochemical conditions by stimulating microbial activity and this can lead to decreases in DO and nitrate, and in some cases mobilisation of iron and other metals.

2.3.3 Natural aquifer treatment and groundwater geochemistry

Worldwide, nitrate and arsenic are two groundwater contaminants which frequently threaten groundwater supply of drinking water. Nitrate may originate from agricultural practices where it readily leaches from the soil under aerobic conditions and contaminates groundwater (Biddau *et al.*, 2019). Non-agricultural urban sources such as wastewater disposal also add a significant nitrogen load to aquifers (Wakida & Lerner, 2005) and this may be in the form of nitrate and/or other species such as organic nitrogen and ammonium. Arsenic contamination, on the other hand, is largely from geogenic sources. Arsenic is ubiquitous in sediments (Smedley & Kinniburgh, 2002), and changes in oxidation-reduction (redox) conditions result in arsenic mobilisation (Fakhreddine *et al.*, 2021).

Bekele *et al.* (2011) studied the water quality changes during treated wastewater infiltration through a 9 m thick vadose zone and compared contaminant concentrations in the downgradient groundwater to the infiltration source water. They found that, with a 4-day residence time in the vadose zone, reduction in concentrations of phosphate (30%), fluoride (66%), iron (63%) and TOC (51%) were achieved while there was no change in the concentration of total nitrogen. Changes in the nitrogen species were found; with total Kjeldahl nitrogen (TKN) - which is the sum of ammonium and organic nitrogen – being converted to nitrate (Bekele *et al.*, 2011), an oxidation process called nitrification. After nitrification, the more mobile form of nitrogen (nitrate) is readily leached to the aquifer. Denitrification requires anoxic conditions which may develop in parts of the vadose zone or in the shallow part of the aquifer if sufficient BDOC is present to allow consumption of available oxygen.

In a long-term study on a soil aquifer treatment (SAT) system where treated wastewater was infiltrated (for the purpose of treatment) through a 20 to 30 m thick vadose zone, it was found that the total nitrogen concentration needs to be kept below 10 mg/L to prevent ammonium and organic nitrogen reaching the aquifer (Mienis & Arye, 2018). The important processes for nitrogen removal were adsorption of ammonium (ion exchange) and denitrification. Ion exchange is not a permanent removal but serves to slow the movement of ammonium which allows for nitrification in the aerobic zone. Ammonium may still be displaced to the aquifer if a change in conditions occurs, resulting in: i) recharge effluent with a higher ionic strength (competition for exchange capacity of the soil); ii) disruption of the recharge regime such that conditions are no longer aerobic; or iii) significant increase in the concentration of ammonium in the recharge water (Mienis & Arye, 2018). The authors conclude that total nitrogen concentration should be kept below 10 mg/L to maintain a sustainable aerobic SAT system.

Aquifer storage and recovery refers to the injection of water into an aquifer and subsequent extraction from the same or nearby well (Maliva, 2020). Arthur, Dabous & Cowart (2002) studied arsenic mobilisation at two such sites where oxygenated water was injected into a reduced aquifer i.e. one that contains little to no oxygen or nitrate in the water and has reduced forms of minerals in the aquifer sediments. They found that arsenic mobilisation occurred during injection and recovery and that more arsenic was mobilised when injected water passed through ‘new’ sediment for the first time than when injected water had passed through sediment previously. The possible pathways to arsenic mobilisation during managed aquifer recharge are summarised by Fakhreddine *et al.* (2021), with the most common pathway being exposure of reduced aquifer sediments (arsenic residing in pyritic minerals) to oxidizing recharge water (containing DO and/or nitrate). This results in adsorption of arsenic onto iron(III) (hydr)oxides (i.e. repartitioning of arsenic) where it is then vulnerable to mobilisation through reductive dissolution of iron(III) (hydr)oxides in the presence of an organic carbon source. Similarly, in oxidised sediments arsenic is likely already adsorbed on iron(III) (hydr)oxides and the introduction of reducing recharge water (water that contains organic carbon) results in reductive dissolution of the iron minerals and mobilization of arsenic (Fakhreddine *et al.*, 2021).

A local example of a natural aquifer treatment (NAT) system is the Atlantis water supply scheme located in the northern part of Cape Town on the west coast of South Africa and has been in operation for nearly five decades (Bugan *et al.*, 2016). Here tertiary treated domestic wastewater and residential stormwater runoff are directed to infiltration basins which recharge the aquifer for later abstraction from a downgradient wellfield. Dissolved organic carbon is naturally present in the groundwater at about 2 mg/L. However, the final abstracted groundwater, which is a blend of natural and recharge water, has a DOC concentration of around 4 mg/L (Tredoux *et al.*, 2011). DOC can influence the redox potential and result in iron mobilisation and can also result in harmful disinfection by-products after chlorination. Iron clogging of production boreholes has been noted as an operational issue. However, the water softening step of the final water treatment removes sufficient iron for use as potable water supply (Tredoux *et al.*, 2011). Iron mobilisation and borehole clogging was studied in Western Cape boreholes including at the Atlantis water supply scheme (Smith, 2006) and it was found that mobilisation is not dependent on the total iron concentration of the aquifer material, but increases in low-pH and low dissolved oxygen groundwater, and is proportional to the amorphous iron oxide fraction in the aquifer material (Smith, 2006). Iron clogging is initiated by oxidation and precipitation, which increases with increasing pH and in the presence of ferrihydrite (an amorphous iron oxide), while microbially mediated oxidation may occur even under low oxygen conditions (Smith, 2006).

2.4 Summary

The CoCT has committed to diversifying water resources and becoming a WSC, including making optimal use of stormwater. The Cape Flats Aquifer will soon become one of CoCTs potable water sources and MAR will be conducted through direct injection of highly treated wastewater. Stormwater infiltration enhancement though retrofitted detention ponds which overlie the CFA may augment aquifer recharge while providing other benefits associated with BGI.

Anthropogenic aquifer recharge includes stormwater infiltration, which may be considered managed aquifer recharge (MAR) if aquifer recharge is the primary function, and effective management of both quantity and quality of recharged groundwater is undertaken. Natural aquifer treatment (NAT) is the intentional use of natural attenuation of contaminants during infiltration and/or transportation of water in an aquifer.

Soil based water treatment has been used in the context of stormwater filtration, infiltration and in NAT using a variety of source waters. Stormwater bioretention systems utilise soil or amended soil (bioretention soil media, BSM) for stormwater filtration and plant growth. Removal of stormwater contaminants including nutrients (nitrogen and phosphate) and conventional metal contaminants (cadmium, chromium, copper, nickel, lead, and zinc) in bioretention systems and by BSM has been the subject of numerous experiments. Further, the treatment of stormwater during infiltration, its effects on groundwater, and the use of aquifers in naturally attenuating contaminants have also been investigated.

Adsorption of metal contaminants and phosphate on soil particles is an immobilisation mechanism which removes these contaminants from infiltrating stormwater. Iron and aluminium (hydr)oxides provide adsorption sites for trace metals and phosphate; however, this capacity may vary (differently for each contaminant) with pH. Organic matter also provides sorption capacity and has been successful for retention of metals; however, leaching of phosphate from organic matter is often of concern and leaching of chromium and copper from organic matter have also been noted.

Nitrogen retention mechanisms are completely different from those of phosphate and metals and are highly dependent on biochemical cycling and redox conditions. Retardation of ammonium transport by cation exchange makes it less mobile than the highly soluble anion, nitrate, and this retardation may retain ammonium in the vadose zone where nitrification can occur. Resulting nitrate may be removed by plant or microbial assimilation or denitrification. Denitrification requires a carbon source and sufficient microbial activity to consume available oxygen before nitrate becomes the best available TEA.

Shallow groundwater environments, such as that of the Cape Flats, are likely to have higher concentrations of organic carbon reaching the water table because i) the VZT is small and ii) the carbon concentration in stormwater runoff may be high in areas impacted by sewer overflows, inadequate sanitation, or industry. Utilisation of nitrate as a TEA in the saturated zone is favourable because this removes nitrate via denitrification. However, sustained supply of organic carbon beyond the availability of nitrate would result in reductive dissolution of iron and manganese minerals. In addition to iron and manganese mobilisation, other trace contaminants such as arsenic adsorbed on the iron and manganese oxides may be released.

3 Research approach

This research formed part of an existing broader project called 'Pathways to Water Resilient South African Cites' (PaWS) undertaken by a transdisciplinary team of researchers at the Universities of Cape Town and Copenhagen. A study site was selected to meet the needs of the transdisciplinary team, in consultation with CoCT's Catchment, Stormwater and River Management Branch and groundwater management consultants, and local community members (Mclachlan *et al.*, 2023). The research approach for the water quality part of the broader project (this dissertation) was driven by two overarching aims: i) evaluate the potential for stormwater treatment during infiltration through the unsaturated soil, and ii) determine whether groundwater quality in the underlying aquifer would deteriorate due to the stormwater infiltration.

The field study provided a natural experiment where observations and monitoring data were used to i) deduce a conceptual hydrochemical model, ii) estimate contaminant removal during infiltration at this site, and iii) observe any adverse effects on groundwater quality. Large-scale soil column experiments were conducted to better understand: i) the soil's ability to treat contaminated stormwater in the during infiltration through different depths and in the saturated zone, ii) the effects of contaminant concentration, stormwater organic carbon and soil media properties on contaminant removal, and iii) potential release of geogenic contaminants from the soil. The soil used in the column experiments is central to this research and is therefore emphasised in bold text in Figure 3-1. It was collected from the study site during installation of the monitoring wells and is the connection between the field study and column experiments. The research approach is laid out diagrammatically in Figure 3-1. It includes physical research activities (blue), planning and thinking activities (pink and orange) conducted as part of this research (solid lines) and as part of the broader project but which have direct impact on this research (dashed lines).

The team research conducted at the study site was a pilot study questioning whether existing monofunctional stormwater detention ponds could be retrofitted and activated to become multifunctional BGI, and asking how this could be achieved. Another area of enquiry was determining how a transdisciplinary team of researchers could conduct this co-research together with local residents and government officials (Tanyanyiwa *et al.*, 2023). While this dissertation focusses on soil and water chemistry aspects, it is important to recognise that the research was part of a complex web of activities that are focused on determining how to increase the functionality of stormwater detention ponds in the South African context.

3.1 Field Study

Groundwater monitoring wells were installed at the study site for the purpose of monitoring water levels and chemistry of the background shallow groundwater, recently infiltrated stormwater, and shallow groundwater downgradient of the infiltration area. Positions and depths of the monitoring wells were decided based on preliminary infiltration swale designs which had two tiers of infiltration areas instead of just one, and the monitoring wells were installed to be positioned in the infiltration areas. However, the final design was modified due to higher-than-expected groundwater levels, and all wells installed before the swale was constructed were downslope from the final installed infiltration swale. An additional shallow well was later installed close to the infiltration swale (Figure 4-6 and Section 4.3).

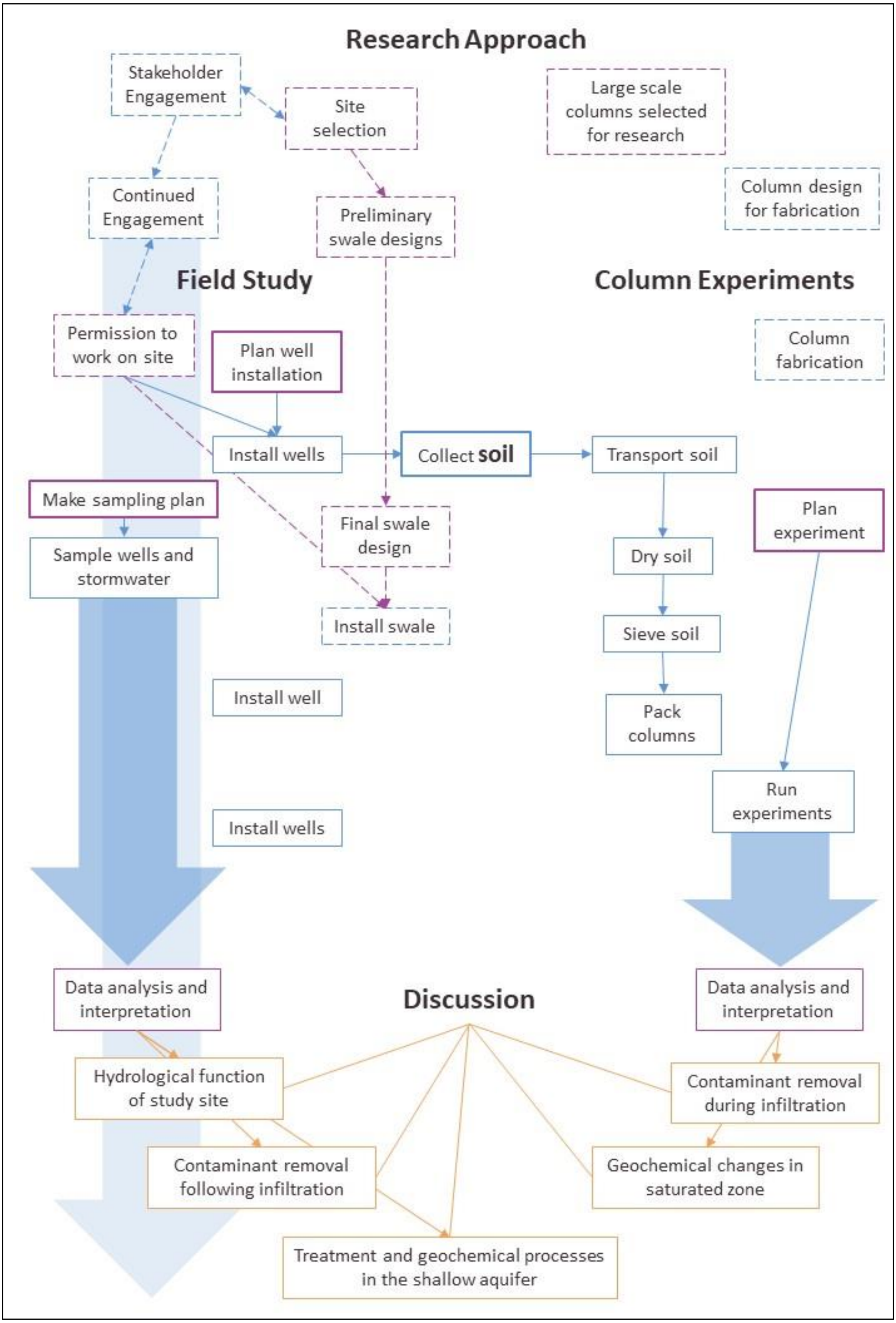

***Figure 3-1**: Diagram of research approach.*

Stormwater samples were also collected, and chloride was used as a tracer to determine the portion of infiltrated stormwater on post rainfall sampling days, which allowed for calculation of the removal of contaminants during infiltration. Changes in shallow groundwater chemistry were monitored in relation to rainfall events and seasons. The complexity of the site, especially regarding soil heterogeneity and hydrological flow paths was initially underestimated. However, a hydrological conceptual model was hypothesised using available data and this served as a background on which to interpret geochemical data. The research objectives for the field study along with data used to meet the objective are summarised in Table 3-1. The first two objectives which are related directly to water quality were established early in the process while the third objective arose during the pilot study.

Table 3-1: *Field study research objectives.*

Objectives	Data used	Explanation
1) Hypothesise a conceptual model of the hydrological functioning of the site.	Soil observations; discrete groundwater levels, temperature, and electrical conductivity; daily rainfall; short duration groundwater level and temperature logging.	Utilization of available data to describe the modes of operation of the system in response to rainfall under different starting groundwater level scenarios.
2) Determine and quantify stormwater treatment during infiltration through soil.	Stormwater and groundwater contaminant and natural tracer concentrations pre and post rainfall event.	Calculate ratio of stormwater and pre-existing groundwater in well, use this to determine % reduction in concentration of contaminant due to infiltration through the soil.
3) Evaluate the geochemical changes in the shallow aquifer below the stormwater infiltration site.	Groundwater chemical monitoring over seasons and in relation to hydrological processes.	Qualitative evaluation of redox processes in the shallow groundwater, where these processes may improve or deteriorate groundwater quality.

During well installation the extracted soil and aquifer sediment (all referred to hereafter as soil) was bagged and transported to UCT for use in the column experiments. Groundwater monitoring was carried out over a period of around 27 months from late June 2021 until late August 2023.

3.2 Column experiment

Field work and column experiments were conducted concurrently for the duration of the column experiment which took place over 20 weeks from mid-February until late June 2022. The large-scale columns contained 1.5 m depth soil from the study site, and synthetic stormwater was loaded and allowed to infiltrate through the full depth of soil. After the first 3 cycles of loading, a saturated zone was created in the bottom 0.5 m of the column and synthetic stormwater was infiltrated through 1.0 m of soil. Before, and finally after 6 cycles, the saturated zone was increased to 1.0 m and infiltration depth was therefore reduced to 0.5 m.

The column experiments consisted of four treatment conditions each conducted in duplicate. Six columns contained soil, and two contained silica sand. Sand columns were included to represent a worst-case scenario where soils contained little to no fines. Synthetic Stormwater (SSW) was prepared with contaminant concentrations representative of a formal residential area (low concentration), concentrations five times higher (high concentration) and high concentrations but without organic carbon. Each SSW composition was used in a pair of soil columns and high concentrations were used in the pair of sand columns. The objectives, data used to investigate each objective, and the controlled variables are described in Table 3-2.

***Table 3-2**: Research objectives for column experiments.*

Objectives	**Data used**	**Controlled variables**
4) Determine the soil/sand media ability to retain Cr, Cu, Ni, Pb, Zn, and P during infiltration of synthetic stormwater through an unsaturated media depth of 0.5 m, 1.0 m and 1.5 m	• Contaminant build up in soil samples at surface, 0.5 m, 1.0 m, and 1.5 m below surface. • Effluent contaminant concentrations after infiltration through 0.5 m, 1.0 m, and 1.5 m soil depths.	• Infiltration depth • Influent contaminant concentrations • Soil *vs* sand as filtration media
5) Determine the effect of dissolved organic carbon (acetate and glycine) in synthetic stormwater on denitrification during infiltration though and storage in saturated soil.	• Effluent N species and C concentrations after infiltration of SSW with and without DOC through soil. • N species and C concentrations in saturated zone samples of treatments with and without DOC in the SSW.	• Presence/absence of organic carbon in synthetic stormwater. • Infiltration depth. • Infiltration through unsaturated zone *vs* saturated zone samples.
6) Determine the relative effect of the media (sand vs soil) and the influent contaminant concentrations (high vs low) in treatment performance.	• Effluent contaminant concentrations after infiltration for treatments A, B and D. • N species and C concentrations in saturated zone samples of treatments A, B and D.	• Media type. • Influent contaminant concentrations. • Infiltration depths.
7) Evaluate the potential for mobilisation of arsenic, iron, and manganese from the soil during infiltration of SSW and after storage of infiltrated SSW in the saturated zone.	• Effluent metal concentrations after infiltration through soil depth. • Saturated zone sample metal concentrations.	• Infiltration depth. • Influent contaminant concentrations. • Infiltration through unsaturated zone *vs* saturated zone. • Presence/absence of organic carbon in synthetic stormwater.

4 Field study

4.1 Introduction

This chapter presents analysis and discussion of the pilot field study conducted at the stormwater detention pond in Mitchell's Plain which was retrofitted with an infiltration trench. As discussed, this work was exploratory and aimed to assess how the retrofitted detention pond functions and what potential changes in shallow groundwater chemistry may result from stormwater infiltration. This chapter introduces the study site, describes the field methods employed for data collection, presents the findings related to the hydrological functioning of the study site and geochemical changes in the subsurface, and discusses next steps and future research needs.

As will be described, shallow groundwater monitoring wells were installed across the site at different depths and were monitored over a 2-year period. The study considered geochemical changes that may occur due to stormwater infiltration such as those resulting from changing redox conditions; and the direct transfer of contaminants (nutrients and metals) from stormwater to groundwater during infiltration.

4.2 Study site description

4.2.1 Location and context

The Cape Flats is a large, relatively flat area of Cape Town which overlies the CFA, and is characterised by multiple different land uses including industrial, commercial, agricultural, formal residential and informal areas, resulting in variability of stormwater runoff quality. Poor stormwater runoff quality, a shallow groundwater table, and sandy soils leave the groundwater highly susceptible to input of contaminants from stormwater as well as other sources.

The CFA is a primary, major, unconfined, shallow aquifer occurring in unconsolidated material. A coarse-textured high hydraulic conductivity paleo channel running from the northeast to the southwest is the most productive part of the aquifer (DWAF, 2008). Clay lenses are common, especially below a portion of the Philippi Horticultural Area (PHA), which in some places limit infiltration, resulting in frequent wet season flooding (Woolf, 2023). The study site is located to the west of the PHA in a formal low-middle income residential area of Mitchell's Plain known as Rondevlei Park. Figure 4-1 shows the boundary of the CoCT and location of the CFA and an outline of the study area. Figure 4-2 shows the location of the study site and extent of its catchment.

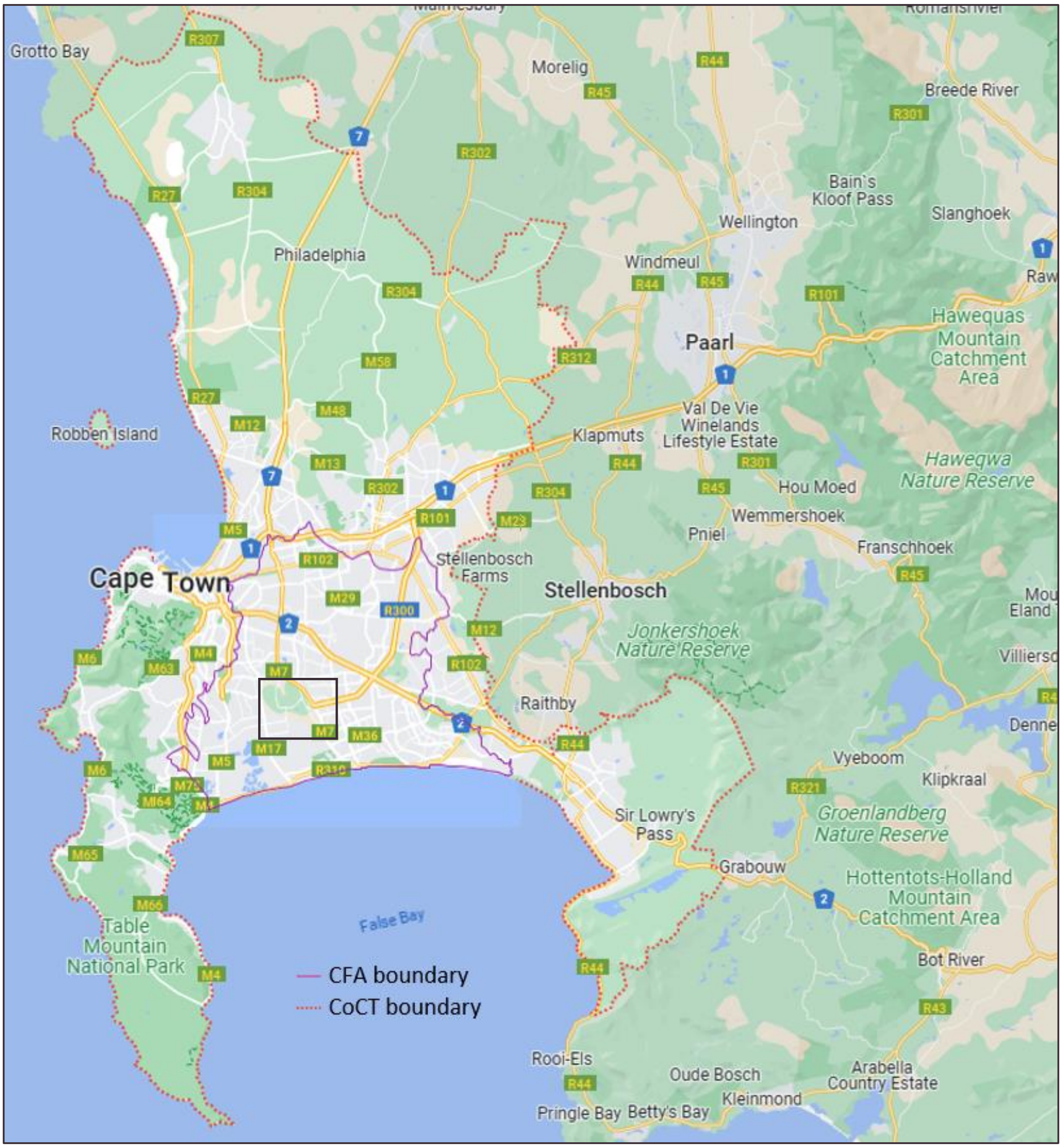

***Figure 4-1:** Boundary of the City of Cape Town and Cape Flats Aquifer. Black square shows extent of Figure 4-2 a). (Image source: Google, 2023)*

The selection of this stormwater detention pond was based on various physical and social factors as it needed to meet the requirements of the transdisciplinary research team. This included soil and hydrogeology suitable for MAR, inlet and outlet positions suitable for the low-cost retrofit (Tanyanyiwa, 2023), and opportunity for meaningful community engagement. One of the selection criteria was the depth to groundwater which needed to be low enough that sufficient space for infiltration was available. However, due in part to the site selection process having taken place at the end of the 2015-2018 ('Day Zero') drought in Cape Town, by the time the experimentation started in 2020 (after two seasons of good rains), the water table below the pond was found to be higher than initially anticipated. The location of this pond next to a school in Mitchell's Plain, Cape Town, gave the option for the safe installation of a weather station and engagement opportunities with learners and residents.

Cape Town has a Mediterranean climate; it receives most of its rainfall in the winter months of May to August and experiences hot and dry summers. The mean maximum air temperature in summer is 26°C although it does often get above 35°C and the mean winter minimum is 7°C (Olivier & Xu, 2019). Historical rainfall records from the Wolfgat Weather Station located 3.5 km from the study site show that the mean annual precipitation in the area is 530 mm (Tanyanyiwa, 2023).

***Figure 4-2**: a) Location of the study site in Mitchell's Plain with stormwater ponds in red; b) map of the local catchment area (gold polygon) and study site (red outline); and c) Study site layout (Image source: Google, 2023).*

4.2.2 Physical characteristics

The study site is a stormwater detention pond which is a usually dry depression designed to attenuate stormwater and reduce flooding. There are two inlets on the eastern side and one outlet leading back to the stormwater network on the western side of the site (Figure 4-2 c)). The pond has a surface area of 9950 m^2 and a depth of about 3.1 m in the centre of the depression. The site receives stormwater runoff from a catchment with surface area of 170 600 m^2 via the two inlets. A much larger volume of water enters the site through the southern inlet which is referred to as the main inlet and was the one sampled in the study. The central and lowest portion of the site is a seasonal wetland which has been completely saturated for part of the year since commencement of work at the site though this may not have been the case before or during the drought. On the southern side of the wetland there is a trench that was constructed by the CoCT's stormwater team which routes water to the outlet to the stormwater network.

Soil and aquifer material encountered during the monitoring well drilling (section 4.3.1) showed that heterogeneous conditions with respect to soil texture are present at the site, and this influences how an infiltrated plume of stormwater will move and spread in the subsurface. While most of the soils were dominated by sands, a layer of finer textured material (higher fraction of clay and silt) was encountered at 1.5 m deep (and then grading back to sand by 2 m bgl) at Positions 3 and 4, on either side of the wetland area. Figure 4-2 c) shows the positions of the monitoring wells, inlets, outlet, and infiltration swale. During sampling of wells at Positions 2, 3 and 4 which had screened sections between 1.5 and 2.5 m bgl the flow rate needed to prevent lowering the water level in the well was noticeably slower than in both shallow and deep wells, which also indicates a low permeability layer at this depth. In the background reference well, no such layer was encountered. Soils in the pond also showed evidence of a fluctuating water table. The grey soil is characteristic of a frequently waterlogged soil where iron oxides have been reduced in anaerobic conditions and removed by water movement. Above this the orange-red soil is characteristic of iron oxide minerals and mottles in the soil usually indicate dissolution and precipitation of iron oxides under anaerobic and aerobic conditions respectively (Figure 4-3).

The groundwater levels in the deepest (middle) part of the pond ranged between surface level and 0.65 m bgl over the research period. The groundwater flow direction is from the NNE to the SSW, and the dry season gradient is 0.005 m/m. The centre of the site was saturated (i.e., the groundwater table was at the surface) from August to December 2021, June to September 2022, and July to August 2023.

4.2.3 Detention pond retrofit

An infiltration swale was constructed along a contour in front of the inlets to retain the incoming stormwater (Figure 4-4) (Tanyanyiwa, 2023; Tanyanyiwa *et al.*, 2023). The infiltration swale receives stormwater from each of the two inlets and was designed to retain 300 mm ponded depth of water before flowing over two 2 m wide weirs at either end of the berm. Construction of the trench and berm was completed in early September 2021. Between November 2021 and April 2023, the trench was frequently undermined by Cape Dune Mole-Rats (*Bathyergus Suillus*) resulting in multiple direct pathways for the stormwater from the infiltration area to the wetland and outlet without infiltrating / filtering through the soil. These mole tunnels reduced the amount of infiltration but did not prevent infiltration all together. In April 2023 a mole barrier, consisting of flexible high-density polyethene (HDPE) sheets was installed on the downgradient side of and along the entire length of the berm to a depth of 1.5 m below the base of the trench. Field observations indicated that this was effective at preventing the Mole-Rats from creating tunnels in the infiltration trench, and water was better retained.

Tanyanyiwa (2023) conducted extensive hydrological modelling based on rainfall data from 2005 to 2022 which demonstrated that: i) Under pre-retrofit conditions 32% of stormwater reaching the site would infiltrate to groundwater; ii) With the addition of the infiltration swale, 51% of stormwater reaching the site would infiltrate to groundwater; iii) Infiltration was limited by the water table and lowering the water table through controlled abstraction (in post-retrofit condition) would result in infiltration of 74% of the stormwater.

Figure 4-3: *Soils encountered during drilling at position 1 (left) position 3 (top right) and mottles in soft soil ped (bottom right).*

Figure 4-4: *The study site during wet (top) and dry (bottom) conditions. In both pictures the forebay area in front of the southern inlet is visible.*

4.3 Field and analytical methods

4.3.1 Groundwater monitoring well installations

Eight groundwater monitoring wells were installed by an environmental drilling company, Envirovac, using a hollow stem auger drill rig and hand auger in June 2021 before construction of the infiltration trench and berm. The wells were constructed out of 63 mm diameter PVC pipe with an end cap to seal it at the top and bottom and a slotted section in the lowest 0.5 m of each well to allow groundwater from that depth to be sampled. Clean filter sand was packed around the slotted section of the well casing, bentonite was used to create a seal above the slotted section and backfill was used to fill around the well above the bentonite seal. A concrete head box was installed around the top of each well and fitted with a closable cover flush to the ground. A diagram of the well construction is given in Figure 4-5.

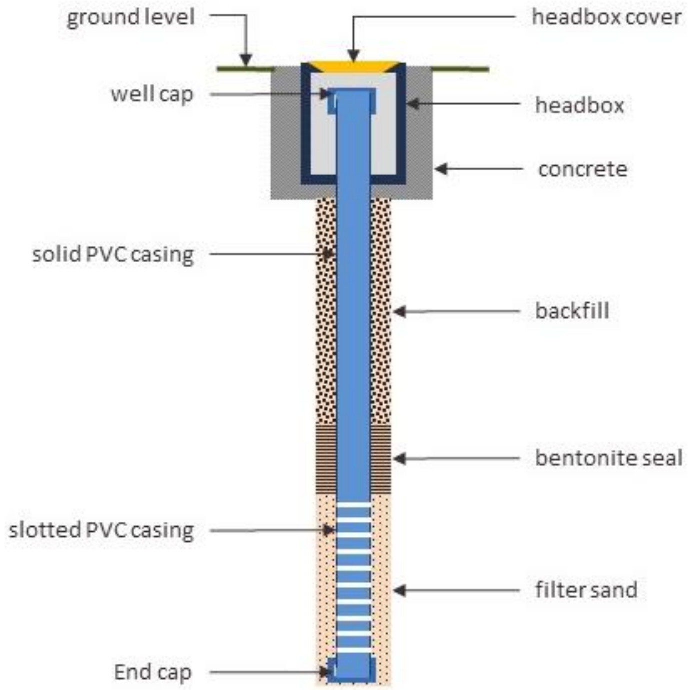

Figure 4-5: *Diagram of monitoring well construction.*

In total twelve monitoring wells were installed at the site, eight before construction of the infiltration swale, one soon after construction and three toward the end of the study period. The first eight monitoring wells were installed in four locations across the site with multiple depths in some locations to intercept the infiltrated stormwater. It was anticipated that early in the rainfall season the groundwater table would be low and a deep well would be in the position to intercept infiltrated stormwater and later in the season the groundwater table may be higher and a shallower well would intercept infiltrated stormwater. In monitoring well Position 1 (outside of the expected infiltration area, Figure 4-6) one well (1D) was installed with a total depth of 3.75 m bgl as a background groundwater reference well. In Position 2, slightly down gradient and approximately halfway between the two inlets, three monitoring wells were installed to depths of 1.5, 2.5 and 3.5 m bgl and were called 2S, 2M and 2D respectively. They were planned to be in the primary infiltration area based on preliminary retrofit designs but ended up being around 1.5 m downgradient from the finally-constructed infiltration swale. In Position 3, on the inlet side of the wetland and around 50 m down-gradient from Position 2, two wells were installed at 1.8 and 2.8 m bgl and were called 3M and 3D respectively. In Position 4, on the outlet side of the wetland, two wells were installed to 1.5 and 2.5 m bgl and called 4M and 4D respectively. The "D" monitoring wells have their screened sections at approximately the same absolute depth, "M" wells at the same depth and the one "S" well is at the shallowest absolute depth. Table 4-1 shows the installed well depths and elevation of the bottom of the wells.

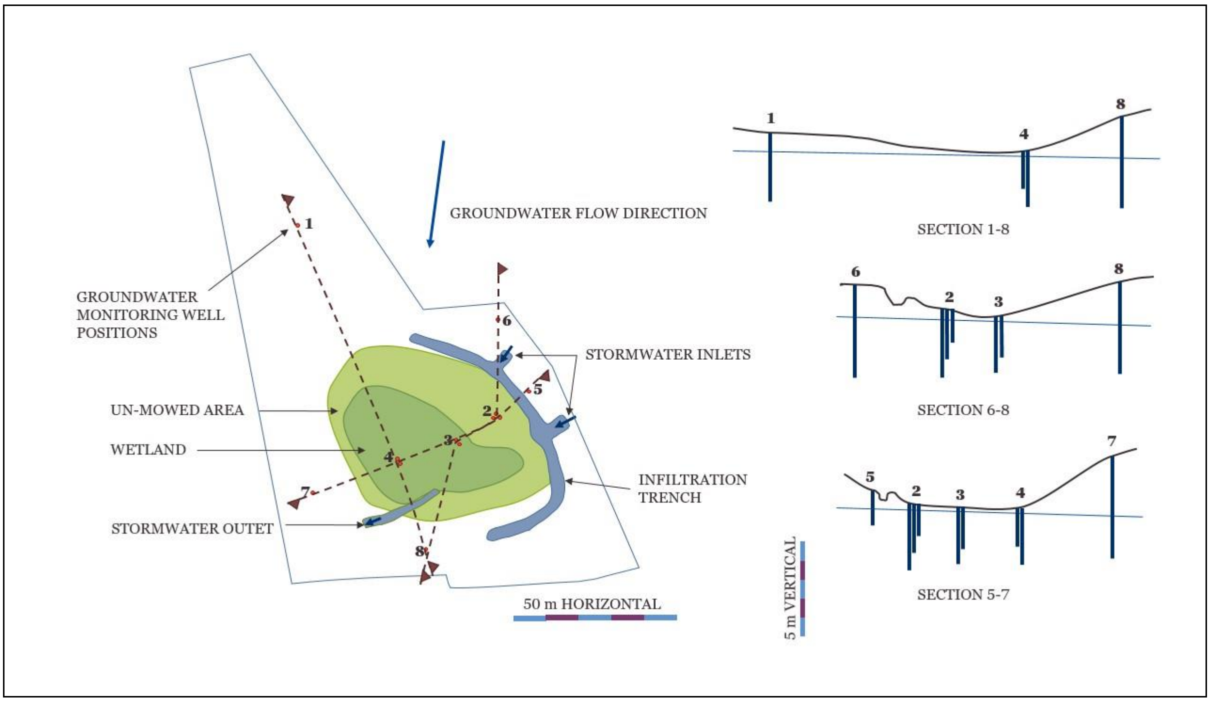

__Figure 4-6:__ Site layout diagram and cross sections. Numbers indicate monitoring well positions.

Table 4-1: *Monitoring well depths and elevation of the bottom of the wells.*

	Deep Wells			**Medium Wells**			**Shallow Wells**		
Position	**Well ID**	**depth (m bgl)**	**elevation of well bottom (m amsl)**	**Well ID**	**depth (m bgl)**	**elevation of well bottom (m amsl)**	**Well ID**	**depth (m bgl)**	**elevation of well bottom (m amsl)**
1	1D	3.83	24.90						
2	2D	3.51	24.63	2M	2.62	26.05	2S	1.63	26.53
3	3D	2.88	24.86	3M	1.80	25.90			
4	4D	2.57	25.19	4M	1.58	26.17			
5							5S	1.90	26.86
6	6D	5.15	25.73						
7	7D	5.31	24.37						
8	8D	5.15	24.41						

After construction of the infiltration swale an additional monitoring well (5S) was installed next to and up gradient of the swale (Position 5 in Figure 4-6), to intercept newly infiltrated stormwater. This well was installed by hand auger to a depth of 1.9 m below ground level with help from local residents and constructed in a similar way to the other wells but using 33 mm diameter HDPE pipe instead of 63 mm PVC due to the smaller size of hand auger available for installation. In March 2023 three new 63 mm diameter PVC wells (with 0.5 m screen as before) were installed by the same drilling company as previously. Monitoring well 6D was installed at Position 6 upgradient (in terms of groundwater flow direction) from the infiltration swale and wells 7D and 8D were installed at Positions 7 and 8 downgradient of the pond area. Monitoring wells 7D and 8D are situated downgradient of the wetland area, and on the downgradient side of the study site in general to further delineate the extent of any water quality impacts. The well depths are included in Table 4-1.

4.3.2 Sampling of groundwater and stormwater

Datry, Malard & Gibert (2004) and Mermillod-Blondin *et al.* (2015) suggest sampling on the day following a significant rainfall event as a way to sample the greatest portion of infiltrated stormwater. Sampling infiltrated stormwater allows for assessment of the contaminant removal during infiltration. On eight occasions during the research period groundwater samples were collected 1 to 3 days after a rainfall event > 3 mm (median 23.6 mm, range 4.8 to 136 mm) which is the minimum rainfall depth required to generate runoff that will reach the site inlets (Tanyanyiwa, 2023). As previously noted, the groundwater table is shallow at the study site and infiltration of stormwater to a significant extent only occurs when the water table is sufficiently low. Furthermore, sampling of infiltrated stormwater requires that the screened section of a monitoring well be located at the right depth and position to intercept the stormwater plume.

Groundwater sampling was conducted 26 times over the monitoring period: on 01 July 2021, every 2 to 4 weeks between 25 August 2021 and 19 October 2022, and approximately every second month between 19 October 2022 and 21 August 2023. Stormwater inlet sampling was conducted 7 times during rainfall events: twice in winter 2021, in autumn and winter 2022, in summer late 2022, and in autumn and winter 2023. Stormwater samples were also collected using the peristaltic pump, with the pump intake tube submerged in the main stormwater inlet while it was flowing. The flow through cell (described below) and water quality probes were used to take measurements of pH, T, EC, DO, and ORP, and samples were collected from the pump outlet safely and easily. Stormwater outlet sampling was conducted 9 times: in winter 2021, four times in spring and once in early summer 2021, and twice in winter 2022. Outlet samples were collected from the seepage flowing into the outlet channel from the wetland/overland flow. Probe readings of outlet samples were taken by holding each probe directly into the water in the outlet channel. Figure 4-7 shows the main (southern) stormwater inlet before and after swale construction with stormwater sampling tube visible.

Groundwater sampling was done using a low flow (≤ 0.5 L/min) sampling technique (USEPA, 1996). A flow-through cell was designed to accommodate the handheld pen-type water quality probes available to take measurements of the parameters in groundwater before the groundwater came in contact with the air. This is especially important for measurement of dissolved oxygen and oxidation-reduction potential (ORP) which can change rapidly on exposure to atmospheric oxygen. The flow through cell was 3D printed using polylactic acid (PLA) for the hard shell and thermoplastic polyurethane for the soft membrane. The flow through cell is show in Figure 4-8.

Figure 4-7: *Stormwater inlet showing overland flow before swale construction (left) and stormwater containment by swale with stormwater sampling tube (right).*

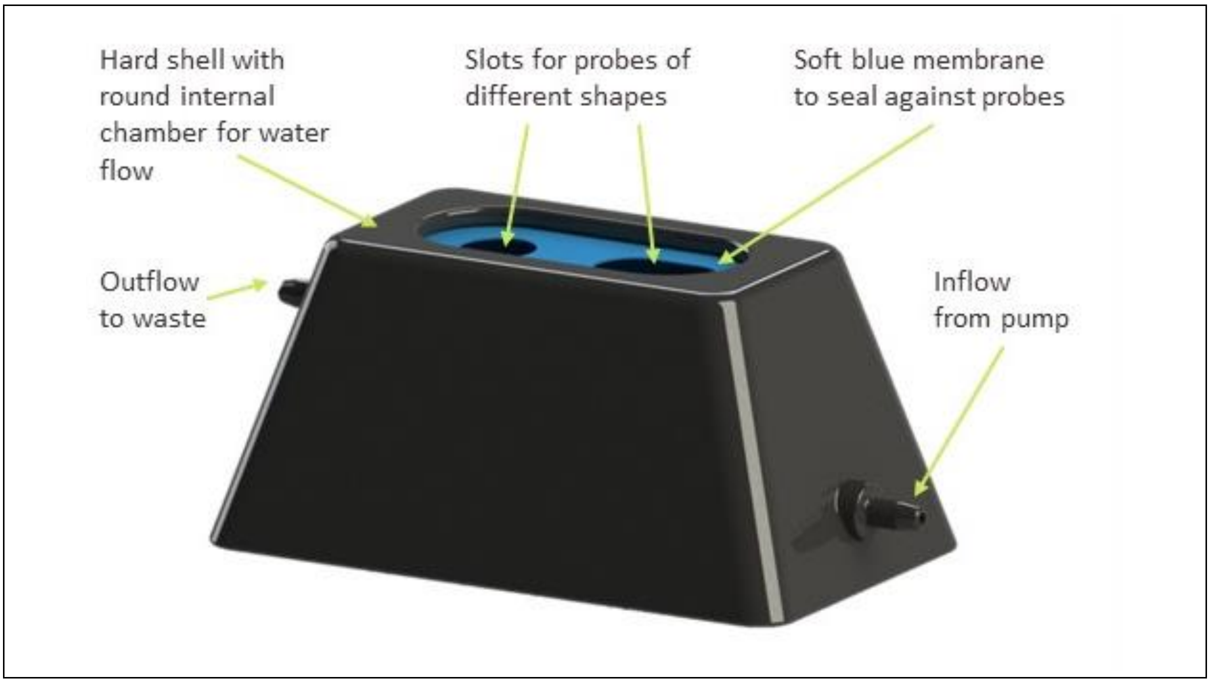

Figure 4-8: *Rendered image of the 3D printed flow-through cell.*

A peristaltic pump (Geotech Geopump™ Series I), compatible soft silicone tubing, and hard polyethylene tubing were used for groundwater sampling. The pump intake depth was the midpoint of the screened section of the well (i.e. 0.25 m from the bottom of the well) and the pump outlet was connected to the flow-through-cell into which the pH and EC probes were inserted. A picture of the sampling set up is shown in Figure 4-9. Monitoring wells were purged until the measurements of pH, T and EC stabilised. Measurements were taken every 3 min until the stabilisation criteria (three consecutive readings with pH within 0.1 units, temperature within 0.5°C and EC within 10%) had been met. Final T, pH and EC measurements were then taken, the probes replaced with DO and ORP probes, and 3 min allowed for removal of any air that may have entered and for readings to settle before taking ORP and DO readings. The pump was left flowing at the same rate, and the outlet disconnected from the flow through-cell for collection of the groundwater samples. Groundwater samples were collected directly from the pump tubing, and all water samples were filtered (where necessary) into relevant bottles which already contained any necessary preserving solution (Section 4.3.3, Table 4-3), and placed in cooler boxes with ice packs for transport to the relevant laboratories. A timeline of the sampling, rainfall and site development is shown in Figure 4-10.

Figure 4-9: *Low flow groundwater sampling set-up.*

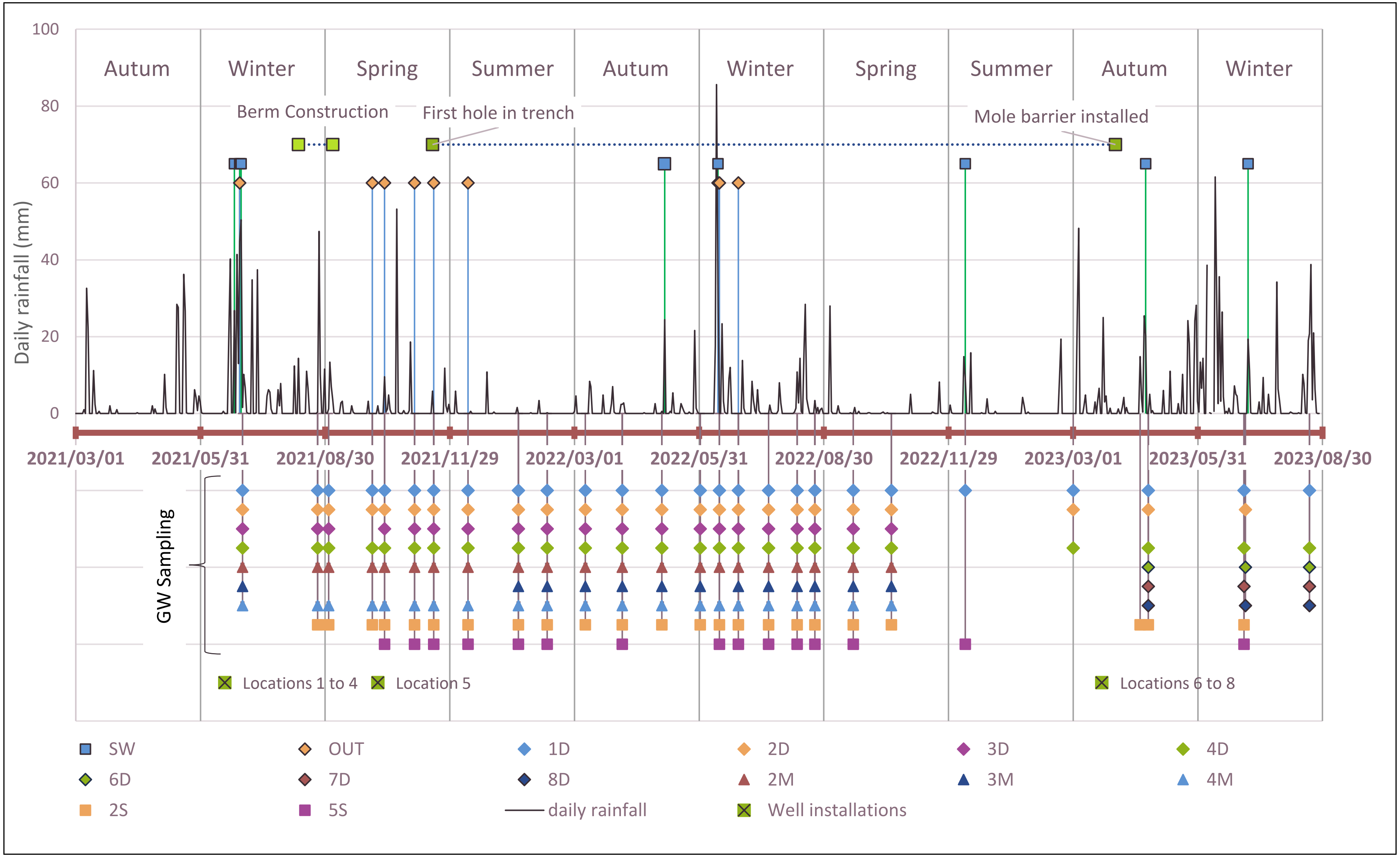

Figure 4-10: *Field study timeline.*

4.3.3 Water quality parameter selection

Stormwater contaminants may be present in dissolved or particulate form, and while particulates are removed though physical settling and filtration, dissolved forms are more mobile and more bioavailable (LeFevre *et al.*, 2015). Dissolved chemical contaminants can be split into three broad classes: i) nutrients, ii) metals, and iii) organic compounds (LeFevre *et al.*, 2015). Nutrients of concern are nitrogen and phosphorous (LeFevre *et al.*, 2015), conventional metal contaminants include cadmium, chromium, copper, lead, nickel, and zinc (Müller *et al.*, 2020), while organic compounds include petroleum hydrocarbons, pharmaceuticals, pesticides, personal care products, illicit drugs, and corrosion inhibitors to name a few (Burant *et al.*, 2018). In this study it was not possible to analyse all possible contaminants therefore only contaminants from classes i) and ii) were investigated and the focus was on dissolved forms. All other analytes were selected to improve understanding of physical and geochemical conditions. The analytical parameters and rationale for their inclusion in this study is shown in Table 4-2.

Table 4-2: *Water quality parameters and rationale for inclusion in study.*

Water quality parameters	Rationale for inclusion in study
pH and T	Master variables which influences geochemical reactions
EC and Cl	Dissolved salt concentration to assist in determining stormwater-groundwater interaction
Dissolved NH4-N, NO3-N, NO2-N, and PO4-P	Inorganic nutrients, contaminants of interest.
TN	Total nitrogen, contaminant of interest.
TOC	Driver of microbial activity and redox processes in subsurface
Fe(II), DO and ORP (and NO3-N)	Indicators of redox conditions in subsurface
Total dissolved metals and phosphorus	Contaminants of interest

Field parameters (pH, EC, DO, and ORP) were measured at all groundwater monitoring events, however not all chemical analytical parameters were analysed at every groundwater sampling round due to time and budgetary constraints. All samples except those for TOC and TN were filtered on site using a 0.45 µm filter, and samples for metals were preserved with 0.5 mL of 7% HCl or HNO_3 as indicated in Table 4-3. The number of groundwater sampling rounds which included analysis of each parameter is also included in Table 4-3.

Table 4-3: *Number of sampling rounds that included analysis of each parameter.*

No of GW sampling rounds	Water quality parameter	Sample Preservation
All 26	pH, EC, DO and ORP	Analyse immediately (on site)
17	Dissolved NH4-N, NO3-N, NO2-N, PO4-P*	Filter on site, analyse within 48 h
17	TOC, and TN	
21	Fe(II)	Filter and acidify with HCl on site
15	Cl	Filter on site
8	Total dissolved metals and P	Filter and acidify with HNO_3 on site

Notes: * PO4-P was analysed by EMT from Jan 2023 due to better detection limits.

4.3.4 Analytical methods

Measurements of T, pH and ORP were done on site using Hanna pen type probes (HI98130 and HI98120) while measurements of DO and EC were done using Ohaus pen type probes (ST20D and ST20C-B). Probes for measurement of pH, DO and EC were calibrated before use, and the ORP probe which uses a silver/silver chloride standard electrode was verified with a standard solution. All probes were thoroughly cleaned after sampling and stored in storage solution (pH and ORP probes) or dry (EC and DO probes).

Nutrient (NH_3-N, NO_2-N, TON and PO_4-P) and chloride concentrations were determined colorimetrically in the UCT Department of Civil Engineering Water Quality Laboratory (WQ Lab) using a Thermo Scientific™ Gallery™ Discrete Analyzer (ThermoFisher Scientific, Massachusetts) and the standard methods of the equipment. The NO_3-N concentration was determined as (TON) – (NO_2-N) where the brackets denote concentrations. Fe(II) concentration was determined using the Hach 1,10-Phenanthroline reagents according to standard method 3500-Fe (APHA, AWWA & WEF, 2017). A Thermo Scientific™ Gallery™ Discrete Analyzer (ThermoFisher Scientific, Massachusetts) was used to measure absorbance of reacted standards and samples and an external calibration curve was constructed and used to calculate Fe(II) concentrations in samples. TOC and TN concentrations were determined by the author in the UCT Centre for Bioprocess Engineering (CeBER) Laboratory using an Analytikjena multi N/C 3100 TOC analyser according to standard method 5310 (APHA, AWWA & WEF, 2017). The method detection limits (MDLs) for these methods were determined according to the USEPA procedure (United States Environemental Protection Agency (USEPA), 2016).

Total dissolved metals and phosphorus were determined by an external laboratory, Element Materials Technology (EMT) using Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) based on standard method 6020A (USEPA, 1994). EMT reported results below the MDL using the text "<" followed by the numerical detection limit.

Method detection limits result in left censored data because the true values below this limit are not known. When externally censored data were in calculations and graphs they were substituted with MDL/2, which was appropriate given the low degree of censoring (<25%) for results used in calculations (Antweiler, 2008, 2015; Verbovsek, 2011). For internal data the actual instrument values below the MDL were used in calculations (Antweiler, 2015). If calculated means were below the method detection limits, they were reported as "< *numerical MDL*".

4.3.5 Hydrological data collection

A weather station was installed on the roof of the school adjacent to the site; however due to connectivity and load-shedding (electricity outages) issues there were large gaps in the measured data. Daily total rainfall data was thus also obtained from the South African Weather Service (SAWS) for a weather station 3.5 km away (Wolfgat). This data had nine missing data points for the period March 2021 to August 2023, seven of which were filled in using data from the project weather station.

The depths to groundwater in the monitoring wells were measured prior to sampling from the well head box cover. Measurements of shallow groundwater depths (where groundwater was visible in the well) were made with a tape measure and measurements of deeper groundwater depths were done with a Water Level Meter (Heron Instruments Inc.). The positions and elevations of the head boxes were surveyed so that the groundwater elevations could be calculated. Groundwater level contours for the deep monitoring wells for specific days were plotted in Surfer® (Golden Software, LLC) to determine the groundwater flow direction and gradient.

Security at the study site is a concern, therefore the use of logging equipment which must remain on site was avoided. However, after nearly two years of monitoring at the site there was no evidence of tampering with the monitoring wells. Four water level and temperature data loggers (Heron dipperLog 128+) were thus deployed at least 0.5 m below the water level in monitoring wells 2S, 2D, 6D, and 7D from 24 April to 26 April 2023. Groundwater level measurements were taken before deployment and after retrieval of the loggers. The data loggers remained in the wells before, during and after a rainfall event before being retrieved. Data from the loggers was downloaded and compensation for atmospheric pressure was done using data from the weather station. The groundwater levels were then calculated from the pressure data and initial measured groundwater level.

4.4 Results and discussion

4.4.1 Hydrogeological conceptual model

Multiple lines of evidence were used to assemble a conceptual model of the hydrogeological functioning of the study site. The data available for this were: i) daily total rainfall; ii) discrete measurements of groundwater levels; iii) two days of water level and temperature measurements every 15 min in 4 monitoring wells; and iv) discrete measurements of groundwater and stormwater EC. Other considerations were the timing of the infiltration trench construction, mole barrier installation and the subsurface soil conditions (section 4.2.2).

Rainfall

Monitoring of the pond took place over three wet seasons: May to August of each 2021, 2022 and 2023, although the first wells were only installed in late June 2021. Daily rainfall data for the Wolfgat station (SAWS) shows that for the period May to August each year, the most rainfall was received in 2021 (629 mm) with a similar amount in 2023 (608 mm), while 2022 received 383 mm. According to long-term rainfall records (2006 to 2021) for Wolfgat weather station, the total annual rainfall received in 2021 was 880 mm, the highest since 2006, while 2022 received 530 mm, the same amount as the mean annual rainfall for that period (Tanyanyiwa, 2023). The total rainfall for January to August 2023 was 795 mm which exceeded the mean annual rainfall of 530 mm. This means that two of the three years over which this study occurred received more rainfall than the mean.

Groundwater levels

The measured groundwater levels were influenced by the period since the last rainfall event and the depth of the monitoring well, as well as the position of the screened interval in relation to the low permeability soil layer. Groundwater levels increased between July and August 2021 reaching the ground surface level by the end of August 2021, and started decreasing from October 2021 with deep wells reaching their lowest 2022 levels in May. In the wet season of 2022 only wells at Position 3 had an extended period (late June to late August) with water levels at the surface, while in 2023 all wells below the level of the infiltration swale (including 1D) had water levels at the surface.

Stormwater infiltration below the infiltration swale is likely to result in some groundwater mounding (see literature review), although the mounding size and duration has not been thoroughly examined. Nonetheless when determining the ambient groundwater flow direction, the water level measurements in deep wells from May 2022 were used because these were after the dry season when mounding, if any, would be at a minimum. These groundwater elevations were plotted in Surfer® (Golden Software, LLC) using the kriging method to generate groundwater contours. The groundwater contours were used to estimate the flow direction (from the NE to SW) and the hydraulic gradient (0.005 m/m). Groundwater levels in the central wetland area fluctuated between 0 and 0.65 m bgl while the water level below the infiltration swale fluctuated between 0.5 and 1.4 m bgl. Monitoring well 1D was assumed to be a reasonable (but not perfect) reference for background shallow groundwater quality as it had not received urban runoff from the stormwater network since installation of the infiltration trench. However, during large rainfall events there may be ponded rainwater in this part of the pond, which infiltrates (diluting the groundwater) or evaporates.

Figure 4-11 (a) shows the water levels in wells 1D (background), and 2S, 2M & 2D (close to the infiltration trench) along with daily rainfall. Water levels in 2S and 2M responded to smaller rainfall events and dropped lower during evapotranspiration periods (e.g., summer to early autumn), while 1D and 2D responded slower to rainfall and were less affected by evaporation. Increased water levels in wells 2S and 2M but not in 2D after a significant rainfall event indicated that the low permeability layer (~1.5 m below the bottom of the pond, Section 4.2.2) slowed water movement in the subsurface. Similarly, evapotranspiration during the dry season decreased the water levels in 2M and 2S while the water level in 2D decreased more slowly and in a similar way to the background water level as indicated by well 1D.

The top of the soil profile in the pond was exposed in the outlet channel (dug out by CoCT's stormwater department) on the south side of the wetland. Seepage from the soil into the channel occurs when the water head is sufficient to overcome the soil pore tension. By comparing the water level in 4M to occasions when the outlet channel was seeping or flowing it was possible to determine the groundwater level (0.2 m bgl measured in well 4M) required for outlet flow from the soil/wetland to occur – see Figure 4-11 (b). A series of cross sections from well 5S to 7D at different times of the year shows the water level changes in deep, medium and shallow wells, Figure 4-12.

Three modes of operation of the study site can thus be described: i) potential groundwater recharge mode where stormwater infiltration recharges groundwater; ii) filtration mode where stormwater infiltration results in further seepage from the water table to the outlet channel and while no net groundwater recharge is achieved the water quality is likely improved by passage through the soil; and iii) peak flow mode where the infiltration swale overflows its weirs and water runs overland to the outlet.

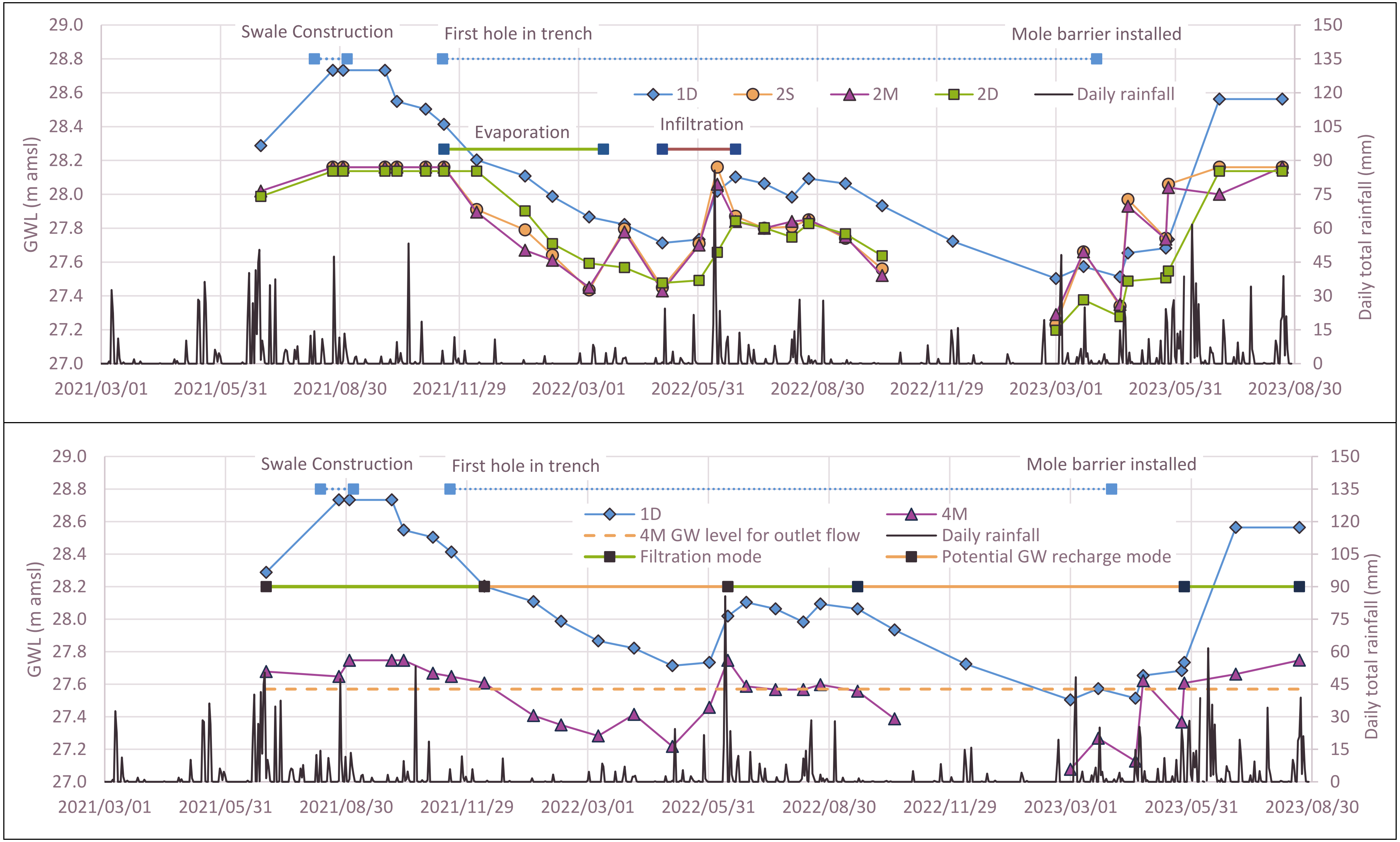

Figure 4-11: *Groundwater elevation over study period in wells 2S, 2M, 2D and 1D (top) and in 4M and 1D (bottom).*

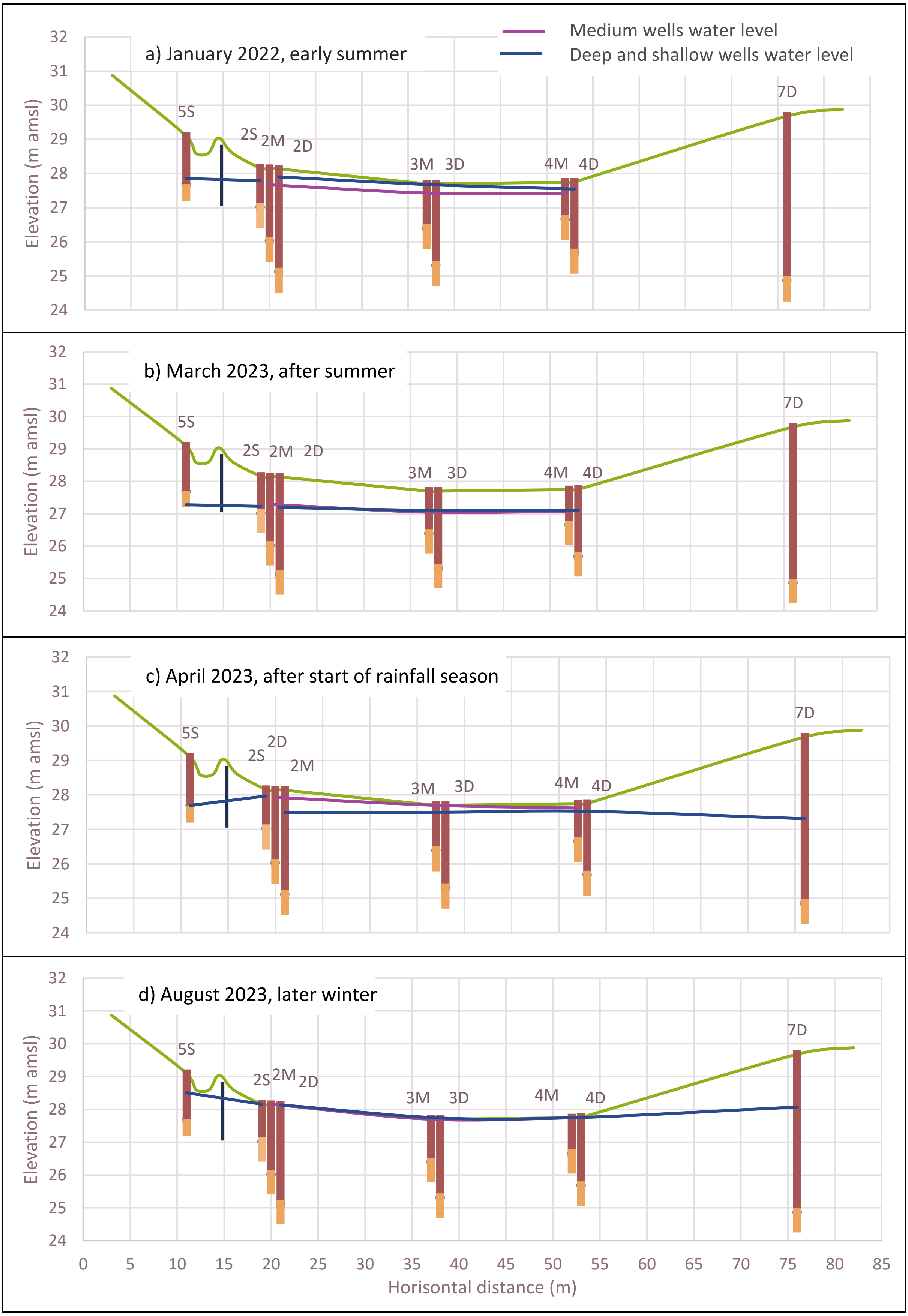

Figure 4-12: *Cross sections showing water levels at different times of the year.*

Logger data – water levels and temperature

During one rainfall event groundwater levels and temperature were recorded every 15 min in four wells using level loggers (Figure 4-13). The groundwater levels increased and decreased rapidly in 2S, and the water level in 2D increased more than that in 6D (position 2 is next to the infiltration swale and position 6 is upstream in terms of groundwater flow from the infiltration swale). The water level in upgradient (6D) and down gradient (7D) wells increased gradually by 10 and 5 cm respectively. This is likely the result of the stormwater mounding and spreading.

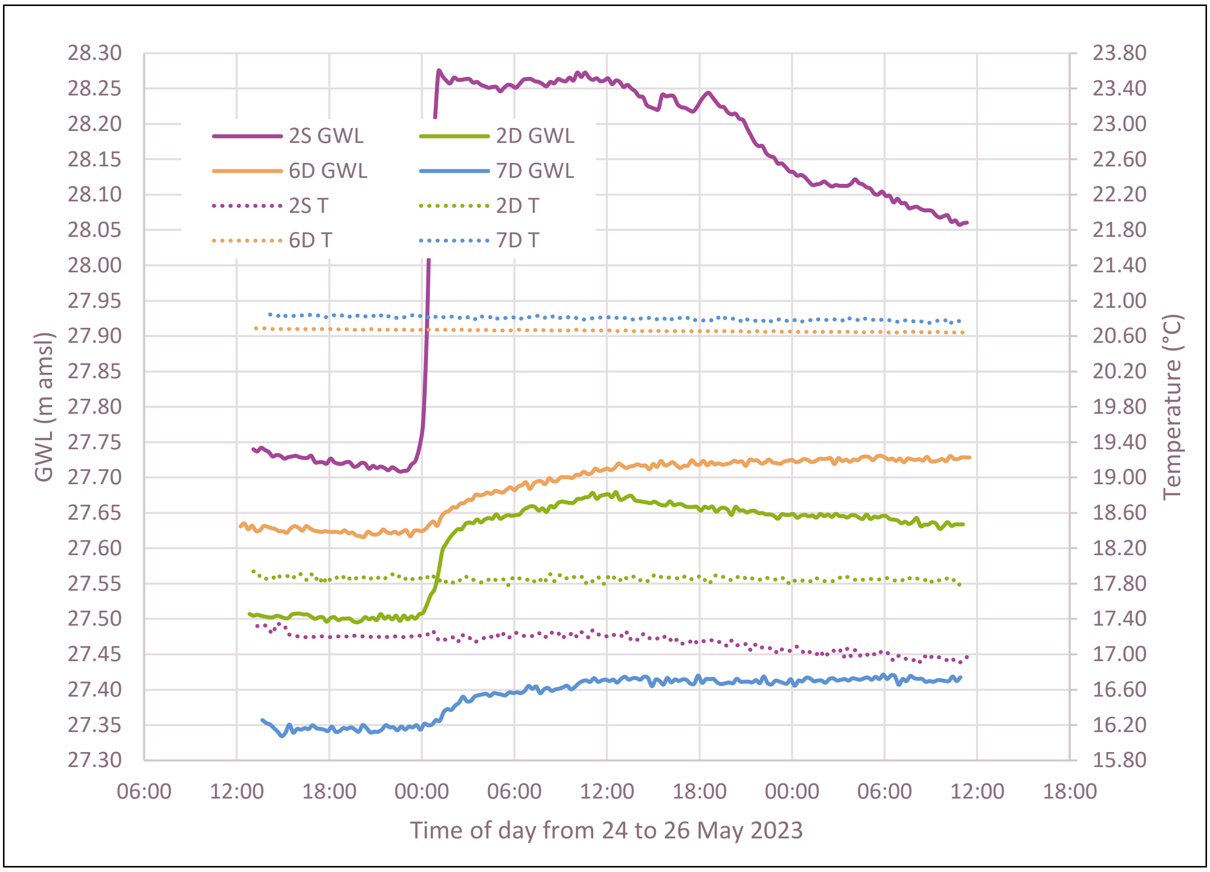

Figure 4-13: *Groundwater elevation and temperature changes in groundwater during a rainfall event.*

Temperature can act as a natural tracer (or surrogate tracer (NRMMC, EPHC, and NHMRC, 2009)) that can be used in surface water-groundwater interaction studies (Cook, 2020). It is very easy to measure and is useful when a temperature difference between the two water bodies of interest exists. Measured temperature in the stormwater ranged from 12.0 to 17.7 °C for late autumn and winter and was 25.3 °C for the summer measurement. The temperatures measured in background well 1D ranged between 16.0 and 21.7 °C over the entire sampling period with a winter mean of 17.0 °C and a summer mean of 21.0 °C.

Incoming stormwater on 23 April and 7 July 2023 had temperatures of 17.8 and 15.2 °C respectively so the stormwater temperature on 24 and 25 May 2023 was likely within that range. The groundwater temperatures measured with the loggers in 6D and 7D were between 20 to 21 °C and the temperatures measured in 2D and 2S were substantially lower at around 17 and 18 °C respectively and closer to the stormwater temperature, possibly indicating some infiltrated stormwater in that location from rainfall earlier in May. As seen in Figure 4-13 the groundwater temperature in well 2S decreases more than the other wells after infiltration of stormwater, possibly indicating that part of the SW plume has reached the depth of the screen interval of this well. However, well 2S is only 1.6 m deep and may therefore also be influenced by the cool surface temperature during the rainfall event to a small extent. When a temperature difference exists between stormwater and pre-existing groundwater, it may be a useful indicator of infiltrated stormwater, especially in conjunction with water level as achieved with water level loggers.

Electrical conductivity

Electrical conductivity (EC) is proportional to total dissolved salt concentration in water and is cost effective and easy to measure. Rainwater has very low dissolved salt concentrations and in general stormwater does too, especially if it has not travelled far or over salt covered surfaces. An exception which is not relevant in this context would be if salt is used to de-ice roads. Groundwater has a higher dissolved salt concentration because minerals in soils and sediments dissolve into the water. At the study site the stormwater had a lower mean dissolved salt concentration than the groundwater (Section 4.4.2, Table 4-5). It follows that stormwater or rainwater infiltration would cause a decrease in EC while evaporation and mineral dissolution would cause an increase in EC. Therefore, the expectation was that wells near the infiltration area would have lower EC, and background wells would have higher EC. Furthermore, the expectation was that infiltration occurring during the rainfall season (May to September) would lower the EC and evaporation occurring during the hot and dry season (December to March) would increase the EC. This, however, was not exactly the case. Table 4-4 shows the EC values in all wells across the site, shaded based on their values with the highest value (184 mS/m) in red, 50th percentile (69 mS/m) in yellow and lowest value (29 mS/m) in green.

Wells in the infiltration area did in general have the lowest EC values. Wells in Position 4 had the highest EC values, and the high values on 1 and 13 June 2022 and on 25 April 2023 correspond to infiltration events (water level in 2S higher than water level in 2D, Figure 4-11). The infiltration event on 5 April 2022 did not result in an EC spike in Position 4, however the rainfall event was small (4.8 mm), and the EC in Position 3 did increase. In the wetland area the water table is shallow and high evapotranspiration rates are expected. It is inferred that these rainfall events (i.e., June 2022 and April 2023) displaced previously concentrated (by evaporation) water into the sampling location for 4M and 4D. When the water table is very high further infiltration is not possible and previously infiltrated water may be above the screened interval of the wells. However, as the water table decreases as it does in summer, this water moves into the sampling depth of wells, which explains the low EC values recorded in December 2021 and August 2022.

Table 4-4: *Electrical conductivity (mS/m) in each well over the monitoring period.*

	Upgradient		**Infiltration area**				**Wetland area**				**Downgradient**	
Well ID	**1D**	**6D**	**5S**	**2S**	**2M**	**2D**	**3M**	**3D**	**4M**	**4D**	**7D**	**8D**
2021/07/01	104				37	44	107	60	150	157		
2021/08/25	65			71	64	67		58	61	68		
2021/09/02	83			72	68	72		64	62	76		
2021/10/04	81			69	76	64			61	80		
2021/10/13	75		74	76	74	59		63	61	69		
2021/11/04	90		69	75	86	73		65	65	83		
2021/11/18	83		79	82	77	64		65	67	87		
2021/12/13	79		48	49	49	41		38	49	74		
2022/01/19	72		60	69	42	57	61	60	69	81		
2022/02/09	66		65	68	80	63	59	61	69	81		
2022/03/09	78			76	79	60	64	66	71	89		
2022/04/05	76		78	56	74	72	63	100	75	88		
2022/05/04	81			74	70	73	65	100	72	85		
2022/06/01	68			73	74	73	63	79	124	151		
2022/06/15	69		34	77	71	78		54	159	137		
2022/06/29	78		51	70	68	75	64	67	106	79		
2022/07/21	79		49	72	68	77	63	66	91	79		
2022/08/11	70		49	69	66	71	61	64	78	68		
2022/08/24	52		40	72	50	57	61	63	77	73		
2022/09/21	69		38	74	62	72	62	65	75	71		
2022/10/19	79			67	62	65	64	67	76	66		
2022/12/12	71		70									
2023/03/01	69					60				70		
2023/04/19				63								
2023/04/25	45	44		29		52				184	59	55
2023/07/04	50	68	54	33		58				58	75	53
2023/08/21	77	72								70	95	64

Note: cells are shaded based on their values with the highest value (184 mS/m) in red, 50th percentile (69 mS/m) in yellow and lowest value (29 mS/m) in green.

Hydrogeological conceptual model

The above data interpretations and descriptions were used to produce the visual conceptual model which is included in Figure 4-14.

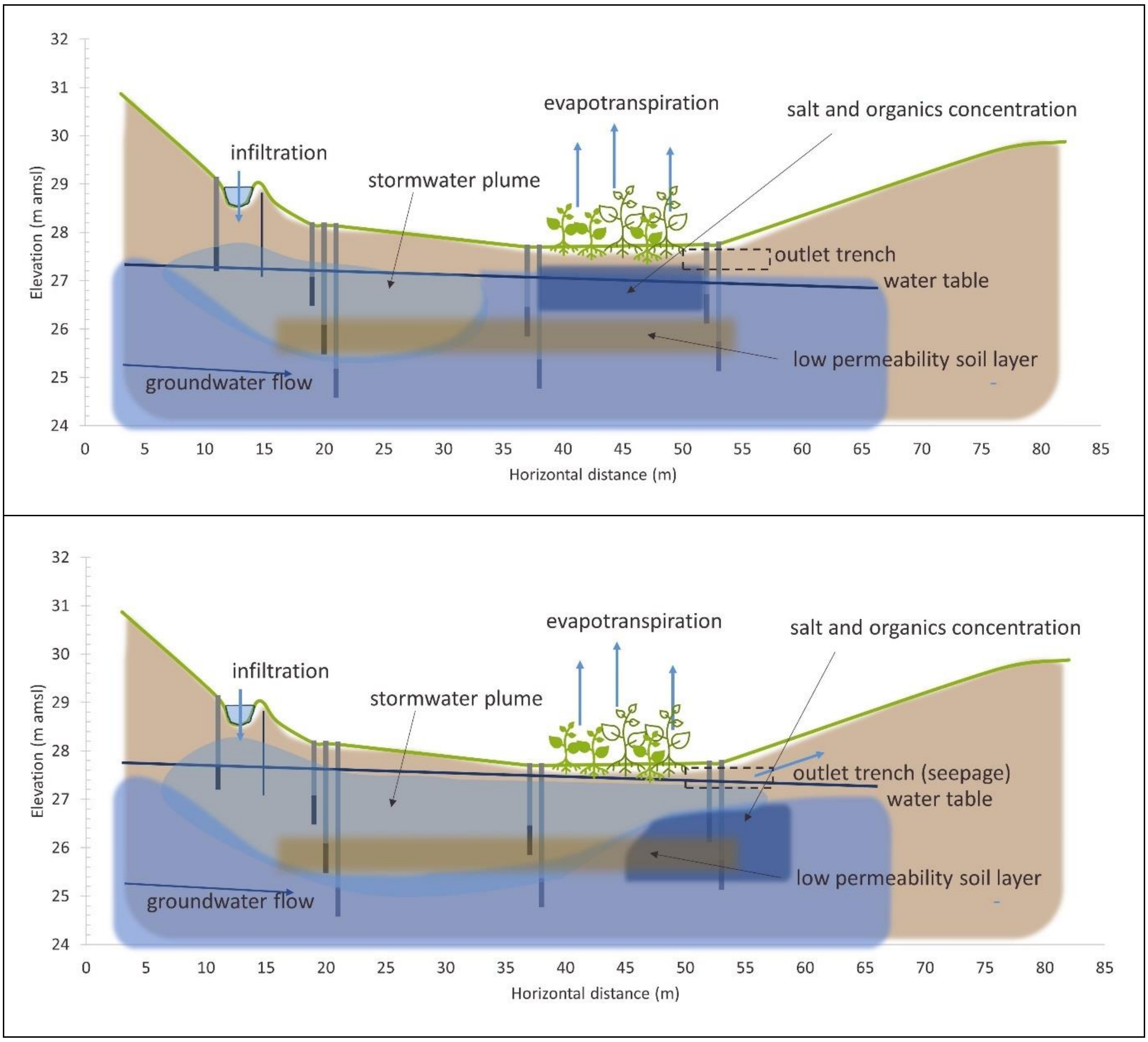

Figure 4-14: *Hydrogeological conceptual model at the start of the wet season (above) and during the middle to late wet season (below).*

4.4.2 Stormwater and groundwater quality

Mean concentrations of physicochemical parameters, dissolved contaminant concentrations and TOC in background groundwater, incoming stormwater and outlet water are presented in Table 4-5, and values which exceed the water quality limits and guidelines presented in Table 2-2 (Section 2.1.1) are indicated. The data show that the stormwater has a lower electrical conductivity (mean of 15.7 mS/m) than the background groundwater, as sampled from monitoring well 1D (mean of 73.4 mS/m). Nutrient concentrations in the stormwater are comparable to those found in other studies for urban stormwater (LeFevre *et al.*, 2015). The background groundwater has lower mean pH, ORP, and lower mean concentrations of DO, TOC, and ammonium compared to the stormwater inflow. However, the background groundwater concentrations of nitrate and nitrite are much higher than that in the stormwater. Stormwater results indicate the presence of TOC which may provide a carbon source for denitrification of the groundwater below the detention pond. The concentration of inorganic nitrogen in the stormwater is slightly above the freshwater aquatic ecosystem limit of 0.5 mg/L as N for oligotrophic conditions (DEAF, 1996c), however it is not a major concern for groundwater quality which already has elevated concentration of nitrogen (in the form of nitrate). Most dissolved metals, arsenic and phosphate were present at higher concentrations in the stormwater than in the groundwater.

In the planning phase of this project, it was not anticipated that there would be sustained flow out of the outlet channel between rainfall events, and since this study is focussed on groundwater quality, sampling of the outlet was not planned. However, samples from the outlet were collected four times, once during a rainfall event when overland flow was occurring and three times during seepage of the wetland and soils. These limited results suggest that the system provides stormwater quality improvement with respect to all nutrients measured, TOC and all dissolved metals except manganese, iron, nickel, and lead (which was below the detection limit in samples). The higher concentrations of dissolved iron and manganese appeared to precipitate out in the outlet channel once the water came into contact with the air.

Table 4-5: *Mean concentrations of dissolved contaminants in upgradient groundwater, stormwater inflow, and outlet.*

	Upgradient GW (1D)			**Stormwater inflow (SW)**			**Outlet (OUT)**		
	Mean	**+/- 95% CI**	**n**	**Mean**	**+/- 95% CI**	**n**	**Mean**	**+/- 95% CI**	**n**
Temp (°C)	18.5	+/- 0.8	26	17.5	+/- 6.1	5	16.4	+/- 5.3	6
pH	6.75	+/- 0.11	26	7.66	+/- 1.42	7	7.39	+/- 0.46	9
EC (mS/m)	73.4	+/- 4.9	26	15.7	+/- 11.4	7	61.9	+/- 22.5	9
ORP (mV)	113	+/- 33	26	163	+/- 135	7	43	+/- 118	9
DO (mg/L)	1.4	+/- 0.4	25	7.4	+/- 3.9	5	4.9	+/- 1.3	8
NH4-N (mg/L)	0.01	+/- 0.01	17	0.34	+/- 0.26	5	0.01	+/- 0.02	4
NO2-N (mg/L)	0.12	+/- 0.04	17	0.04	+/- 0.02	5	<0.001		4
NO3-N (mg/L)	[abc]15.2	+/- 1.7	17	[b]0.7	+/- 0.6	5	0.5	+/- 1.4	4
TIN (mg/L)	[abc]15.3			[b]1.1			[b]0.5		
TN (mg/L)	20.4	+/- 4.8	16	2.4	+/- 2.0	7	2.4	+/- 4.9	4
PO4-P (mg/L)	<0.11		16	[b]0.27	+/- 0.25	5	<0.11		4
TOC (mg/L)	2.7	+/- 1.7	17	[a]25.1	+/- 29.8	7	7.0	+/- 5.9	4
Cl (mg/L)	51.9	+/- 4.6	15	7.9	+/- 9.2	5	22.8		2
Al (µg/L)	6.3	+/- 5.7	5	[b]36.0	+/- 9.9	4	[b]10.9		2
As (µg/L)	1.7	+/- 2.0	6	3.3	+/- 2.2	4	1.6		2
Cr (µg/L)	<0.2		5	0.9	+/- 1.8	3	0.6		2
Cu (µg/L)	<1		5	[b]9	+/- 20	3	<1		2
Fe (µg/L)	18.6	+/- 28.6	6	26.9	+/- 45.4	3	[ad]1072.1		2
Pb (µg/L)	<0.4		5	<0.4		4	<0.4		2
Mn (µg/L)	1.7	+/- 0.9	6	1.7	+/- 4.2	3	[c]24.7		2
Ni (µg/L)	0.5	+/- 0.1	6	0.3	+/- 0.5	3	1.3		2
TP (µg/L)	[b]19	+/- 13	6	[b]160	+/- 117	4	[b]18		2
Zn (µg/L)	[b]10	+/- 6	5	[b]81	+/- 148	3	[b]5		2

Note: a = exceeds drinking water standard, b = exceeds value for aquatic ecosystems, c = exceeds value for irrigation, and d = exceeds value for industrial use. "<" indicates concentration below laboratory detection limits. All analytes are dissolved except TOC. The 95% confidence intervals are included.

The concentrations of inorganic nutrients in all the monitoring wells, stormwater, and outlet are shown in box and whisker plots in Figure 4-15. Based on the limited data collected for the outlet, results indicate the outlet water quality is improved compared to incoming stormwater for phosphorus. Outlet water quality is also improved compared to stormwater and groundwater for total inorganic nitrogen (TIN). Similar plots for the other water quality parameters are presented in Appendix A.

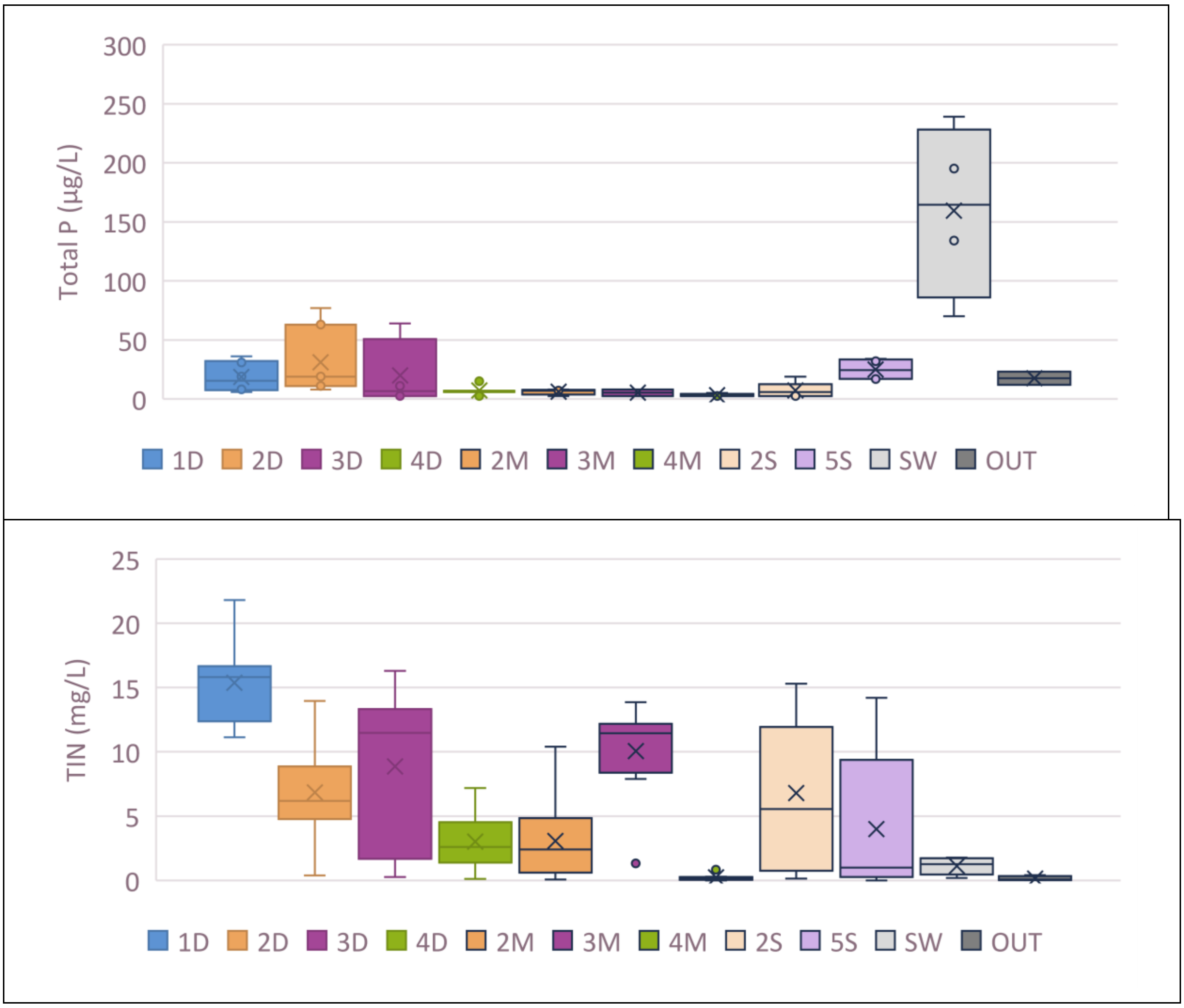

Figure 4-15: *Box and whisker plots for total inorganic nutrients P and N for all monitoring points.*

4.4.3 Treatment during infiltration

Chloride is commonly used as a natural tracer in groundwater systems because its behaviour can be assumed to be conservative (Clark, 2015), i.e. it does not take part, to any significant extent, in biogeochemical reactions in the subsurface (Tredoux, Cavé & Engelbrecht, 2004). In examining stormwater infiltration to groundwater Cl^- is useful because the stormwater typically has a much lower concentration of Cl^- than groundwater (as is the case here) and thus a two-end member mixing model Equation 3 (Cook, 2020) can be used to determine the proportion of previously existing groundwater in the sampled wells:

$$f_{GW} = \frac{[Cl]_{MW} - [Cl]_{SW}}{[Cl]_{GWref} - [Cl]_{SW}}$$ *Equation 3*

where:

f_{GW} is the fraction of water in the monitoring well that is previously existing groundwater,

$[Cl]_{MW}$ is the Cl$^-$ concentration in the monitoring well,

$[Cl]_{SW}$ is the mean Cl$^-$ concentration in the stormwater, and

$[Cl]_{GWref}$ is the Cl$^-$ concentration of the pre-existing groundwater.

Evaluation of the dilution effect of stormwater on the groundwater is important because it can be used to differentiate between dilution of contaminants and other remediation processes such as sorption, precipitation, and biodegradation. The chloride data were used to determine the fraction of infiltrated stormwater in monitoring wells 2S and 5S on days where chloride concentrations were low indicating recent stormwater infiltration. For stormwater infiltration to reach the sampling zone of the well (i.e., the screened section, bottom 0.5 m) the volume of infiltrating stormwater should create a large enough plume to reach the sampling zone. If the starting water level (before rain event) is high a larger volume of water is required to displace the existing groundwater. The concentration of chloride in the monitoring well immediately before the rainfall was not measured for each infiltration event. Instead, chloride data were plotted (Figure 4-16) to visually determine (based on groupings of concentrations and rainfall in preceding days) when concentrations could be considered "background or pre-existing" (highest concentrations) and when concentrations had been reduced by stormwater infiltration. Alternatively, data from 1D could have been used as reference groundwater; however, this is likely to be a less accurate estimation of groundwater previously existing in that well.

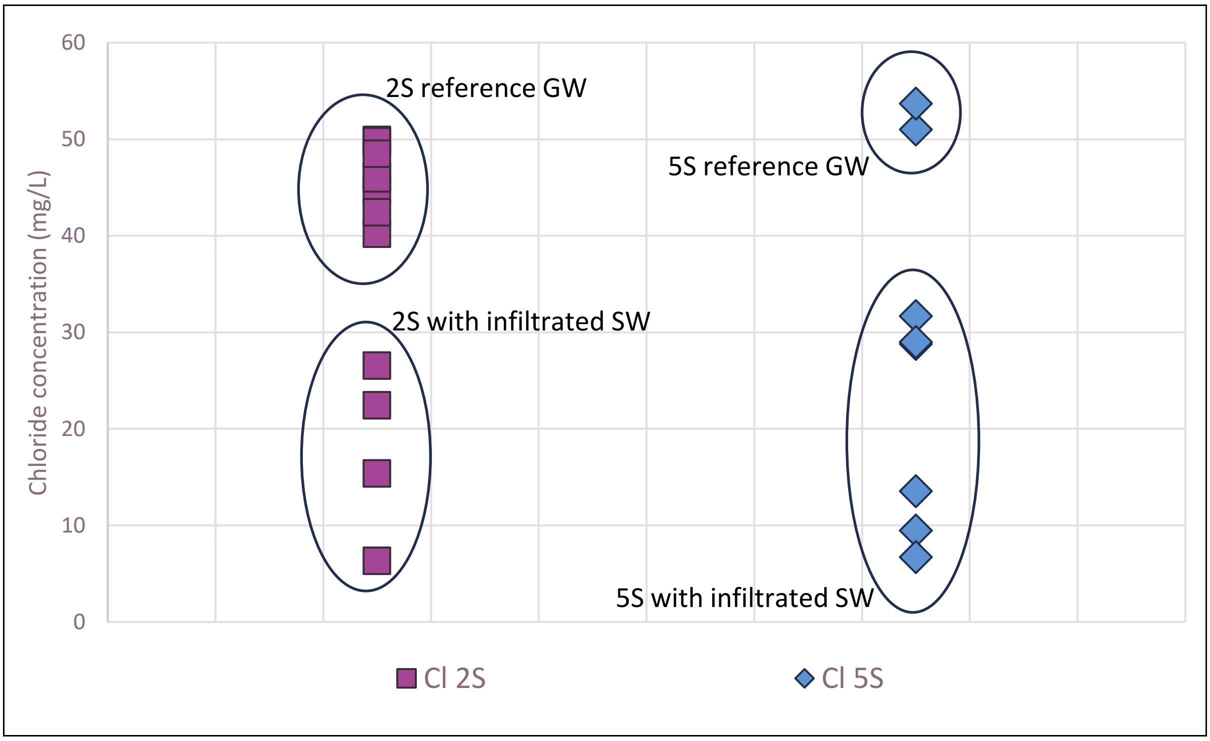

***Figure 4-16**: Chloride concentration in 2S and 5S to determine reference groundwater samples.*

The two-end member mixing model (Equation 3) was applied using the mean SW chloride concentration, and mean reference GW chloride concentrations for each 2S and 5S monitoring wells. The calculated fractions of groundwater and stormwater are presented in Table 4-6.

***Table 4-6**: Fractions of pre-existing groundwater and recently infiltrated stormwater in shallow monitoring wells.*

Sample Point	Sample Date	f_{GW}	f_{SW}
2S	2022/04/05	0.38	0.62
2S	2022/06/01	0.49	0.51
2S	2023/04/25	0.00	1.00
2S	2023/07/04	0.20	0.80
5S	2022/01/19	0.47	0.53
5S	2022/06/15	0.04	0.96
5S	2022/08/24	0.00	1.00
5S	2022/09/21	0.13	0.87
5S	2022/12/12	0.53	0.47
5S	2023/07/04	0.47	0.53

These fractions were used to calculate a theoretical concentration of each contaminant that would be present in the monitoring well if no treatment processes had taken place, i.e. the concentration obtained by mixing stormwater and groundwater in the fractions calculated above. The percent removed during infiltration was then calculated using Equation 4:

$$\%Removed = \frac{C_t - C_a}{C_t} \times 100 \qquad \textit{Equation 4}$$

where:

C_t	is the theoretical contaminant concentration in the monitoring well, and
C_a	is the actual contaminant concentration in the monitoring well.

The mean of the individual % removed is shown in Table 4-7 along with the mean actual and mean theoretical concentrations. Given that for TON (NO2 + NO3) the concentration was higher in the groundwater than in the stormwater, the % removed for TON is an improvement in groundwater quality.

***Table 4-7:** Mean actual and theoretical concentrations of contaminants in shallow monitoring wells after SW infiltration.*

	2S			5S		
	mean C_a	mean C_t	mean %Removed	mean C_a	mean C_t	mean %Removed
NH4-N (mg/L)	0.03	0.26	88	0.01	0.27	95
TON (mg/L)	0.4	3.1	74	2.6	2.2	13
TOC (mg/)	2.0	18.6	90	3.3	18.7	80
TP (µg/L)	10	118	92			
Al (µg/L)	5.5	27.1	83			
Zn (µg/L)	5.1	60.5	91			

4.4.4 Groundwater chemistry

Redox potential, pH and temperature are fundamental properties which control geochemical reactions, chemical speciation, and mineral solubility. Temperature influences biogeochemical reaction rates, including degradation of organic carbon. Organic carbon is the main electron donor which microorganisms in the subsurface use to make energy. This requires a TEA such as oxygen which will become reduced, (in the case of oxygen to water) as shown in Equation 5 where CH_2O represents a carbohydrate (Strawn, Bohn & O'Connor, 2020). Inorganic electron donors are less abundant in soils and may be oxidised by chemotrophs or abiotically: nitrification is an example of a this (Strawn, Bohn & O'Connor, 2020).

$$O_2 + CH_2O \rightarrow CO_2 + H_2O \qquad \textit{Equation 5}$$

The oxidation of organic carbon by microbes consumes TEAs in the groundwater which changes the geochemical conditions and therefore the chemical and mineral speciation potentially impacting groundwater quality. Understanding how organic carbon concentrations in the groundwater are influenced by recharge is necessary to build a conceptual understanding of the system. Examination of the most common redox active species (i.e., TEAs and their reduction products) gives insight into geochemical reactions which may influence the groundwater quality.

Temperature and pH

The logger data presented in Section 4.4.1 showed the usefulness of temperature measurements in monitoring stormwater infiltration where it can act as a tracer when sufficient temperature difference exists between the stormwater and groundwater. Water temperature at the study site varied with depth below the ground surface and across seasons, with deeper groundwater having a more stable temperature. In winter, the measured temperature increased with depth while in summer, water temperature decreased with depth. During autumn and spring, the temperature was more stable across the site. Box and whisker plots of the temperature measurements in each well and stormwater split over four seasons are shown in Figure 4-17.

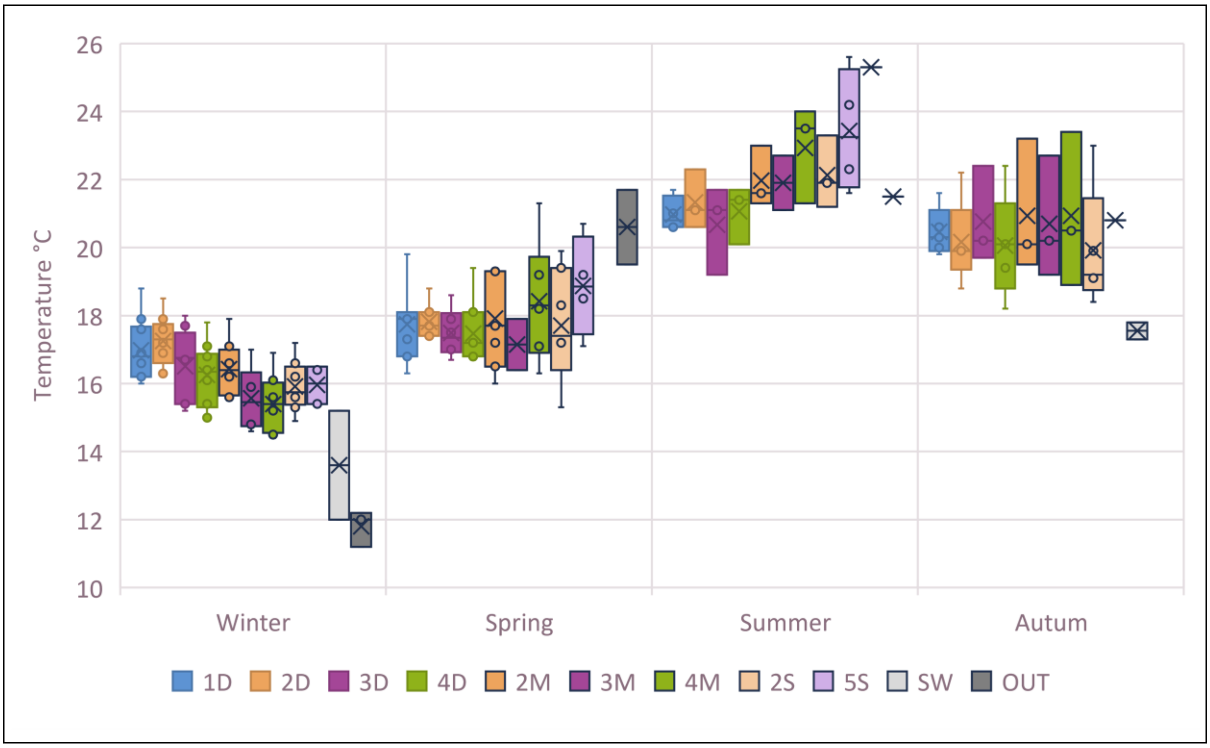

Figure 4-17: *Boxplots of temperature in groundwater and stormwater in each seasons.*

Linear regression was used to test if monitoring well depth (MWD) significantly predicted mean groundwater temperature (GWT) during summer and winter. The fitted regression model was GWT = 23.844 - 0.8152*(MWD) for summer and GW temperature = 14.136 + 0.8685*(MWD) for winter. The overall regression was statistically significant for summer (R2 = 0.5288, F(1, 7) = 7.855, p = 0.026) and winter (R2 = 0.9277, F(1, 10) = 128.37, p < 0.001). The trends for summer and winter suggest that at some depth the groundwater temperature is stable. By plotting the temperature range (highest – lowest) in each well against the well depth the depth at which temperature is expected to be stable is approximately 7.5 m bgl. Graphs showing these regression lines are included in Appendix B.

The mean pH in the background monitoring well (1D) was lower than in wells in Positions 2-5 (Figure 4-18). Wells on the infiltration swale side of the wetland (Positions 2, 5, and 3) had higher mean pH than wells at Position 4. One-way ANOVA showed that there was a significant difference in mean pH between at least two monitoring wells (F(8, 178) = 6.6, p < 0.001). Individual t-tests were conducted to compare the mean pH in 1D to each other well and after applying Bonferroni adjustment the mean pH in 1D was significantly different from the mean pH all other wells expect 4D. This suggests that the infiltration of stormwater resulted in a slight increase in the pH measured in groundwater. Stormwater pH measurements were spread over a larger range than groundwater pH.

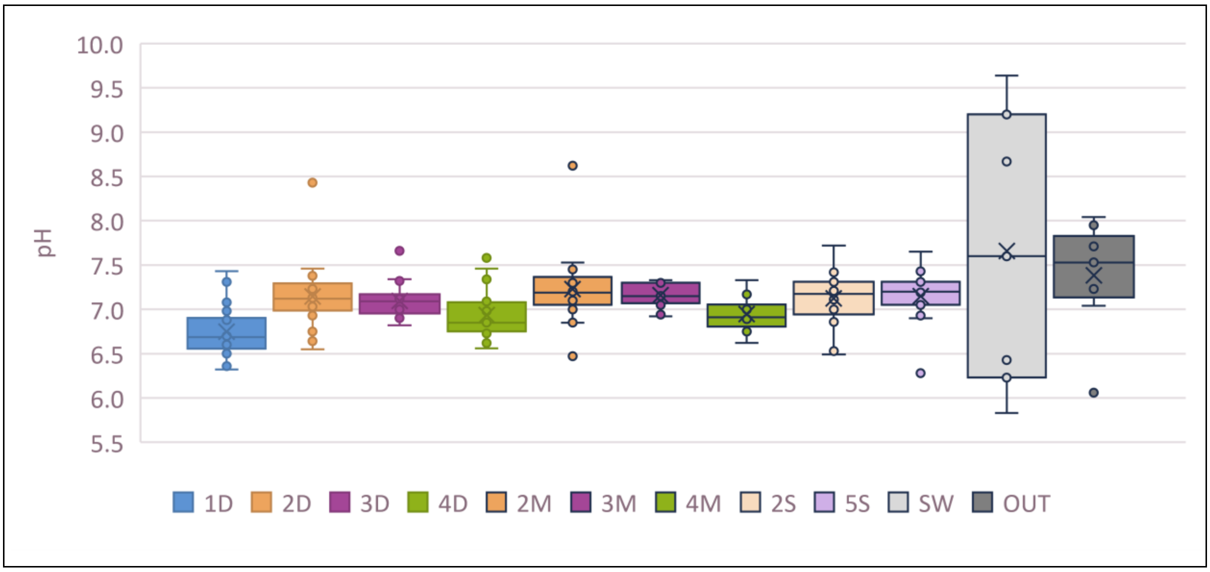

Figure 4-18: *pH in groundwater and stormwater over monitoring period.*

Organic carbon

As shown in Section 4.4.3, 80 to 90% of the TOC was removed during infiltration, and although the mean TOC concentration in the stormwater was 25.1 mg/L the highest concentration of TOC detected in the shallow wells (2S and 5S) was 5.9 mg/L. The TOC concentrations in all wells at the study site for the whole monitoring period were between <0.5 and 13.1 mg/L with a mean of 2.0 mg/L and median of 1.1 mg/L, and as shown in the box and whisker plot in Figure 4-19, the dataset contained outliers. The outlier TOC concentrations were found in monitoring wells 1D, 3D, 4D, and 4M, and in monitoring wells 3D, 4D, and 4M these often co-occurred with EC spikes. The graph shown in Figure 4-20 shows TOC and EC spikes in these monitoring wells. Interestingly the TOC and EC spikes in 4D and 4M seem to correspond to the wet seasons. One hypothesis for this is that evaporation during the dry season increases the EC in the wetland area, and SW infiltration in the wet season moves this high EC water into the sampling location of wells at Position 4. The TOC may originate from decaying organic matter and microbial byproducts in the wetland area which are concentrated during the warm dry season and move into the sampling location in the wet season. However, this relationship requires further research.

Linear regression was performed in Microsoft Excel to test if EC significantly predicted TOC concentration over all monitoring data, and individually for the monitoring wells (excluding 6D, 7D and 8D which only have 3 data points each). The overall regression was statistically significant (R^2 = 0.12, F (1, 121) = 16.05, $p < 0.001$) although the low R^2 shows that EC does not explain all the variability of TOC. The regression results for the individual wells are shown in Table 4-8. In 4M and 4D EC is positively correlated with TOC and appears to be a good predictor of TOC. In wells closer to the infiltration area EC was negatively correlated with TOC concentrations, this may indicate TOC inputs derived from stormwater.

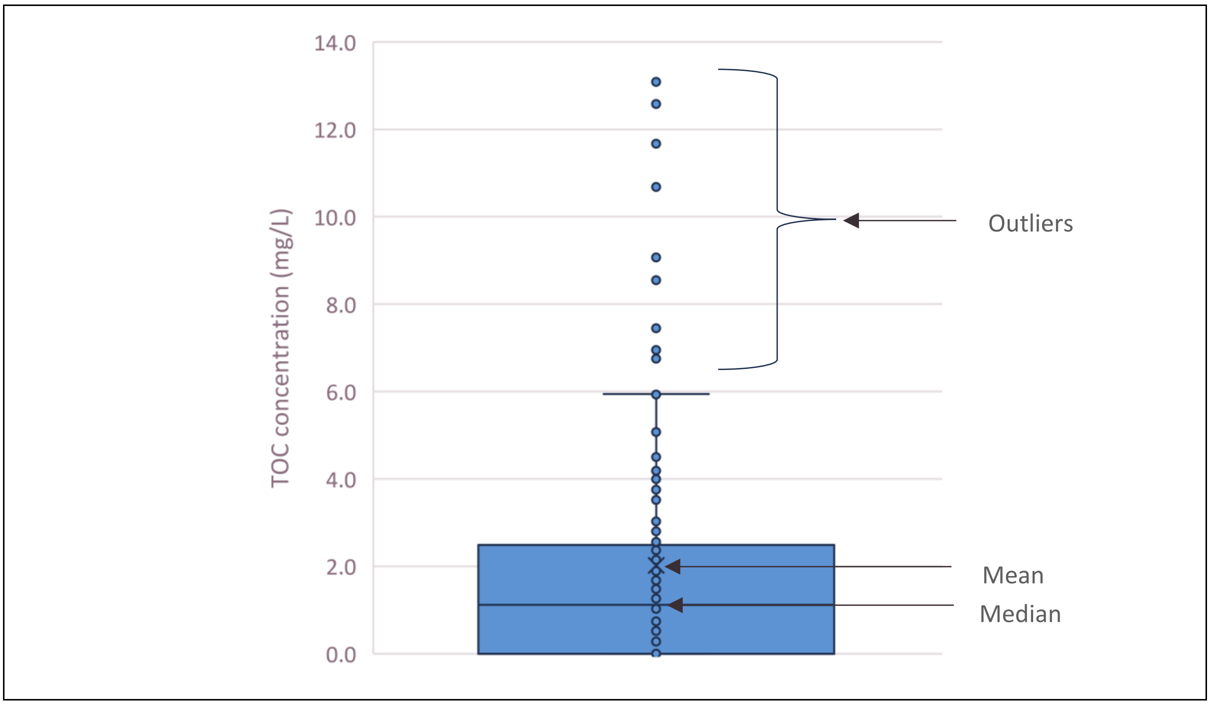

Figure 4-19: *Box and whisker plot of all TOC data.*

Table 4-8*: Results of regression analysis of EC and TOC in individual wells.*

	Ref GW	**Shallow infiltration area**		**Infiltration area**		**Before wetland**		**After wetland**	
	1D	**5S**	**2S**	**2M**	**2D**	**3M**	**3D**	**4M**	**4D**
R^2	0.02	0.18	0.41	**0.65**	0.21	0.53	0.46	**0.79**	**0.69**
P-value	0.61	0.26	0.02	**0.001**	0.09	0.03	0.02	**<0.001**	**<0.001**
coefficient	positive	negative	negative	**negative**	negative	positive	positive	**positive**	**positive**
df	1, 15	1, 7	1, 11	**1, 10**	1, 13	1, 7	1, 9	**1, 10**	**1, 14**
F	0.28	1.51	7.60	**18.83**	3.38	7.80	7.63	**37.79**	**29.48**

Note: Bold results are highly significant (p<0.001), results in normal text are significant (p<0.05) and greyed results are not statistically significant.

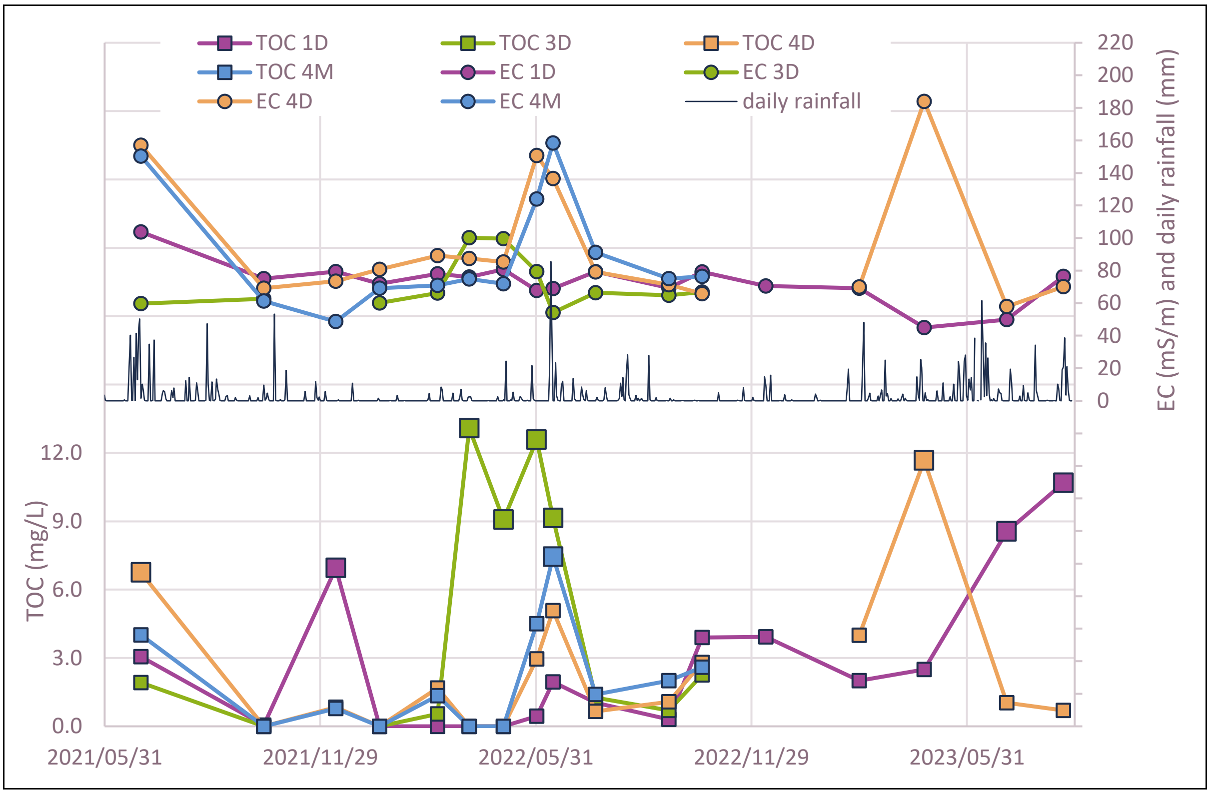

Figure 4-20: *TOC, EC, and total daily rainfall over the monitoring period for MWs 1D, 3D, 4D, and 4M.*

Redox conditions and groundwater denitrification

Measurements of the redox potential (ORP) in water indicate the tendency of the system to reduce or oxidise the chemicals present (Strawn, Bohn & O'Connor, 2020) and are made by measuring the potential difference between an indicator electrode and a reference electrode (APHA, AWWA, WEF, 2017). ORP is measured in mV, and a higher reading means a more oxidising environment, and a lower reading indicates a reducing environment. These measurements are more reliable for some redox couples (for example Fe^{2+}/Fe^{3+}) than others (McBride, 1994, page 245-250), and are influenced by other factors such as reversibility of reactions, concentrations of species and the number and variety of redox couples present. ORP can be useful to identify changes in redox conditions (especially for the Fe^{3+} - Fe^{2+} redox couple) (McBride, 1994).

To evaluate the redox conditions, it is useful to also evaluate concentrations of TEAs and/or their reduction products. The most energetically favourable TEAs are utilised first, and the sequence of utilisation generally followed is (Strawn, Bohn & O'Connor, 2020):

$$O_2 > NO_3^- > Mn^{4+} > Mn^{3+} > Fe^{3+} > SO_4^{2-} > CO_2 > H^+$$

In the case of iron and manganese, the electron acceptors are insoluble oxides, and the reduction product is soluble and is the species that can be evaluated in groundwater. In this study the redox indicators measured were DO, nitrite and dissolved ferrous iron (Fe(II)). The interpretation of redox conditions used in this study is based on McMahon & Chapelle (2008) and is laid out in Table 4-9. Clearly defined redox zones were not always found at the study site due to the soil heterogeneity and surface water influence, however investigating the changes in redox conditions can improve understanding of the chemical processes in the shallow groundwater.

***Table 4-9:** Interpretation of redox conditions in the subsurface (after McMahon & Chapelle, (2008)).*

Water quality parameter concentrations	Interpretation	Comments
≥1 mg/L DO; <100 µg/L Fe(II)	Oxic	
<1 mg/L DO; ≥0.5 mg/L NO_3^- -N; <100 µg/L Fe(II)	Anoxic, nitrate reducing	Conditions needed for denitrification provided available electron donor
<1 mg/L DO; <0.5 mg/L NO_3^- -N; ≥100 µg/L Fe(II)	Anoxic, iron reducing	
Other	Mixed	Heterogeneous subsurface and influence of SW infiltration. Multiple processes at once.

Although other researchers have used stable nitrogen isotopes and/or quantification of dissolved nitrogen gasses to quantify denitrification in groundwater (Smith *et al.*, 2004; Green *et al.*, 2008; O'Reilly, Chang & Wanielista, 2012), this study was not designed to quantify denitrification. However, since denitrifying bacteria are ubiquitous in soils, the existence of nitrate reducing conditions, the presence of an electron donor and the decrease in the concentration of nitrate all indicate that denitrification is occurring at the site.

The DO concentration across most of the site remained low (≤ 1 mg/L) from winter of 2021 (when monitoring started) until the end of summer 2022. It increased over autumn of 2022 and has subsequently remained above 1 mg/L, apart from occasional dips. The graphs in Figure 4-21, Figure 4-22, Figure 4-23 and Figure 4-24 show the concentrations of redox species and ORP over time in wells 1D, 2S, 4D and 4M respectively.

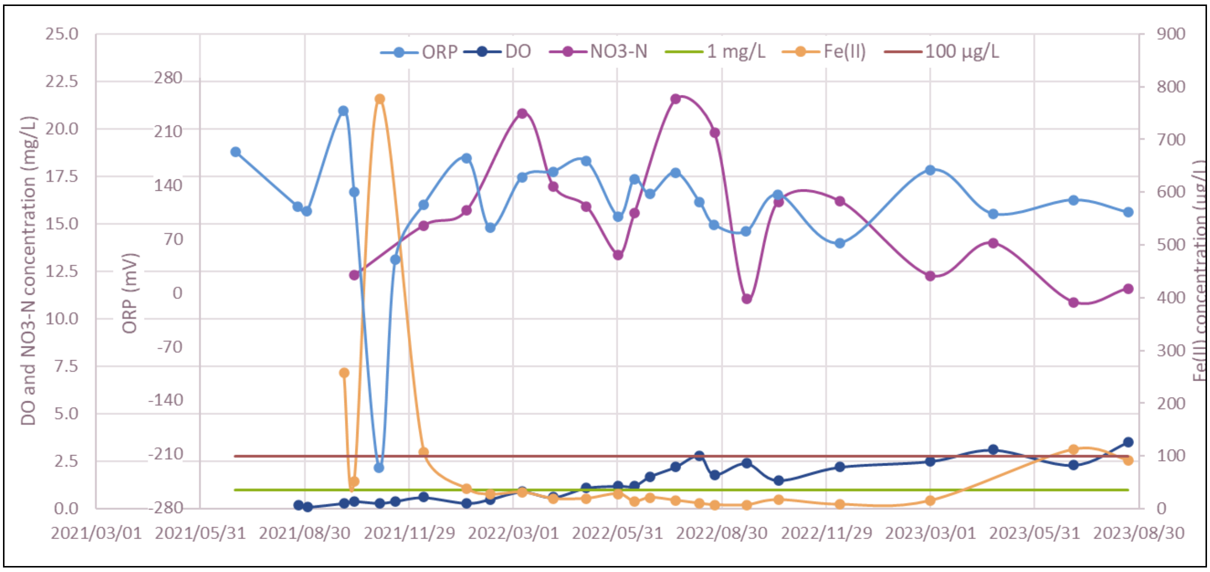

***Figure 4-21:** Variation of the redox indicators in well 1D over the monitoring period.*

The background monitoring well 1D had anoxic nitrate reducing conditions from October 2021 until April 2022 (mid-spring to early autumn) and oxic conditions from May 2022 to July 2022 (mid-autumn into winter). The measured ORP stayed positive apart from one negative reading of -228 mV (4 November 2021) which corresponded with a spike in Fe(II) concentration (777 µg/L), suggesting a temporary shift from nitrate reducing to iron reducing or mixed conditions (nitrate was not tested on this day). A similar decrease in ORP may have occurred at other times in between sampling events, however reducing conditions are not sustained because nitrate is quickly replenished by background groundwater, and this buffers the redox conditions.

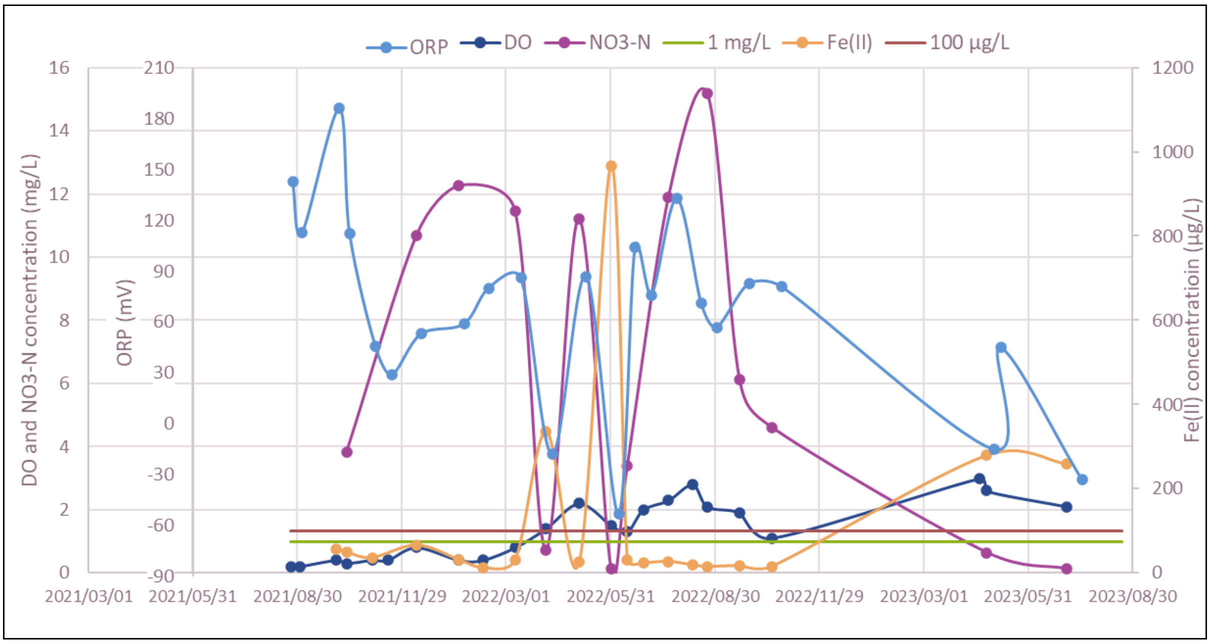

Figure 4-22: *Variation of the redox indicators in well 2S over the monitoring period.*

Monitoring well 2S receives infiltrated stormwater after rainfall events. While stormwater is oxygenated it also carries a carbon load which serves to drive the oxygen levels down by stimulating microbial activity. Redox conditions in 2S are often mixed due to the mixing of water sources and relative reaction rates of biogeochemical processes. To distinguish between nitrate dilution and denitrification the chloride concentrations were used to determine f_{GW} in the monitoring well (section 4.4.3). A 74% reduction in groundwater TON concentration was found after rainfall events. This denitrification appears to be a direct result of stormwater TOC input as an electron donor and often leads to temporary iron reducing conditions. Between rainfall events the background groundwater replenishes nitrate (and probably dissolved oxygen) which prevents the occurrence of sustained reducing conditions.

Monitoring well 4D is in the wetland area near to the outlet trench and as discussed above experienced a spike in EC and TOC in the winter period. The nitrate concentrations in well 4D were lower than in well 1D and they decreased in June 2022 and April 2023 corresponding to the TOC and EC spike. The ORP remained positive and redox conditions were relatively stable compared to other wells. It is hypothesised that the proximity to the wetland environment provides a steady supply of labile organic carbon (and possibly other electron donors) for denitrification, but further research is required to verify this.

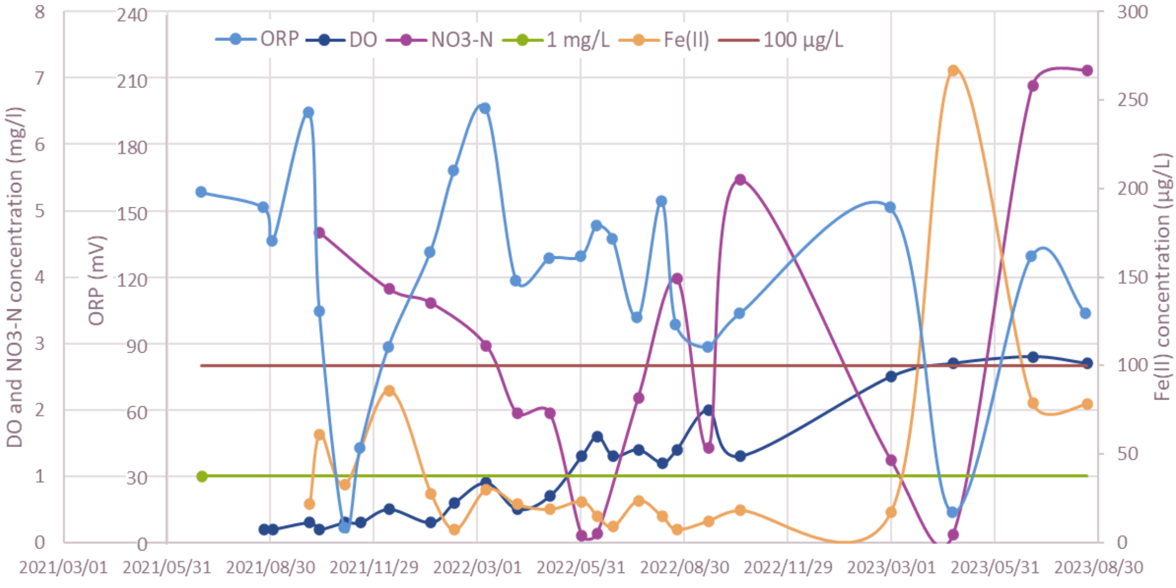

Figure 4-23: *Variation of the redox indicators in well 4D over the monitoring period.*

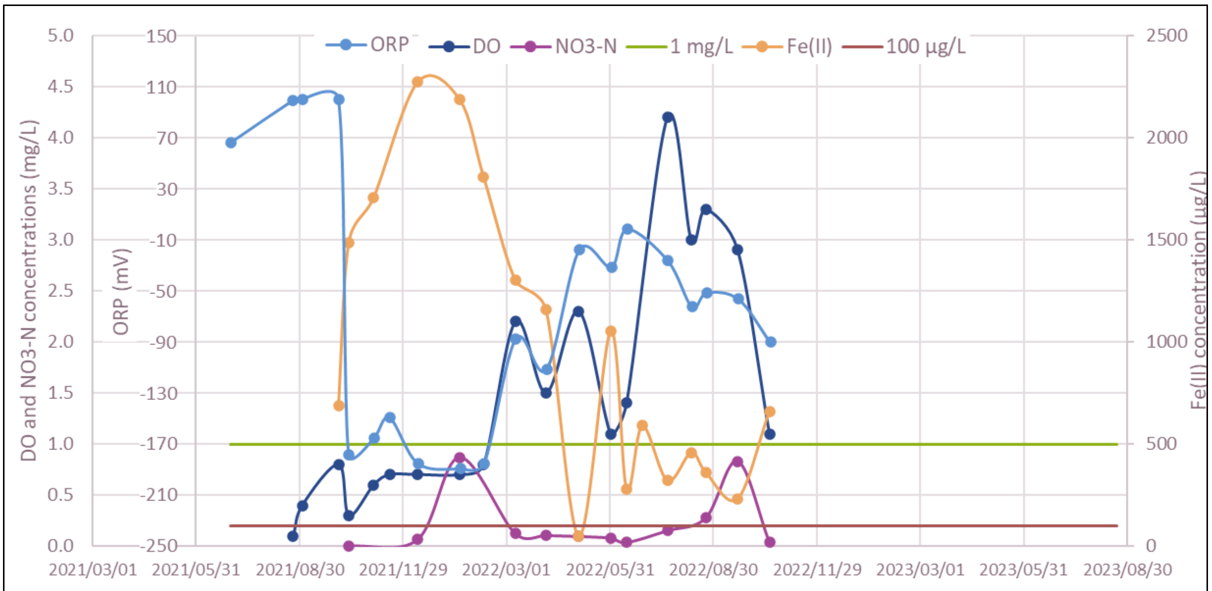

Figure 4-24: *Variation of the redox indicators in well 4M over the monitoring period.*

Monitoring well 4M is also in the wetland area, but its screened section is between 1 and 1.5 m deep intersecting with the low permeability layer. The ORP in this well was low and remained negative from October 2021 to October 2022. The Fe(II) concentration was usually high and nitrate concentration was consistently very low (<1 mg/L). The low permeability layer prevents rapid movement of background groundwater nitrate into the sampling location of 4M. Because there is no nitrate to buffer the redox potential the next available electron acceptor (ferric iron) is utilised and a rise in dissolved ferrous iron occurs. The TOC concentration and EC spike in 4M corresponded with a measurable decrease in DO concentration in June 2022.

4.5 Key findings

When the water table is above the 0.2 m bgl in well 4M seepage of water from the wetland soil into the outlet trench occurs and from the limited number of outlet samples collected results suggest improved water quality compared to the incoming stormwater. Further infiltration under elevated groundwater conditions can occur because the infiltration swale is at a higher elevation than the wetland, however this results in more seepage to the outlet channel. When the water table is lower than 0.2 m bgl as measured in well 4M, infiltration results in groundwater recharge. Under both conditions water quality improvement is expected.

During infiltration an effective contaminant concentration reduction (after accounting for dilution effects) of 80 to 95% was determined for dissolved ammonium, phosphorus, aluminium, zinc, and TOC. Other stormwater contaminants were usually below the method detection limits in the stormwater, groundwater, or both and no meaningful concentration reductions could be determined. Furthermore, the input of stormwater organic carbon may improve groundwater quality at this study site by providing a carbon source for denitrification.

The groundwater temperature was influenced by seasons, increased with depth below the ground level in winter, and decreased with depth in summer. pH in the background groundwater was higher than in groundwater below the infiltration and wetland areas. Groundwater organic carbon concentrations were influenced by stormwater infiltration events, however, the stormwater itself is unlikely to be the main organic carbon source. The wetland and biological functions in the soil may produce mobile organic carbon which is utilised in reduction reactions. Elevated background groundwater nitrate concentrations buffer the redox conditions where soil permeability allows. The results suggest that at this study site stormwater infiltration is unlikely to deteriorate the groundwater quality.

This field study adds to the limited number of studies investigating water quality impacts of stormwater infiltration in shallow groundwater environments where surface-water groundwater interaction is expected, and the role of BGI for urban water quality management in these environments.

4.6 Limitations

Groundwater monitoring in this study was limited to discrete sampling events and conditions between sampling events are therefore unknown. Fluctuations in groundwater levels and water quality parameters occurring between these events have not been measured and cannot be included in data analysis and interpretations. Similarly, the positioning of monitoring wells and their depths provide discrete measurement points. Well positions were limited to the study site, including the background well. There was no monitoring data from before the retrofit, so it is difficult to evaluate the effect of the infiltration trench itself compared to the previous monofunctional detention pond.

While chloride is a useful natural tracer, its use is limited because upgradient detention ponds may infiltrate stormwater which will influence the background chloride levels in the shallow groundwater. A tracer study utilising a tracer such as fluorescein or bromide added to the infiltration trench during an infiltration event would provide better understanding of the site hydrology and groundwater-surface water interactions.

5 Column experiments

5.1 Introduction

Column experiments have been used by researchers to evaluate treatment performance of various media for the removal of stormwater contaminants. Some of these experiments operated largely unsaturated columns which were loaded periodically with a drying period in between (Hsieh, Davis & Needelman, 2007b; Hatt, Fletcher & Deletic, 2008; Barrett, Limouzin & Lawler, 2013), while some were saturated columns with continuous flow (Bertelkamp *et al.*, 2014; von Rohr *et al.*, 2014). Barrett, Limouzin & Lawler (2013) used unsaturated columns with and without a submerged zone in the lower portion of the column to simulate the saturated zone in a biofiltration system. The columns used also varied in size from 14 cm to 80 cm diameter, and the media used also varied from natural soils of various texture to some with amendments to filter sand or engineered materials. Column experiments are in no way standardised, and their design is dependent on the nature of the study.

The aim of the column experiments as part of this research was to determine the treatment effect of the soil/aquifer sediment (hereafter referred to as soil) during infiltration of synthetic stormwater through an unsaturated depth of 0.5 m, 1.0 m and 1.5 m, and investigate geochemical changes in the stormwater after storage in a saturated zone. Soil column experiments were designed to represent the vadose zone in the stormwater detention basins to determine the possible treatment effect that the vadose zone may have on contaminants in the infiltrating stormwater. While it is not possible to precisely mimic the conditions at the site, the experiment, which operated for 18 weeks, was designed to represent a typical wet season with the water table (represented by the top of a saturated zone in the columns) increasing every 6 weeks. Loading of the columns was done by flooding the top of the column with 9 L of synthetic stormwater (SSW) (i.e., a depth of 300 mm in the 200 mm diameter column), and then allowing for infiltration as occurs in the infiltration trench on site (Section 5.4.1). While in the field study samples are only taken from a saturated zone via a groundwater monitoring well, in the column experiments it was possible to take samples of water that had passed through the unsaturated depth of soil, as well as samples from the saturated zone. Column experiments also allowed for higher concentrations of contaminants than those present in the stormwater at the study site to be used.

Four key questions for the column experiments were laid out in the introduction (Section 1.5), and these questions are addressed and answered in the results and discussion sections of this chapter (Sections 5.5.2 to 5.5.5).

5.2 Experimental design

Lewis & Sjöstrom (2010) divided types of soil column experiments along two lines; 1) packing method (packed or monolithic), and 2) operation condition (saturated or unsaturated). Packed columns utilise disturbed soil, which is processed and then packed into the column, while monolithic columns require careful extraction of an undisturbed soil core with the exact diameter of the columns, and careful repositioning into the column while preserving the soil structure. Where soils are very sandy, such as at the study site, the soil structure is undeveloped, and an undisturbed monolithic core is unnecessary and every difficult to obtain. Therefore, a packed column was the obvious choice. Since the aim of this experiment was partly to understand the effective treatment during infiltration through the vadose zone processes, it had to be run under largely unsaturated conditions, or at least conditions that to some extent mimic the periodic infiltration of a head of water. Sampling unsaturated columns requires either that a suction be applied to the sampling port to overcome the soil pore tension, or that the column be operated using a free-drainage approach which necessitates that a (temporary) saturated zone, at least the thickness of the capillary fringe, must develop above the sampling point such that a sample may freely drain from the column (Lewis & Sjöstrom, 2010). Since these columns are large and aim to represent the entire vadose zone, the free-drainage approach was suitable, and the development of a temporary saturated zone above the permanently saturated zone is in line with the reality of the site.

To compare different infiltration depths or vadose zone thickness (VZT), it was necessary to have sampling ports at different depths (0.5 m, 1.0 m and 1.5 m) below the surface of the soil; however, as previously discussed a temporary saturated zone would need to be created above the sampling port so that a sample could freely drain from the column. Hatt, Fletcher & Deletic (2008) inserted a small piece of pipe that was sliced in half lengthways from the sampling port of an unsaturated column into the media to intercept some of the water flow as it infiltrated. This method has the potential to disturb the packing of the column and cause preferential flow paths, so an alternative method was devised. Since the water table below the infiltration trench at the site is expected to rise over the course of the rainfall season it was deduced that a similar condition could be utilised in the column. Thus, over the course of the experiment a permanently saturated zone was allowed to develop and grow, which allowed collection of saturated zone samples as well as collection of free-drainage samples from the higher sample ports.

Table 5-1: *Overview of the four experimental conditions.*

Experiment	A		B		C		D	
Column #	A1	A2	B1	B2	C1	C2	D1	D2
Media	soil	soil	soil	soil	soil	soil	sand	sand
SSW	low	low	high	high	high no OC	high no OC	high	high

5.3 Experimental setup

5.3.1 Column construction

Eight soil columns were constructed from 2 m long, 200 mm diameter PVC pipe with a cap sealing them at the bottom and were supported by a steel frame. Each column was fitted with three sample ports located at 0.5 m, 1.0 m, and 1.5m from the soil surface (Figure 5-1). The 1.5 m sample port was at the bottom of the column, and a 0.5 m space was left above the soil/sand for loading the columns. The sample ports consisted of a 2 cm diameter opening in the column wall to which a PVC block with a 2.5 cm threaded opening was glued. A round filter (loose weave cotton material) was inserted into the block before the PVC valve fitting was screwed into the block. The inside surfaces of the columns were roughened with 80 grit sandpaper to reduce the tendency for preferential flow paths down the side of the column as per Lewis & Sjöstrom (2010).

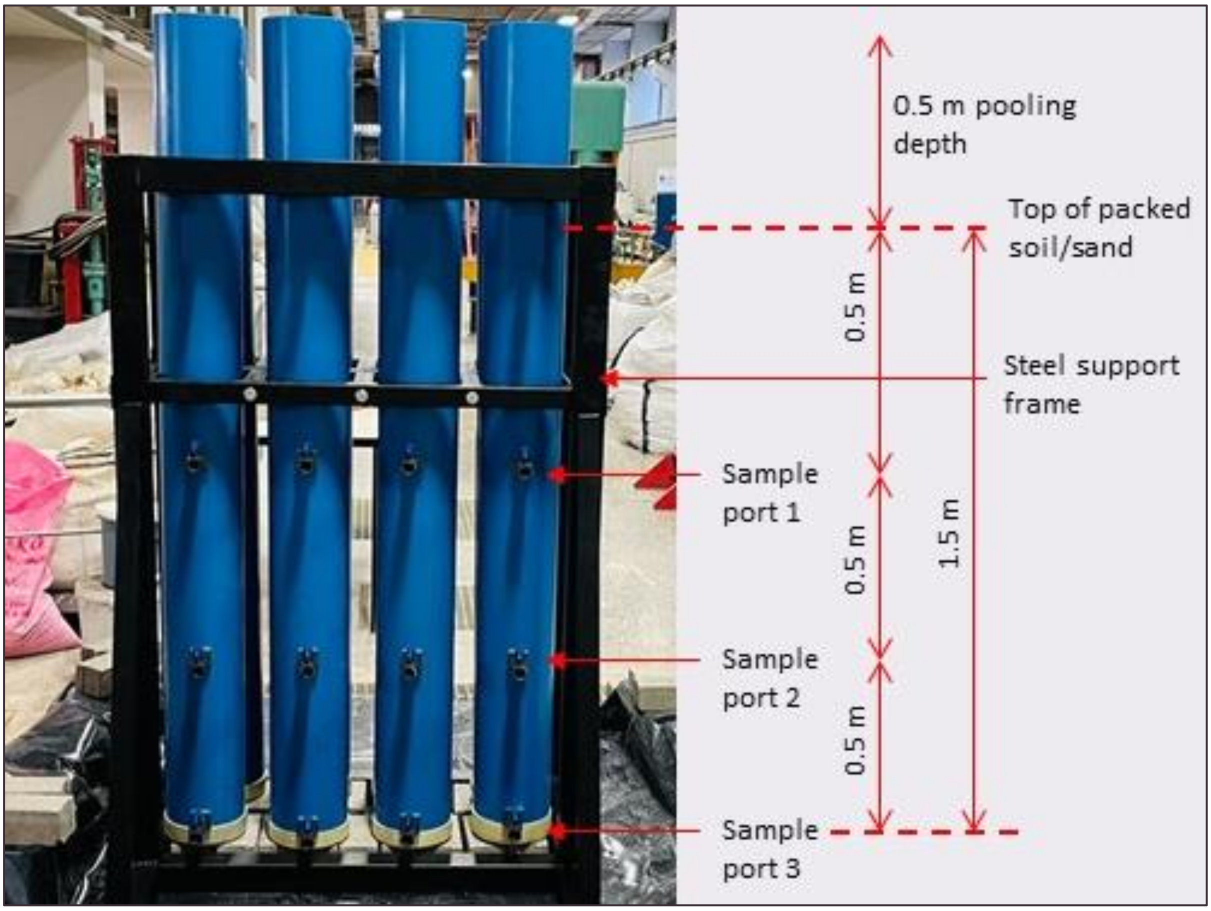

Figure 5-1: *Eight experimental columns back-to-back in steel support frame.*

5.3.2 Soil and sand media

Bioretention systems often make use of engineered biofiltration soil media (BSM) or natural soils which are typically soils of the textural class sandy loam (Davis *et al.*, 2006; Hsieh, Davis & Needelman, 2007b; Hatt, Fletcher & Deletic, 2008), recommended by Australian guidelines for fine media filtration (Hatt, Fletcher & Deletic, 2008). Soil textural classes are based on the fractions of sand (0.05 to 2 mm diameter), silt (0.002 to 0.05 mm diameter) and clay (<0.002 mm diameter) particles in the soil (Ritchey, McGrath & Gehring, 2015). Clay minerals have a high specific surface area because of the small particle size, and clay surfaces are negatively charged which gives soil its cation exchange capacity (CEC) which is important for retention of metal cations. Organic matter and metal oxides are also important for contaminant removal.

Soil/aquifer sediment (referred to as soil) from the study site was collected from depths of 0 m to 3.8 m below the ground surface during installation of the monitoring wells on 18 June and 8 October 2021. The soil was placed into bags, transported to UCT and stored until the 16 November 2021. The soil was air dried before crushing clumps, sieving through a 2 mm mesh size sieve to remove all particles larger than sand, and homogenised by mixing in large bags. Six columns were packed with soil and two were packed with silica sand and both media were sampled in triplicate for analysis of media properties and contaminants listed in Table 5-2. Media properties are presented in Section 5.5.1, Table 5-5.

***Table 5-2**: Descriptions and rational for soil and sand analysis.*

Analysis	Description	Reason
Five fraction soil texture	Particle size fractions for clay, silt, fine sand, medium sand, and coarse sand	Important for reporting and comparison between media and with other studies
Bulk density	Mass of soil per volume as packed	To ensure sufficient packing and comparison to other studies
Porosity	The volume of pore space as a fraction of total volume (packed)	To calculate soil column pore volume and for repeatability of experiment
CEC	Moles of negative exchange sites in the soil	Important property in soil for retention and mobility of cations
Total organic carbon	Total carbon in soil that is present as part of organic matter	Organic matter in soil plays an important role in retention and sorption of chemical species
pH	pH measured in a 1:2 soil:water extract	Fundamental property of the soil and will influence chemistry
Easily extractable contaminants (NH_4^+, NO_3^-, NO_2^-, TN, TOC, and metals)	Extractable by a 1:2 soil to 1M KCl solution	To determine the baseline mass of mobile contaminants
Total concentrations (metals and P)	Total element concentrations	Total mass of elements in soil which may become mobile under certain conditions such as organic matter decomposition or dissolution of minerals

Five fraction soil texture, CEC and TN were analysed by an external laboratory (Bemlab) using their standard methods. Total metals and TP concentrations were analysed by EMT by ICP-OES (EPA Method 200.7, 6010B and BS EN ISO 11885 2009) after acid digestion using Aqua Regia reflux. Bulk density and porosity of the packed columns were determined using 0.5 m test columns as described in section 5.3.3. pH was measured in a 1:2 soil:water solution after shaking and allowing to stand for 10 min. The easily extractable contaminants (present in soil pore water and weekly adsorbed on media particles (O'Reilly, Chang & Wanielista, 2012)) were extracted using 1M KCl in a 1:2 soil:liquid ratio (75 g soil in 150 mL KCl). The slurry was briefly stirred every 10 min for 1 hour and allowed to settle for 30 min. The supernatant liquid was removed with a syringe and filtered using a 0.45 µm filter. The extracts were analysed using the methods described for water sample analysis in Section 4.3.4.

5.3.3 Packing the columns

Two 0.5 m test columns of 200 mm diameter were used to practice the packing method and to determine the packed bulk density and porosity of each media. The test column was fitted with an end cap and weighed before packing. A full 10L bucket of soil was then added to each test column and a poker/needle vibrator (commonly used in concrete works) was used to vibrate and compact the soil in the column for 90 seconds. Once the test column was packed it was again weighed to determine the mass of the packed column. Water was then added until the column was completely saturated, but no free water was present above the media. The addition of water resulted in slight additional compaction of the media, and the final height of the packed media was measured. Equation 6 was used to determine the bulk density and Equation 7 was used to determine the porosity of the packed media (assuming a density of 1 g/cm for tap water).

$$\rho_b = \frac{m_{packed} - m_{empty}}{\pi r^2 h} \qquad \text{Equation 6}$$

ρ_b is the bulk density of the packed column,
m_{packed} is the mass of the packed column,
m_{empty} is the mass of the empty column,
r is the radius of the column, and
h is the height of packed media in the column.

$$n = \frac{V_V}{V_T} = \frac{(m_{saturated} - m_{packed}) \times \rho_w}{\pi r^2 h} \qquad \text{Equation 7}$$

n is the porosity,
V_v is the volume of voids,
V_T is the total volume, and
$m_{saturated}$ is the mass of the packed column saturated with water.

Ideally a bulk density between 1 and 2 g/cm^3 (depending on the soil texture) should be achieved if the column has been sufficiently packed (Lewis & Sjöstrom, 2010). (Note: $n = \rho_b/\rho_s$)

Once the test column had been used to practice packing and determine bulk density and porosity of each media the eight experimental columns were packed, six with soil and two with sand up to 1.5 m above the bottom of the column. After addition and vibration of each bucket measure of media the top of the packed media was lightly scratched to ensure incorporation with the next layer of media.

5.3.4 Synthetic stormwater composition and preparation

Concentrations of contaminants in stormwater vary due to several factors such as land use, rainfall intensity and duration, and presence of point source contaminants (Goonetilleke *et al.*, 2005; LeFevre *et al.*, 2015; Müller *et al.*, 2020). For this study the concentrations of contaminants for the synthetic stormwater (SSW) were based on previous local data and international studies. The low concentration solution represented a formal residential catchment such as the one that feeds the study site, and the high concentration was approximately five times higher for all contaminants representing a generally worse water quality scenario but still within the formal residential land use contaminant range.

CoCT data for the Zeekoe catchment (a catchment overlying the south-western portion of the CFA, adjacent to Mitchell's Plain) was used to determine the concentrations of nutrients in a formal residential catchment, and DOC concentration was taken from that reported for stormwater at the Atlantis MAR site (Tredoux *et al.*, 2009). Dissolved metal concentrations were based on those reported in Pitt *et al.* (1995). Details on the determination of representative concentrations can be found in Appendix C.

SSW with only dissolved contaminants of interest was used as it has the advantage of not causing blockages and column failure associated with adding solids to the column (Hatt, Fletcher & Deletic, 2008) and the influent concentrations were more consistent because sorption of dissolved contaminants before column loading is avoided. Furthermore dissolved phase pollutants are more mobile (and therefore more likely to reach the groundwater) than solids-associated contaminants which are usually readily removed by physical filtration (LeFevre *et al.*, 2015).

The organic carbon was added using a combination of sodium acetate (and later potassium acetate) and glycine, which was also a source of organic nitrogen. Initially sodium acetate was used, however after cycle one clogging in the columns was observed and a change to potassium acetate relieved and reversed the issue. For treatment group C no organic carbon was added (Table 5-1) and to keep the total nitrogen concentration consistent additional ammonium was added. Nitrogen was added as nitrate, nitrite, ammonium, and organic N (except in treatment C which had only inorganic nitrogen species). Phosphate and five metal contaminants (Cr, Cu, Pb, Zn and Ni) were added to the SSW while four elements (As, Al, Mn, and Fe) were not added but were monitored in column effluent as they could be mobilised from the soil and sand media. To keep the total dissolved solid concentration consistent between the treatments, a higher concentration of background electrolyte was added to the SSW for treatment group C. The target concentrations for the SSW preparations are detailed in Table 5-3; actual concentrations were determined for each batch during the study. Note that for cycle zero only background electrolyte was used.

Four stock solutions: 1) ammonium, 2) other nutrients (nitrate, nitrite, and phosphate), 3) metals, and 4) background electrolyte, were prepared in 1 L volumetric flasks and transferred to plastic storage bottles. SSW was prepared in 25 L plastic jerry cans by filling them with deionised water nearly to the 20 L mark, adding the relevant amounts of the pre-prepared stock solutions and weighed out potassium acetate and glycine, and then making up to the 20 L mark with deionised water before mixing by shaking the containers. One 20 L batch was used for each pair of columns on each loading day.

Table 5-3: *Target concentrations of contaminants and chemicals used in the SSW preparations.*

Contaminant	**Chemical used**	**Low**	**High**	**High with no C**
DOC	potassium acetate	10.10	50.50	0
DOC	glycine	3.43	17.15	0
Total DOC		**13.53**	**67.65**	**0**
NO3-N	KNO3	1.20	6.00	6.00
NO2-N	NaNO2	0.20	1.00	1.00
NH4-N	NH4Cl	0.50	2.50	12.50
Organic N	glycine	2.00	10.00	0
Total N		**3.90**	**19.50**	**19.50**
PO4-P	K2HPO4	0.22	1.10	1.10
Total P		**0.22**	**1.10**	**1.10**
Cr (µg/L)	CrK(SO4)2 · 12H2O	2	10	10
Cu (µg/L)	CuSO4 · 5H2O	14	70	70
Pb (µg/L)	PbCl2	2	10	10
Ni (µg/L)	NiCl2	2	10	10
Zn (µg/L)	ZnCl2	84	420	420
Total metals (µg/L)		**104**	**520**	**520**
Background electrolyte	KCl	100	100	470
Relevant Experiment		**A**	**B & D**	**C**

Note: Concentrations are in mg/L unless otherwise indicated.

5.4 Experimental procedure

5.4.1 Loading the columns

A 0.3 m ponding depth is the designed depth allowed at the site due to the sand berm (Mclachlan *et al.*, 2023). Given the column diameter of 200 mm, 9 L of SSW was required to achieve the 0.3 m ponding above the column, and this was set as the standard loading volume. Thus one 20 L batch of SSW was enough to load two columns and have some remaining for sampling. The columns were loaded by decanting the relevant SSW into a 9 L watering can, and carefully sprinkling water to avoid disturbing the surface of the soil.

5.4.2 Experimental cycles

The column experimental procedure was designed to represent a typical wet season while maintaining regular intervals between experimental runs to keep consistency during the experiment. Rainfall events vary in duration, volume, and intensity and to determine a regular schedule this needs to be generalised. Tanyanyiwa (2023) determined that at least 3 mm of rainfall in a day was required to generate runoff that would pond in the infiltration swale at the study site. Daily total rainfall for the period 21 May to 21 September for the years 2013, 2014, and 2016-2018 for the Wolfgat weather station were used. Analysis of the rainfall data showed that the number of days where less than 3 mm of rainfall was recorded was 477 (out of 615 days in total) or, on average, 11 days out of 14. This means that on average during the wet season runoff is expected to reach the infiltration trench on 3 days out of every 14. Rainfall may occur on one, two or more consecutive days with six being the maximum number of consecutive days observed in the dataset. For this experiment the three rainfall days in each cycle were consecutive and followed by 11 non-rainfall days.

The experiment was conducted over 20 weeks and consisted of a Cycle zero followed by nine 14-day experimental cycles. Due to the slow infiltration rate in the soil columns and limited pooling depth, columns were loaded on Days 1 and 2, water remained ponded on Day 3 and samples were collected on Days 2, 3 and 4. The columns were allowed to dry out for the remainder of each cycle. During the nine cycles a saturated zone was created and increased in depth to represent the rising water table seen at the site. Cycles 1 to 3 had no saturated zone, cycles 4 to 6 had 0.5 m saturated zone and cycles 7 to 9 had 1.0 m saturated zone. A schematic diagram of a column with increasing saturated zone is shown in Figure 5-2.

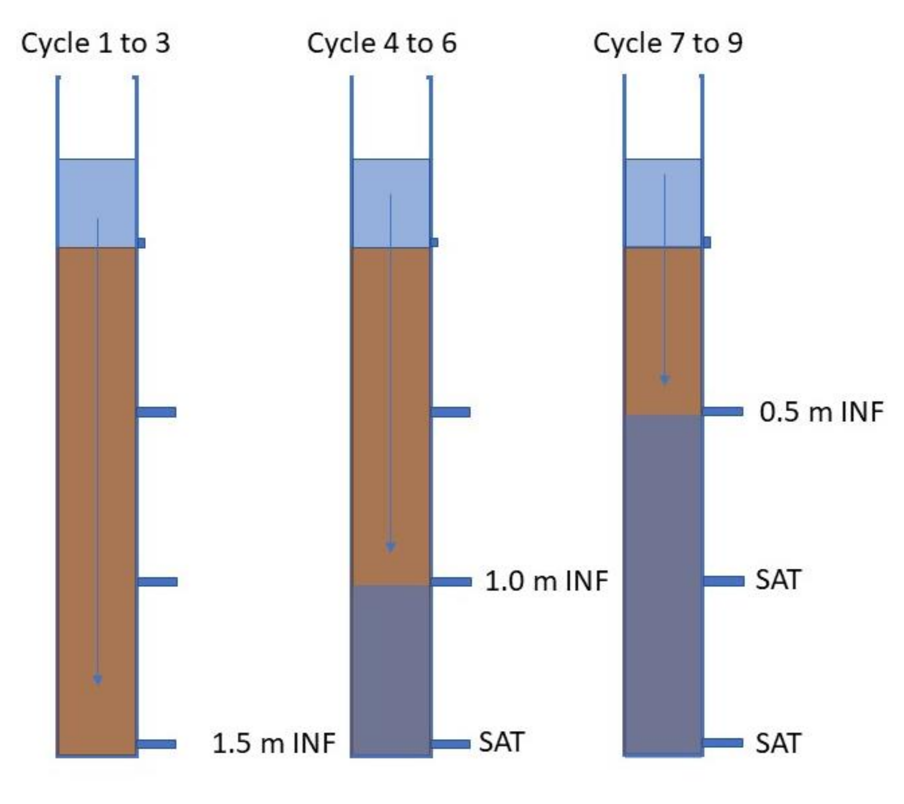

Figure 5-2: *Schematic diagram of a column during the cycles of the experiment. 'INF' indicates sample collected after infiltration through the media and 'SAT' indicates samples collected from the saturated zone.*

5.4.3 Sample collection and analysis

Two types of samples were collected during this experiment; samples of infiltrated freely draining water which are indicated as 'INF', and samples of water from the saturated zone which are indicated as 'SAT'.

- During Cycles 1 to 3: 1.5 m INF samples were taken from Sample port 3 (the lowest sample port) after infiltration through the full 1.5 m media depth.
- At the start of Cycle 4: Sample port 3 was closed and a 0.5 m saturated zone was created in the lowest portion of the column.
- During Cycles 4 to 6: 1.0 m INF samples were taken from Sample port 2 (the middle sample port) after infiltration through 1.0 m media depth and SAT samples were taken from Sample port 3 on Day 4 only.
- At the start of Cycle 7: Sample port 2 was closed and the saturated zone was extended to a depth of 1.0 m.
- During Cycles 7 to 9: 0.5 m INF samples were taken from Sample port 1 (the top sample port) after infiltration through 0.5 m depth and SAT samples were taken from Sample ports 2 and 3 on Day 4 only.

During collection of INF samples the flow rates were recorded by measuring the volume of water removed over a timed period. At the end of INF sampling on Days 2 & 3 the sample ports were closed to prevent water flowing out overnight. Sample ports were always closed after collecting SAT samples. All water samples from the columns and batches of SSW were collected into clean plastic jugs and subsampled into clean sample bottles. Water samples were preserved and analysed for parameters listed in Table 5-4. Analytical methods are the same as those described in Section 4.3.4.

Table 5-4: *Column experiment water quality analysis.*

Water quality parameter	Sample Preservation	Analytical lab
TOC and TN	Analyse as soon as possible	CeBER, UCT
Dissolved NH4-N, NO3-N, NO2-N,	Filter immediately, analyse within 48 h	WQ Lab, UCT
Total dissolved metals and P	Filter immediately and acidify with HNO_3	EMT, external lab

Soil samples were collected two weeks after the collection of the last water samples. These samples were collected from the soil/sand surface, and through each of the sample ports for a total of four samples per column. Samples were allowed to air dry before being analysed for easily extractable metals and P, and total metals and total P. Analytical methods were the same as those described in Section 5.3.2.

5.4.4 Experimental issues

Three experimental issues were encountered and were addressed as follows.

1) *Leaks*. During cycle zero while loading the first column leaks were noted at the square block which attaches the sample port to the column. Loading was paused and all columns were sealed with silicone sealant, and loading resumed in the afternoon. After loading the columns, several of the sampling ports leaked at the valve thread where the filter was installed. Between Cycles 0 and 1 PTFE tape was used to seal the screw threads of the leaking sample ports.
2) *Blockage*. During Cycle 1 the turbidity of water samples from columns A1, A2, B1, and B2 was high and flow rate from these columns was slowing. Since sodium ions can cause dispersal of clays in soil (McBride, 1994 pg 280) the sodium acetate (organic carbon source) in the SSW was replaced with potassium acetate from Cycle 2 onward. The sample turbidity improved, and the flow rate did not worsen.
3) *Filter failure*. On Day 1 of Cycle 5 the first failure of the sample port filter occurred (columns B1 and B2), and some soil slurry came out of the sample port. This was fixed by removing the sample port and replacing the filter, taking care to stop the flow of water and soil while working. After this other sample ports failed in a similar manner and were fixed as soon as this occurred so that normal sampling could continue.

5.5 Results and discussion

5.5.1 Properties of the soil and sand media

Engineered SuDS often utilise natural or engineered soil media for its physical properties and treatment performance. Sandy loam, loamy sand and sand are the textural classes frequently recommended for BSM. The textural classifications, sandy loam, loamy sand and sand have 50% to 70%, 70 to 85%, and >85% sand respectively (Ritchey, McGrath & Gehring, 2015). The soil used in this study is classified as sand (well graded) with only 5.8% clay and 2% silt which is in line with international guidelines for BSM (Woods-Ballard *et al.*, 2007). The silica sand used is classified as coarse sand, which is suitable for a worst-case scenario where the lack of clay minerals is expected to provide worse treatment. Table 5-5 shows the properties of the soil and sand used in the columns.

Table 5-5: *Properties of the soil and sand used in the columns.*

Property	**Soil**	**Sand**
Five fraction soil texture (particle size range)		
Clay (%) (<0.002 mm)	5.8 ± 0.0	0.6 ± 1.0
Silt (%) (0.002-0.05 mm)	2.0 ± 0.0	2.0 ± 2.0
Fine sand (%) (0.05-0.25 mm)	39.3 ± 1.7	3.0 ± 2.7
Medium sand (%) (0.25-0.5 mm)	33.2 ± 0.4	4.6 ± 2.4
Coarse sand (%) (0.5-2.0 mm)	19.6 ± 0.1.7	90.0 ± 4.0
Classification	sand	coarse sand
CEC (cmol$_c$/kg)	2.0 ± 0.2	1.6 ± 0.3
Total organic carbon (%)	0.4 ± 0.1	0.2 ± 0.1
pH (1:2)	6.9 ± 0.2	7.8 ± 0.1
Bulk density (g/cm^3)	1.39	1.46
Porosity (unitless)	0.29	0.32

Note: standard deviation indicated where three samples were analysed.

Flow rates

Flow rates for Day 3 of each cycle were compared between column pairs and between Experiments A and B, B and C, and B and D (Table 5-1). Paired t-tests were performed (alpha = 0.05) to compare flow rates in each duplicate pair of columns and no significant differences between the column pairs were found ($p > 0.05$ for all pairs). This indicates that the columns pairs showed acceptable repeatability.

One-way ANOVA showed that there was a significant difference in mean flow rates between at least two treatment conditions ($F(3, 68) = 12.2$, $p < 0.001$). Individual t-tests were conducted to compare the mean flow rate in Experiment B to Experiments A, C, and D and after applying Bonferroni adjustment significant differences in flow rate were found between Experiments B and D ($p = 0.001$) (as expected) and between Experiments B and C ($p = 0.014$), while no significant difference was found between Experiments A and B ($p = 0.608$).

All columns had an initial decline in flow rate between Cycle 1 and Cycle 2. During Cycles 4-6 (Sample port 2) and Cycles 7-9 (Sample port 1) flow rates from the soil columns were impacted to some extent by filter failure issues however overall no major changes to flow rates over the 20 week experiment were found (Figure 5-3).

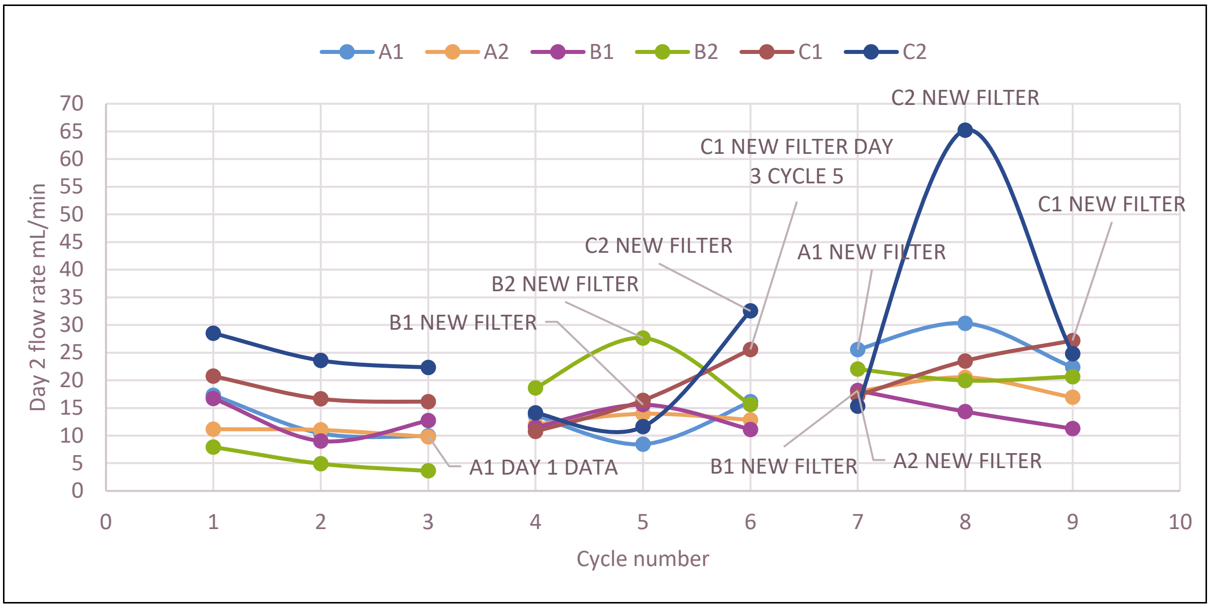

Figure 5-3: *Day 3 flow rates from soil columns and filter replacements.*

5.5.2 Retention of added metals and phosphate

Retention of the added metals and P by the media is an important treatment process. To determine whether this was occurring the accumulation of these contaminants in the media was examined, along with the concentrations in the column effluent after infiltration through each depth of soil or sand.

Soil and sand analysis post column experiments

A change in total concentration from before to after the column experiment indicated a build-up (and retention) of contaminants in the soil/sand. Most of the contaminant retention occurred at the soil surface for P, Zn, Ni and Cu. Cr retention, however, increased at the surface and was highest at 0.5 m depth. Pb concentrations remained below the laboratory detection limit. Table 5-6 presents mean contaminant concentrations for soil before and at each depth from all soil columns, and Figure 5-4 shows contaminant concentrations at each depth for soil and sand. Soil had a higher starting concentration of P, while sand had higher Ni and Cr to start with. Soil showed measurable build-up of P, Zn, Ni, Cr and Cu at the surface while sand did not show measurable build-up of any contaminants. This suggests that the soil has higher capacity than the sand to retain these contaminants through adsorption processes which is likely a result of the presence amorphous iron oxides and clay particles.

Table 5-6: *Mean contaminant concentrations in soil at different depths before and after column experiments.*

Contaminant	Soil before	Surface	0.5 m depth	1.0 m depth	1.5 m depth
P (mg/kg)	137 ± 4	**170 ± 16**	130 ± 14	139 ± 30	131 ± 32
Zn (mg/kg)	<5	**64 ± 33**	5 ± 1	<5	<5
Pb (mg/kg)	<5	<5	<5	<5	<5
Ni (mg/kg)	0.8 ± 0.5	**2.1 ± 0.7**	1.6 ± 0.6	1.3 ± 0.4	1.0 ± 0.3
Cu (mg/kg)	2 ± 1	**6 ± 4**	<1	<1	<1
Cr (mg/kg)	19 ± 8	25 ± 20	**35 ± 24**	16 ± 9	12 ± 4

Note: mean ± standard deviation. The highest mean concentration for each contaminant is in bold.

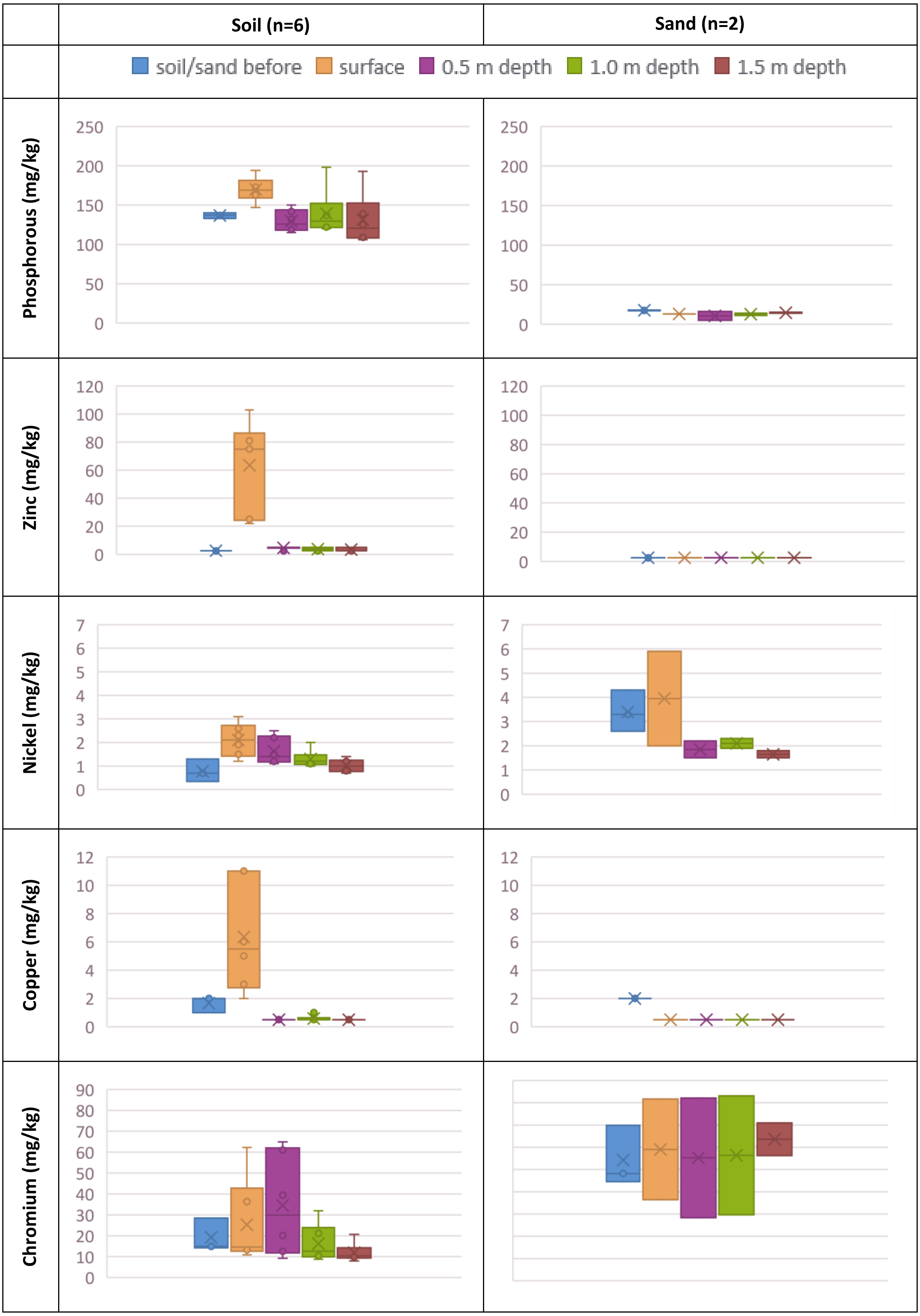

Figure 5-4: *Box and whisker plots of total contaminant concentration in soil and sand before and after experiments at different depths.*

The surface contaminant concentrations for each experiment are shown in Table 5-7. For all contaminants except Zn the mean surface concentrations were highest in Experiment C. Pb was consistently undetected and may be present at concentrations below the method detection limit.

Table 5-7: *Mean concentrations of contaminants in the surface media samples and after the column experiments.*

Contaminant	A	B	C	soil before	D	sand before
P (mg/kg)	155	169	**186**	137	13	18
Zn (mg/kg)	24	**92**	75	3	3	3
Pb (mg/kg)	<5	<5	<5	<5	<5	<5
Ni (mg/kg)	1.6	2.1	**2.7**	0.8	4.0	3.4
Cu (mg/kg)	3	6	**11**	2	1	2
Cr (mg/kg)	13.7	23.6	**38.6**	19.2	59.1	54.2

Note: values in bold indicate the largest increase in contaminant concentration for each contaminant.

Soil samples were also analysed for their easily extractable concentrations as described in section 5.3.2. These concentrations are about three orders of magnitude lower than total concentrations and therefore do not contribute substantially to the total concentrations and indicated that most of the retained contaminants were not readily mobile. The most notable result was the presence of Pb in all the post experiment sand sample extracts (0.009 to 0.1 mg/kg once related back to the mass of soil used), while no Pb was detected in the post experiment soil sample extracts or any of the before column samples. Box and whisker plots of extractable contaminant concentrations are shown in Appendix D.

Column influent and effluent concentrations from infiltration experiments

As described in Section 5.4.2 columns were each loaded twice and sampled three times every 14 days. Loading was done on Days 1 and 2 and samples of the infiltrated water were taken on Days 2, 3, and 4. In the first 3 cycles samples were taken from Sample port 3 (1.5 m below soil surface), from Sample port 2 (1.0 m below soil surface) in Cycles 4-6 and from Sample port 1 (0.5 m below soil surface) in Cycles 7-9. This means that the 1.5 m infiltration depth was the first set of samples collected, and that there had already been 6 cycles passing through the column before the 0.5 m infiltration depth samples were collected. Box and whisker plots for contaminant influent and effluent concentrations are presented in Figure 5-5 and Figure 5-6. The concentrations of P, Pb, Ni and Cr in soil column effluent after 1.5 m infiltration depth were higher than in effluent after 0.5 and 1.0 m infiltration depth. The reason for this may differ between contaminants, but it is possible that the first few times the column was loaded some metals leached from the soil. Cycle 0 was conducted before Cycle 1 where all columns were loaded twice with SSW consisting of background electrolyte only. The results from this back up the leaching hypothesis for P, Ni and Cr, and suggest Pb requires more cycles to start leaching. For the other two metals (Zn and Cu) it seems that Cycle 0 was sufficient to remove the leachable concentrations. The leaching of contaminants from soil columns has been shown in other studies; for example Kranz *et al.* (2022) found that when columns were flushed for the first time Pb, Cd, Cr, Cu, Ni and Zn were leached from the columns, and some metals demonstrated a second flush after several pore volumes, even when the influent contained no metals.

For each experiment the effluent concentration from each infiltration depth (sample port) was compared using one-way ANOVA, and if a difference between infiltration depths was found a Turkey's Honestly Significant Difference (Turkey HSD) test was conducted to determine which depths differed from which others. Results for the significance testing along with mean concentrations ± 95% confidence intervals are presented in Table 5-9.

Table 5-9 The mean concentration-based removal for added metals and P after infiltration through 0.5 m of soil was 94%. For sand the removal was 65% in 0.5 m infiltration depth, but this improved to 86% after 1.0 m infiltration. The percent removals for each of the added metals and P after infiltration through 0.5 m for each experiment is shown in Table 5-8. Percent removals for other depths are shown in Appendix E. The concentrations used in this study, while representative of residential urban runoff, were not, even for the high concentration, as high as may be found in road runoff (Robertson, 2017). Furthermore, the capacity of the soil to keep retaining metals over years of loading has not been investigated here. Since the measurable build-up of metals was only found at the surface of the soil, there is likely more soil depth capable of retaining metals below this.

***Table 5-8**: Percent removal for added metals and P after infiltration through 0.5 m media depth.*

	Experiment A	Experiment B	Experiment C	Experiment D
P	92	98	99	21
Zn	75	95	97	76
Pb	>82	>93	>95	>94
Ni	>90	96	99	44
Cr	79	97	95	90
Cu	92	98	99	65

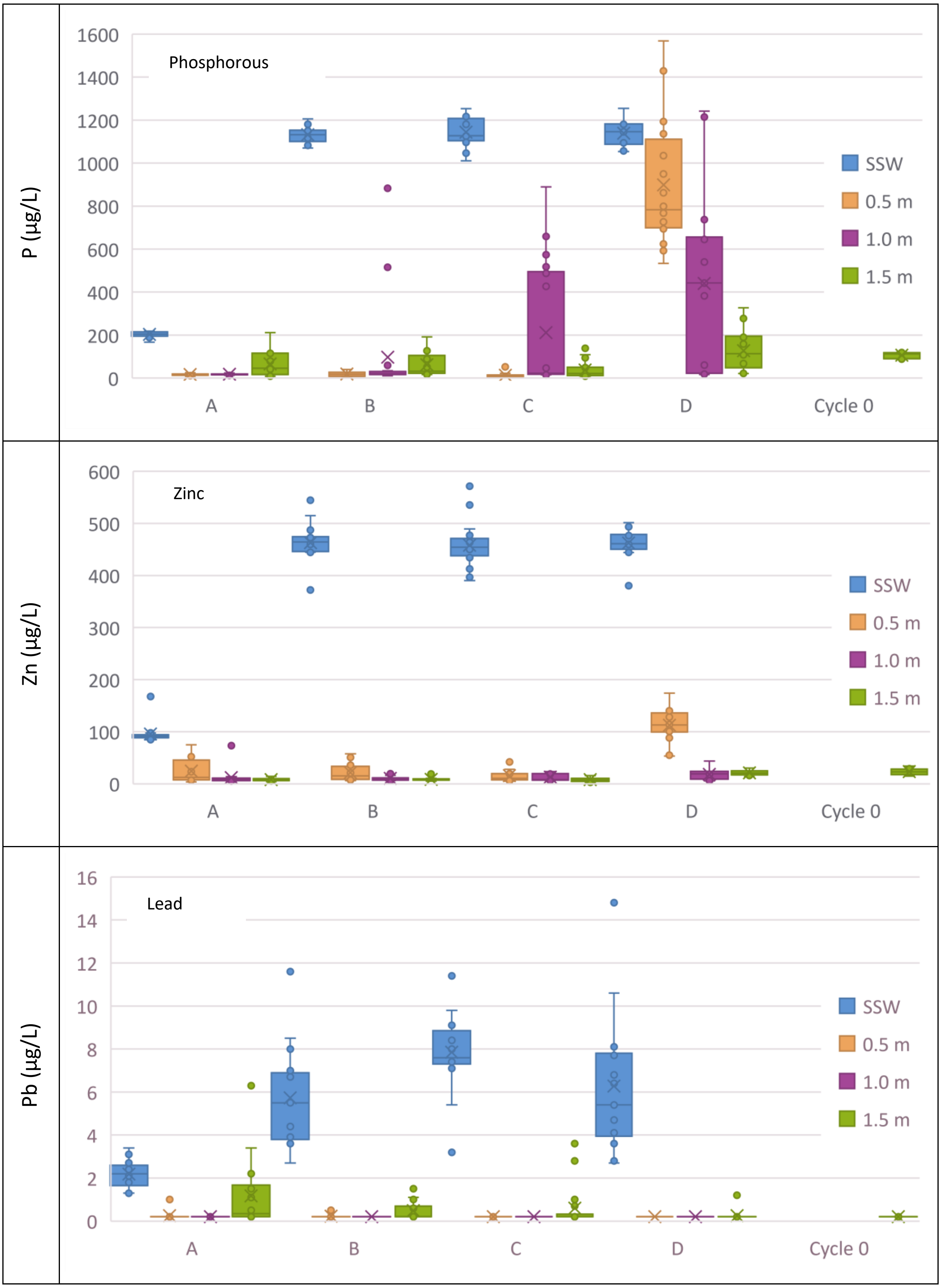

Figure 5-5: *Concentrations of P (top), Zn (middle) and Pb (bottom) in SSW and INF samples for each depth.*

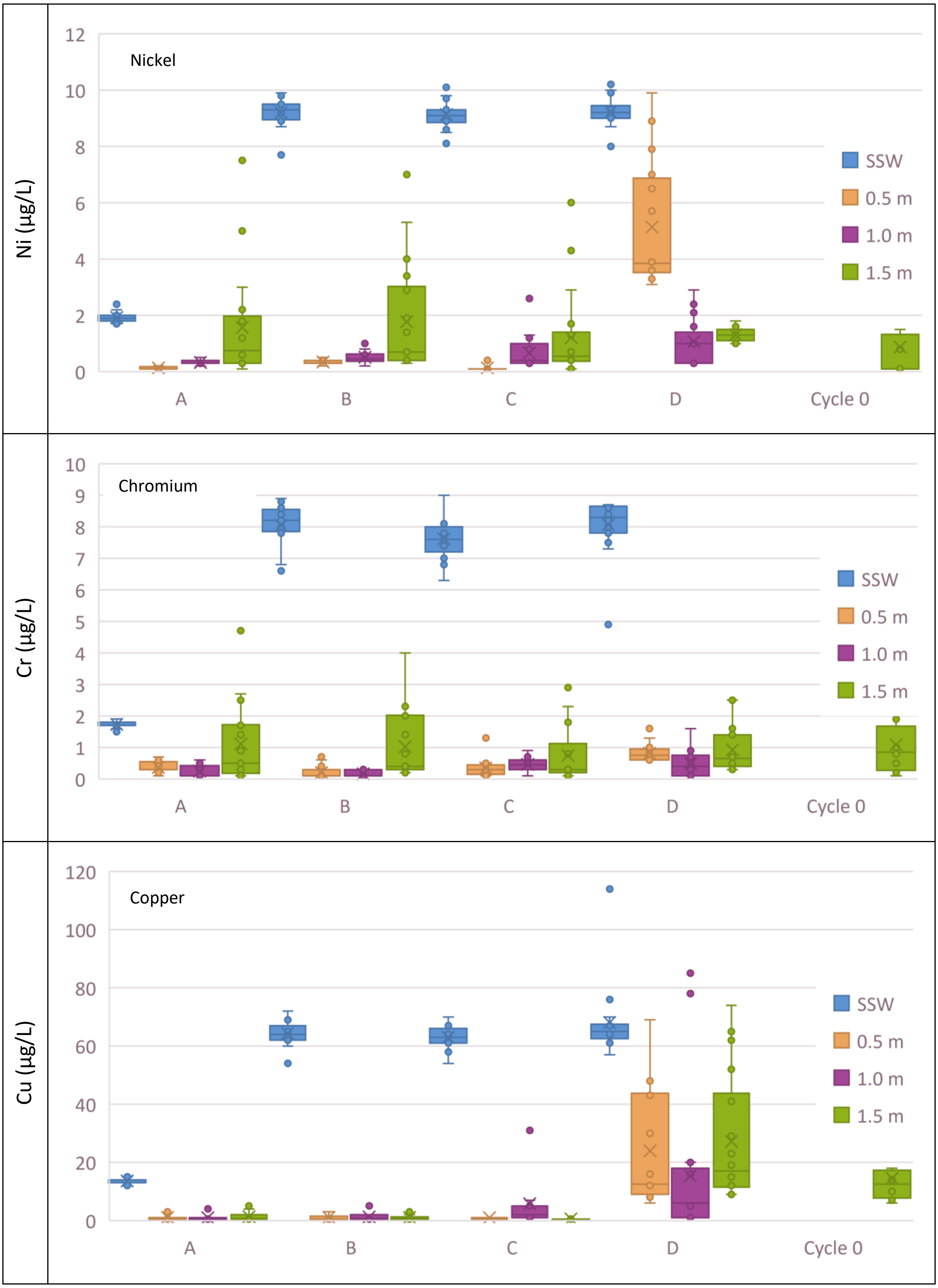

Figure 5-6: *Concentrations of Ni (top), Cr (middle) and Cu (bottom) in SSW and INF samples for each depth.*

Table 5-9: *Mean contaminant concentrations in SSW and effluent after infiltration through each depth.*

Experiment A	**P**	**Zn**	**Pb**	**Ni**	**Cr**	**Cu**
SSW	203 ± 7	95 ± 10	2.2 ± 0.3	1.9 ± 0.1	1.7 ± 0.1	14 ± 1
Infiltration depth						
0.5 m	16 ± 2	24 ± 12	<0.4	<0.2	0.4 ± 0.1	1 ± 0.5
1.0 m	17 ± 2	12 ± 8	<0.4	0.3 ± 0.03	0.3 ± 0.1	1 ± 0.4
1.5 m	76 ± 28	8 ± 1	1.2 ± 0.8	2 ± 1	1 ± 0.6	1 ± 0.6
ANOVA p-value	<0.001	0.013	0.005	<0.001	0.002	0.616
Turkey HSD						
0.5 m vs 1.0 m	no	no	no	no	no	-
0.5 m vs 1.5 m	yes	yes	yes	yes	yes	-
1.0 m vs 1.5 m	yes	no	yes	yes	yes	-
Experiment B	**P**	**Zn**	**Pb**	**Ni**	**Cr**	**Cu**
SSW	1132 ± 20	463 ± 18	5.7 ± 1.2	9.2 ± 0.3	8.0 ± 0.4	64 ± 2
Infiltration depth						
0.5 m	19 ± 6	22 ± 9	<0.4	0.3 ± 0.05	0.2 ± 0.1	1 ± 0.4
1.0 m	98 ± 113	10 ± 2	<0.4	0.5 ± 0.1	0.2 ± 0.05	1 ± 0.6
1.5 m	62 ± 26	9 ± 2	0.5 ± 0.2	1.8 ± 1.0	1.0 ± 0.5	1 ± 0.4
ANOVA p-value	0.24	<0.001	0.006	<0.001	<0.001	0.765
Turkey HSD						
0.5 m vs 1.0 m	-	yes	no	no	no	-
0.5 m vs 1.5 m	-	yes	yes	yes	yes	-
1.0 m vs 1.5 m	-	no	yes	yes	yes	-
Experiment C	**P**	**Zn**	**Pb**	**Ni**	**Cr**	**Cu**
SSW	1144 ± 34	458 ± 23	7.9 ± 0.9	9.1 ± 0.2	7.6 ± 0.3	63 ± 2
Infiltration depth						
0.5 m	13 ± 6	16 ± 6	<0.4	<0.2	0.3 ± 0.1	<1
1.0 m	212 ± 145	13 ± 3	<0.4	0.7 ± 0.3	0.5 ± 0.1	6 ± 5
1.5 m	38 ± 19	8 ± 2	0.6 ± 0.5	1.2 ± 0.8	0.7 ± 0.4	<1
ANOVA p-value	0.002	0.017	0.058	0.010	0.087	0.013
Turkey HSD						
0.5 m vs 1.0 m	yes	no	-	no	-	yes
0.5 m vs 1.5 m	no	yes	-	yes	-	no
1.0 m vs 1.5 m	yes	no	-	no	-	yes
Experiment D	**P**	**Zn**	**Pb**	**Ni**	**Cr**	**Cu**
SSW	1140 ± 29	462 ± 14	6.3 ± 1.6	9.2 ± 0.3	8.1 ± 0.5	68 ± 6
Infiltration depth						
0.5 m	898 ± 160	113 ± 17	<0.4	5.1 ± 1.2	0.8 ± 0.2	24 ± 11
1.0 m	440 ± 203	18 ± 5	<0.4	1.1 ± 0.4	0.5 ± 0.2	15 ± 13
1.5 m	128 ± 45	21 ± 2	<0.4	1.3 ± 0.1	0.9 ± 0.4	27 ± 11
ANOVA p-value	<0.001	<0.001	-	<0.001	0.047	0.296
Turkey HSD						
0.5 m vs 1.0 m	yes	yes	-	yes	no	-
0.5 m vs 1.5 m	yes	yes	-	yes	no	-
1.0 m vs 1.5 m	yes	no	-	no	yes	-

Note: ± 95% confidence interval. Units are µg/L.

5.5.3 The effect of organic carbon in the SSW on nitrogen removal

The concentrations of nitrogen species and organic carbon in SSW and effluent from each infiltration depth for Experiments B and C are shown in Figure 5-7 and percent removals at each depth are shown in Figure 5-8. In the first 0.5 m of infiltration high rates of nitrification resulted in nitrate accumulation in both experiments. In the 0.5 m and 1.0 m depths in both experiments the rate of denitrification is less than the rate of nitrification resulting in higher nitrate concentrations than what was in the SSW. Nitrate accumulation has been reported elsewhere, for example Hatt, Fletcher & Deletić (2007) found increased concentrations of nitrate in column effluents following dry periods when nitrification in could occur in the column experiments. At wastewater infiltration sites nitrate accumulation was also found together with decreases in ammonium and/or organic nitrogen after infiltration through the vadose zone (Bekele *et al.*, 2011; Mienis & Arye, 2018). For Experiment C this is true at the 1.5 m depth too, and only 10% total nitrogen removal was achieved after 1.5 m infiltration. For Experiment B total nitrogen removal was achieved at all three infiltration depths, with 50% removal for the 1.5 m depth. This suggests that organic carbon in infiltrating stormwater, or at least the readily biodegradable portion of it, may be important for nitrogen removal during infiltration.

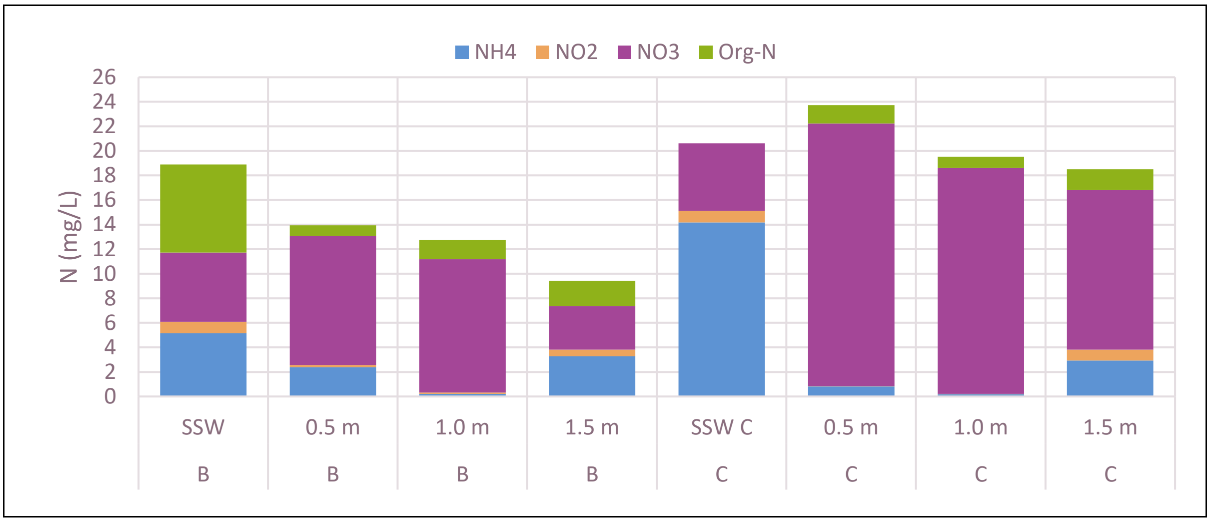

Figure 5-7: *Mean concentrations of nitrogen species in SSW and after infiltration through each soil depth for experiments B and C.*

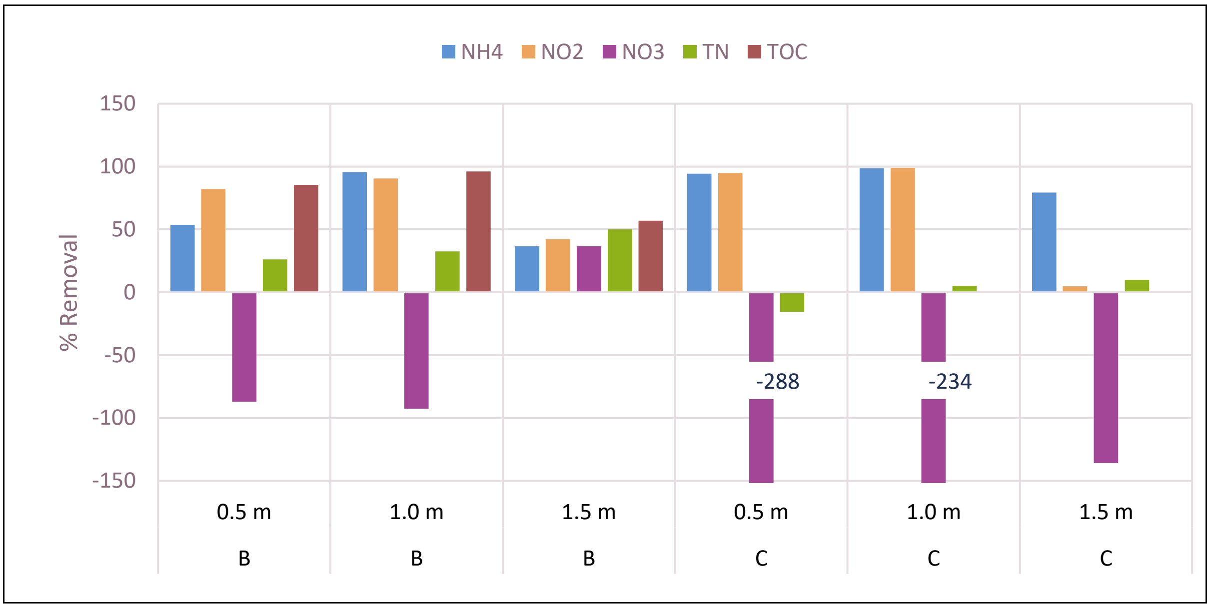

Figure 5-8: *Percent removals of nitrogen species and TOC during infiltration with (B) and without (C) organic carbon in SSW.*

The higher percent removal of ammonium achieved in Experiment C compared to Experiment B after 0.5 m infiltration is most likely due to ammonification of the organic nitrogen which was present in the SSW of Experiment B and not in Experiment C.

The saturated zone could be split into 3 parts based on the cycle in which it was sampled, and the sample port used, as shown in Figure 5-9. Mean total concentrations and breakdown of the nitrogen species in each part of the saturated zone are shown in Figure 5-10 and percentage removals are shown in Figure 5-11. The first saturated zone samples were taken on Day 5 of Cycles 4-6 from Sample port 3 which was 0.5 m below the top of the saturated zone and received water after 1.0 m infiltration. Here both experiments achieved 88% total nitrogen removal and had ammonium as the dominant nitrogen species. During Cycles 7-9 samples were again taken from Sample port 3 and, because the saturated zone was never drained and the only water removed was that taken for sampling, this water had also infiltrated through 1.0 m but had been in the saturated zone for longer.

A small increase in ammonium concentration in samples from Sample port 3 in Cycles 7-9 suggests that ammonification occurred in the saturated zone, but nitrification was limited. The biggest difference between experiments was in the upper part of the saturated zone sampled in Cycles 7-9 from Sample port 2, where water reached the saturated zone after only 0.5 m infiltration depth. In Experiment B complete denitrification occurred and only a small amount of ammonium and organic nitrogen remained, while in Experiment C denitrification was not sufficient and nitrate concentration was higher than the SSW concentration.

Two-way ANOVA was used to determine the effect of organic carbon in the SSW and infiltration depth on the effluent concentrations of nitrogen species and TOC, and to determine the effect of added organic carbon in the SSW and saturated zone part (Figure 5-9) on the effluent concentration of the same analytes. Overall, the column effluent after infiltration had significantly higher concentrations of nitrate and total nitrogen in Experiment C compared to Experiment B, while ammonium and organic carbon were significantly higher in Experiment B.

			Time		
			Cycle 1-3	Cycle 4-6	Cycle 7-9
Depth below soil surface	0.5 m	sample port 1			
	1.0 m	sample port 2			P2 C7-9
	1.5 m	sample port 3		P3 C4-6	P3 C7-9

***Figure 5-9**: Saturated zone split into three parts.*

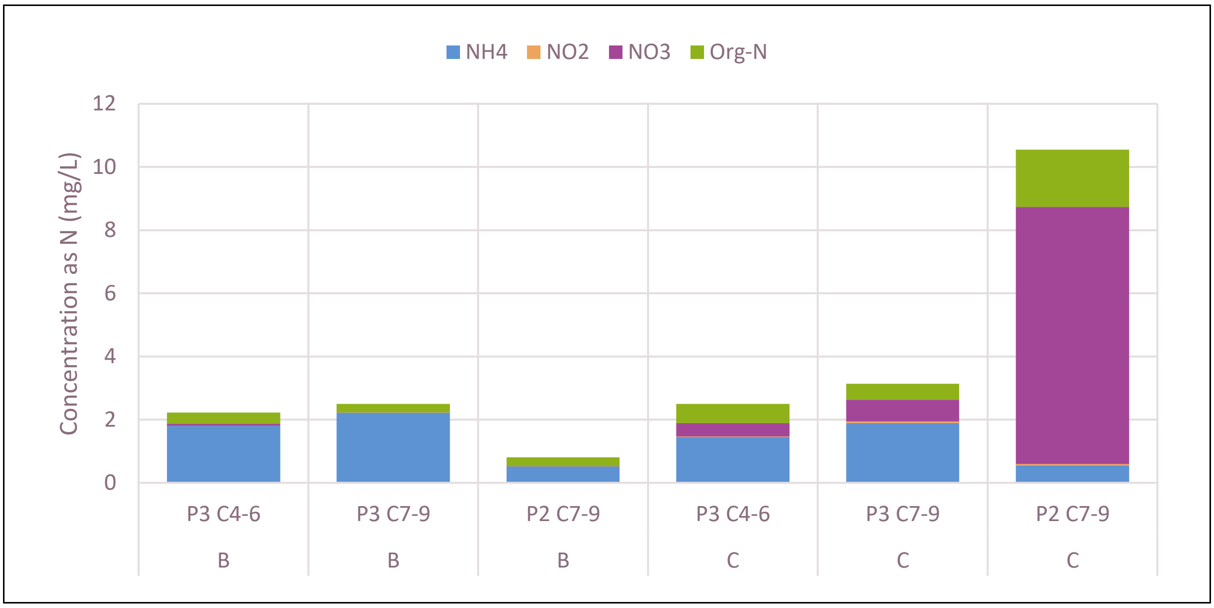

***Figure 5-10:** Concentrations of nitrogen species in column samples from the saturated zone for Experiments B and C.*

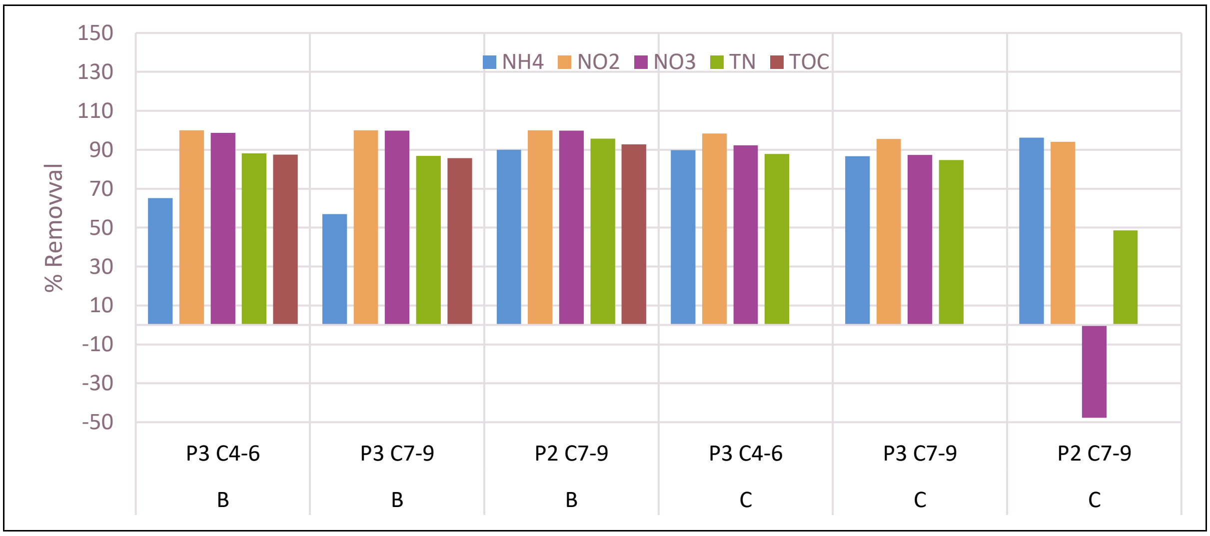

***Figure 5-11:** Percentage removal of nitrogen species and TOC in saturated zone with (B) and without (C) organic carbon in the SSW.*

In the saturated zone there was no difference between the treatments for ammonium concentration but for nitrite, nitrate and total nitrogen Experiment C had significantly higher concentrations. Mean concentrations and 95% confidence intervals for infiltration and saturated zones are given in Table 5-10. The percent removals for each depth, mean concentrations for each depth and complete ANOVA results can be found in Appendices E, F, and G respectively.

Table 5-10: *Mean concentrations of nitrogen species after infiltration and in the saturated zone.*

	after infiltration through soil			saturated zone		
	B	**C**	**p-value**	**B**	**C**	**p-value**
ammonium as N	2.0 ± 0.5	1.3 ± 0.4	0.002	1.5 ± 0.4	1.3 ± 0.3	0.069
nitrite as N	0.27 ± 0.26	0.35 ± 0.30	0.685	<0.001	0.038 ± 0.027	0.012
nitrate as N	8.3 ± 3.8	17.6 ± 4.1	0.001	0.03 ± 0.02	3.1 ± 2.3	0.001
total N	12.0 ± 3.8	20.6 ± 4.0	0.003	1.8 ± 0.4	5.4 ± 2.6	0.001
organic carbon	13.3 ± 4.9	6.0 ± 3.3	0.004	7.3 ± 1.5	4.5 ± 0.8	<0.001

Note: ± 95% confidence interval. P-values < 0.05 indicates statistically significant difference between the respective means from Experiments B and C. Units are mg/L.

The organic carbon concentration in Experiment B was significantly higher than in Experiment C for the infiltration effluent samples and from the saturated zone (Table 5-10). Results for each depth and each part of the saturated zone are shown in Figure 5-12. Organic carbon concentrations after 1.5 m infiltration were likely higher due to leaching of soil organic carbon.

Soil organic carbon can be mobilised by infiltrating water and this together with organic carbon from the stormwater may be utilised for denitrification. Readily biodegradable organic carbon in stormwater may increase nitrogen removal during infiltration and in the saturated zone below small infiltration depths; however, deeper infiltration depths may allow mobilisation of more organic carbon from the soil and result in less dependence on stormwater organic carbon for denitrification. Soil organic carbon mobilisation in the saturated zone may also be important.

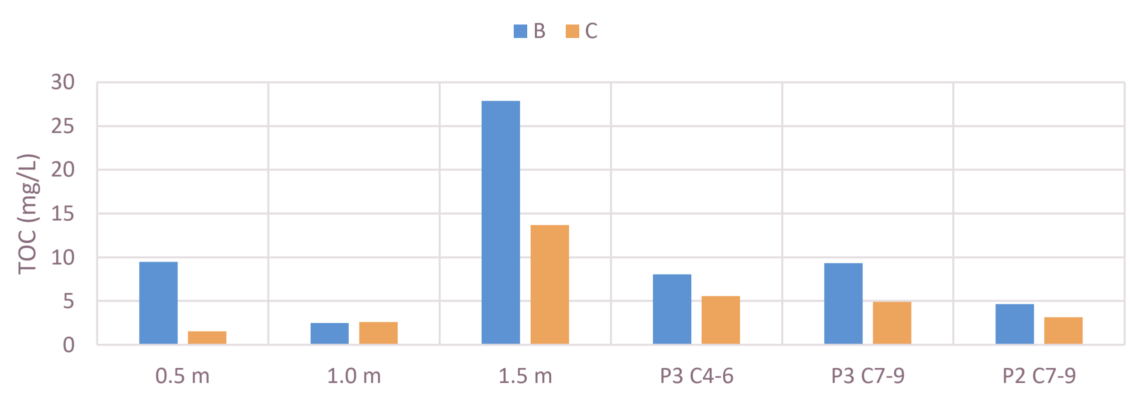

Figure 5-12: *Organic carbon concentrations in column effluent after infiltration through each depth and in saturated zone.*

5.5.4 The effect of the media and the SSW contaminant concentrations

This experiment used two different concentrations of contaminants in the SSW, i.e., one representing a typical residential catchment and the other using a theoretical 5x higher concentration to investigate how contaminant concentration impacts treatment during infiltration storage and in the saturated zone. Further, to represent a worst-case scenario where the soil is coarse-textured and contains less organic matter, metal oxides, and clay minerals, clean silica sand was used in place of soil in Experiment D to determine whether treatment was still possible.

Two-way ANOVA was used to determine the effect of SSW concentration and infiltration depth on effluent concentrations for the added metals and P. Results showed that the SSW metal and P concentrations had no significant effect on the effluent concentrations in Experiments A and B. Two-way ANOVA showed that the media type, however, had a significant effect on the effluent concentrations; for Experiment D added metal and P concentrations were significantly higher than Experiment B (except Pb). For Pb results were mostly below the MDL, but low concentrations were detected in the 1.5 m infiltration depth samples for the soil columns. Box and whisker plots for each metal and P are shown in Figure 5-13. These results indicate that the soil properties are important for retention/adsorption of these contaminants. The main difference in media properties which may influence contaminant adsorption is the clay content and particle size distribution of the sand fraction. The soil had a higher clay content (5.8 % compared to 0.6%) and a higher proportion of fine and medium sand (Table 5-5). The concentration of contaminants in the infiltrating water (SSW), at least for the range of concentrations used, did not significantly affect the effluent concentrations. A table showing the mean concentration of each metal and P for each depth is included in Appendix F, and results from the two-way ANOVA are included in Appendix G. As previously noted, the percent removals at each depth for these contaminants are included in Appendix E.

A two-way ANOVA was performed to determine the effect of SSW concentrations (Experiments A and B) and infiltration depth / saturated zone on effluent contaminant concentrations. Analysis of the SSW concentration effect showed that after infiltration the effluent TN and TOC in Experiments B were significantly higher than in Experiment A. In the saturated zone no significant difference between the mean TN or TOC concentration due to high and low SSW concentration was found (Table 5-11). Similarly, two-way ANOVA was used to compare the media effects on TN and TOC concentrations. After infiltration there was no difference in the mean concentrations of TN and TOC, however in the saturated zone samples from the soil columns (Experiment B) had significantly higher TOC concentrations and significantly lower TN concentrations than the sand columns (Experiment D). All results from the two-way ANOVA can be found in Appendix F. Percent removals for each depth and the saturated zone from each experiment for nitrogen species and TOC are shown in Appendix E.

Table 5-11: *Effect of SSW concentration on effluent TN and TOC concentrations.*

	Experiment A	**Experiment B**	**Experiment D**	**A vs B**	**B vs D**
SSW concentration	Low	High	High	Low vs high	High
Media	Soil	Soil	Sand	Soil	Soil vs sand
	Mean effluent concentrations (mg/L)			**p-value**	
TN (INF samples)	4.4	12.0	13.9	**<0.001**	0.364
TOC (INF samples)	7.1	13.3	11.3	**0.016**	0.469
TN (SAT samples)	1.6	1.8	12.5	0.130	**<0.001**
TOC (SAT samples)	9.1	7.3	3.8	0.128	**<0.001**

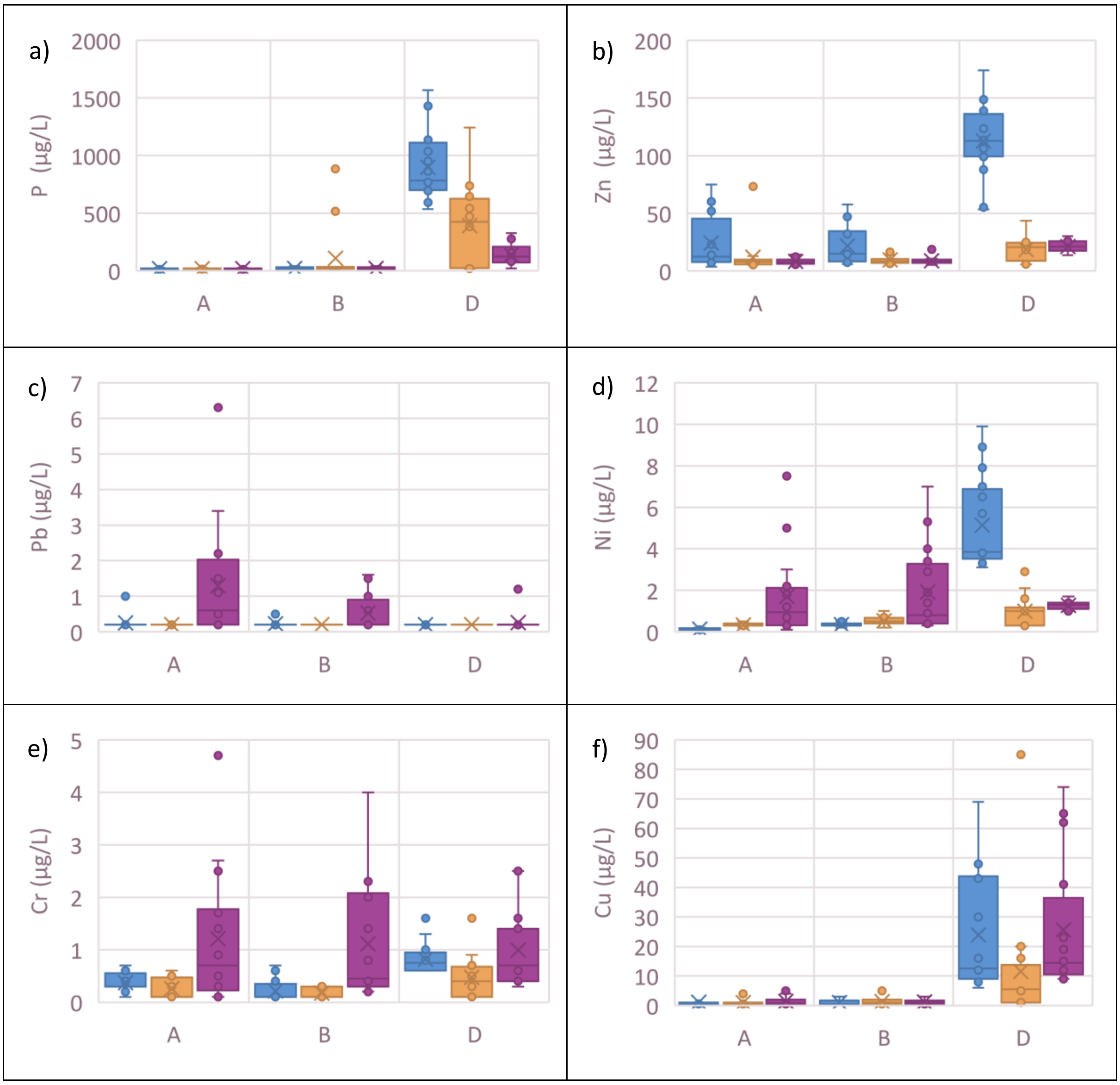

Figure 5-13: *Box and whisker plots of a) phosphorous, b) zinc, c) lead, d) nickel, e) chromium, and f) copper in column effluent from each infiltration depth for Experiments A, B and D.*

Figure 5-14 shows the nitrogen species concentrations and percent removals at different depths and in the saturated zone. For Experiments A and B nitrification seems to be the dominant process in the first 1.0 m infiltration resulting in removal of ammonium and nitrite and build-up of nitrate. At the same time there is an increase in organic N between 0.5 m and 1.0 m indicating organic N mobilisation from the soil which is also evident in the 1.5 m depth. By the 1.5 m depth ammonification and incomplete denitrification results in an increase in ammonium and nitrite and decrease in nitrate. In Experiment A the total nitrogen increases with infiltration depth while the opposite is true of Experiment B. In the saturated zone complete denitrification takes place with total nitrogen removal rates of 61% and 90% for Experiments A and B respectively. A similar residual amount of ammonium and organic nitrogen remains in the saturated zone in both experiments.

The comparison between Experiment B (soil) and Experiment D (sand) nitrogen species is quite stark (Figure 5-15). While no significant difference between total nitrogen concentrations during infiltration was found, the concentrations of the individual species did differ significantly. For Experiment D ammonification is dominant in the first 1.0 m leading to accumulation of ammonium and decrease in organic nitrogen. By the 1.5 m depth there is a combination of ammonification, nitrification, and denitrification (likely occurring on different days) which results in accumulation of nitrite and nitrate although complete nitrification is not achieved. In the saturated zone there is no net denitrification in Experiment D, and overall nitrogen removal was only 35%. This may be due to the lower TOC concentration in the saturated zone in Experiment D or other factors such as smaller microbe populations, lower clay content, or faster infiltration rates. Results suggest that soil/ media properties are more important than influent concentration for overall removal of nitrogen in the saturated zone. During infiltration nitrification is the dominant process in soils and since this does not result in TN removal, high SSW concentrations result in higher TN after infiltration. However, once in the saturated zone denitrification in soil resulted in similar final TN concentration for both high and low SSW concentrations.

Figure 5-14: *Nitrogen species concentration in Experiments A and B (top), percentage removals in Experiment A (middle) and in Experiment B (bottom).*

Figure 5-15: *Nitrogen species concentration in Experiments B and D (top), percentage removals in Experiment B (middle) and in Experiment D (bottom).*

5.5.5 Mobilisation of As, Fe, and Mn

Changes to the geochemical conditions in the aquifer from artificial recharge can lead to mobilisation of naturally occurring contaminants (NRMMC, EPHC & NHMRC, 2009; Fakhreddine *et al.*, 2021). Arsenic is of particular concern as it is toxic even in small quantities, while Fe and Mn pose operational risks associated with clogging of abstraction boreholes as has been seen to be a problem in the Atlantis water supply scheme (Bugan *et al.*, 2016).

Arsenic is ubiquitous in sediments (Smedley & Kinniburgh, 2002), and changes in redox conditions result in arsenic mobilisation (Fakhreddine *et al.*, 2021). The possible pathways to arsenic mobilisation during managed aquifer recharge are summarised by Fakhreddine *et al.* (2021), with the most common pathway being exposure of reduced aquifer sediments (arsenic residing in pyritic minerals) to oxidizing recharge water (containing DO and/or nitrate). This results in sorption of arsenic onto iron(III) (hydr)oxides (i.e. repartitioning of arsenic) where it is then vulnerable to mobilisation through reductive dissolution of iron(III) (hydr)oxides in the presence of an organic carbon source. Similarly, in oxidised sediments arsenic is likely already adsorbed on iron(III) (hydr)oxides and introduction of reducing recharge water (water that contains organic carbon) results in reductive dissolution of the iron minerals and mobilization of arsenic (Fakhreddine *et al.*, 2021).

Iron and manganese are also ubiquitous in soils and neither these nor arsenic thus needed to be added to the synthetic stormwater feeds in order that their mobilisation could be studied. Iron and manganese are redox active species which are present as oxide and hydroxide minerals in their oxidised forms and dissolved (and therefore mobile) in their reduced form.

Two-way ANOVA was performed to determine the effect of infiltration depth / saturated zone and SSW composition on the concentrations of arsenic, iron, and manganese. Results showed that there was a significant interaction effect for iron (p=0.023) and manganese (p=0.021), but not for arsenic (0.141). Both the infiltration depth / saturated zone and SSW composition had statistically significant effects on the concentrations of all three elements. The two- way ANOVA results can be found in Appendix F. Mean concentrations for each element (± 95% confidence interval) for each infiltration depth and saturated zone (INF 0.5 m, INF 1.0 m, INF 1.5 m and SAT) and for each SSW composition (Experiments A, B and C) are shown in Table 5-12. The box and whisker plots in Figure 5-16 show differences between each infiltration depth and the saturated zone for each SSW composition for the three elements.

Table 5-12: *Mean concentrations of arsenic, iron and manganese in INF depth and SAT (experiments A, B and C), and in Experiments A, B and C (INF depths and SAT).*

	Arsenic	Iron	Manganese
Infiltration depth / saturated zone			
INF 0.5 m	3.1 ± 1.1	94.6 ± 52.7	5.1 ± 2.2
INF 1.0 m	4.3 ± 1.5	95.9 ± 49.8	15.7 ± 6.7
INF 1.5 m	**20.1 ± 3.4**	887.8 ± 146.8	19.1 ± 3.3
SAT	13.7 ± 1.6	**1519.8 ± 249.2**	**31.8 ± 3.1**
SSW composition			
Experiment A	10.5 ± 2.4	449.2 ± 141.6	13.9 ± 3.2
Experiment B	**13.6 ± 2.5**	**842.7 ± 208.1**	**21.4 ± 3.6**
Experiment C	6.9 ± 2.2	656.8 ± 200.5	18.5 ± 5.4

Note: ± 95% confidence interval. Units are µg/L.

Since no arsenic, iron or manganese were added in the SSW these elements were mobilised from the soil and higher concentrations were released in the saturated zone (except arsenic) compared to after infiltration and from Experiment B compared to other experiments. This suggests that increased organic carbon input may increase the risk of mobilisation of these contaminants in the aquifer.

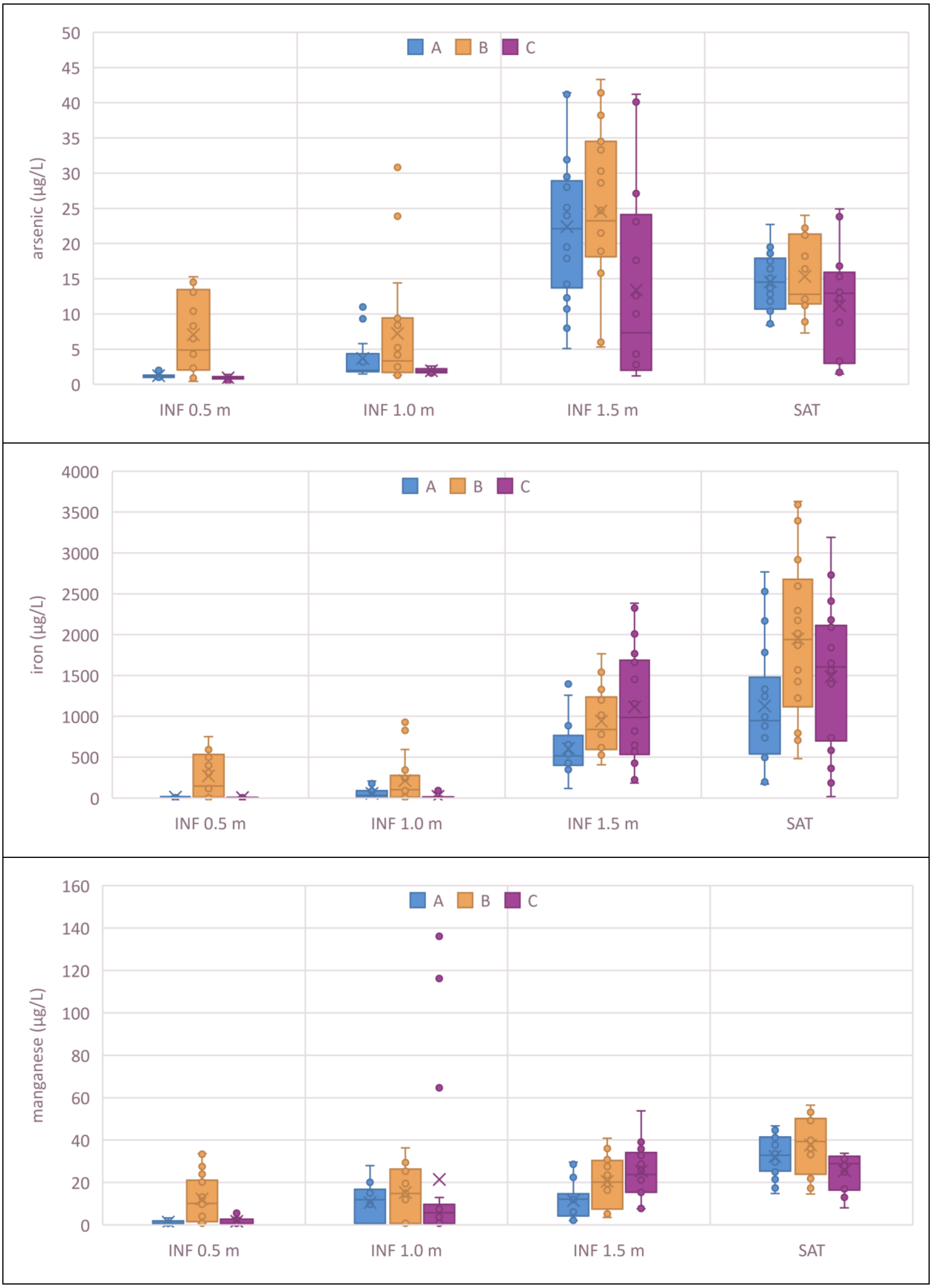

Figure 5-16: *Box and whisker plots showing arsenic (top), iron (middle) and manganese (bottom) concentrations in the INF and SAT samples in Experiments A, B and C.*

5.6 Key findings

Soils were able to effectively retain P, Zn, Pb, Ni, Cr and Cu during infiltration through the first 0.5 m depth of soil and at the concentrations tested for one rainfall season. Accumulation of P, Zn, Ni, and Cu was found in soil samples from the surface of the columns while only Zn accumulated slightly in the 0.5 m depth soil sample. Measurable accumulation in sand was not found.

The distribution of nitrogen species changes with depth, and at the shallower infiltration depths (0.5 m and 1.0 m) nitrate concentration increased compared to SSW for all soil experiments. Organic carbon in the SSW improved total nitrogen removal during infiltration (50% removal compared to 10% without for 1.5 m infiltration). In the saturated zone total nitrogen was better removed with (90%) and without (74%) added organic carbon in SSW. Organic carbon in the SSW allowed denitrification to commence higher in the profile instead of waiting for organic carbon to be released / mobilised from the soil. This suggests that stormwater organic carbon (if readily biodegradable) may be useful for denitrification during infiltration through shallow soil depths.

Arsenic and iron mobilisation occurred to a greater extent in the saturated zone and when organic carbon was added to the SSW. Thus, the organic carbon load from stormwater may also increase the likelihood of arsenic and iron mobilisation in the groundwater.

There was little difference between the final concentrations of P, Zn, Pb, Ni, Cr and Cu after infiltration for the low *vs* high concentrations (Experiments A & B), however the sand performed significantly worse than the soil in removing these contaminants. During infiltration the concentrations of nitrogen species in the low concentration experiment increased with depth indicating leaching from the soil. However, in the saturated zone there was little difference in mean total nitrogen concentration between Experiments A & B. Of note was that for Experiment D the mean saturated zone total concentration was 6-fold higher again, demonstrating that media properties were important for contaminant removal. Overall, the media (sand *vs* soil) was more important than the input concentrations in contaminant removal performance.

5.7 Limitations

The clean silica sand drained much faster than the soil and so the media would have had more time to dry between loadings. As described in section 5.4.4 column leaks were an issue and although fixed as soon as possible may have caused some differences in the results. Furthermore, clogging of the columns during cycle one may have resulted in altered flow paths due to movement of fine material.

This study did not test the total capacity of the media to retain added metals and phosphorous therefore the long-term performance is unknown. However, at the low concentrations typical of residential areas there is likely high capacity in the soil.

6 Discussion

As part of its commitment towards becoming a water sensitive city, the CoCT endeavours – through its Water Strategy – to conserve and protect water resources for people and the environment (CoCT, 2019). The vison of becoming a WSC inspires continuous improvement, new thinking, and innovation for better urban water management (Fisher-Jeffes *et al*., 2017). This vision is about holistic water management which considers the entire water cycle, and utilises fit-for purpose water in a centralised and decentralised manner (CoCT, 2019).

The CFA is a large primary aquifer underlying a significant portion of the Cape Town metropolitan area and offers potential for storage of infiltrated stormwater (Okedi, 2016) which otherwise flows into the city waterways and ultimately, out to sea. Dispersed stormwater infiltration through enhancement of existing infrastructure could have multiple benefits for communities, ecosystems, biodiversity and groundwater recharge. This research investigated the impact of stormwater infiltration on shallow groundwater quality, where the limited infiltration depth meant that processes in both the unsaturated and saturated soil required investigation.

Assessment of water quality should be made based on its suitability for an intended purpose, e.g., human consumption, irrigating crops, or sustaining an aquatic ecosystem. Even within these uses there is further nuance such as the crop type, soil type, water storage method or sensitivity of specific plants and organisms. Inorganic nutrients, for example, are known to cause eutrophic conditions in surface water bodies at low concentrations (0.025 mg P /L and 2.5 mg N /L) but nitrogen is safe for human consumption and irrigation at much higher concentrations, and phosphate is not part of the water quality limit or guidelines for these uses. Phosphate in particular is a major concern for surface water bodies in Cape Town (Day *et al*., 2020) therefore stormwater runoff from urban areas may be unsuitable for surface water ecosystems but may be suitable for infiltration to groundwater and subsequent re-use.

Phosphate adsorption in soil often occurs on oxide minerals via inner-sphere bonding. Although outer-sphere electrostatic attraction may occur initially, increasingly stronger adsorption occurs over time (Strawn, Bohn & O'Connor, 2020). This process is not limited to the vadose zone and in the saturated zone there may be more time for adsorption and/or precipitation to occur as was found by Barrett, Limouzin & Lawler (2013). However, if dissolution of phosphate-retaining mineral oxides occurs (due to geochemical changes such as development of reducing conditions or changes in pH) phosphate may be re-mobilised until suitable adsorption surfaces are again available. Results from both the field study and laboratory experiments showed that the soil from the Cape Flats is capable of phosphate adsorption during infiltration and soils could potentially be utilised as a phosphate filter to protect surface water quality. Other adsorbable contaminants (i.e., zinc, lead, nickel, chromium, copper, aluminium) were also well retained. While the retention of metal contaminants by soils (albeit not this specific soil) has been demonstrated in many studies (Davis *et al.*, 2003; Hatt, Fletcher & Deletic, 2008, 2009; Li & Davis, 2009; Paus *et al.*, 2014; Li *et al.*, 2018; Hamedani *et al.*, 2021; Kranz *et al.*, 2022), phosphate retention has had variable results, although most phosphate leaching from BSM has been attributed to organic amendments (Bratieres *et al.*, 2008; Paus *et al.*, 2014; Hamedani *et al.*, 2021; Kranz *et al.*, 2022).

During this research a monofunctional stormwater detention pond was retrofitted with an infiltration swale and was transformed into a large bioretention system within the detention pond utilising existing natural soil as bioretention media and vegetation which grew naturally at the site. The groundwater fluctuated between 0 and 0.65 m below the wetland, however, since the infiltration swale was at a higher elevation, infiltration of retained stormwater occurred even during high water table periods. While groundwater recharge was limited during high water table periods, the site provided stormwater quality improvement opportunity by functioning as a bioretention system. The water seeping from the wetland soil into the outlet channel may be infiltrated stormwater, preexisting groundwater or a combination of both, and a tracer study should be conducted to differentiate this. Outlet stormwater quality was not initially included in the field study; however, the limited data collected suggest a reduction in concentrations of organic carbon, inorganic nitrogen, phosphate, and most metals studied in the outlet flow compared to the incoming stormwater.

Nitrification of ammonium to nitrate occurred in the soil columns during infiltration through the first 1.0 m of soil, and this was followed by denitrification which removes nitrogen from the system. Where organic carbon was added to the SSW denitrification occurred during infiltration, however where soil organic matter was the only carbon source, denitrification during infiltration was limited. Denitrification in the saturated zone in the experiment without organic carbon in the SSW achieved 75% total nitrogen removal, much better than the 35% TN removal in the saturated zone of the sand columns. Where sand was used as the column media both nitrification and denitrification were less effective even though organic carbon was added to the SSW. At the study site ammonium was removed during infiltration and stormwater organic carbon appeared to be a carbon source for denitrification in the infiltration zone. The soil cation exchange capacity slows ammonium movement during infiltration, thus increasing the opportunity for nitrification especially during the dry periods between rainfall events (Hatt, Fletcher & Deletić, 2007), but nitrification may be decreased by: competition from other cations in the infiltrating water (because they occupy exchange sites), occurrence of anaerobic conditions, or an increase in ammonium concentration (Mienis & Arye, 2018). At the study site 88 to 95% ammonium removal occurred during infiltration, however the incoming stormwater ammonium and total nitrogen concentrations were relatively low (0.34 and 2.4 mg N/L respectively) and slightly lower than those used in the column experiment (0.5 and 3.9 mg N/L respectively). Nitrification is not limited to the vadose zone, it is however limited to aerobic conditions. Therefore, if other stormwater detention ponds with higher ammonium and organic nitrogen concentrations in their catchments are to be used for infiltration an aerobic pre-treatment step may be required.

Denitrification is the major removal pathway for nitrogen and occurs in anoxic conditions where a bioavailable carbon source is present. Soil organic carbon may be suitable as demonstrated in the column experiment saturated zone. Mobilization and release of (biodegradable) organic carbon in the groundwater below the study site appeared to be linked to stormwater infiltration and evaporation cycles, especially around the wetland area. This may offer some nitrate removal for shallow groundwater as suggested by the consistently lower nitrate concentration in monitoring well 4D compared to other ‘deep’ wells. Overall nitrogen removal during stormwater infiltration requires both nitrification and denitrification which needs oxic and anoxic conditions, in that sequence. If a high ammonium concentration were present a greater oxic zone may be required for sufficient nitrification.

This research contributed to the understanding of stormwater quality management using BGI in shallow groundwater conditions. Restoring some functionality of the natural hydrological cycle in an urban environment with shallow groundwater is a challenging concept because the shallow groundwater is vulnerable to contamination. However, some contaminants may be better remediated by soils and aquifer transport than in surface water bodies. Restoring the connection between surface water and groundwater where appropriate and allowing space and time for nature could have water quality benefits above and below the ground. Further research is needed to understand the limits and capacities of nature-based water treatment strategies in these shallow groundwater environments.

7 Conclusions and recommendations

7.1 Conclusions

The groundwater table at the study site was shallow, remaining < 0.65 m below the centre of the site (wetland area) and reaching the ground level seasonally in this area. It remained > 0.5 m below the infiltration swale which was at a higher elevation. When the water level below the wetland was < 0.2 m seepage to the outlet did not occur and net groundwater recharge was achieved; however, when the groundwater level was higher seepage to the outlet channel produced outflowing stormwater. Outflow stormwater had lower mean concentrations than incoming stormwater for most of the contaminants measured.

Both the field and column experiments results suggest that the soil has potential to retain significant portions of adsorbable contaminants (i.e. phosphate, zinc, lead, nickel, chromium, copper, aluminium) from a formal residential catchment runoff during infiltration through a relatively small soil depth of 0.5 m. Phosphorus removal exceeded the 45% reduction target set out in the Stormwater Impacts Policy (CoCT, 2009) after infiltration through only 0.5 m of soil (92-99% removal). By comparison the sand column experiment achieved only 21% phosphorus removal in the first 0.5 m but this increased to 61% by the 1.0 m depth. In the field study it was estimated that 92% of the phosphate was retained during infiltration.

Stormwater organic carbon may improve denitrification during infiltration and in the saturated zone, however soil organic carbon may be an equally important carbon source. Soil organic carbon availability and mobilization may be influenced by stormwater infiltration and other processes in shallow saturated soils such as evaporation and microbial metabolism. Groundwater nitrate concentrations were lower in all other wells compared to the background well, suggesting denitrification of the groundwater was occurring, and reduction in nitrate concentrations after stormwater infiltration in the shallow infiltration wells was greater than what would result due to dilution.

Stormwater infiltration appears to increase the groundwater pH slightly but significantly and leads to fluctuations in the redox conditions in the localised infiltration area. Groundwater temperature was highly correlated with the well depth (m bgl) in which it was measured in summer and winter, and this may influence microbiological and chemical processes. Iron, arsenic, and manganese mobilisation in the column experiment was increased by the presence of organic carbon in the SSW. However, although there was some localised and time limited iron mobilization at the study site no groundwater quality deterioration was found; and some groundwater quality improvement through denitrification may be occurring. At the study site the background groundwater nitrate concentration buffered the redox conditions preventing further iron mobilisation while utilising the nitrate.

Contaminants which are removed by adsorption processes during stormwater infiltration (metals and phosphate) were well retained by soils at the typical concentrations for a formal residential catchment, and at five times higher concentrations. Total nitrogen and TOC were not well removed during infiltration, and higher influent concentration lead to higher effluent concentrations. However, in the saturated zone removal rates were good and final concentrations were similar for typical and five times typical formal residential catchment concentrations. The sand column experiment resulted in less retention of adsorbable contaminants during infiltration lower removal nitrogen removal in the saturated zone. This suggests that, if soil properties are similar, stormwater from more polluted catchments could also be suitable for infiltration.

7.2 Recommendations

This research contributed to the limited knowledge on the impact of stormwater infiltration on shallow groundwater quality, and the role of BGI in water quality improvement. Water quality is a key consideration in the transition to a water resilient city, and increased stormwater infiltration should not be done without due consideration of the impact on groundwater quality. In a developing world context where 'stormwater' quality is highly variable careful consideration and further research is required to ensure protection of surface water and groundwater quality.

Based on this research enhanced infiltration of stormwater from relatively small (neighbourhood scale) formal residential catchments such as the one in this study is unlikely to pose a significant threat to groundwater quality (for the contaminants studied here), therefore this should be encouraged. Stormwater with higher contaminant concentrations may also be suitable for infiltration, however further research is required to determine the concentration limits and determining factors for suitability of a particular site.

For more contaminated stormwater research should focus on targeted interventions and site conditions needed for specific contaminants or groups of contaminants so that the contaminant profile of the catchment can inform the design of the retrofit. For example, runoff impacted by inadequate sanitation may contain high ammonium, phosphate, and organic carbon (oxygen demand) and without sufficient nitrification may result in ammonium contamination in an anoxic aquifer. If iron oxides are reduced and the iron mobilised this may limit the phosphate adsorption capacity in the aquifer. A nitrification step before infiltration may be required, unless a thick, well aerated vadose zone is present at the infiltration site. Where the carbon load is high soil re-oxygenation periods (for example between infiltration events, due to seasonal water table fluctuations or induced by targeted groundwater pumping) may help to prevent sustained reducing conditions and the associated risk of geogenic contaminant mobilization. Long term studies on adsorption and retention of adsorbable contaminants are required to determine the load and concentration capacity limits of the soils, as well as the conditions which may mobilise previously retained contaminants.

Implementation of BGI as a water resilience strategy could be a useful tool to address water quality issues through targeted, well-informed, nature-based interventions. This requires understanding the capacity and limits of not only the soil, but of the whole nature-based system with its multiple interconnected factors. The selection of detention ponds for stormwater infiltration (from a water quality perspective) should be targeted to protect both freshwater ecosystems and groundwater as far as possible. The design interventions should be based on site specific factors such as groundwater level and fluctuations, soil conditions, inlet and outlet position and elevation, and the stormwater contaminant profile. In a developing world context, a water sensitive city transition is complicated by many factors, and poor urban runoff quality due to, *inter alia*, inadequate sanitation services is an important issue which warrants further research.

The study site also provided a useful case for an ongoing (separate) investigation of the occurrence of trace organic contaminants and microorganisms in stormwater and groundwater and these topics are important areas of research. The retention and degradation of trace organic contaminants in BGI such as this is an important area for future research. Continued monitoring and investigation at the study site could be conducted to better understand stormwater-groundwater interactions and water treatment processes in the wetland area. More research is required to understand the stormwater quality improvement from inlet to outlet and how this is influenced by the groundwater. Carefully designed tracer studies may assist in determining if the water that seeps into the outlet is recently infiltrated stormwater or if it is previously existing groundwater, and whether this changes over the seasons and with water table fluctuations. Temperature and level loggers may be a useful tool to understand the movement of stormwater in the subsurface. Finally, similar research should be conducted at other stormwater infiltrations sites overlaying the CFA, and in other areas with shallow urban groundwater.

The study site saw a complete socio-ecological transformation over the study period. In addition to the swale construction, “no mow” areas were demarcated and, in combination with some wetter years the wetland flourished and along with it came many indigenous species of flora and fauna. Future research should investigate the role of plants in improving water quality in BGI. While contaminant uptake is important, other factors such as how plants interact with and change the soil, support the growth of beneficial microbes, and release organic carbon into the system should also be investigated.

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Appendices

A. Water quality parameters measured in the field study

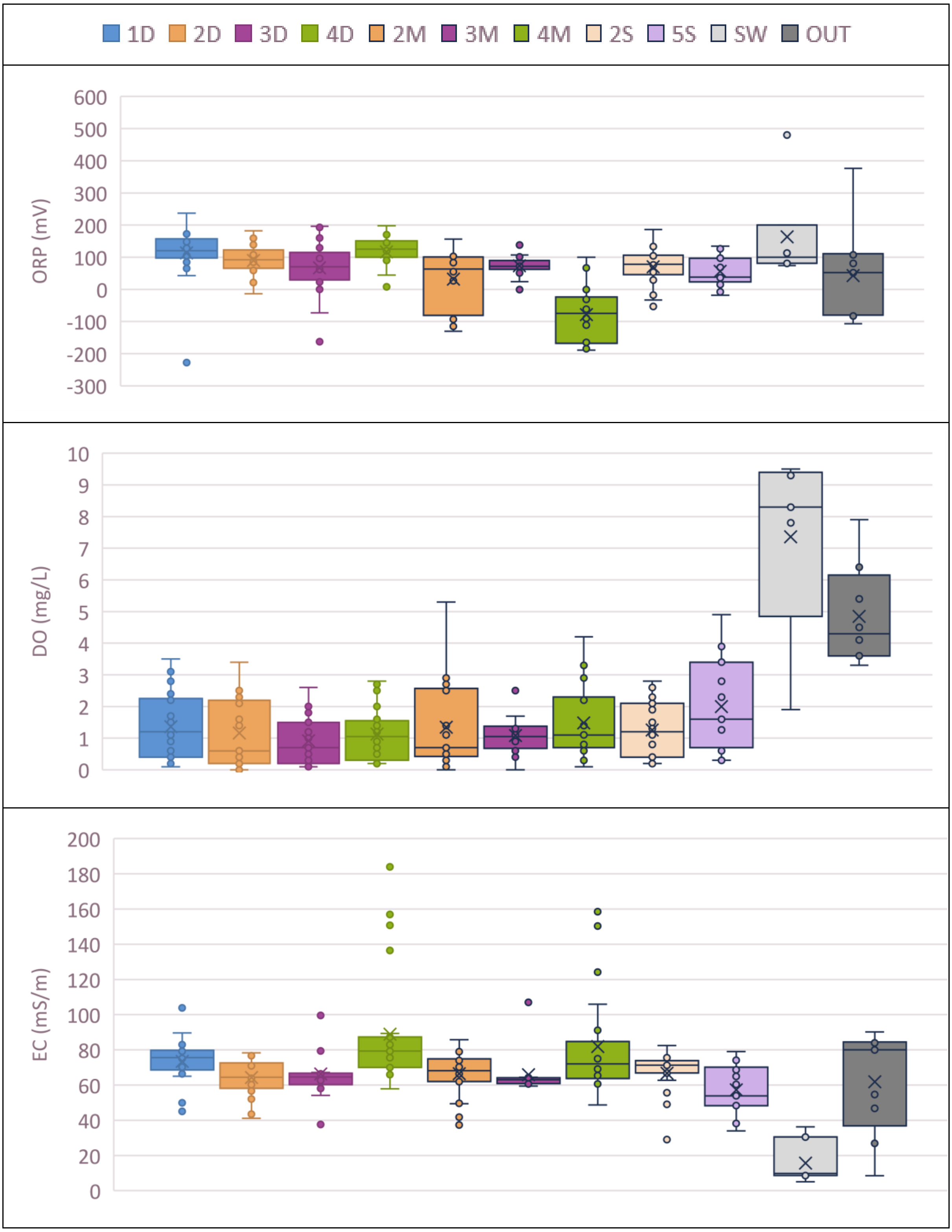

***Figure A-1**: Water quality parameters in monitoring wells and stormwater: ORP (top), DO (middle) and EC (bottom).*

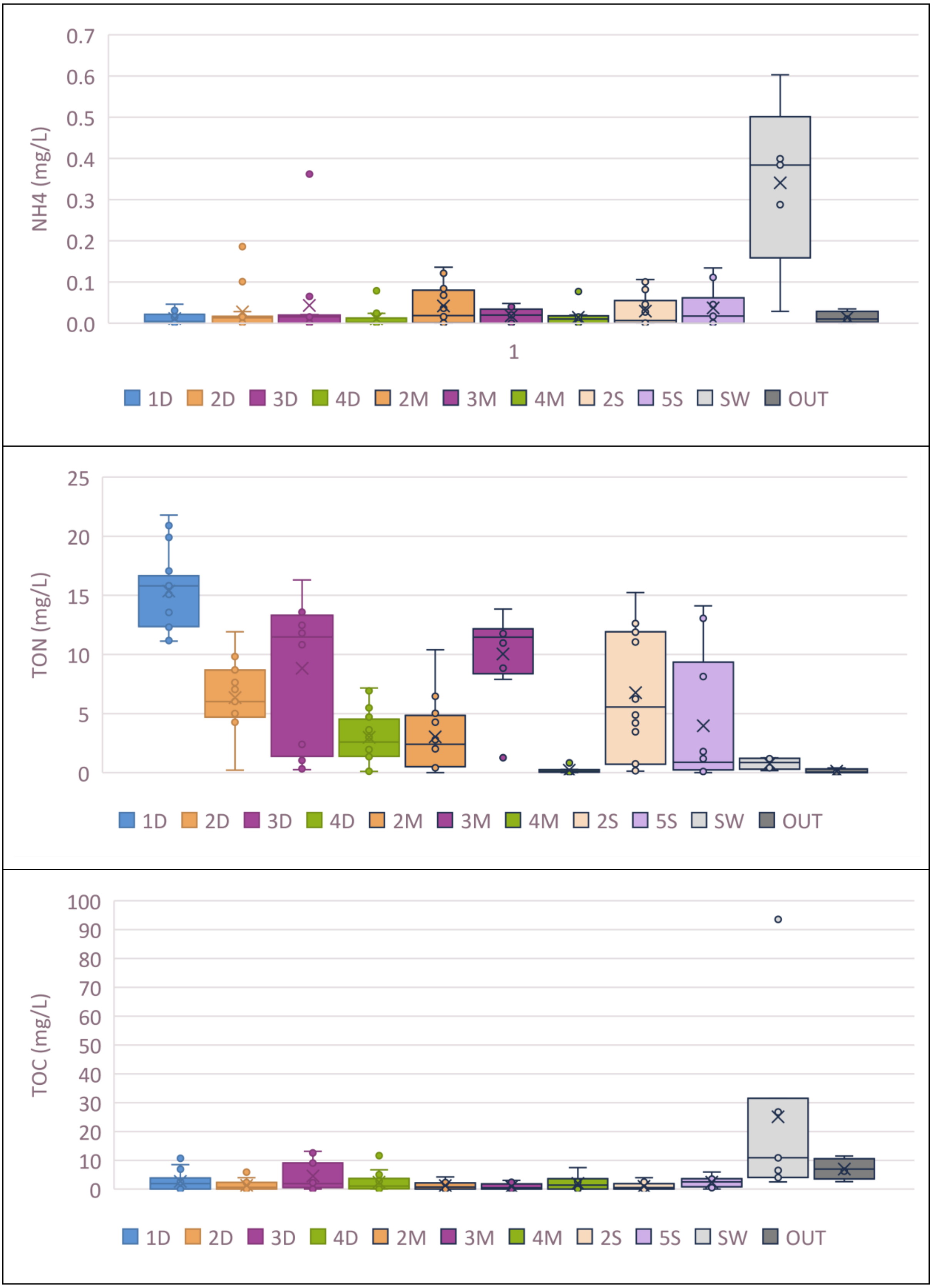

Figure A-2: *Water quality parameters in monitoring wells and stormwater: ammonium (top), total oxidised nitrogen (middle) and total organic carbon (bottom).*

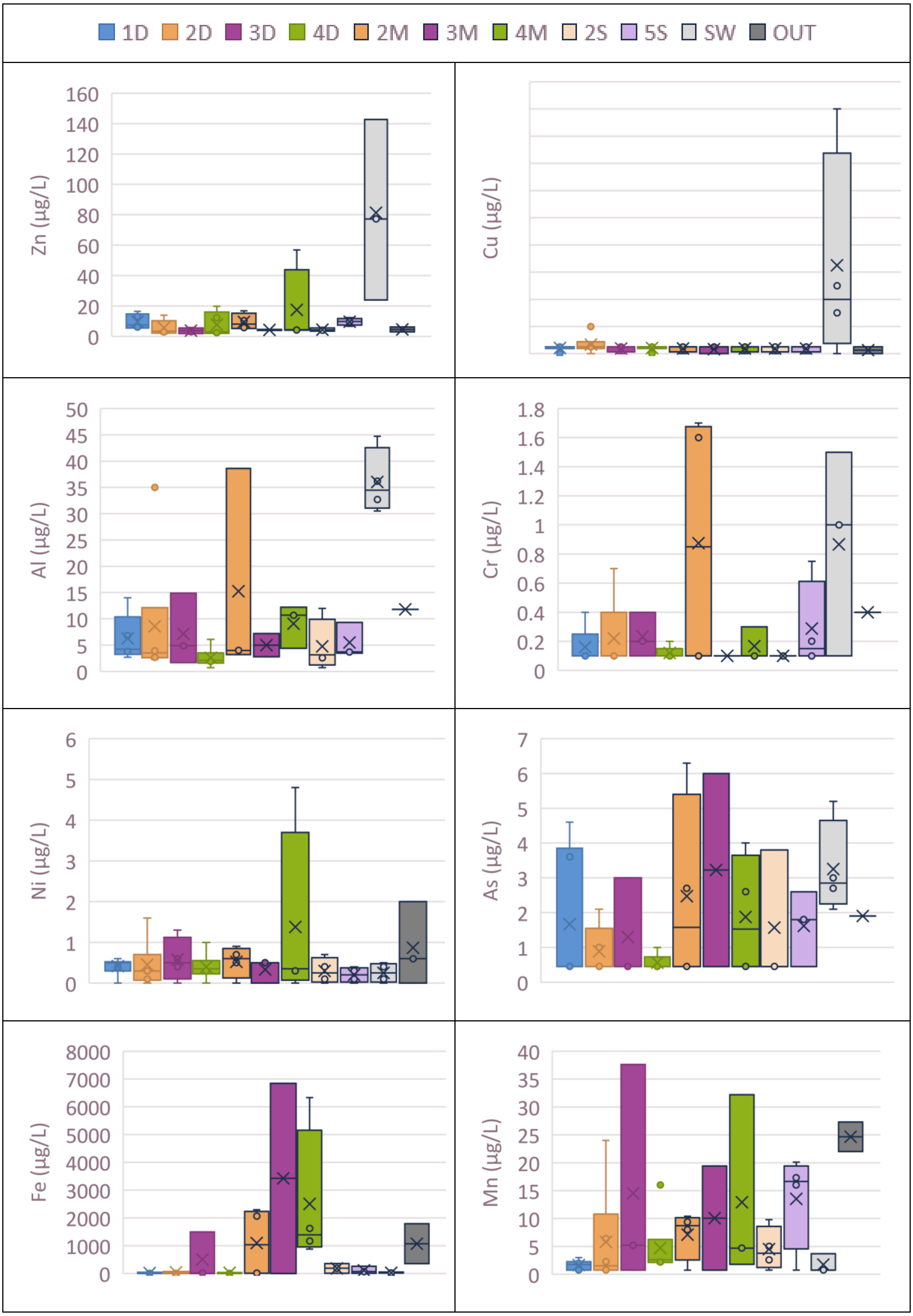

Figure A-3: *Concentrations of metals in monitoring wells and stormwater.*

B. Change in groundwater temperature with depth

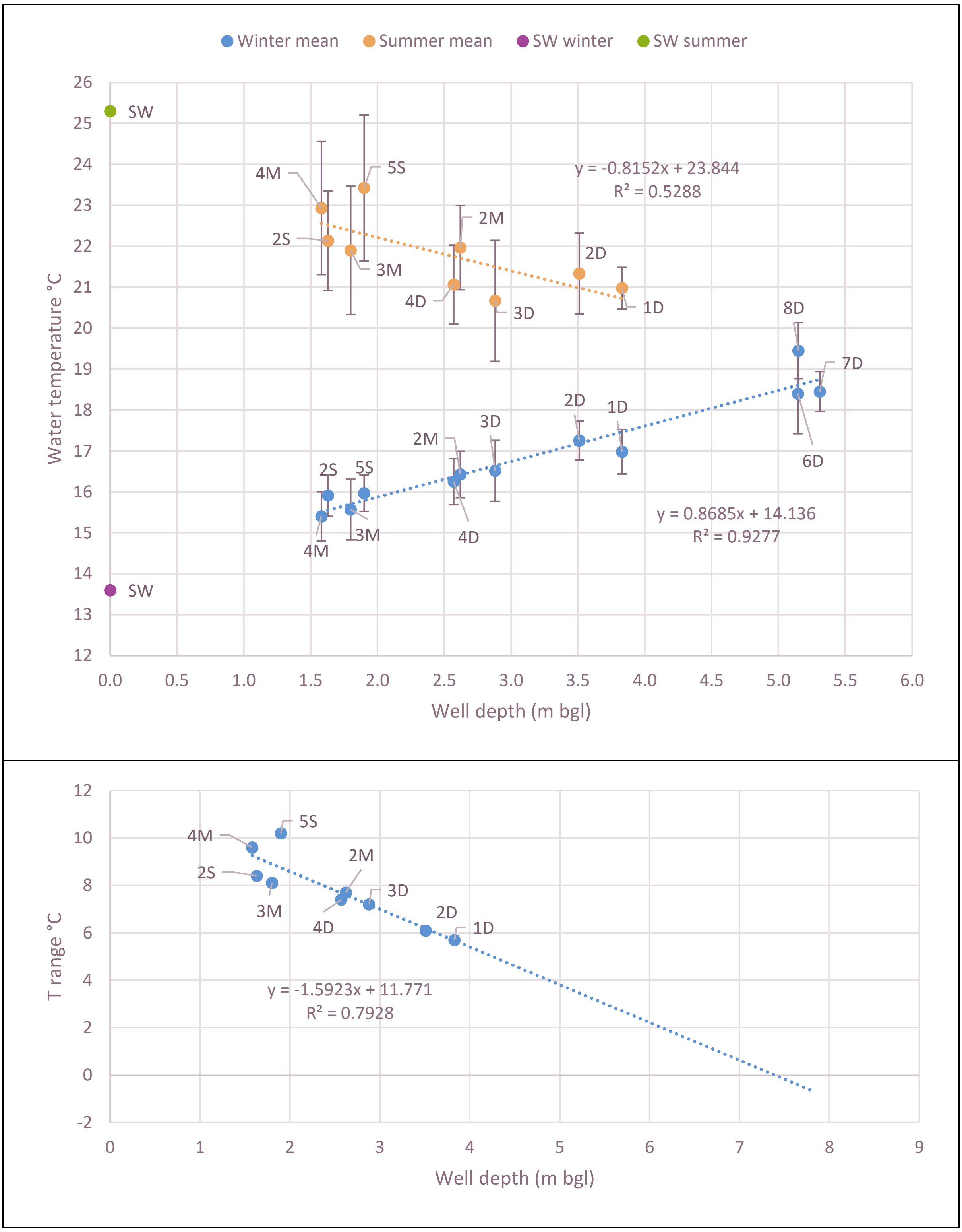

Figure B-1: *Change in mean groundwater temperature with well depth in summer and winter (top) and temperature range in monitoring wells with well depth extended to theoretical depth where groundwater temperature is stable (bottom).*

C. Determination of representative SSW concentrations.

The CoCT has 14 sampling points for the Zeekoe catchment, which is an important catchment on the Cape Flats. Dzurume, (2020) assigned one or more land uses land cover (LULC) associations to each sampling point based on a GIS and Google Earth study. Using these assignments, all points which were not associated with (and therefore assumed to be not impacted by) informal residential, industrial or farmland were excluded, and of the remaining points those which were associated with formal residential were analysed. Median concentrations from this dataset were used as the concentrations for nutrients representative of a formal residential area.

Pitt *et al.*, (1995) analysed stormwater samples from 9 different local source areas for total and dissolved concentrations of metals. Dissolved metal concentrations were used and results from storage areas, vehicle servicing and loading docks were removed as these are not typical of a residential area. Mean of the dissolved values for remaining data were used, however the low concentration for Cu was doubled because it was originally too close to the laboratory method detection limit.

D. Extractable concentrations of contaminants in media after column experiments

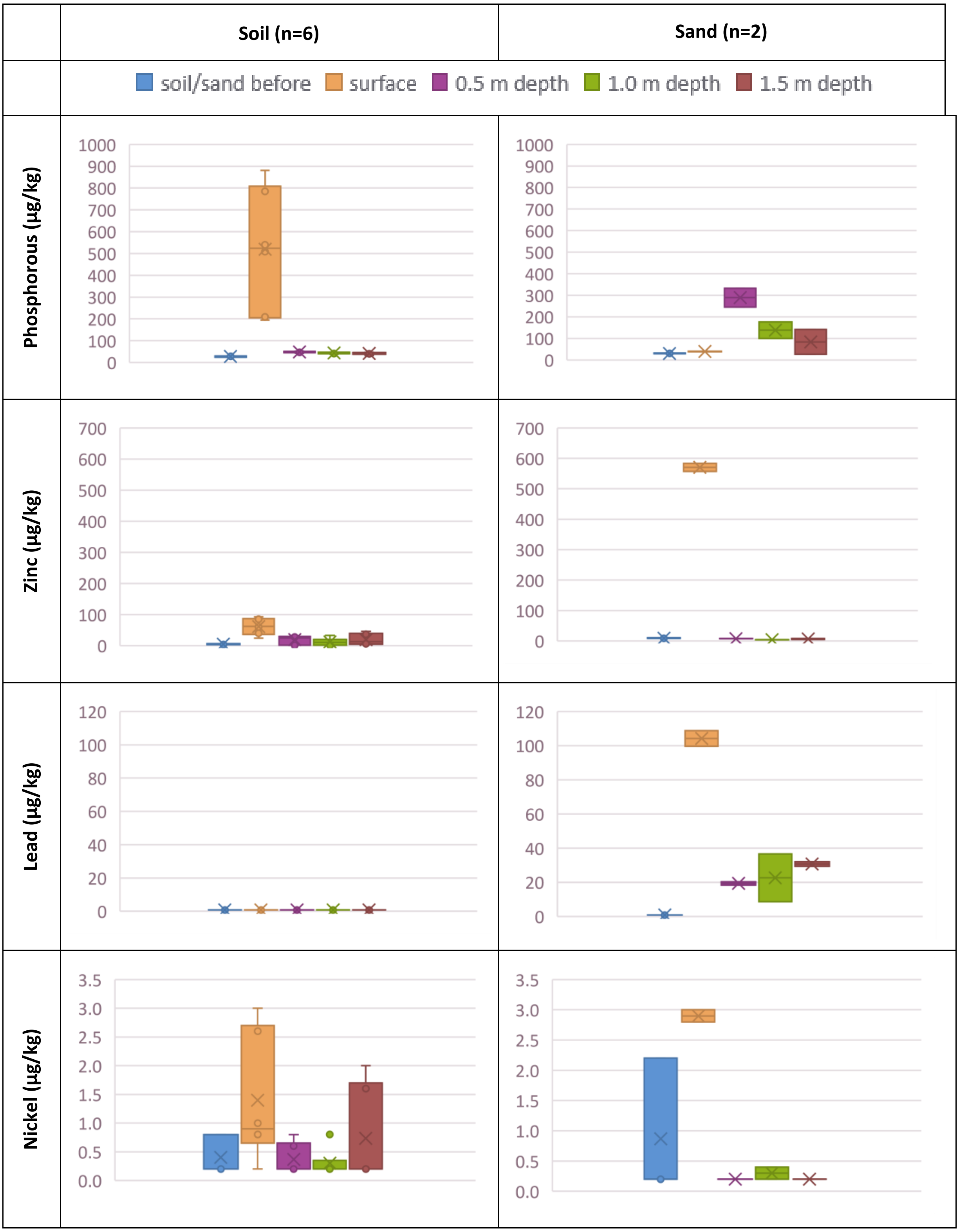

Figure D-1: *Concentrations of extractable contaminants in sand and soil before and after column experiments.*

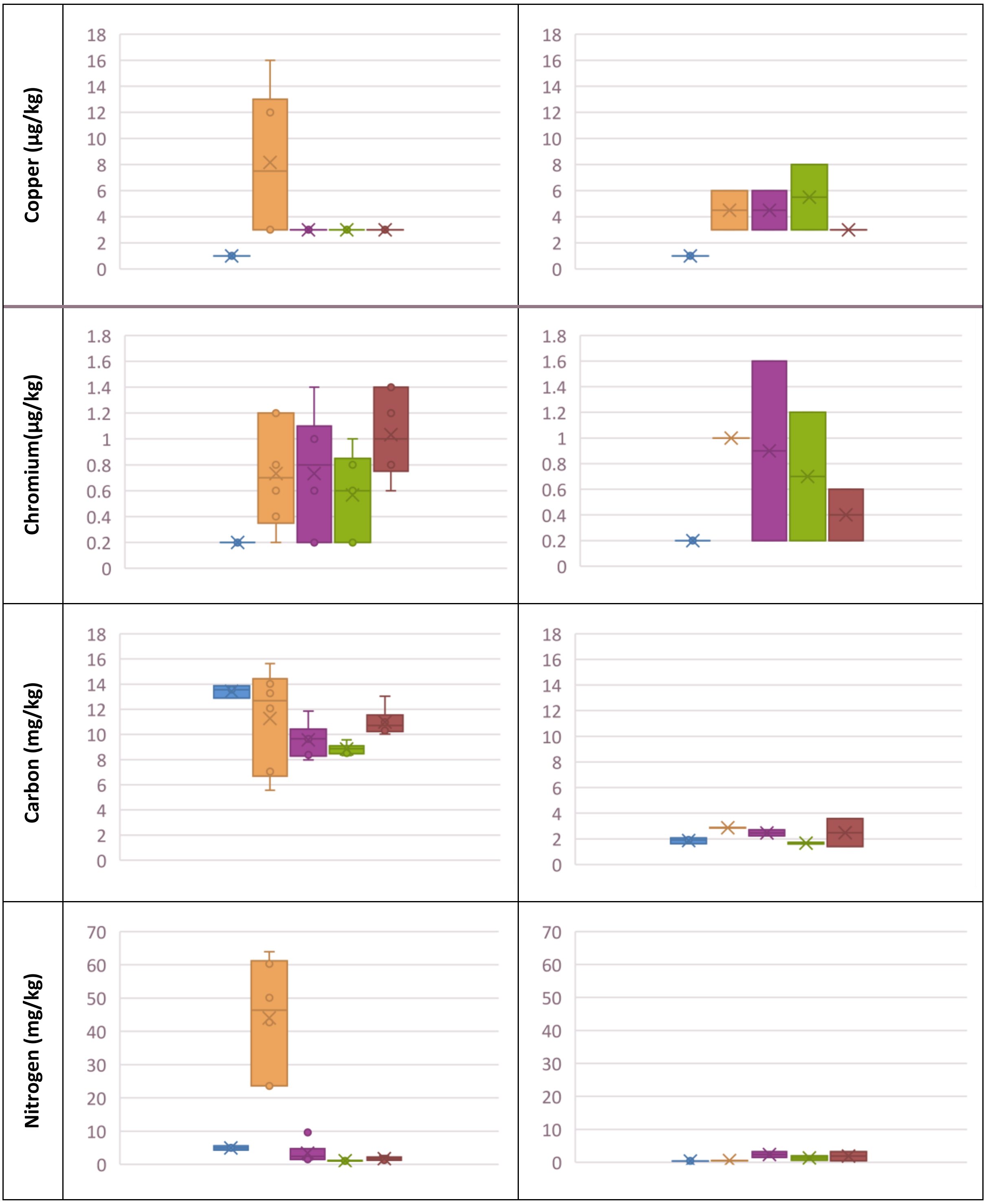

Figure D-1: *Concentrations of extractable contaminants in sand and soil before and after column experiments (continued).*

E. Percent removals of contaminants in column experiments

Table E-1: *Percent removals of metals and phosphate in column experiments after infiltration through 0.5, 1.0, and 1.5 m depth of media.*

Exp.	Media	SSW conc.	INF depth	P	Zn	Pb	Ni	Cr	Cu
A	Soil	Low	0.5 m	92	75	>82	>90	79	92
A	Soil	Low	1.0 m	91	87	>82	83	86	>93
A	Soil	Low	1.5 m	92	91	46	18	36	90
B	Soil	High	0.5 m	98	95	>93	96	97	98
B	Soil	High	1.0 m	91	98	>93	94	>98	98
B	Soil	High	1.5 m	95	98	91	81	87	98
C	Soil	High, no C	0.5 m	99	97	>95	99	95	99
C	Soil	High, no C	1.0 m	81	97	>95	93	94	91
C	Soil	High, no C	1.5 m	97	98	92	87	90	>98
D	Sand	High	0.5 m	21	76	>94	44	90	65
D	Sand	High	1.0 m	61	96	>94	88	94	77
D	Sand	High	1.5 m	89	95	>94	86	89	60

Table E-2: *Percent removals of nitrogen species and organic carbon in column experiments after infiltration through 0.5, 1.0, and 1.5 m depth of media and in the saturated zone.*

Exp	Media	SSW conc.	INF/SAT	NH4-N	NO2-N	NO3-N	TN	TOC
A	Soil	Low	0.5 m	98	98	-111	24	87
A	Soil	Low	1.0 m	89	88	-149	-12	80
A	Soil	Low	1.5 m	-124	-168	-1	-40	-36
A	Soil	Low	SAT	-3	99	97	61	28
B	Soil	High	0.5 m	54	82	-87	26	85
B	Soil	High	1.0 m	96	90	-93	33	96
B	Soil	High	1.5 m	37	42	37	50	57
B	Soil	High	SAT	71	100	99	90	89
C	Soil	High, no C	0.5 m	94	95	-288	-15	
C	Soil	High, no C	1.0 m	99	99	-234	5	
C	Soil	High, no C	1.5 m	79	5	-136	10	
C	Soil	High, no C	SAT	91	96	44	74	
D	Sand	High	0.5 m	-24	62	33	29	78
D	Sand	High	1.0 m	-37	25	24	25	87
D	Sand	High	1.5 m	21	-31	10	30	83
D	Sand	High	SAT	7	84	-15	35	94

F. Tabulated mean concentrations from column experiments

Table F-1: *Mean concentrations of added metals and P.*

Exp	Media	SSW conc.	INF depth	P	Zn	Pb	Ni	Cr	Cu
A	Soil	Low	0.5 m	16	24.3	<0.4	<0.2	0.4	1
A	Soil	Low	1.0 m	18	11.9	<0.4	0.3	0.3	1
A	Soil	Low	1.5 m	16	8.2	1.3	1.7	1.2	1
B	Soil	High	0.5 m	19	21.6	<0.4	0.4	0.2	1
B	Soil	High	1.0 m	107	9.6	<0.4	0.5	<0.2	1
B	Soil	High	1.5 m	19	8.9	0.5	1.9	1.1	1
D	Sand	High	0.5 m	898	112.7	<0.4	5.1	0.8	24
D	Sand	High	1.0 m	391	18.6	<0.4	1.0	0.5	12
D	Sand	High	1.5 m	139	21.2	<0.4	1.3	1.0	26

Table F-2: *Mean concentrations on nitrogen species and TOC.*

Exp	Media	SSW conc.	INF/SAT	NH4	NO2	NO3	TN	TOC
A	Soil	Low	0.5 m	0.02	0.004	2.5	3.1	1.6
A	Soil	Low	1.0 m	0.12	0.022	3.0	4.5	2.5
A	Soil	Low	1.5 m	2.43	0.500	1.2	5.6	17.1
A	Soil	Low	P3_C4-6	1.37	<0.001	0.1	1.8	8.7
A	Soil	Low	P3_C7-9	1.65	0.004	<0.1	2.3	15.2
A	Soil	Low	P2_C7-9	0.32	0.001	0.0	0.6	3.4
B	Soil	High	0.5 m	2.39	0.169	10.5	13.9	9.5
B	Soil	High	1.0 m	0.22	0.090	10.8	12.8	2.5
B	Soil	High	1.5 m	3.26	0.548	3.6	9.4	27.9
B	Soil	High	P3_C4-6	1.80	<0.001	0.1	2.2	8.1
B	Soil	High	P3_C7-9	2.22	<0.001	<0.1	2.5	9.3
B	Soil	High	P2_C7-9	0.51	<0.001	<0.1	0.8	4.7
C	Soil	High, no C	0.5 m	0.80	0.070	21.4	23.7	1.6
C	Soil	High, no C	1.0 m	0.20	0.025	18.4	19.5	2.6
C	Soil	High, no C	1.5 m	2.92	0.945	13.0	18.5	13.7
C	Soil	High, no C	P3_C4-6	1.45	0.016	0.4	2.5	5.6
C	Soil	High, no C	P3_C7-9	1.90	0.043	0.7	3.1	4.9
C	Soil	High, no C	P2_C7-9	0.54	0.056	8.1	10.5	3.2
D	Sand	High	0.5 m	6.47	0.363	3.7	13.7	14.4
D	Sand	High	1.0 m	7.18	0.714	4.3	14.4	8.4
D	Sand	High	1.5 m	4.13	1.253	5.0	13.6	11.1
D	Sand	High	P3_C4-6	3.76	0.335	9.3	15.8	2.6
D	Sand	High	P3_C7-9	4.93	0.017	4.1	9.7	4.4
D	Sand	High	P2_C7-9	5.85	0.119	5.9	11.9	4.3

Table F-3: *Mean concentrations of arsenic, iron, and manganese in column effluent.*

Exp	SSW conc.	INF depth	As	Fe	Mn
A	Low	INF 0.5 m	1.2	9.3	1.3
A	Low	INF 1.0 m	3.7	55.9	10.5
A	Low	INF 1.5 m	22.4	605.3	11.5
A	Low	SAT	14.6	1126.2	32.2
B	High	INF 0.5 m	7.1	269.3	12.3
B	High	INF 1.0 m	7.2	211.6	15.3
B	High	INF 1.5 m	**24.6**	942.0	20.5
B	High	SAT	15.3	**1947.7**	**37.6**
C	High, no C	INF 0.5 m	0.9	5.3	1.7
C	High, no C	INF 1.0 m	1.9	20.3	21.4
C	High, no C	INF 1.5 m	13.4	1116.1	25.4
C	High, no C	SAT	11.2	1485.6	25.5

Note: highest mean for each contaminant is bolded

G. Statistical results from column experiments

Table G-1: *Results from two-way ANOVA: The effect of SSW concentration and media on concentrations of added metals and P.*

Effect of SSW concentration (Experiment A *vs.* B) and infiltration depth on effluent concentrations				**Effect of the media (Experiment B *vs.* D) and infiltration depths on effluent concentrations**			
ANOVA - P				**ANOVA - P**			
Source of Variation	*df*	*F*	*P-value*	*Source of Variation*	*df*	*F*	*P-value*
SSW concentration	1	2.481	0.119	Media	1	94.278	<0.001
Infiltration depth	2	2.197	0.117	Infiltration depth	2	24.847	<0.001
Interaction	2	2.052	0.134	Interaction	2	27.408	<0.001
Within	90			Within	90		
Total	95			Total	95		
ANOVA - Zn				**ANOVA - Zn**			
Source of Variation	*df*	*F*	*P-value*	*Source of Variation*	*df*	*F*	*P-value*
SSW concentration	1	0.254	0.615	Media	1	140.973	<0.001
Infiltration depth	2	10.351	<0.001	Infiltration depth	2	123.386	<0.001
Interaction	2	0.146	0.864	Interaction	2	72.211	<0.001
Within	90			Within	90		
Total	95			Total	95		
ANOVA - Pb				**ANOVA - Pb**			
Source of Variation	*df*	*F*	*P-value*	*Source of Variation*	*df*	*F*	*P-value*
SSW concentration	1	3.276	0.074	Media	1	4.331	0.040
Infiltration depth	2	10.059	<0.001	Infiltration depth	2	6.978	0.002
Interaction	2	3.048	0.052	Interaction	2	3.096	0.050
Within	90			Within	90		
Total	95			Total	95		
ANOVA - Ni				**ANOVA - Ni**			
Source of Variation	*df*	*F*	*P-value*	*Source of Variation*	*df*	*F*	*P-value*
SSW concentration	1	0.783	0.379	Media	1	34.543	<0.001
Infiltration depth	2	16.834	<0.001	Infiltration depth	2	19.379	<0.001
Interaction	2	0.000	1.000	Interaction	2	40.354	<0.001
Within	90			Within	90		
Total	95			Total	95		
ANOVA - Cr				**ANOVA - Cr**			
Source of Variation	*df*	*F*	*P-value*	*Source of Variation*	*df*	*F*	*P-value*
SSW concentration	1	0.589	0.445	Media	1	4.791	0.031
Infiltration depth	2	17.710	<0.001	Infiltration depth	2	13.216	<0.001
Interaction	2	0.026	0.974	Interaction	2	3.070	0.051
Within	90			Within	90		
Total	95			Total	95		
ANOVA - Cu				**ANOVA - Cu**			
Source of Variation	*df*	*F*	*P-value*	*Source of Variation*	*df*	*F*	*P-value*
SSW concentration	1	0.010	0.920	Media	1	39.814	<0.001
Infiltration depth	2	0.379	0.686	Infiltration depth	2	2.065	0.133
Interaction	2	0.560	0.573	Interaction	2	2.217	0.115
Within	90			Within	90		
Total	95			Total	95		

Table G-2: *Results from two-way ANOVA: The effect of SSW concentration (Experiment A vs. B) and INF/SAT on nitrogen species and TOC.*

Effect of SSW concentration and infiltration depth on effluent concentration				**Effect of SSW concentration and saturated zone depth/time on concentration in saturated zone**			
ANOVA - NH4-N				**ANOVA - NH4-N**			
Source of Variation	*df*	*F*	*P-value*	*Source of Variation*	*df*	*F*	*P-value*
SSW concentration	1	31.707	<0.001	SSW concentration	1	10.285	0.003
Infiltration depth	2	63.799	<0.001	Sat zone depth/cycle	2	55.654	<0.001
Interaction	2	11.668	<0.001	Interaction	2	0.802	0.458
Within	90			Within	30		
Total	95			Total	35		
ANOVA - NO2-N				**ANOVA - NO2-N**			
Source of Variation	*df*	*F*	*P-value*	*Source of Variation*	*df*	*F*	*P-value*
SSW concentration	1	0.332	0.566	SSW concentration	1	1.324	0.259
Infiltration depth	2	3.432	0.037	Sat zone depth/cycle	2	0.838	0.443
Interaction	2	0.049	0.952	Interaction	2	0.838	0.443
Within	90			Within	30		
Total	95			Total	35		
ANOVA - NO3-N				**ANOVA - NO3-N**			
Source of Variation	*df*	*F*	*P-value*	*Source of Variation*	*df*	*F*	*P-value*
SSW concentration	1	9.968	0.002	SSW concentration	1	0.100	0.754
Infiltration depth	2	2.269	0.109	Sat zone depth/cycle	2	38.438	<0.001
Interaction	2	0.933	0.397	Interaction	2	0.004	0.996
Within	90			Within	30		
Total	95			Total	35		
ANOVA - TN				**ANOVA - TN**			
Source of Variation	*df*	*F*	*P-value*	*Source of Variation*	*df*	*F*	*P-value*
SSW concentration	1	14.058	<0.001	SSW concentration	1	2.420	0.130
Infiltration depth	2	0.119	0.888	Sat zone depth/cycle	2	31.268	<0.001
Interaction	2	1.011	0.368	Interaction	2	0.183	0.833
Within	90			Within	30		
Total	95			Total	35		
ANOVA - TOC				**ANOVA - TOC**			
Source of Variation	*df*	*F*	*P-value*	*Source of Variation*	*df*	*F*	*P-value*
SSW concentration	1	6.017	0.016	SSW concentration	1	2.449	0.128
Infiltration depth	2	24.289	<0.001	Sat zone depth/cycle	2	18.008	<0.001
Interaction	2	1.612	0.205	Interaction	2	3.610	0.039
Within	90			Within	30		
Total	95			Total	35		

Table G-3: *Results from two-way ANOVA: The effect of the media (Experiment B vs. D) and INF/SAT on nitrogen species and TOC.*

Effect of Media and infiltration depth on effluent concentration				**Effect of Media on concentration in saturated zone**			
ANOVA - NH4-N				**ANOVA - NH4-N**			
Source of Variation	*df*	*F*	*P-value*	*Source of Variation*	*df*	*F*	*P-value*
Media	1	170.361	<0.001	Media	1	95.339	<0.001
Infiltration depth	2	2.572	0.082	Sat zone depth/cycle	2	1.809	0.181
Interaction	2	33.297	<0.001	Interaction	2	8.917	0.001
Within	90			Within	30		
Total	95			Total	35		
ANOVA - NO2-N				**ANOVA - NO2-N**			
Source of Variation	*df*	*F*	*P-value*	*Source of Variation*	*df*	*F*	*P-value*
Media	1	8.157	0.005	Media	1	6.491	0.016
Infiltration depth	2	4.708	0.011	Sat zone depth/cycle	2	2.309	0.117
Interaction	2	0.796	0.454	Interaction	2	2.309	0.117
Within	90			Within	30		
Total	95			Total	35		
ANOVA - NO3-N				**ANOVA - NO3-N**			
Source of Variation	*df*	*F*	*P-value*	*Source of Variation*	*df*	*F*	*P-value*
Media	1	4.077	0.046	Media	1	35.171	<0.001
Infiltration depth	2	1.085	0.342	Sat zone depth/cycle	2	2.116	0.138
Interaction	2	1.917	0.153	Interaction	2	2.004	0.152
Within	90			Within	30		
Total	95			Total	35		
ANOVA - TN				**ANOVA - TN**			
Source of Variation	*df*	*F*	*P-value*	*Source of Variation*	*df*	*F*	*P-value*
Media	1	0.832	0.364	Media	1	176.201	<0.001
Infiltration depth	2	0.534	0.588	Sat zone depth/cycle	2	5.345	0.010
Interaction	2	0.385	0.682	Interaction	2	5.350	0.010
Within	90			Within	30		
Total	95			Total	35		
ANOVA - TOC				**ANOVA - TOC**			
Source of Variation	*df*	*F*	*P-value*	*Source of Variation*	*df*	*F*	*P-value*
Media	1	0.528	0.469	Media	1	19.964	<0.001
Infiltration depth	2	8.974	<0.001	Sat zone depth/cycle	2	3.053	0.062
Interaction	2	7.539	0.001	Interaction	2	4.011	0.029
Within	90			Within	30		
Total	95			Total	35		

Table G-4: *Results from two-way ANOVA: The effect of SSW carbon (Experiment B vs. C) and INF/SAT on nitrogen species and TOC.*

Effect of SSW carbon and infiltration depth on effluent concentration				**Effect of SSW carbon on concentration in saturated zone**			
ANOVA - NH4-N				**ANOVA - NH4-N**			
Source of Variation	*df*	*F*	*P-value*	*Source of Variation*	*df*	*F*	*P-value*
Carbon in SSW	1	9.890	0.002	Carbon in SSW	1	3.566	0.069
Infiltration depth	2	65.178	<0.001	Sat zone depth/cycle	2	65.529	<0.001
Interaction	2	5.339	0.006	Interaction	2	1.171	0.324
Within	90			Within	30		
Total	95			Total	35		
ANOVA - NO2-N				**ANOVA - NO2-N**			
Source of Variation	*df*	*F*	*P-value*	*Source of Variation*	*df*	*F*	*P-value*
Carbon in SSW	1	0.165	0.685	Carbon in SSW	1	7.239	0.012
Infiltration depth	2	5.292	0.007	Sat zone depth/cycle	2	0.711	0.499
Interaction	2	0.702	0.498	Interaction	2	0.711	0.499
Within	90			Within	30		
Total	95			Total	35		
ANOVA - NO3-N				**ANOVA - NO3-N**			
Source of Variation	*df*	*F*	*P-value*	*Source of Variation*	*df*	*F*	*P-value*
Carbon in SSW	1	10.795	0.001	Carbon in SSW	1	12.861	0.001
Infiltration depth	2	2.813	0.065	Sat zone depth/cycle	2	8.729	0.001
Interaction	2	0.114	0.892	Interaction	2	8.879	0.001
Within	90			Within	30		
Total	95			Total	35		
ANOVA - TN				**ANOVA - TN**			
Source of Variation	*df*	*F*	*P-value*	*Source of Variation*	*df*	*F*	*P-value*
Carbon in SSW	1	8.935	0.004	Carbon in SSW	1	11.751	0.002
Infiltration depth	2	0.967	0.384	Sat zone depth/cycle	2	4.017	0.028
Interaction	2	0.101	0.904	Interaction	2	8.928	0.001
Within	90			Within	30		
Total	95			Total	35		
ANOVA - TOC				**ANOVA - TOC**			
Source of Variation	*df*	*F*	*P-value*	*Source of Variation*	*df*	*F*	*P-value*
Carbon in SSW	1	8.708	0.004	Carbon in SSW	1	15.316	<0.001
Infiltration depth	2	20.677	<0.001	Sat zone depth/cycle	2	8.144	0.001
Interaction	2	2.771	0.068	Interaction	2	1.397	0.263
Within	90			Within	30		
Total	95			Total	35		

Table G-5: *Results from two-way ANOVA: The effect of SSW composition (Experiments A, B and C) and infiltration depth / saturated zone on concentrations of arsenic, iron, and manganese.*

ANOVA - Arsenic			
Source of Variation	*df*	*F*	*P-value*
INF depth or SAT	3	66.487	<0.001
SSW composition	2	15.186	<0.001
Interaction	6	1.629	0.141
Within	204		
Total	215		
ANOVA - Iron			
Source of Variation	*df*	*F*	*P-value*
INF depth or SAT	3	92.838	<0.001
SSW composition	2	10.071	<0.001
Interaction	6	2.497	0.024
Within	204		
Total	215		
ANOVA - Manganese			
Source of Variation	*df*	*F*	*P-value*
INF depth or SAT	3	28.540	<0.001
SSW composition	2	4.543	0.012
Interaction	6	2.546	0.021
Within	204		
Total	215		