Reactive solute transport in urban karst-like environments: Implications for the design and layout of stormwater infiltration systems

Amir BEHROOZI

ORCID: 0000-0003-4198-0335

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Environmental, Hydrology and Water Resources Discipline, University of Melbourne
Abstract

Cities around the world make major investments to mitigate the impacts of urban stormwater, such as flash flooding and degradation of receiving waters. Stormwater infiltration systems are popular worldwide, particularly in suburban and peri-urban areas, given their potential to improve water quality and reduce peak flows, while at the same time recharge groundwater and stream baseflows. The benefit of this investment is, however, somewhat uncertain, because little is known about the fate of infiltrated water and associated solutes in an urban area, where the complex network of underground infrastructure and its surrounding permeable trenches provide preferential flow paths for the infiltrated water and associated solutes. The overall goal of this research is to better understand the potential for mobilization of infiltrated stormwater pollutants in urban subsurfaces, which is achieved through the following research questions:

1. What is the effect of soil clay mineralogy on the transport of reactive solutes?

2. How do gravel filled preferential flow paths affect reactive solutes transport in soils? or what is the impact of the urban karst on the transport of reactive solutes?

I used a combination of laboratory experiments and modeling approach to answer the above questions. First, I investigated the reactive transport of solutes (exemplified by zinc) using single solute batch tests. I found that 2:1 clay minerals (e.g., muscovite) in natural soil significantly contribute to zinc sorption. I also found that the maximum sorption capacity of soil that contains varied clay type fractions cannot be directly predicted from individual mineral types reported in the literature. I then investigated the transport of zinc through natural soil using column tests to better mimic the natural systems. I observed that zinc was highly retarded in the natural soil due to relatively high clay content and its mineralogy including a significant fraction of muscovite. I observed a dispersed asymmetrical breakthrough of zinc with long tailings in the columns. Fitting the asymmetric breakthrough curves of zinc with the HYDRUS-1D numerical model suggested that chemical non-equilibrium sorption was dominant. The modeling results also showed that the batch sorption data cannot be
directly used in a transport model when the residence time of a reactive solute in the soil is not long enough to reach equilibrium. This result reinforces the necessity of using flow-through experiments to better approximate field conditions by simulating the dynamic transport of reactive solutes through natural soils with varied clay mineralogies.

Finally, I used a preferential flow cell representing urban infrastructure to examine the impact of preferential flow paths on zinc transport. I then applied HYDRUS-1D to predict the zinc breakthrough curve through the low-permeability field soil (single medium) in the larger flow cell. Comparing the modeled breakthrough curve within the homogeneous condition in the large flow cell with that experimentally observed in the preferential flow case, I found that the breakthrough of zinc was much faster and displayed a greatly different shape due to preferential flow path. While transport through the preferential column was fast, there was a significant movement of water and zinc into the low-permeability media, due to radial diffusion. Predicted radial diffusion of zinc from an approximate solution substantially overestimated the fate and transport of zinc into the low-permeability region.

The results of this thesis suggest that stormwater managers should consider soil clay mineralogy and the existence of underground infrastructure when designing and locating stormwater infiltration systems so that these systems protect and restore rather than degrade – water quality of urban streams. Without such understanding, stormwater infiltration could have unintended negative consequences, including the potential to mobilize solutes from soils and groundwater into surface waters.
Declaration of Authorship

This is to certify that:

i. the thesis comprises only my original work towards the PhD except where indicated in the preface.

ii. where I have consulted the published work of others, this is always clearly attributed.

iii. due acknowledgment has been made in the text to all other material used.

iv. the thesis is less than 100,000 words in length, exclusive of tables, maps, bibliographies, and appendices.

Amir BEHROOZI
Melbourne, November 2019
Preface

This thesis presents the research carried out during my candidature (2015-2019) and the reported results are original. The research was supervised by Dr. Meenakshi Arora, Prof. Tim Fletcher, Prof. Andrew Western and Dr. Justin Costelloe from Melbourne University.

Publications obtained from this thesis are as follows:

CHAPTER 3

“Understanding the impact of soil clay mineralogy on the fate of reactive solutes”
Amir Behroozi, Meenakshi Arora, Tim D. Fletcher, Andrew W. Western, Justin F. Costelloe

CHAPTER 4

“The transport of reactive solutes in porous media”
Amir Behroozi, Meenakshi Arora, Tim D. Fletcher, Andrew W. Western

CHAPTER 5

“Transport of reactive solutes through the urban karst”
In progress.
Amir Behroozi, Meenakshi Arora, Tim D. Fletcher, Andrew W. Western
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The work presented in this thesis is the result of almost four years of intensive effort with the assistance of a number of people and organizations to whom I express my sincere gratitude. My supervisors, Dr. Meenakshi Arora, Dr. Justin Costelloe, Prof. Tim Fletcher, and Prof. Andrew Western, whose valuable guidance and continuous support and encouragement helped me to achieve this significant goal in my life. In addition, thanks to the Chair of my advisory committee A/Prof. Angus Webb for his insightful and constructive comments.

I owe a special thanks to Dr. Justin Costelloe, one of my supervisors who sadly passed away during my PhD research. Despite his illness, he spent many hours of his precious time, giving me advice with his gentle guidance. Indeed, his mentorship transformed my academic experience. God bless him.

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I received technical assistance from personnel funded in part by Melbourne Water, under the Melbourne Waterway Research-Practice Partnership (http://mwrpp.org). I am grateful to all members of the Waterway Ecosystem Research Group (WERG) at the University of Melbourne, Peter J. Poelsma, Robert B. James, Matthew Burns, Genevieve M. Hehir, Jeremie Bonneau and Mike Sammonds for their help during all stages of my candidature with their practical knowledge and vast experience. I would also like to thank Brad Snibson, client services team leader from the ALS group, and Murray Joseph from Sibelco Australia Ltd. Co. for assistance with my laboratory tests.

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Chapter 1 – Introduction
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1.1 Background

Urbanization — and in particular the creation of impervious areas and constructed stormwater drainage systems — results in the degradation of urban streams through changes to hydrology and water quality and, ultimately, of ecosystem structure and function (King et al., 2011; Pitt et al., 1999). Such effects are commonly referred to as the ‘urban stream syndrome’ (Walsh et al., 2005a). Urban stormwater is a major source of pollutants, which, in combination with changes to flow regimes, results in the widespread degradation of receiving waters (Walsh et al., 2005b), depriving urban communities of the ecosystem services provided by healthy urban streams. The degradation occurs both as a result of changes to flow regimes (Poff et al., 1997) and the degradation of water quality (Roy et al., 2009). Urban streams typically have more ‘flashy’ flows, with frequent large peaks (FIGURE 1.1), yet decreased baseflows or dry weather flows, depriving aquatic organisms of habitat.
FIGURE 1.1: Contrasting subsurface flow pathways and streamflow response of (A) pre-urban hillslope and (B) urban hillslope with stormwater infiltration.

To protect and restore urban streams, various stormwater management approaches such as ponds, stormwater wetlands, rain gardens, and infiltration systems (basins or trenches) have been used internationally, to reduce runoff and restore baseflows, while also reducing the generation, mobilization, and transport of solutes (Fletcher et al., 2013). Stormwater infiltration systems are the most widely used control measures worldwide. In these systems, runoff from impervious areas is captured and infiltrated into soils, either through unvegetated sand or gravel media or vegetated loamy-sand media, with the aim of reducing pollutant concentrations before water infiltrates into the surrounding soils (Hamel et al., 2013). Despite the increasing use of stormwater infiltration in tackling the urban stream syndrome, very little is known about how it influences stream water quality, and in turn what consequences it might have for stream ecosystems. Such understanding is vital because stormwater infiltration could have unintended consequences, including the potential to introduce pollution into
groundwater and subsequently into surface waters (Barraud et al., 1999; Dechesne et al., 2004; Foulquier et al., 2009; Le Coustumer et al., 2007). Indeed, major investments in protecting and restoring urban catchments through stormwater retrofit (e.g., Fletcher et al., 2010) may not deliver the desired restoration of ecosystem structure and function, and may even exacerbate current degradation (Roy & Bickerton, 2012).

1.2 Problem statement

Infiltration-based systems provide substantial localized (‘point-source’) additions to the subsurface water store, with the potential to generate significant contributions to groundwater and lateral flow. There is increasing evidence (Kirchner, 2003), however, that such systems fail to restore both flow and water quality regimes, due to the gross disturbance of subsurface flow paths caused by urban underground infrastructure (e.g., water, sewer and gas pipelines, communications conduits) and their associated gravel trenches; collectively referred to as the ‘urban karst’ (Soulsby et al., 2014). These highly permeable trenches potentially lead to short-circuiting of the soil and rapid transport of water and its associated solutes (Roy & Bickerton, 2012) to streams. Given these uncertainties, predicting the impacts of stormwater infiltration on the water quality of receiving waters remains a great challenge.

The number and variety of solutes in urban areas can be large, with potentially major effects on aquatic ecosystems including situations where the groundwater contributes to streamflows (Roy & Bickerton, 2012). These solutes may result from existing, or legacy land uses, including past agriculture and horticulture, as well as present and past industrial, commercial and residential activity or fully exhausted stormwater
infiltration media. There is thus a risk that solutes might be transported into surface waters, undermining attempts to restore stream ecosystems. This risk, however, is poorly understood, because of the uncertainty in pollutant fate and mobilization in soils and urban flow paths.

The design of stormwater infiltration systems – and particularly their location in the landscape – therefore requires an understanding of infiltrated stormwater potential to transport solutes from soils to the stream. While there is a developing understanding of the role of different flow pathways in mobilizing solutes in natural catchments, it is believed that this knowledge cannot be directly transferred to the significantly altered urban landscape, where flow pathways are likely to be highly influenced by the heterogeneity of soils and infrastructure. This PhD thesis focuses on addressing this gap in understanding the effect of soil types and urban karst on the pollutant fate and transport in soils.

1.3 Research objectives and questions

The overall goal of this research is to better understand the potential for mobilization of infiltrated stormwater solutes in urban subsurfaces. The results of this research will provide an improved quantitative understanding of the transport of solutes (zinc was chosen as a representative solute for this study) to underpin the location and design of stormwater infiltration systems so that they deliver on their objective – to improve the health of urban streams.
To achieve this research goal, the main objective is:

- to investigate the movement of reactive solutes (exemplified by zinc) in soils of urban areas where preferential flow paths (the urban karst) dominate.

One way to look at this is to initially understand the transport behavior of reactive solutes in natural soils, such as the effect of clay mineralogy. Once determined, I use such information as a foundation for the urban karst results. Thus, I first need:

- to understand the role of soil clay mineralogy on the fate of reactive solutes; and
- to evaluate the transport of reactive solutes in porous media in a dynamic system.

Based on the research objectives defined, this research attempts to address the following research questions:

3. What is the effect of soil clay mineralogy on the transport of reactive solutes?

4. How do gravel filled preferential flow paths affect reactive solutes transport in soils? Or what is the influence of the urban karst on the transport of reactive solutes?

Answering the above questions will provide waterway and stormwater managers with improved knowledge to better employ stormwater infiltration systems in a way that protects and restores – rather than degrades – water quality of urban streams.
1.4 Research approach

This research is structured around three work packages (FIGURE 1.2), corresponding to the fundamental research objectives identified in the previous section. Results from WP1 and WP2a feed into WP2b. The results of the first two work packages are then used as a basis to compare with those obtained from WP3.

<table>
<thead>
<tr>
<th>Research objectives</th>
<th>Work packages</th>
</tr>
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<tbody>
<tr>
<td><strong>Objective 1</strong> Understanding the role of soil clay mineralogy on the fate of reactive solutes</td>
<td>1: Batch tests to determine the maximum sorption capacity of soil</td>
</tr>
<tr>
<td><strong>Objective 2</strong> Evaluating transport of reactive solutes in porous media via a flow-through system</td>
<td>2a: Column tests to determine the dispersion coefficient along with the sorption parameters</td>
</tr>
<tr>
<td><strong>Objective 3</strong> Investigating the transport of reactive solutes due to the preferential flow paths</td>
<td>2b: Numerical model of solute transport using values from WP1 and WP2a</td>
</tr>
<tr>
<td></td>
<td>3: Column test using a gravel filled preferential flow zone surrounded by the natural soil</td>
</tr>
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</table>

**FIGURE 1.2**: Research conceptual framework.

The natural soil used for the laboratory experiments was collected from a peri-urban area referred to as the “Dobsons Creek Catchment”. This catchment is approximately 1300 hectares with 9.8% (~10%) imperviousness and is located approximately 40 km east of Melbourne, Victoria (Bonneau et al., 2018).
Up until 2010, most impervious surfaces in Dobsons Creek were directly drained via a conventional stormwater drainage system. From 2010 onwards, the Dobsons Creek catchment has been partially retrofitted with various stormwater control measures of which the “Wicks Reserve Infiltration Basin” is the largest system, with an area of 2,000 m² (FIGURE 1.3 and FIGURE 1.4). The Wicks Reserve infiltration basin receives water draining from nearly half of the impervious surfaces in the Dobsons Creek catchment. Inflows to the basin pass through a large gross pollutant trap and flow via a sedimentation basin to a vegetated infiltration cell.

This catchment has been selected as a study site for this project, because it is the subject of an existing stormwater retrofit experiment, which is funded by local, state and Commonwealth government, and with extensive instrumentation as well as datasets already in place (Walsh et al., 2015). Since infiltration-based systems are ubiquitous there, the risk of flushing solutes from such systems into the groundwater and their subsequent movement into streams is particularly high as opposed to dense inner-city landscapes (Hamel et al., 2013).
FIGURE 1.3: Map of Wicks Reserve infiltration basin (Image source: Google Earth).

FIGURE 1.4: Conceptual diagram of Wicks Reserve infiltration basin.
1.5 Thesis structure

This PhD thesis comprises six chapters. Introduction, literature review, three result chapters, and a summary, discussion, and conclusion chapter. Chapters 3, and 4 are journal articles that have been submitted at the time of thesis submission. Chapter 5 has been also prepared as a journal article and is ready for submission. A brief outline of different chapters is as follows.

**Chapter 2 - Literature review**

Chapter 2 presents a detailed literature review to provide an understanding of the existing knowledge and gaps. Previous studies provide clear evidence that infiltration systems are efficient at mitigating peak flows and volumes of stormwater delivered to urban streams. There is also a good understanding of the interaction of solutes with filter media and the potential for transport to groundwater. However, there is little evidence of whether infiltrated reactive solutes (e.g., metals) have the potential to reach the stream. This uncertainty is due to a lack of experimental data about the movement of infiltrated reactive solutes and a lack of knowledge about complex urban subsurfaces. From this literature review, two research questions were identified:

- What is the effect of soil clay mineralogy on the transport of reactive solutes? *(Chapters 3 and 4)*

- How do gravel filled preferential flow paths affect reactive solutes transport in soils? Or what is the influence of the urban karst on the transport of reactive solutes? *(Chapter 5)*
The results chapters then set out to answer these questions.

Chapter 3 - Understanding the role of clay mineralogy on the fate of reactive solutes

Chapter 3 is an article in review in the journal ‘Water Science and Engineering’. The overall capacity of soils containing varied clay minerals to sorb reactive solutes (e.g., zinc) has not been studied in the literature and there was a lack of understanding on to what extent the soil clay mineralogy contributes to zinc ion sorption. To address this gap, single solute batch tests were carried out to determine the maximum sorption capacity \((q_m)\) of two soils with different mineralogy in removing zinc ions. Zinc was chosen as a representative solute due to its ubiquitousness in the urban groundwaters. The zinc sorption process in soils was described by the most widely used isotherms (Freundlich and Langmuir). The isothermal sorption data obtained from these analytical models were utilized to parametrize a numerical model of zinc transport. The results showed that clay mineralogy has a significant impact on the movement and fate of zinc in the subsurface and must be taken into account when implementing stormwater infiltration techniques to reduce the risk of groundwater contamination.

Chapter 4 - The transport of reactive solutes in porous media

Chapter 4 is an article in review in the journal ‘Geoderma’. This work aimed to answer the first research question but in flow-through systems [dynamic systems].

Laboratory soil columns were homogeneously packed with the natural soil to better mimic the sorption and transport behavior of reactive solutes such as zinc in field
conditions and to provide estimates of sorption parameters that are not possible to determine from batch studies. The factors influencing solute transport including the sorption and reaction parameters of the soil and the axial dispersion coefficient (through running a conservative tracer using chloride) were obtained through the 1D dynamic systems. A dispersed asymmetrical front was observed during zinc transport through the soil columns, indicating the presence of a non-equilibrium sorption process in the columns. The sorption data obtained from both the batch and column laboratory tests were then used with the numerical model HYDRUS-1D to evaluate the zinc transport processes. While the use of isothermal parameters from batch tests in HYDRUS-1D poorly predicted the zinc breakthroughs, column results fitted very well them. The results of Chapter 3 and Chapter 4 showed that though batch tests are necessary to determine the maximum adsorption capacities of soils towards zinc ions, running column tests is of greater importance to better predict the zinc transport in the field conditions.

**Chapter 5 – Transport of reactive solutes through the urban karst**

Chapter 5 has been already prepared as a journal article and is ready for submission. As mentioned, there is a lack of knowledge about the potential of urban underground infrastructure to provide preferential flow paths and rapidly transmit water and solutes to streams.

This chapter aimed to answer research question 2: what is the influence of the urban karst on the transport of reactive solutes?
There is evidence of a contribution from the infrastructure in transmitting water and its associated solutes to streams in urban catchments; in stark contrast to the behavior observed in the undeveloped catchments (Kim et al., 2008). To investigate the role of the urban karst on the zinc mobilization, a preferential flow cell was packed with media with two distinct hydraulic conductivities. A highly permeable 1.5 cm diameter gravel core filled the middle of the column, surrounded by the natural soil. The zinc breakthroughs showed an entirely different shape and timing compared with those for the smaller scale homogeneous columns in the absence of the gravel core (see Chapter 4). The column was dissected and soil samples from different points along the column and at different radii were taken to track the spread of zinc. The results showed a higher concentration of zinc in the soil adjacent to the gravel core, with declines towards the outer edge of the core. This task provided data to develop a model of reactive solute transport in media of varying hydraulic conductivities in the future.

Chapter 6 – Summary, discussion, and conclusion

This chapter synthesizes the overall results of the thesis, discusses the limitations of the laboratory experiments, and makes recommendations for the extension of this work for future studies. Practical implications are also discussed and the overarching conclusions provided.
1.6 Bibliography


Chapter 2 – Literature review
Chapter 2 - Stormwater infiltration and the transport of solutes - a review

2.1 Chapter perspective

Chapter 2 discusses the stormwater management challenges caused by urbanization and then provides an overview of the aims of current infiltration-based strategies to protect and restore urban stream in terms of flow regime and water quality. The review of the literature identifies that stormwater infiltration systems might fail to deliver their objectives in protecting and restoring the health of waterways, without a critical understanding of the fate and transport pathways of pollutants that emanate from them. In doing so, it reviews the factors affecting the fate of infiltrated pollutants in urban subsurfaces including geology and soil characteristics (e.g., the impact of clay minerals through sorption processes), as well as existing subsurface infrastructure. Subsequently, it investigates the available tools such as experiments and models to understand the fate and transport of solutes. To conclude, it identifies the gaps in the literature and research opportunities to resolve the gaps encountered.
2.2 Introduction

2.2.1 Urban sprawl

The population of the world is currently 7.3 billion and is expected to increase between 9.6 and 12.3 billion by the end of this century (Gerland et al., 2014). A huge influx of people have now immigrated to cities: the share of urbanites is already over 50% today and is projected to increase by 30% until 2050 (United Nations, 2013).

Cities are growing in many areas across the world. The dynamics of urban expansion is associated with high population growth and rural exodus in countries with a developing economy. For instance, the size of the urban areas of Kinshasa-Brazzaville and Manila respectively extended 4 and 7.1 times from 1975 to 2010 (Taubenböck et al., 2012). In countries with a developed economy, the ‘urban sprawl’, driven by the desire of people to have a detached house and a block of land, leads to ever-growing cities (Wu & Thompson, 2013). As an illustration, 416 km² of land was sealed between 2001 and 2006 in the US part of the Gulf of Mexico region (Xian et al., 2012).

Australia is not an exception, following similar trends with the population increasing from 10 million back in 1960 to 24 million people now. This figure is expected to double by 2050 (Australian Bureau of Statistics, 2013). To accommodate this rapidly growing population, impervious areas are increasing in both infill developments as well as in new suburbs, sealing agricultural lands on the brink of cities (Coffee et al., 2016), leading to less pervious landscapes.
2.2.2 The urbanization problem

Urbanization results in highly disturbed landscapes. With urbanization, pervious surfaces (which dominate vegetated areas such as forests and agricultural lands) are replaced with impervious areas such as roads, rooftops, and parking spaces. The creation of impervious surfaces has substantial effects on catchment hydrology, with increased runoff rates and volumes, and loss of infiltration (Fletcher et al., 2013; Shuster et al., 2005). The change in the impervious-pervious surface balance and therefore in the flow regime also causes erosion, degradation of stream ecosystems and associated reduced biodiversity (Brabec et al., 2002; Roy et al., 2008). This may be due to changes in pollutant transport pathways, and reductions in water residence times (Collin & Melloul, 2003; Dietz & Clausen, 2008).

2.2.3 Stormwater management approaches

The combination of an increasing population and water demand (Vörösmarty et al., 2000) means that fast-growing cities will require better water management. The conventional way to manage excess surface runoff caused by urbanization is the use of constructed stormwater networks, which convey runoff to receiving waters. The consequences of this conventional approach are highly altered flow and water quality regimes (Barron et al., 2013). Urban stormwater drained directly to streams via conventional man-made drainage systems contains a large number of pollutants that are recognized as primary degraders of urban stream ecology (King et al., 2011; Vietz et al., 2014; Wright et al., 2011).
In contrast to conventional stormwater management techniques which primarily aimed to evacuate water out of cities by pipes and channels, more recent sustainable approaches also attempt to mitigate impacts on flow and water quality regimes (Burns et al., 2012), while maintaining the flood mitigation performance of the traditional approach. It is hypothesized that with such interventions, it should be possible to return stream ecosystems towards a more natural ecological condition (Walsh et al., 2015). A wide range of stormwater control measures (SCMs) has been developed, such as grass swales, ponds, stormwater wetlands, infiltration systems, and stormwater harvesting systems. Of the range of SCMs available, stormwater infiltration systems are arguably the most widely used stormwater management technique to mitigate runoff and restore lost baseflows, while also reducing water quality disturbance (Fletcher et al., 2013). Stormwater infiltration systems include rain gardens, pervious pavements, infiltration trenches, basins, and wells. They are constructed to intercept stormwater runoff and allow it to infiltrate, recharging groundwater and restoring clean, filtered baseflows to urban streams (Hamel et al., 2013). Baseflows are critical to stream health; loss of baseflow (caused by impervious areas reducing infiltration) causes habitat loss and local extinction of aquatic fauna (Poff et al., 1997).

2.3 Impact of stormwater infiltration

2.3.1 Site-scale

2.3.1.1 The quality of water piped in Vs. out

The quality performance of individual stormwater infiltration systems (FIGURE 2.1, Marker 1) has been well documented (Bratieres et al., 2008; Dallman & Spongberg,
The results broadly show that infiltrated pollutants are intercepted in the topsoil of the stormwater infiltration systems by allowing solids to settle, through sorption, and chemical and biological transformation. Infiltrated pollutants from stormwater infiltration systems are thus assumed to have a minimal effect on soil and groundwater quality. However, the fate of solutes which accumulate within infiltration systems is ambiguous (Mikkelsen et al., 1997) since the results of different studies are often inconsistent, with some studies reporting considerable groundwater pollution (e.g., Fischer et al., 2003), while others find no pollution of surrounding soil and groundwater (e.g., Bardin et al., 2001). Thus, the risk of local soil and groundwater pollution due to stormwater infiltration cannot be neglected by stormwater managers.

2.3.1.2 Local soil and groundwater quality

The movement of infiltrated solutes underneath infiltration systems has become a concern for underlying soil and groundwater quality (FIGURE 2.1, Marker 2). Infiltrated stormwater has been identified as a major potential source of soil and groundwater contamination (e.g., Clark & Pitt, 2007). The range of solutes of concern is broad, and consists of nutrients (i.e. nitrate and phosphorus), pesticides, heavy metals (e.g. lead, zinc, copper, chromium and cadmium), organics (i.e. petroleum hydrocarbons), pathogens (i.e. faecal coliform, viruses, and other bacteria) and dissolved salts (Mikkelsen et al., 1994; Pitt et al., 1999) with an increasing focus on micro-pollutants (Bressy et al., 2012; De Keyser et al., 2010; Flanagan et al., 2019). Pitt et al. (1999) claimed that the extent of the impact of infiltrated solutes on soil and
groundwater quality depends on the likely existence of elements in the stormwater, their mobility through soils and the filtration media used.

Infiltrated solutes accumulated in the interior of the filtration media may be re-infiltrated in the underlying soil and groundwater (Barraud et al., 1999; Li et al., 2018; Pitt et al., 1995). Mason et al. (1999) concluded that infiltrated metals such as zinc and lead from an artificial infiltration site could be further transported through the deeper soil layers of the vadose zone in the long-term, providing evidence that the filtration media could be exhausted over time, thus not fully capturing metals and polluting underlying soil.

For highly mobile water-soluble pollutants, downward mobility is such that soils are unable to act as filters. Therefore, these pollutants can enter the saturated zone, and contaminate the groundwater (Weiss et al., 2008). Nutrients (Voisin et al., 2018), salts (Casey et al., 2013), pesticides, pharmaceuticals, and polycyclic aromatic hydrocarbons (Cabeza et al., 2012; Fram & Belitz, 2011) have been observed in groundwater adjacent to stormwater infiltration sites, highlighting the importance of the mobility of pollutants when assessing groundwater contamination risk.

Regardless of whether local soil and groundwater contamination from infiltrated pollutants are considered as a risk, Roy and Bickerton (2012) suggested that stream baseflow and water quality at a larger scale could also be degraded by enhanced infiltrated stormwater because of the flushing and transport of legacy solutes already present in soils and groundwater. Understanding the fate of infiltrated pollutants would thus help to better assess the groundwater contamination risk.
2.3.2 Catchment-scale

2.3.2.1 Stream baseflow and water quality

Infiltration systems are efficient at mitigating peak flows, runoff volume and loads of solutes (Appleyard, 1993; Birch et al., 2005; Ferguson, 1998; Liu et al., 2015). These site-scale outcomes, however, may not be sufficient to fulfill the catchment-scale baseflow and water quality objectives (Walsh et al., 2012) since processes generating baseflow are highly complex. Only a few studies have been undertaken into the relationship between stormwater infiltration and baseflow hydrology at the catchment scale (see a review by Hamel et al., 2013). In addition, the indirect effect of altered baseflow on stream water quality has been largely ignored. Loperfido et al. (2014) implemented a range of infiltration measures in a distributed manner that led to the increased baseflow as a result of recharging groundwater. Bhaskar et al. (2016) observed considerably increased baseflow in a catchment retrofitted with many stormwater control measures, such as infiltration systems. Both studies show that stormwater infiltration increases stream baseflow under some circumstances, but the impact on stream water quality was not specified.

There are significant uncertainties relating to the fate of infiltrated pollutants in urban environments, regarding both the extent to which the contaminants are mobilized or immobilized within the soil or where there are potential interactions with subsurface infrastructure. Given these uncertainties, the fate of locally infiltrated pollutants within the soils and groundwater and their impact on stream water quality is still unclear. There is no established approach to predict the extent to which infiltrated
pollutants from the source-control infiltration system will affect stream water quality. The lack of confidence about the fate of infiltrated pollutants is due to inadequate knowledge of how urban characteristics impact the transport of pollutants. These characteristics influence stream water quality in urban catchments. They are natural features such as geology, soil type and its capacity for natural attenuation of a pollutant in the subsurface (Hamel et al., 2013) and anthropogenic factors such as spatial features of infrastructure that make diverse groundwater pathways (Bonneau et al., 2018). More experimental data is thus needed to give better insight into the relationship between site-scale and catchment-scale water quality objectives.
FIGURE 2.1: Different scales at which infiltration systems have been studied. Marker (1): At the site-scale: within infiltration systems, Marker (2): At the site-scale: just beneath infiltration systems and Marker (3): At the catchment-scale: downstream of infiltration systems (modified from Bonneau et al., 2017).
2.4 Properties affecting the transport of solutes in porous media

2.4.1 Geology and soil — a house for a variety of clay minerals

The transport behavior of solutes in soil has long been a core interest of many researchers motivated by the possibility of soil and groundwater pollution through contaminant leaching. The fate and transport of pollutants do not only depend on the physicochemical properties of the solutes but the soil sorption properties determined by characteristics such as clay fraction content, and mineralogical composition (Dube et al., 2001). Sorption plays a fundamental role in the advective-dispersive transport of solutes. The separation process of a given pollutant from the liquid phase (i.e., water) and its accumulation at the surface of a solid phase (i.e., soil particles) is called adsorption (Slejko, 1985) (FIGURE 2.2). The inorganic colloidal fraction of soil has the most important role in sorption/adsorption, given its mineral particles (Crini & Badot, 2011).
2.4.1.1 Clay and clay minerals

The term “clay” refers to the materials with a grain size lower than 2 μm, and also to the family of minerals with similar chemical compositions and crystal structural features (Bergaya & Lagaly, 2013). Clays are aluminosilicate minerals which are composed of colloidal fractions of sediments, rocks, and water (Mockovčiaková & Orolínová, 2009). Clay minerals are a mixture of carbonates, silica, metal oxides, and metal ions (Bhattacharyya & Gupta, 2008). They consist of an interconnected silicate sheet linked to a second sheet consisting of a grouping of metallic atoms such as calcium, magnesium and sodium, oxygen, and hydroxyl (Mitchell & Soga, 2005). The 1:1 clay mineral type includes one tetrahedral silica sheet, alternating with one octahedral alumina sheet, while the 2:1 clay mineral type consists of one octahedral
alumina sheet, sandwiched between two tetrahedral silica sheets (Bhattacharyya & Gupta, 2008).

Clays have a variety of physical characteristics, such as plasticity, cohesion, fineness of grain, and capacity of the surface to sorb pollutants present in water (Odoma et al., 2013). Surface chemistry of clays, their complex porous structure and mineralogy, and also their ability to scavenge pollutants by taking up cations and anions through ion exchange and adsorption, make clays suitable for adsorbing pollutants (Mitchell & Soga, 2005).

Clays and clay minerals are divided up into two groups; kaolin (e.g., kaolinite), and smectite (e.g., montmorillonite, illite, bentonite, muscovite, vermiculite, etc.) (Dondi et al., 2014; Shichi & Takagi, 2000). Kaolin clays (the 1:1 type layer) have a strong bonding resulting in its high chemical stability, relatively low cation exchange capacity and low expansion coefficient (Miranda-Trevino & Coles, 2003). Smectite clays (the 2:1 type layer) possess a very weak bonding between silica sheets, however, they have much more total surface area (due to the existence of the internal surface area), expansive properties and higher adsorption capacity than the kaolin clays (Bedoui et al., 2008).

2.4.1.2 Clay — a superb adsorbent for all kinds of solutes?

The use of natural clay minerals as potential adsorbents in the removal of different pollutants from water has been studied extensively (TABLE 2.1). Results from the literature confirm that clays and their minerals have excellent potential as efficient
adsorbents to mitigate the concentrations of various pollutants, specifically cations such as heavy metal ions, from water. This is because most of the clay minerals are negatively charged. They are extensively applied to adsorb positively charged ions from water (Uddin, 2017). Yuan et al. (2013) concluded that the adsorption of heavy metals is largely influenced by direct bonding between negatively charged minerals on the surface of the clays and metal cations.

On the other hand, research on the adsorption of anions (e.g., nitrate) by natural clay minerals is really sparse (see a review by Bhatnagar & Sillanpää, 2011), with only a few studies in the literature that investigate the removal of nitrate from water by treated (modified) clay minerals (Bagherifam et al., 2014; Mena-Duran et al., 2007; Özcan et al., 2005). Xi et al. (2010) evaluated natural (e.g., bentonite and kaolinite) and organic surfactants modified clay minerals for nitrate adsorption. The authors found that untreated natural bentonite and kaolinite did not remove nitrate ions from the solution. However, the adsorption capacities of modified clays were found to improve greatly. Nitrate ions cannot be removed by clays and their minerals because they are negatively charged and thus repelled from the negatively charged clay surfaces.
TABLE 2.1: Research on adsorptive removal of different types of solutes from water sources - use of natural clay as an effective adsorbent.

<table>
<thead>
<tr>
<th>Pollutant type</th>
<th>Sorbent type</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pharmaceuticals (e.g., tetracycline) and metals (e.g., Cu(II))</td>
<td>Montmorillonite</td>
<td>Wang et al. (2008)</td>
</tr>
<tr>
<td>Pharmaceuticals (e.g., tylosin)</td>
<td>Montmorillonite, Bentonite, Illite, Kaolinite</td>
<td>Bewick (1979)</td>
</tr>
<tr>
<td>Metals such as Cd(II), Cu(II), Ni(II), and Pb(II)</td>
<td>Bentonite</td>
<td>Anna et al. (2015)</td>
</tr>
<tr>
<td>Metals such as Cu(II) and Zn(II)</td>
<td>Bentonite</td>
<td>Bouazza et al. (2018)</td>
</tr>
<tr>
<td>Metals such as Pb(II), Ni(II), Cd(II) and Cu(II)</td>
<td>Kaolinite</td>
<td>Jiang et al. (2010)</td>
</tr>
<tr>
<td>Metals such as Zn(II), Cd(II), Mg(II) and Cr(III)</td>
<td>Vermiculite</td>
<td>Da Fonseca et al. (2006)</td>
</tr>
<tr>
<td>Suits of metals</td>
<td>Montmorillonite and Vermiculite</td>
<td>Dos Anjos et al. (2014)</td>
</tr>
<tr>
<td>Organics (e.g., phenol)</td>
<td>Montmorillonite</td>
<td>Djebbar et al. (2012)</td>
</tr>
<tr>
<td>Pesticides such as metalaxyl and tricyclazole</td>
<td>Bentonite</td>
<td>Azarkan et al. (2016)</td>
</tr>
<tr>
<td>Pesticide called paraquat</td>
<td>Bentonite</td>
<td>Sidhoum et al. (2013)</td>
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2.4.1.3 An overview of experiments and modeling approaches

Many batch tests have been conducted under different experimental conditions to explore the adsorptive characteristics of natural clay minerals on the sorption and transport of pollutants (Chang et al., 2012; Franus & Wdowin, 2010; Hefne et al., 2008; Karapinar & Donat, 2009; Mohsenipour et al., 2015; Rao & Kashifuddin, 2016). Zacaroni et al. (2015) investigated the application of natural clay (a mixture of quartz and chlorite-vermiculite-montmorillonite) in the removal of copper(II). The amount of copper(II) adsorbed per unit weight of clay was found to be 10.8 mg g⁻¹, resulted in
a 68.7% removal (pH: 5.5 and temperature: 22 °C). Similarly, Khalfa et al. (2016) experimented on the removal of lead(II) using a natural clay sample (the minerals were not specified) from the area located in south-east Tunisia and found a 21.107 mg of lead(II) adsorbed per gram of clay at pH 6.0. Both studies quantified the adsorption capacities of clay minerals in removing metal ions but the overall sorption capacity of the entire soil with a wide range of grain size distribution and clay mineralogies remains poorly understood.

Column experiments and transport models have also been widely used to better understand and predict the sorption and transport of solutes in natural soils in a saturated medium (Jellali et al., 2010; Ladu & Zhang, 2011; Smaranda et al., 2017; Yang et al., 2013). Chotpantarat et al. (2011) explored the sorption and transport of heavy metal ions through a clayey soil (the mineralogy was not specified) running both batch and column experiments. The use of batch-determined sorption parameters in the HYDRUS-1D code showed sharp concentration fronts which lagged the experimental data. They found that the sorption coefficients from column studies were better to elucidate the asymmetrical shape of the breakthrough curves with long recessions, indicating the existence of the chemical non-equilibrium conditions.

2.4.2 The urban karst — a network of preferential flow paths

Urban subsurfaces are highly disturbed by underground infrastructure including water supply mains and manifolds, sewer and gas pipes, trenches, communication conduits, and deep foundations in high-density cities (Attard et al., 2016; Schirmer et al., 2013). The interaction between groundwater flow and the network of subsurface
infrastructure has been referred to as the ‘urban karst’ (Kaushal & Belt, 2012). Trenches are excavated across the urban environment to place utilities including stormwater and sewer pipelines, water mains, and gas and electricity networks. Pipelines and cables sit within the backfill layer typically composed of coarse aggregates with better compaction and stability features than fine aggregates. Buried pipelines are typically surrounded by highly permeable material such as gravel or sand (Sharp et al., 2003).

These highly permeable trenches are characterized by large voids and high porosity spaces with little clay content. The urban karst is an extensive network of megapores (Bonneau et al., 2017), able to intercept, potentially store, and rapidly transmit water and pollutants (White, 2002). Sharp (2003) found that hydraulic conductivities around the pipelines were two or three orders of magnitude higher than that of local soil, forming networks of hyper-permeability paths for groundwater and the contaminants it carries. As suggested by Engel-Yan et al. (2005), urban karst influences the way water and its associated solutes move through urban landscapes.

2.4.2.1 The urban karst effect --- an example of field observation

Stormwater infiltration systems are typically situated in peri-urban landscapes, and located within meters of subsurface infrastructure. The urban karst is generally shallow, within just a few meters of the surface. In the case of a shallow water table, the lateral transport of groundwater might be intercepted by the urban karst (Goldscheider & Drew, 2007). The proximity of gravel trenches and infiltration systems thus enhances the risk of human-made shortcuts for infiltrated water and pollutants.
Any interception of water and contaminant flow by the underground infrastructure can cause a rapid transfer of water through the preferential flow paths. This could also result in the quick transport of pollutants without getting sorbed on the soil sediments (White, 2018). These pollutants may thus be flushed into surface waters at a much greater rate than those in natural (non-urban) landscapes (FIGURE 2.3). Bonneau et al. (2018) monitored the groundwater level in two monitoring bores upslope and downslope of a sewer line in the proximity of the infiltration system in a peri-urban catchment (Melbourne, Australia). Whereas the depth of groundwater table in monitoring bore upslope of a sewer line fluctuated during summer, a bore located downgradient of a sewer line was dry, showing evidence of interception between the plume of infiltrated stormwater and the highly permeable trench around the sewer line.

The widespread application of infiltration systems in the context of incomplete knowledge about interactions with other infrastructure poses several risks. The acceleration of water flow due to highly permeable trenches could potentially drain infiltrated solutes into streams. Understanding the potential mobilization and transport of solutes when interacting with the urban karst has been largely neglected, and thus more experiments in this area would help to better understand the efficiency of stormwater infiltration as a strategy to protect and restore urban streams.
FIGURE 2.3: The potential impact of the urban karst on the transport path of pollutants. The infiltration system (G) receiving stormwater from the impervious area (A). Components of the urban karst (sewer, water mains, etc.) (C) surrounded by gravel trenches (D). Expected pathway of infiltrated stormwater and its associated pollutants (E) to the stream (F) with potential shortcuts (B) (Bonneau et al., 2017).

2.5 Summary - the gaps and resulting questions

This review has demonstrated that complete pollutant treatment is unlikely via infiltration systems, and thus stormwater pollutants of concern such as heavy metals could travel with the plume of infiltrated stormwater, percolating down the filter media and exfiltrating from the filter media into the local environment. The degree to which pollutants can be removed from the much more extensive filtration through the surrounding soils between the system and the stream is still unclear. The movement of these pollutants is also susceptible to influences by the network of pipelines and their associated highly permeable trenches. This network could potentially undermine
the aim of using stormwater infiltration to protect the health of waterways through more natural flow and water quality regimes.

Since the use of stormwater infiltration is becoming increasingly common, it is crucial to understand the fate of infiltrated water and its associated pollutants in urban environments. In an urbanizing world, protecting the urban groundwater-stream system can support healthy stream ecosystems. Groundwater and stream water are not separate entities of the hydrological systems and can interact in a variety of landscapes. Thus, practical stormwater management approaches need to assess the heterogeneity of underlying soil and uncertainty of urban subsurface pathways. In general, the literature review suggests that the following issues associated with stormwater infiltration in urban areas have not received much attention:

**Gap 1.** The presence and movement of pollutants in the soils due to existing or past land uses also pose a challenge of getting these pollutants remobilized by the plume of infiltrated water.

The first gap leads to **Research Question 1** (tackled in Chapters 3 and 4).

1. What is the effect of soil clay mineralogy on the transport of reactive solutes?

My hypothesis is that clay mineralogy plays a pivotal role in sorbing metal ions and therefore should be considered when implementing infiltration systems to mitigate the risk of groundwater and subsequently stream water contamination.
**Gap 2.** The presence of highly permeable subsurface infrastructure commonly found in urban areas, where stormwater capturing is most practiced, may lead to the rapid transmission of infiltrated water and pollutants it carries.

This gap is addressed by answering **Research Question 2** (tackled in Chapter 5).

2. How do gravel filled preferential flow paths affect reactive solutes transport in soils? Or what is the influence of the urban karst on the transport of reactive solutes?

My hypothesis is that the existence of karst-like flow paths accelerates the transmit of solutes through the subsurface, thus degrading urban stream ecosystems.
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Chapter 3 – Understanding the impact of soil clay mineralogy on the fate of reactive solutes
Chapter 3 – Understanding the impact of soil clay mineralogy on the fate of reactive solutes

3.1 Chapter perspective

In Chapter 3, the zinc sorption characteristics of the two soil types, a natural soil and a synthetic soil, are investigated through laboratory batch experiments whereby clay minerals act as the adsorbent. Clay mineralogy of the natural soil is measured by the X-ray diffractometer and then used as a reference to make the synthetic soil. The particle size distribution of the synthetic soil is closely approximated to that of the natural soil. The maximum sorption capacity of soils for removing zinc is compared kinetically and in equilibration to examine the zinc sorption potential of the two soil types under optimal operating conditions. The type of soil clay minerals determines the extent of the movement of the metals in the subsurface that should be taken into account prior to implementing stormwater infiltration systems.
3.2 Introduction

As a result of urbanization, much of the once-permeable soil surface through which infiltration could occur is replaced with impervious areas, leading to less groundwater recharge and increased runoff (Pitt et al., 1999). The increased imperviousness is recognized as a primary cause of flash flooding and degradation of receiving waters (Walsh et al., 2005); depriving urban communities of the ecosystem services provided by healthy urban streams. Since the early 1990s, there has been growth in the use of alternate stormwater management approaches involving nature-based stormwater control measures (Fletcher et al., 2015). These approaches include swales, porous pavements, wetlands, ponds, and infiltration systems (basins and trenches). Among these, infiltration systems are arguably the most extensively applied stormwater control measure worldwide, in part for their assumed ability to intercept stormwater and allow it to infiltrate, recharging groundwater and ultimately restoring clean, filtered baseflows by removing solids before they reach receiving waters (Barraud et al., 1999; Hamel et al., 2013; Roy & Bickerton, 2012; Weiss et al., 2008).

There is, however, evidence of unintended consequences occurring from infiltration systems, including the potential to introduce a variety of pollutants into the soil and groundwater and subsequently leading to pollution of receiving waters (Fischer et al., 2003). Pollutants that may lead to groundwater contamination via infiltration systems include non-metals/anions, pesticides, metals/cations and organics (e.g., petroleum hydrocarbons), along with pathogens such as fecal coliforms, viruses, and bacteria (Clark & Pitt, 2007). Pollution by heavy metals is of great concern to water managers, given that metals are typically stable, persistent in nature and detrimental to a variety
of biota (Inglezakis et al., 2003). Among the metals, zinc is important from an environmental toxicology point of view, as it finds its way into water from numerous sources (ATSDR, 2005). Alloway (2013) claimed that probability of zinc transmission to groundwater is higher than other metals.

Short-term studies have demonstrated the effectiveness of stormwater infiltration systems in mitigating heavy metal concentrations from uncontaminated stormwater runoff. There are, however, documented cases of failure when elevated levels of heavy metals in stormwater are introduced to infiltration systems from industrial waste (Teta & Hikwa, 2017), fertilizers (Srilert et al., 2013), and animal manure (Ogiyama et al., 2005) or when the long-term accumulated heavy metals in biofilters within infiltration systems are not appropriately maintained (regenerated or replaced). Such failures undermine the ability of the infiltration systems to reduce heavy metal pollution, potentially resulting in leaching to subsurface layers (Al-Ameri et al., 2018). The fate and transport of metals leached out from the infiltration systems are governed by the surrounding soil media features. The extent of metal removal downstream of such systems then depends on several factors, including porous media surface area, soil type, clay mineralogy, and surface charge (Bhattacharyya & Gupta, 2008b; Ijagbemi et al., 2009; Jiang et al., 2010).

Clay minerals, an important constituent of soil, play a pivotal role in removing heavy metals through separating them from the aqueous solution. Clays are hydrous aluminosilicates which make up the colloidal fraction (< 2µm) of soil (Velde, 1995). The high specific surface area, chemical, and mechanical stability and high cation
exchange capacity make them an excellent sorbent to immobilize heavy metal ions (Uddin, 2017). Clay minerals can be generally classified into two main groups, namely the kaolin and smectite groups. Kaolin such as Kaolinite and other 1:1 clay minerals include silica tetrahedral sheets and octahedral hydroxide sheets in a 1:1 ratio (Xu et al., 2018). Kaolinite possesses a strong bond between the layers, and there is no interlayer swelling, relatively low cation exchange capacity and low expansion coefficient (Miranda-Trevino & Coles, 2003). On the other hand, smectites, including muscovite, vermiculite, montmorillonite, and illite, consist of two silica tetrahedral sheets with an octahedral sheet in between (Brigatti et al., 2013); that is a 2:1 ratio. The 2:1 clay mineral types have an interstitial zone leading to weak bonding between silica sheets, much more expansive properties and much higher sorption capacity than the kaolin type clays (Barton, 2002).

Several studies have reported that zinc can be removed by sorption onto the specific clay minerals (Kyzioł-Komosińska et al., 2014; Wencui et al., 2017), but there is lack of understanding of the impact of clay mineralogy on the overall sorption capacity of the soil. Infiltration-based stormwater control measures are commonly designed by predicting the sorption capacity of soil for a particular metal using the clay sorption capacities available in the literature, without a proper understanding of the natural interactions that might occur in the environment. This study aims to address this gap in our understanding of the effect of clay mineralogy on the sorption behavior of soils. The results of this study will help inform designers of infiltration systems, and in understanding the fate of heavy metals in the subsurface.
To achieve this aim, a series of laboratory batch experiments were conducted to determine the maximum sorption capacity of soils with different clay mineralogy for zinc. Two sets of soils; the natural soil collected from a peri-urban catchment and the synthetically-made soil were used to study their sorption behaviors. The main constituents of the natural soil were quartz, kaolinite, and muscovite, while the synthetic soil was composed of quartz and kaolinite. The operating conditions for sorption, including soil dose, agitation time, solution pH and metal ion concentration, were optimized to determine the maximum sorption capacity of the soils. The results were then compared to assess the relative zinc sorption potential of the two soil types under optimal operating conditions, and the observed sorption capacity of the soil was compared with the sorption capacity predicted on the basis of available literature.

3.3 Materials and methods

3.3.1 Soil collection and preparation

We collected a weathered natural soil from a peri-urban catchment, 40 km east of Melbourne, Victoria. We oven-dried the soil at 105 °C until a constant weight was achieved (72 h). The soil was then manually crushed and mechanically sieved, removing grains with a diameter larger than 2000 µm. To provide a comparison with the natural soil containing a mix of clay minerals, and thereby develop a better understanding of the impact of soil clay mineralogy in sorbing zinc, a synthetic soil with total clay content similar to natural soil was prepared by mixing quartz (silica flour and sand) and kaolinite provided by Sibelco Australia Ltd. Co. The quartz fraction consisted of water-washed high purity silica sand. Kaolinite produced from
selectively mined, and stockpiled raw material was added to the sand. The particle size distribution of the synthetic soil was similar to the silt-sand distribution of the natural soil.

3.3.2 Soil characterization

3.3.2.1 XRD measurement and particle size distribution

The phase composition of the collected soil was determined using a Bruker D8 Advance X-ray diffractometer (XRD) with Ni-filtered Cu Kα radiation using the method described in Warren (1990). We back-loaded the sample into a standard sample holder for analysis. The diffraction data were obtained between 5° and 85° with a step size of 0.02° 2θ and the scan rate of 1 s per step. The resulting peaks and intensities of each mineral were then compared with the powder diffraction files published by the International Centre for Diffraction Data (Jenkins et al., 1986). This information was used to make the synthetic soil of similar total clay content. The particle size distribution was measured using a Beckman-Coulter LS 13 320 Laser Particle Size Analyzer. As the instrument can only run an aqueous phase, the sample needed to be disaggregated in a wet paste form prior to analysis, by soaking for 24 h using Calgon.

3.3.2.2 Cation exchange capacity

We estimated the cation exchange capacity (CEC) of each soil using the test method 15B1 (Rayment & Lyons, 2011). Exchangeable cations in the soil were initially replaced by neutral ammonium ions by filtration through a Buchner funnel. In doing so, 5 g of
air-dry soil sample was mixed with 50 mL of 1 M NH₄Cl at pH 7 in a 100 mL plastic extraction container. The solution was then securely capped, and shaken using an end-over-end tumbler for two hours. An ashless Whatman qualitative filter paper was fitted to a Buchner funnel with the aim of delivering the extract into another 100 mL plastic container. During the filtering stage, the vacuum was kept off until all the extract was added to the Buchner funnel to submerge the soil. The vacuum was then turned on to draw the extract through the filter paper. The remaining soil in the extraction container was then transferred onto the filter paper, aided by a squirt bottle filled with 1 M NH₄Cl extracting solution. Soil washing with the solution was continued until 100 mL of extract was collected. The extract was then analyzed by ICP-OES¹ (Optima 4400, Perkin Elmer, USA) for the determination of exchangeable cations. Subsequently, ammonium ions in the soil were displaced with K-Ca (15% potassium nitrate and 6% calcium nitrate) solution, and the resulting extract was analyzed for ammonium, expressed as NH₄-N (mg L⁻¹). For this, 80 mL of 0.1 M HNO₃ was added to the plastic container and leached with K-Ca displacing solution that evenly passed through the soil to make up 200 mL of extract. The retained extract was used to calculate the CEC from the following equation:

\[
\text{CEC (meq NH}_4^+/100\text{g}) = 7.143 \times \frac{SV}{m} \tag{3.1}
\]

Where \( S \) is the concentration of \( \text{NH}_4^- \)-N in the extract (mg L⁻¹), \( V \) is the volume of extract taken (L) and \( m \) is the mass of the soil (g).

¹ Inductively Coupled Plasma-Optical Emission Spectrometer
3.3.3 Preparation of sorbate solutions

The sorption experiments were carried out by using synthetic solutions containing known concentrations of zinc ions. The stock solutions of 100 mg L\(^{-1}\) zinc were prepared by dissolving 0.444 g of ZnSO\(_4\).7H\(_2\)O, in one liter deionized water. The solutions at the desired concentrations were then prepared by appropriate dilution with deionized water.

3.3.4 Zinc leaching test

It is essential to ensure that collected natural soil does not contain Zinc that can leach out while running batch experiments. To determine the potential leachability of the residual zinc from the natural soil, we agitated 50 mL deionized water dosed with 0.25 g of the natural soil for three hours at a stirring speed of 250 rpm. Samples were filtered through a 0.45 µm syringe filter after agitation, and ICP-OES determined the concentrations of zinc and in the filtrate. We also sent the natural soil to an external laboratory for leachability testing to confirm the results. The external laboratory utilized a slightly different method of extraction. Water was initially extracted from soil samples by a 1:5 S/W ratio. Soluble salts were then leached from a soil sample by the continuous suspension of the soil in water for one hour using an end-over-end tumbler at 30 rpm (Rayment & Lyons, 2011). The resultant water extract was then analyzed to determine concentrations of soil metals using ICP-MS\(^2\).

---

\(^2\) Inductively Coupled Plasma-Mass Spectrometry
3.3.5 Equilibrium batch tests

Laboratory-scale batch tests were carried out to evaluate the effects of soil dose, agitation time, pH and initial metal concentration on the zinc sorption by the natural and synthetic soils. We performed the experiments at room temperature (22 ±2 °C) in 100 mL Pyrex flasks. The blank tests were initially done at the beginning of each experiment to ensure there is no major contamination source or loss of zinc via adsorption of the glass fibers. The initial batches aimed to optimize the soil dosage and the agitation time required to achieve equilibrium, followed by batches to study the effect of pH and initial concentrations. A stirring speed of 250 rpm was chosen (Burham & Sayed, 2016) using a digital orbital shaker, to provide complete mixing between aqueous and solid phases. The solutions were filtered after the equilibrium time, and residual zinc concentrations in the supernatant liquid were then determined by ICP-OES. All experiments were done in triplicate. The average of the three measured values was taken, with an experimental error, less than 4% for the instrument used.

3.3.5.1 Effect of soil dose

The soil dose is an important parameter in determining the sorption capacity of a soil for a fixed initial concentration of the sorbate at the given operating conditions. The effect of soil mass on the amount of zinc sorbed onto the natural soil was determined by placing different doses of soil (1 to 50 g L⁻¹) in different flasks containing 50 ml of stock solution. All flasks were mechanically agitated at room temperature and a constant speed of 250 rpm for 180 minutes. At this time, the samples were then filtered,
and the filtrates were analyzed for the residual zinc concentrations. The optimum soil doses determined in this step were used for remaining batch runs.

3.3.5.2 Effect of agitation time (determination of equilibrium time)

Equilibrium is attained when the concentration of metals in the aqueous solution remains nearly constant, as the rate of sorption is equal to desorption. Determination of equilibrium time is an important step, so that remaining batches could be run for sufficient duration to achieve equilibrium. 100 mg of zinc per liter was chosen as initial concentrations, and the optimum soil dose of 5 g L\(^{-1}\) (0.25 g soil + 50 mL sorbate solution) was used for all flasks. We checked the zinc sorption with time at various agitation times: 5, 10, 15, 20, 25, 30, 45, 60, 90, 120, 150 and 180 min by sequentially removing one flask off the shaker. We then filtered the suspension through a 0.45 µm syringe filter, and the filtrate was analyzed for residual zinc concentration.

3.3.5.3 Effect of solution pH

The pH of groundwater samples collected from the study site ranged from 6.5 to 7.5. However, a wider range of pH (4-9) was chosen to examine the sorption behavior of metal in soil so that the study results can be used for other sites that might have acidic or alkaline groundwater. These values are within the pH range observed for urban stormwater (Duncan, 1999). During these tests, the initial zinc concentration and soil dose were fixed to 100 mg L\(^{-1}\) and 5 g L\(^{-1}\), respectively. The pH adjustment was carried out using 0.1 M HCl and NaOH solutions. The added volume did not exceed 1% of the initial solution volume; therefore no volume correction was used. The pH was
measured using a Hach HQ40D portable multimeter with an accuracy of ±0.002 pH that was calibrated with standard solutions.

3.3.5.4 Effect of initial aqueous concentration

We also examined the effect of initial metal concentrations through equilibrium and kinetic models, to study the effect of varying concentrations on zinc sorption. A range of initial concentrations for zinc was chosen as 5, 10, 15, 20, 40, 60, 80 and 100 mg L\(^{-1}\). This range was taken because more realistic concentrations of zinc (< 5 mg L\(^{-1}\)) could not be selected as initial ICP-MS analyses showed a limitation of the instrument in detecting the post-adsorption liquid phase zinc ions. Very high concentrations of zinc have been also reported in the literature (Charles & Tapiwa., 2017; Galitskaya et al., 2017). Each batch was run with a fixed soil dose of 5 g L\(^{-1}\) for the pre-determined equilibrium time. The suspensions were filtered through 0.45 µm syringe filters and then analyzed to determine the residual zinc concentrations.

3.3.6 Estimation of the amount of sorbed zinc and the removal efficiency

The amount of zinc sorbed per unit mass of the sorbent, \(q_t\) (mg g\(^{-1}\)) at a given time (t) and the removal efficiency (%E) were quantified as follows:

\[
q_t = (C_0 - C_t)V/m
\]  \hspace{1cm} (3.2)

\[
%E = (C_0 - C_t) \times 100/C_0
\]  \hspace{1cm} (3.3)

where \(C_0\) and \(C_t\) (mg L\(^{-1}\)) are the initial and at time ‘t’ metal ion concentrations in the aqueous phase, respectively, \(V\) is the volume of the aqueous solution (L) and \(m\) is the mass of the used sorbent (g).
3.3.7 Sorption isotherm models

In general, a sorption isotherm is a curve describing the phenomenon governing the release or mobility of a substance from the aqueous phase to a solid phase at a constant temperature and pH (Limousin et al., 2007). Two of the most widely used isotherm models, the Langmuir, and Freundlich (Treybal, 1980), were applied to determine the maximum sorption capacity of the two soils. The Langmuir model assumes that sorption takes place uniformly on the active sites of the sorbent and no further sorption can occur once all the sites are occupied. It is also assumed that the sorbate removal from liquid phase occurs on a homogeneous surface by monolayer sorption without interactions between sorbed molecules. Alternatively, the Freundlich model is an empirical equation, assuming that the sorption occurs onto a heterogeneous surface.

The equations corresponding to each model and their linearized forms are presented in TABLE 3.1, where $q_e$ is the amount of metal sorbed at equilibrium (mg g$^{-1}$), $q_m$ is the maximum amount of metal that can be sorbed (mg g$^{-1}$), $C_e$ is the concentration of metal in the liquid phase at equilibrium (mg L$^{-1}$), and $K_l$ is the Langmuir sorption constant, which is related to the sorption energy (L mg$^{-1}$). In the linearized form of the Langmuir model, the values $K_l$ and $q_m$ can be determined from the intercept and slope of the straight line, on a plot of $C_e/q_e$ versus $C_e$. The key parameter of the Langmuir model is the dimensionless equilibrium parameter, known as the separation factor, $R_L$ (Weber & Chakravorti, 1974).

$$R_L = 1/(1+K_lC_0) \quad (3.4)$$
The value of $R_L$ indicates whether the isotherm shape is favourable ($0 < R_L < 1$), unfavourable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$) (Foo & Hameed, 2010).

For the Freundlich model, $K_f$ is a coefficient indicative of the sorption capacity, and $n$ is sorption intensity (Treybal, 1980). $K_f$ and $n$ can be estimated from the intercept and slope of a linear curve on a plot of Log $q_e$ versus Log $C_e$ (TABLE 3.1).

### TABLE 3.1: Original, linearized forms and parameters of the used isotherms.

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Original form</th>
<th>Linearized form</th>
<th>Plots</th>
<th>Deduced parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$q_e = q_m K_l C_e / (1 + K_l C_e)$</td>
<td>$C_e / q_e = 1 / (K_l q_m) + C_e / q_m$</td>
<td>$C_e / q_e$ vs $C_e$</td>
<td>Slope: $q_m$ Intercept: $K_l$</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$q_e = K_f C_e^{1/n}$</td>
<td>Log $q_e = \log K_f + 1/n \log C_e$</td>
<td>Log $q_e$ vs Log $C_e$</td>
<td>Slope: $n$ Intercept: $K_f$</td>
</tr>
</tbody>
</table>

### 3.3.8 Sorption kinetics

Sorption kinetics modeling is very useful to better understand the sorption mechanism of zinc onto selected soils. A large number of kinetic models have been proposed in the literature (Al-Degs et al., 2006; Bereket et al., 1997; Unuabonah et al., 2016). Two well-known models; pseudo-first-order, and pseudo-second-order kinetic models have been utilized in this study to investigate soil-metal interaction over time.

The pseudo-first-order generally governs the sorption over the first few minutes where the number of metal ions outnumbers the number of sorption sites available on clay surfaces (Lagergreen, 1898). It is given below by Eq. (3.5) and its linear form by Eq. (3.6):

$$\frac{dq_t}{dt} = K_1 (q_e - q_t)$$  \hspace{1cm} (3.5)
Ln (q_e - q_t) = Ln q_{eq} - K_1 t \quad (3.6)

where q_t and q_e are the amounts of sorbed metal at time t (min) and equilibrium (mg g^{-1}), K_1 is the equilibrium rate constant of pseudo-first-order (min^{-1}), and q_{eq} is the theoretical metal equilibrium concentration for the pseudo-first-order model onto sorbent. In the linear form, K_1 and q_{eq} can be determined from the slope and intercept of a linear fit to a plot of Ln (q_e - q_t) versus t.

The pseudo-second-order model is also based on the sorption capacity of sorbent and predicts “chemical sorption” behavior over the whole time of the sorption process (Ho & McKay, 1998). The equations corresponding to the pseudo-second-order model are:

\[
\frac{dq_t}{dt} = K_2 (q_e - q_t)^2 
\]

\[
t/q_t = 1/(K_2 q_{eq}^2) + t/q_{eq} \quad (3.8)
\]

where K_2 is the equilibrium rate constant of pseudo-second-order (g mg^{-1} min^{-1}), and q_{eq} is the theoretical metal equilibrium concentration for the pseudo-second-order model onto sorbent. K_2 q_{eq}^2 is also referred to as the initial sorption rate (h) (mg g^{-1} min^{-1}). In the linear form, K_2 and q_{eq} can be computed from the intercept and slope of a linear curve, respectively on a plot of t/q_t versus t.

The best-fit model was chosen based on the regression correlation coefficient (R^2) of the plots, residual plots and the coherence between the computed and experimental q_e values for the kinetic models.
3.4 Results and discussion

3.4.1 Soil characterization

3.4.1.1 XRD measurements and particle size distribution

The XRD spectra (FIGURE 3.1) indicated that the natural soil is composed of quartz-kaolinite-muscovite minerals (74% quartz and 26% of all clay types combined). Using the natural soil mineralogical composition as a reference, the synthetic soil was made up of 76% quartz (goethite percent was added to quartz as it also behaves in an inert way), and 24% kaolinite. TABLE 3.2 presents the weight percent of the crystalline phases for the natural soil as well as for the synthetic soil. The synthetic soil does not contain muscovite and thus provides a good basis for comparison. The grain size distribution as shown in FIGURE 3.2 was: 24.46% < 2 µm, 43.62% < 20 µm, 55.6% < 50 µm, 62.13% < 75 µm, 76.97% < 149 µm, 88.34% < 210 µm, 97.61% < 420 µm, 100% < 841 µm. The median particle size quantified for the natural soil was 36 µm.

![FIGURE 3.1: XRD diffractogram of the analyzed natural soil.](image-url)
TABLE 3.2: Semi-quantitative results for identified crystalline phases for the natural soil and the synthetic soil.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Phase</th>
<th>Quartz</th>
<th>Kaolinite</th>
<th>Muscovite</th>
<th>Vermiculite</th>
<th>Goethite</th>
</tr>
</thead>
<tbody>
<tr>
<td>The natural soil</td>
<td></td>
<td>74</td>
<td>13</td>
<td>10</td>
<td>&lt;1</td>
<td>2</td>
</tr>
<tr>
<td>The synthetic soil</td>
<td>76 (includes goethite)</td>
<td>24</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

FIGURE 3.2: Particle size distribution of natural soil using Beckman-Coulter LS 13 320.

3.4.1.2 Cation exchange capacity

The CEC values of the natural soil and the synthetic soil were found to 13 and 5.2 meq/100g, respectively. The CEC of the natural soil was 2.5 times higher than that of the synthetic soil, potentially due to the presence of muscovite in the natural soil. Although only 24% of the synthetic soil is composed of kaolinite, the CEC value is within the range reported in the literature, i.e., 3-15 meq/100g at pH 7 for pure kaolinite (Grim, 1968).
3.4.2 Zinc leaching test

The leachability tests indicated that the natural soil did contain small concentrations of zinc. The results from the external laboratory also confirmed that the natural soil contained only 20 mg kg\(^{-1}\) of zinc. Therefore, we applied correction factors in computing the sorption rates of metals onto natural soil.

3.4.3 Effect of experimental conditions

3.4.3.1 Effect of soil dose

The amount sorbed per unit mass of soil decreased as soil dose increased (Arias & Sen, 2009) for doses higher than 5 g L\(^{-1}\) (FIGURE 3.3). The reduction of measured sorption capacity with the increase in soil mass is likely due to particle aggregation, resulting in an overlapping of the sorption sites and a decrease in the total surface areas available (Shukla et al., 2002). This may also desorb some of the zinc that is only loosely and reversibly bound to the carbon surface. Another reason may be due to unsaturation of adsorption sites through the adsorption reaction.

On the contrary, zinc removal efficiency increased with higher soil loading (FIGURE 3.4), likely because the higher amount of soil in the aqueous solution increases the overall availability of exchangeable sites for metal ions (Jain et al., 2009). So we need to find a balance between two to find the optimal dose.
FIGURE 3.3: Effect of soil dose on the sorption of zinc by the natural soil. Initial concentration: 100 mg L\(^{-1}\); agitation time: 3 h; agitation speed: 250 rpm; temperature of solution: 22 ± 2 °C.

FIGURE 3.4: Effect of soil dose on the removal of zinc by the natural soil. Initial concentration: 100 mg L\(^{-1}\); agitation time: 3 h; agitation speed: 250 rpm; temperature of solution: 22 ± 2 °C.
3.4.3.2 Effect of agitation time

The results presented in FIGURE 3.5 show that zinc interacts with the clays rapidly and sorption is almost instantaneous (occurring within 5 minutes of contact time). After this contact time, zinc uptake remains constant, and no further sorption takes place for either soil type. Therefore, the equilibrium time is found to be less than 5 minutes. This rapid sorption is likely due to the increased concentration gradient between metal ions in aqueous and solid phases (Afroze et al., 2016). Hence, both the natural and synthetic soils are characterized by a swift zinc sorption process. The results also show that the natural soil has a much higher zinc sorption capacity (2.34 mg g\(^{-1}\)) than the synthetic soil (0.34 mg g\(^{-1}\)), respectively. The lower sorption capacity of the synthetic soil is attributed to the 1:1 clay mineral type used and the absence of muscovite (Sánchez-Martín et al., 2008).

FIGURE 3.5: Effect of contact time on zinc sorption. Initial concentration: 100 mg L\(^{-1}\); soil dose: 0.25g/50mL; agitation speed: 250 rpm; temperature of solution: 22 ± 2 ℃.
3.4.3.3 Effect of solution pH

Three main regions are apparent in the zinc uptake by the natural and synthetic soils with pH (FIGURE 3.6). In the first region, from pH 4.0 to 6.0, the sorption of zinc remained almost constant. In the second region, where the pH increases from 6.0 to 7.0, the zinc sorbed onto the natural soil increased from 1.38 to 2.26 mg g\(^{-1}\). This increase was far less noticeable for the synthetic soil. At pH > 7.0 (third region), the sorption capacity of zinc onto both soils increased rapidly and reached a very high maximum (~19.64 mg g\(^{-1}\)) at pH 9. Unuabonah et al. (2016) studied the sorption of zinc by modified kaolinite clay and observed a rapid increase in the percentage of zinc sorbed within the pH range of 6.0-9.0.

The variations in sorption with pH can be due to the potential competition between the metal ions and H\(^+\) ions for sorption sites onto the clay fractions of the soil. At lower pH values, H\(^+\) ions compete strongly with the metal ions, causing a decrease in the sorption of the metals from solution (Altin et al., 1999). On the other hand, at higher pH, more sites become more available for the metal ions, enhancing the sorption (Taty-Costodes et al., 2003).

The presence of metal hydroxyl species and the dissolution of Al(III) from the aluminosilicate layers could also explain this behavior (Ören & Kaya, 2006). As the pH increases above 7.0, precipitation of the insoluble metal hydroxides may occur, apparently leading to a significant increase in metal ion removal. At pH higher than 7.0, zinc ions may form complexes with OH\(^-\) such as Zn(OH)\(_2\), Zn(OH)\(_3\)^- and Zn(OH)\(_4\)^2- and consequently precipitate onto the clay structure (Kaya & Ören, 2005). This could
also explain higher zinc sorption at pH above 7.0 (Jiang et al., 2009). As the results show a strong pH dependence, further batch experiments were carried out at a pH of 7.0.

![Graph showing the effect of solution pH on zinc sorption. Initial concentration: 100 mg L\(^{-1}\); soil dose: 0.25g/50mL; agitation time: 5 min; agitation speed: 250 rpm; temperature of solution: 22 ± 2 °C.]

**FIGURE 3.6:** Effect of solution pH on zinc sorption. Initial concentration: 100 mg L\(^{-1}\); soil dose: 0.25g/50mL; agitation time: 5 min; agitation speed: 250 rpm; temperature of solution: 22 ± 2 °C.

3.4.3.4 Effect of initial zinc concentration

The number of zinc sorbed per unit mass of soil increases with increasing metal ion concentration in aqueous solution (FIGURE 3.7). Raising the initial concentrations from 5 to 100 mg L\(^{-1}\) led to an increase in sorption capacities from 0.83 to 2.57 mg g\(^{-1}\) for zinc in the natural soil. A similar trend was also observed for the synthetic soil, where capacities varied from 0.1 to 0.36 mg g\(^{-1}\) for zinc when initial concentrations shifted from 5 to 100 mg L\(^{-1}\). The simplest explanation of these trends is that there is
an increased metal concentration gradient between aqueous solutions and the clay particles. Similar results have also been reported for other metals e.g. Cu(II) by natural bentonite (Veli & Alyüz, 2007) and Pb(II), Cd(II) and Ni(II) by kaolinite and montmorillonite (Gupta & Bhattacharyya, 2008).

**FIGURE 3.7**: Effect of initial aqueous concentration on zinc sorption onto the natural and synthetic soils. Initial concentrations: 5-100 mg L\(^{-1}\); soil dose: 0.25g/50mL; agitation time: 5 min; agitation speed: 250 rpm; pH: 7.0; temperature of solution: 22 ± 2 °C.

### 3.4.4 Sorption isotherms

The Langmuir and Freundlich models fit the experimental data very well for the natural and synthetic soils (FIGURE 3.8). This can be also observed from residual plots, indicating random residuals for either of the two models. The monolayer Zn sorption capacity, \(q_m\), of the natural soil (2.68 mg g\(^{-1}\)) was far more than that in the
synthetic soil (0.41 mg g\(^{-1}\)) (TABLE 3.3). The \(R_L\) values for zinc concentrations in the range of 5 -100 mg L\(^{-1}\) were computed as 0.54 and 0.78, showing favorable conditions for the sorption of zinc onto the soils. In addition, larger values of the equilibrium coefficient, \(K_l\), were obtained for zinc sorption onto the natural soil, compared with the synthetic soil. This indicated the stronger interactions between zinc and the natural soil, implying the significant role of the muscovite in sorbing zinc ions, as compared to the kaolinite.

The Freundlich sorption constant, \(n\), was evaluated as 4.014 and 2.478 for the natural and synthetic soils (TABLE 3.3); falling within the typical range of 2 < \(n\) < 10 which shows the selected soil types preferentially sorbed zinc ions. The Freundlich sorption constant, \(K_f\), was larger for the natural soil (Zn(II): 0.870 mg\(^{1-(1/n)}\) L\(^{1/n}\) g\(^{-1}\)), compared with that of the synthetic soil (Zinc(II): 0.058 mg\(^{1-(1/n)}\) L\(^{1/n}\) g\(^{-1}\)). This result confirms that the natural soil in the presence of the 2:1 clay mineral has been found to sorb much more than the synthetic soil with no 2:1 clay minerals. Gupta and Bhattacharyya (2008) studied the sorption of Pb(II), Cd(II) and Ni(II) on kaolinite and montmorillonite, and found montmorillonite to sorb much more than kaolinite.

The results also indicate that values of the sorption capacities and sorption coefficients of different soils cannot be directly obtained and extrapolated from those reported in the literature even though the operating conditions are similar. For instance, Chai et al. (2017) reported that 6.35 and 79.2 mg of zinc were removed per unit mass of natural kaolinite and bentonite, respectively. However, in a natural environment when dealing with the subsurface soils, the relative weight percentage of the dominant
minerals will define the overall sorption capacity. The zinc sorption capacity of the natural soil studied in this research was found to be 2.68 mg g⁻¹, significantly different from the predicted sorption capacity of 9.53 mg g⁻¹, as per Chai et al. (2017). This may be due to the multitude of other interactions that might happen in the natural environment. These results suggest that it is important to determine the sorption capacity of the whole soil for a given site, instead of relying on the sorption capacities available in the literature to account for all the potential interactions specific to that site.

**TABLE 3.3:** The Langmuir and Freundlich coefficients for zinc sorption onto the natural and synthetic soils. Initial concentrations: 5-100 mg L⁻¹; soil dose: 0.25g/50mL; agitation time: 5 min; agitation speed: 250 rpm; pH: 7.0; temperature of solution: 22 ± 2 ºC.

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Soil</th>
<th>Langmuir coefficients</th>
<th>Freundlich coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>qₘ (mg g⁻¹)</td>
<td>Kₗ (L mg⁻¹)</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>Natural</td>
<td>2.684</td>
<td>0.171</td>
</tr>
<tr>
<td></td>
<td>Synthetic</td>
<td>0.410</td>
<td>0.055</td>
</tr>
</tbody>
</table>
3.4.5 Sorption kinetics

TABLE 3.4 lists the calculated parameters and the coefficients obtained from the kinetic models for zinc sorption. The correlation coefficients for the pseudo-second-order were greater than 0.99 for both the soils, indicating an almost perfect fit of data with the second-order kinetic model (FIGURE 3.9). The calculated $q_e$ values also agreed very well (deviations from -19.4 to -11.3%) with the experimental data, confirming the good performance of the pseudo-second-order model to describe zinc
sorption behavior onto the selected soils (TABLE 3.4). The results suggest that the sorption of zinc ions is largely governed by the chemical sorption or chemisorption through the sharing or exchange of electrons between zinc and soils (Ho & McKay, 2002). The initial sorption rate, $h$, for the sorption of zinc, was significantly higher onto the natural soil than the synthetic soil (5.20 and 0.07 mg g$^{-1}$ min$^{-1}$, respectively). This indicated that the natural soil sorbed zinc from the aqueous solution far more rapidly than the synthetic soil did.

![Figure 3.9](image)

FIGURE 3.9: Pseudo-first and -second-order reaction kinetics for zinc sorbed onto the natural and synthetic soils. Initial concentration: 100 mg L$^{-1}$; soil dose: 0.25g/50mL; agitation speed: 250 rpm; pH: 7.0; temperature of solution: 22 ± 2 °C.
TABLE 3.4: Kinetic parameters for zinc sorption onto the natural and synthetic soils. Initial concentration: 100 mg L\(^{-1}\); soil dose: 0.25g/50mL; agitation speed: 250 rpm; pH: 7.0; temperature of solution: 22 ± 2 °C.

<table>
<thead>
<tr>
<th>Kinetic models</th>
<th>Parameters</th>
<th>Zn(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>The natural soil</td>
</tr>
<tr>
<td>Pseudo-first-order</td>
<td>Experimental (q_e) (mg g(^{-1}))</td>
<td>2.57</td>
</tr>
<tr>
<td></td>
<td>(K_1 \times 10^3) (min(^{-1}))</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>Theoretical (q_{el}) (mg g(^{-1}))</td>
<td>0.035</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.846</td>
</tr>
<tr>
<td></td>
<td>Deviation (%)</td>
<td>-98.6</td>
</tr>
<tr>
<td></td>
<td>(K_2) (g mg(^{-1}) min(^{-1}))</td>
<td>1.00</td>
</tr>
<tr>
<td>Pseudo-second-order</td>
<td>(h) (mg g(^{-1}) min(^{-1}))</td>
<td>5.20</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>Deviation (%)</td>
<td>-11.3</td>
</tr>
</tbody>
</table>

3.5 Conclusions

Transport and leaching of heavy metals in the subsurface from the filtration media of stormwater infiltration systems through the underlying soil can affect the quality of receiving waters and have a detrimental impact on their ecosystems. Understanding the degree to which heavy metals can be transported through the soils and regolith between the infiltration systems and stream can help improve the design and location of the infiltration systems for the most benefit. The potential removal of heavy metals by the soils is highly dependent on the clay mineralogy of the soil as well as other interacting factors at a given site.

We investigated the zinc sorption potential of two clay soils. The soils were similar in total clay content but different in mineralogy. The isothermal sorption data showed
the general applicability of the Freundlich and Langmuir models for describing zinc sorption onto the selected soils. The kinetic simulation indicated that zinc sorption process followed pseudo-second-order kinetics, which is strongly supported by the consistency of equilibrium concentrations calculated by the kinetic model and experimental values. From the kinetic and isothermal studies, it can be concluded that, while the interactions were predominantly chemically modulated in nature, the sorption sites were non-uniform and non-specific.

We calculated the sorption capacity for the soils tested. Under experimentally verified optimal operating conditions, the zinc sorbed onto the natural soil was 6.5-fold larger than the synthetic soil, showing that the 2:1 clay mineral type (i.e., muscovite) strongly contributes to the sorption of zinc ions. Furthermore, the use of adsorptive capacities of kaolinite and bentonite (as a representative for the 1:1 and 2:1 clay minerals) based on the literature overestimated the overall sorption capacity of the natural soil by 3.5 times, suggesting that individual mineral sorption capacities cannot be directly used to estimate capacities for natural soils with a mixture of clay minerals.

The results of this work demonstrate the importance of soil clay mineralogy in the fate of pollutants such as metals. These results, therefore, have significant implications for the design and layout of stormwater infiltration systems. We suggest that the potential sorption characteristics of the underlying soil, their purity and composition should be in the design process to minimize the risk of contamination of water resources. The experiment also has implications for other pollutant remediation approaches relying on clay soil sorbing heavy metals or other pollutants from flowing water.
3.6 Bibliography


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Chapter 4 – The transport of reactive solutes in porous media
Chapter 4 – The transport of reactive solutes in porous media

4.1 Chapter perspective

In Chapter 4, particular attention is paid to the laboratory column experiments to study the sorption process of zinc ions in the saturated medium. The sorbed zinc mass is calculated for each breakthrough curve using the trapeze method and applied in the isotherm sorption models to re-quantify the sorption coefficients. The obtained sorption parameters from both batch and column experiments are employed in the HYDRUS-1D to compare the performances of the equilibrium and non-equilibrium models to describe the sorption behavior of zinc in the natural soil. Importantly, sensitivity analysis for the main transport and reaction parameters is conducted to investigate their influences on the zinc transport process. The results of this chapter demonstrate the extent of reactive solute attenuation as a function of the amount of clay content and the type of its mineralogy in a more realistic dynamic condition.
4.2 Introduction

Although infiltration systems are used globally to manage the volume, rate, and quality of stormwater, there remains much uncertainty about their impact on the local environment. Pollution of underlying soil and groundwater with heavy metals just below and near the infiltration systems is a potential threat to the environment (Durin et al., 2007). In the long term, zinc has been shown to be transported through the deeper soil layers below an artificial infiltration site (Mason et al., 1999). In another study, the probability of zinc transmission to groundwater was determined to be higher than for other heavy metals (Alloway, 2013). Zinc that has leached into the groundwater and soil can subsequently be mobilized through the subsurface with potentially major impacts on aquatic ecosystems where the groundwater contributes to streamflows (Roy & Bickerton, 2012). The fate of zinc from stormwater infiltration systems thus remains a fundamental question about their long-term environmental benefit.

Sorption is one of the most important processes that governs the transport of metals in soil (Hinz & Selim, 1994; Liu et al., 2006). Considering the heterogeneous nature of soil sorption sites, metal sorption is mostly assumed to be non-linear if metal concentrations are high (Tsang et al., 2007). Likewise, the fate and transport of many solutes such as metals in soils are sensitive to sorption non-linearities (Serrano, 2003). Non-linearity in sorption sites may cause solutes to arrive at a monitoring point faster or slower than predicted by linear models. Bolt (1982) investigated the transport of metals in soils that is subject to non-linear equilibrium and non-equilibrium sorption.
Batch experiments have extensively been applied to explore the sorption of metals in soils under equilibrium conditions (Kaya & Ören, 2005; Mellah & Chegrouche, 1997; Veli & Alyüz, 2007). A major benefit of batch experiments is that they allow significant simplification in the conceptual and mathematical framework of a solute transport model (Kookana et al., 1994). The applicability of batch experiments in studying solute transport, however, has been questioned because the local equilibrium generally observed in batch studies depends on several factors, including a high solution to soil ratio, shaking, as well as centrifugation, which are not representative of transport conditions. There is evidence that the hydrodynamic parameters in solute transport processes cannot be obtained in this way (Gaber et al., 1995; Mao & Ren, 2004; Pang & Close, 1999).

In contrast, column experiments are performed under a continuous flow system to more closely emulate the sorption behavior of metals in field conditions and to provide more sorption parameters that are not available from batch studies (Goel et al., 2005). Non-linear sorption reactions in a heterogeneous soil may have an impact on the shape of breakthrough curves (hereafter BTCs; the variations of concentrations versus time), causing long back tails or sharp front ends. For a laboratory column packed with soil, the measured BTCs demonstrated an early arrival and extensive tailing (Berkowitz et al., 2006). Pang et al. (2002) observed that the BTCs of Cd, Zn, and Pb in alluvial gravel columns showed extensive tailings, suggesting that chemical non-equilibrium sorption conditions occurred in the columns. A large number of computer models (e.g., CXTFIT, HYDRUS-1D, MARCO, SIMULAT, VADOFT) with various degrees of complexity and dimensionality have been applied to simulate this
type of non-equilibrium solute transport. Among them, HYDRUS-1D has been widely used to describe BTCs and determine the principal processes involved in solute transport in the subsurface (Šimůnek et al., 1998).

The overall aim of this research was to enhance the understanding of contaminant transport in the subsurface and explore the best possible approach for accurate prediction of contaminant fate and transport. This objective was achieved through a series of steps; 1) experimentally quantify the sorption parameters of zinc during its transport through natural soils using two approaches (i.e., batch and column experiments), 2) evaluate the significance of the non-equilibrium processes in the zinc transport, and 3) analyze the sensitivity of the simulation results to the main transport and reaction parameters. We performed batch and column tests to understand processes governing the leaching of metals (exemplified by Zn) from the soil. The BTCs were then modeled using the HYDRUS-1D software with non-linear isotherm parameters derived from batch and column experiments. Information obtained from this study can be used to describe the transport of metals into the subsurface and thus better design the size and location of infiltration systems.

4.3 Materials and methods

4.3.1 The preparation of field soil samples and reagents

The natural soil was collected from a peri-urban catchment in Melbourne, Australia, where a large stormwater infiltration basin has been the subject of previous research (Bonneau et al., 2018). It was initially oven-dried, ground and mechanically sieved.
We measured the particle size distribution (consisting of 24.46% clay) using a Beckman-Coulter LS 13 320 Laser Particle Size Analyzer. The mean and median particle diameters were 93 and 36 µm. The soil was thus categorized as sandy clay loam. The mineralogical composition was determined by an X-ray diffractometer (Warren, 1990), indicating that the soil is composed of quartz-kaolinite-muscovite minerals. We also estimated the average saturated hydraulic conductivity as being in the order of $10^{-8}$ m s$^{-1}$ using the falling head test (ASTM D5084-03). The mean porosity was 0.41 cm$^3$ cm$^{-3}$ and cationic exchange capacity 13 meq/100 g (Rayment & Lyons, 2011). We sent the soil to a NATA-accredited laboratory to determine the legacy amount of zinc accumulated. The soil was almost free of zinc (20 mg kg$^{-1}$). Synthetic zinc solutions were prepared by diluting stock solutions containing 100 mg L$^{-1}$ of zinc with deionized water. We prepared the stock solutions by dissolving 0.444 g of ZnSO$_4$·7H$_2$O in one liter deionized water. We then measured the zinc concentrations using an inductively coupled plasma-optical emission spectrometer (ICP-OES) (Optima 4400, Perkin Elmer, USA).

4.3.2 Batch assays to determine the isotherm sorption parameters

One of the essential parameters needed to simulate the leachability of zinc is the sorption isotherm coefficients (Fetter, 2000). A sorption isotherm is a curve explaining the phenomenon governing the release or mobility of a substance from the liquid phase to a solid phase at a constant temperature and pH (Limousin et al., 2007). We quantified these coefficients for the natural soil using batch experiments. Two batch sets were initially conducted to determine the optimum soil dose (5 g L$^{-1}$) and the equilibrium time (5 min). In another experiment, aliquots of 0.25 g soil were agitated
with 50 mL zinc sulfate heptahydrate (ZnSO₄·7H₂O) containing 5, 10, 15, 20, 40, 60, 80 and 100 mg L⁻¹ zinc for 5 min at room temperature (22 ± 2 ºC) and a stirring speed at 250 rpm. The solutions were filtered through 0.45 µm syringe filters and then analyzed using ICP-OES to determine zinc concentrations. Each batch experiment was done in triplicate with an instrumental error less than 4%. The amount of sorbed zinc per unit mass of the natural soil at equilibrium time, qₑ, (mg g⁻¹) was calculated as follows:

\[
qₑ = \frac{(C₀ - Cₑ)V}{m} \quad (4.1)
\]

where \(C₀\) and \(Cₑ\) (mg L⁻¹) are aqueous zinc concentrations at the initial and equilibrium time, respectively, \(V\) is the volume of the aqueous solution (L) and \(M\) is the mass of the soil layer material (g).

Based on the batch sorption experimental results, the zinc sorption isotherms on the natural soil were analyzed using two sorption models, the Freundlich, and Langmuir models (Twarakavi et al., 2008). The sorption process was described based on the regression correlation coefficient (R²) of the plots, and the residual plots. The general form of the sorption behavior can be described by the following equation:

\[
S = \frac{K_d C^β}{1 + \eta C^β} \quad (4.2)
\]

where \(S\) is the concentration of zinc sorbed into the solid phase at equilibrium (mg g⁻¹), \(C\) is the liquid phase resident concentration of zinc at equilibrium (mg L⁻¹), and \(K_d\), \(β\) and \(η\) are the soil-water distribution coefficient, the Freundlich exponent and the Langmuir coefficient, respectively. The last three parameters referred to as the “solute reaction parameters” that can be computed either from batch or column
experiments. When $\beta = 1$, Eq. (4.2) becomes a Langmuir isotherm, and when $\eta = 0$, the equation becomes a Freundlich isotherm.

4.3.3 Column experiments

4.3.3.1 Experimental setup

When the affinity of the metal to the soil is high, the retardation factor can be very high and the resulting duration of column experiments impractically long (Miretzky et al., 2006). In order to keep experiments to a reasonable duration, we used small columns. We performed column experiments in plastic tubes with a length of 10 cm and an internal diameter of 1.2 cm (FIGURE 4.1). The columns were packed with the soil and compacted by gently tapping to reach a field soil bulk density of 1.55 g cm$^{-3}$. The bulk density of the soil was estimated by ASTM D7263-09 using undisturbed soil taken from the field. The soil mass used for each column was about 10.5 g. We used 2 cm of glass wool at each boundary of the columns to ensure uniform water distribution. A peristaltic pump (Precision Pump Co., Baoding, China) ensured the upward flow of deionized water, chloride as a conservative tracer and zinc solutions. We injected the solutions from the bottom of the columns to avoid preferential flow pathways. Despite this, it was yet likely to observe preferential flow paths inside the soil core due to the very high head pressure exerted to the inlet of the columns as a result of small dimensions used. To evaluate this, we packed a separate column with the soil using a red dye tracer (rhodamine).
4.3.3.2 Chloride tracer and zinc sorption experiments

We conducted conservative tracer experiments (Grisak & Pickens, 1981) to determine the longitudinal dispersivity ($\alpha_L$) and hydrodynamic dispersion coefficient ($D_L$) of the field soil. For the start, deionized water was injected at a flow rate of 5 $\mu$L min$^{-1}$ for 12 h to fully saturate the soil column. A conservative tracer, chloride (Cl$^-$), with a concentration of 200 mg L$^{-1}$ and a flow rate of 50 $\mu$L min$^{-1}$ was then pumped into the column using up-flow mode. These experiments were stopped when the measured chloride concentrations at the outlet of the column equaled that being injected into the
column. We measured the influent and effluent chloride concentrations using IC3-1100 (Dionex). The measured data were then plotted as BTCs. At the end of the experiment, the soil was leached for 24 h with deionized water to ensure that there was no residual salinity in the column.

Once the columns were completely washed out, zinc sorption experiments were conducted and zinc concentrations in the effluent were measured through the analysis of 5 mL aqueous solutions sampled over time. Six separate columns were packed with the soil to investigate the effect of influent zinc concentration on its sorption capacity. For this, the influent aqueous concentrations were fixed at 10, 20, 40, 60, 80, and 100 mg L\(^{-1}\). The experiments were stopped when the effluent zinc concentration reached that of the solution entering the column, which indicates that all sorption sites were fully saturated. The decision was made not to employ replication of the experiments due to the very low hydraulic conductivity of the soil and thus time constraints. According to Eq. (4.3), the area under the curve \((1 - C/C_0)\) until the bed saturation is proportional to \(q_s\). The sorbed zinc mass, \(q_s\) (mg g\(^{-1}\)) was calculated as following (De Freitas et al., 2017):

\[
q_s = \frac{C_0 Q}{1000 M} \int_0^\infty \left(1 - \frac{C}{C_0}\right) dt
\]

in which \(C_0\) and \(C\) are the influent and effluent zinc concentrations (mg L\(^{-1}\)), \(Q\) is the feed solution flow rate (mL min\(^{-1}\)), and \(M\) is the soil mass used in the column (g).

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4.3.4 HYDRUS-1D model description

We used the finite element software package HYDRUS-1D to numerically solve the transport equations for the reactive solute transport process in the soil column (Šimůnek & van Genuchten, 2008). Reactive solutes dissolved in groundwater are transported in the soil through processes called advection, dispersion, and reaction (sorption, ion exchange, etc.). Advection will cause a reactive solute to carry along with the flowing groundwater. Dispersion also known as hydrodynamic dispersion is the mutual effects of diffusion and longitudinal dispersion. Diffusion will cause a reactive solute to spread out with moving from areas of higher to lower concentration even in the absence of groundwater flow while longitudinal dispersion will cause a solute-containing groundwater to move in the direction of the flow path (Fetter, 2000). The governing solute transport equations are described briefly below.

4.3.4.1 Equilibrium transport model

The general one-dimensional advection-dispersion-reaction equation in saturated, homogeneous porous media under steady-state flow condition can be expressed by Miller and Weber (1984):

\[
R \frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} - q \frac{\partial C}{\partial x}
\]  

(4.4)

in which \( R \) is the retardation factor, \( C \) (M L\(^{-3}\)) is the solute concentration in the liquid phase, \( x \) (L) is length, \( t \) (T) is time, \( D_L \) (L\(^2\) T\(^{-1}\)) is the hydrodynamic dispersion coefficient, \( q \) (L T\(^{-1}\)) is Darcy’s velocity, and \( \theta_s \) (L\(^3\) L\(^{-3}\)) is the porosity for saturated
media. The retardation factor and the hydrodynamic dispersion coefficient can be also expressed as below (Šimůnek et al., 2008):

\[
R = 1 + \frac{B_d}{\theta_s} S'(C) \quad (4.5)
\]

\[
D_L = \frac{q}{\theta_s} \alpha_L \quad (4.6)
\]

where \(B_d\) (M L\(^{-3}\)) is the soil bulk density, \(S'(C)\) is the first derivative of a solute concentration sorbed in the solid phase (M M\(^{-1}\)), and \(\alpha_L\) (L) is the longitudinal dispersivity. The retardation factor is equal to 1 for conservative tracers such as chloride.

4.3.4.2 Chemical non-equilibrium models - CNEMs

Numerous studies have provided evidence that chemical non-equilibrium sorption processes help to better simulate solute transport in a heterogeneous porous medium (Hou et al., 2018; Jellali et al., 2010; Kookana et al., 1994; Pang & Close, 1999; Van Genuchten & Wagenet, 1989). The interaction between sorbate and sorbent are relatively slow in comparison with the required residence time in such non-equilibrium transport models. As a result, the sorbate takes a long time to reach equilibrium during the sorption process. The 2-site CNEM splits the solid phase into two fractions, one that achieves equilibrium instantaneously (type-1 sites) and the other one in which time-dependent kinetic interaction between solid and liquid phase occurs (type-2 sites) (Ptacek & Gillham, 1992). The total sorption on both fractions, \(S\) (M M\(^{-1}\)), is given by (Simunek et al., 2005):

\[
S = S^e + S^k \quad (4.7)
\]
where $S^e$ (M M$^{-1}$) on type-1 sites is assumed to be instantaneous, while $S^k$ (M M$^{-1}$) on the remaining type-2 sites is considered to be a first-order kinetic process. At equilibrium, sorption on type-1 sites is described by the general equation of the form:

$$S^e = f_e \frac{K_d C^\beta}{1 + \eta C^\beta}$$  \hspace{1cm} (4.8)

whereas sorption on sites type-2 is expressed by a first-order kinetic equation as:

$$\frac{\partial S^k}{\partial t} = \omega \left[ (1-f_e) \frac{K_d C^\beta}{1 + \eta C^\beta} - S^k \right]$$  \hspace{1cm} (4.9)

where $f_e$ (-) is a fraction of sorption sites which is at equilibrium with the liquid phase, $K_d$ (L$^3$ M$^{-1}$) is the sorption isotherm coefficient, and $\omega$ (T$^{-1}$) is the first-order rate coefficient. Assuming solute degradation is negligible, the solute transport equation for the 2-site CNEM is given by:

$$R \frac{\partial C}{\partial t} + \frac{B_d}{\theta_s} \frac{\partial (S^e + S^k)}{\partial t} = D_l \frac{\partial^2 C}{\partial x^2} \frac{q}{\theta_s} \frac{\partial C}{\partial x}$$  \hspace{1cm} (4.10)

The 2-site model reduces to the 1-site kinetic model when $f_e = 0.0$.

### 4.3.5 Model assumptions – boundary and initial conditions

The transport of the conservative tracer, chloride, and zinc in the soil columns were simulated using the assumption that the porosity of the saturated soil is constant along the column ($\theta_s = 0.41$ cm$^3$ cm$^{-3}$). For water flow, the columns were subjected at both upper and lower boundaries to a constant pressure head. For solute transport simulation, the concentration flux boundary condition was applied to the upper
boundary, and zero concentration gradient was set to the lower boundary. The soil packed in the columns was assumed to be free of zinc.

4.3.6 Initial values of soil hydraulic and solute reaction parameters

Soil hydraulic parameters include the residual soil porosity ($\theta_r$), saturated soil porosity ($\theta_s$), the soil water retention parameters ($\alpha$, and $n$), saturated hydraulic conductivity ($K_s$) and tortuosity ($I$). Here, $\theta_s$ and $K_s$ were experimentally determined as 0.41 cm$^3$ cm$^{-3}$ and 9×10$^{-3}$ cm h$^{-1}$, respectively for the soil. The other parameters $\theta_r$, $\alpha$, $n$, and $I$ were also determined from the sand, silt, and clay distribution, and bulk density using neural network predictions via the Rosetta method (summarized in Table 1; Simunek et al., 2005). The average longitudinal dispersivity $\alpha_L$ was estimated from the chloride BTC data, and then the inverse parameter estimation method was used to calibrate this parameter. We also used the chemical non-equilibrium model to estimate the sorption parameters ($K_d$ and $\eta$) and non-equilibrium parameters ($f_e$ and $\omega$) for the transport of zinc. The column-determined sorption coefficients were then compared with the coefficients obtained from batch tests.

TABLE 4.1: The hydraulic parameters of the soil for the experimental columns: $\alpha$ is the inverse of the air-entry value, and $n$ is the pore-size distribution index.

<table>
<thead>
<tr>
<th>Particle size distribution</th>
<th>Bulk density (g cm$^{-3}$)</th>
<th>Soil texture (International)</th>
<th>$\theta_r$ (cm$^3$ cm$^{-3}$)</th>
<th>$\alpha$ (cm$^{-1}$)</th>
<th>$n$</th>
<th>$I$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand (%)</td>
<td>Silt (%)</td>
<td>Clay (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>56.38</td>
<td>19.16</td>
<td>24.46</td>
<td>1.55</td>
<td>Sandy clay loam</td>
<td>0.0636</td>
<td>0.0214</td>
</tr>
</tbody>
</table>
4.3.7 Optimization algorithm

We used the Levenberg-Marquardt non-linear parameter optimization method (Marquardt, 1963) in the inverse mode in HYDRUS-1D to solve the governing equations for zinc transport through the soil. This procedure allows zinc transport parameters to be estimated either sequentially or simultaneously from observed concentrations by numerical inversion of the advection-dispersion equation. The objective function $\phi$ to be minimized during the parameter estimation is defined as (Šimůnek et al., 1998):

$$\phi(a) = \sum_{j=1}^{n_b} w_j \left[ (O_j(t_j) - P_j(t_j,a)) \right]^2$$

(4.11)

where $n_b$ is the total number of observations in a particular measurement set; $j$ is the ordinal number of time steps; $O_j(t_j)$ are specific observations at time $t_j$; $P_j(t_j,a)$ are the corresponding model predictions for the vector ‘$a$’ of the optimized parameters; and $w_j$ is a weighting factor associated with a particular data point assumed to be 1.0 in this work.

4.3.8 Simulation and Sensitivity of zinc transport and reaction parameters

The root mean squared error (RMSE), and the correlation coefficient ($r^2$) were calculated to reflect the appropriateness of curve fitting. We conducted a systematic sensitivity analysis following the equation presented by Lu et al. (1999) to evaluate the impacts of parameter uncertainty for the model results. One particular parameter was
varied from its calibrated reference value in each run to observe its isolated effect on simulation results while keeping all other parameters constant.

\[ X_k = \frac{\frac{\partial y}{\partial a_k}}{\frac{\Delta a_k}{a_k}} \sim \frac{[y(a_k+\Delta a_k)-y(a_k)]}{y(a_k)} \]  

(4.12)

where \( X_k \) is the sensitivity coefficient of the model-dependent variable \( y \) with respect to the \( k \)th parameter; and \( y(a_k) \) and \( y(a_k+\Delta a_k) \) are the values of the dependent variable obtained for the base case and the perturbed-parameter case, respectively. We used the calibrated model as the base case, and the parameters were perturbed to 20% over the base case.

4.4 Results and discussion

4.4.1 Preferential flow paths

The flow pathways of red dye were visible after the wetting of the surface to 1 cm column depth. The soil core was dissected to check whether the red dye flowed uniformly through the soil (FIGURE 4.2). We observed a uniform movement pattern of the red dye through the soil, indicating that no preferential flow paths were present in the column.
4.4.2 Chloride BTC

The chloride median BTC was almost symmetrical (FIGURE 4.3), showing that equilibrium transport occurred in the columns and that immobile water was not essential for transport under the hydraulic conditions employed (Hou et al., 2018). The longitudinal dispersivity ($\alpha_L$) of the soil was estimated as 0.28 cm and inversely calibrated using an equilibrium model in HYDRUS-1D (Šimůnek et al., 2008). The comparison between the experimental data of chloride median BTC and predicted relative concentration also indicated that there were no significant differences in the dispersivity values (TABLE 4.2). Thus, the calibrated value of the dispersivity was used in the subsequent modeling of zinc BTCs. At the column scale, the longitudinal
dispersivity is correlated with the mean grain size diameter and soil heterogeneity (Jellali et al., 2003). The small value of $\alpha_L$ shows that the soil was homogeneously packed.

TABLE 4.2: Transport parameters obtained from the chloride tracer experiments using the equilibrium model in HYDRUS-1D (q: Darcy’s velocity; $D_L$: dispersion coefficient; $\alpha_L$: longitudinal dispersivity; $\theta_s$: saturated water content; $r^2$: correlation coefficient for the regression of observed versus fitted concentrations; a: calibrated parameters; calibrated values are given in parenthesis).

<table>
<thead>
<tr>
<th>q (cm h$^{-1}$)</th>
<th>$D_L$ (cm$^2$ h$^{-1}$)</th>
<th>$\alpha_L$ (cm$^a$)</th>
<th>$\theta_s$ (cm$^3$ cm$^{-3}$)</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>1.43</td>
<td>0.28 (0.31)</td>
<td>0.41</td>
<td>0.99</td>
</tr>
</tbody>
</table>

FIGURE 4.3: Fitted and observed median BTC of the conservative tracer (chloride) experiments (chloride concentration: 200 mg L$^{-1}$, the temperature of the influent solution: 22 ± 2 °C, flow rate: 50 $\mu$L min$^{-1}$).
4.4.3 Zinc transport

The Darcy’s velocity, \( q \), was varied in the range of \( 1.98 - 2.52 \text{ cm h}^{-1} \). This variation could be due to variations in column soil packing, which differs from one experiment to another and/or due to the presence of the glass wool at the column boundaries (Jellali et al., 2010). The amount of zinc sorbed onto the soil, \( q_s \), calculated by Eq. (4.3) gradually increased from \( 2.6 \) to \( 3.2 \text{ mg g}^{-1} \) with increasing influent zinc concentrations (TABLE 4.3). This is because the binding sites became more rapidly saturated when the influent zinc concentration increases (Chowdhury et al., 2012). For instance, 400 pore volumes were required to reach breakthrough \((C/C_0 = 0.05)\) for \( C_0 = 10 \text{ mg L}^{-1} \), while only half of this (200 pore volumes) was needed for \( C_0 = 20 \text{ mg L}^{-1} \) (FIGURE 4.4).

![Figure 4.4: Zinc relative concentration versus pore volume for different influent concentrations (temperature of the influent solutions: \( 22 \pm 2 \text{ ºC}, \) flow rate: \( 50 \text{ µL min}^{-1} \)).](image-url)
TABLE 4.3: Physico-chemical and sorption parameters of the natural soil used for zinc transport study (L: soil length; q: Darcy’s velocity; B_d: soil bulk density; θ_s: soil porosity in saturated media; R_area: the area under the curve (1-C/C_0) estimated from Trapezoidal Rule Integration; q_s: the amount of sorbed zinc).

<table>
<thead>
<tr>
<th>Zn(II) (mg L⁻¹)</th>
<th>L (cm)</th>
<th>q (cm h⁻¹)</th>
<th>B_d (g cm⁻³)</th>
<th>θ_s (cm³ cm⁻³)</th>
<th>R_area</th>
<th>q_s (mg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.78</td>
<td>6.0</td>
<td>1.98</td>
<td>1.52</td>
<td>0.426</td>
<td>915.48</td>
<td>2.611</td>
</tr>
<tr>
<td>21.87</td>
<td>6.0</td>
<td>2.52</td>
<td>1.47</td>
<td>0.445</td>
<td>459.74</td>
<td>2.698</td>
</tr>
<tr>
<td>41.83</td>
<td>6.0</td>
<td>2.43</td>
<td>1.53</td>
<td>0.422</td>
<td>259.54</td>
<td>2.871</td>
</tr>
<tr>
<td>62.12</td>
<td>6.0</td>
<td>2.24</td>
<td>1.49</td>
<td>0.438</td>
<td>176.05</td>
<td>2.892</td>
</tr>
<tr>
<td>82.63</td>
<td>6.0</td>
<td>2.31</td>
<td>1.49</td>
<td>0.438</td>
<td>139.99</td>
<td>3.059</td>
</tr>
<tr>
<td>102.67</td>
<td>6.0</td>
<td>2.02</td>
<td>1.51</td>
<td>0.430</td>
<td>95.21</td>
<td>3.201</td>
</tr>
</tbody>
</table>

4.4.4 Simulation of zinc transport in HYDRUS-1D

4.4.4.1 Prediction of zinc BTCs using batch-determined sorption data

As a wide range of zinc concentrations was used, we expected to see the impact of non-linearity of zinc sorption onto the soil. While the sorption data for the soil fitted well to both isotherm models, the Freundlich model fitted slightly better than the Langmuir model (FIGURE 4.5). This is in agreement with the results obtained from residual plots, indicating more systematic errors for the Langmuir model into the soil. The sorption parameters, K_d and β, determined from the intercept and slope of the straight line of the Freundlich model were 0.87 mg⁻¹⁻¹ β L⁻¹ g⁻¹ and 0.25 (-), respectively. For the Langmuir model, K_d and η were estimated to 0.46 L g⁻¹ and 0.17 L mg⁻¹. The high K_d values from batch tests are consistent with the grain size distribution and clay mineralogy of the soil used, which has clay particles of muscovite type, playing a pivotal role for zinc sorption (Buss et al., 2004).
FIGURE 4.5: Linearized forms of isotherms and residual plots for zinc sorption. Soil dose: 0.25g/50mL; and agitation time: 5 min.

4.4.4.2 Application of non-linear isotherms in HYDRUS-1D using equilibrium model

Although the Freundlich model showed a better agreement with the experimental data (see details in Chapter 3), the curve-fitted BTCs using the Langmuir isotherm explained the experimental results better than the Freundlich isotherm. Thus, the equilibrium model in HYDRUS-1D employed the Langmuir parameters ($K_d$ and $\eta$) derived from batch tests and the calibrated dispersivity ($\alpha$) value from the chloride tracer test (FIGURE 4.6(a-f)). The zinc BTCs in equilibrium became sharp due to the non-linearity of the isotherm used (Kookana et al., 1994). All simulated BTCs appeared to lag behind the experimental data at their initial stages. The predicted zinc BTCs
using batch sorption parameters were unable to describe zinc transport through the soil under equilibrium conditions, implying that the residence time in the soil was not long enough to reach equilibrium.

We also compared the batch-determined sorption coefficients with the column-determined sorption coefficients. The $K_d$ and $\eta$ values obtained from fitting the column experimental results were greater than those derived from the batch tests (TABLE 4.4). The differences in the estimated values from batch and column tests might be either due to a difference in the solution ratios in the system or flow schemes (Chotpantarat et al., 2011). The asymmetrical shape of the zinc BTCs (FIGURE 4.6 (a-f)), may be due to the existence of non-equilibrium conditions in the system.

<table>
<thead>
<tr>
<th>Laboratory experiment type</th>
<th>Freundlich model</th>
<th>Langmuir model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_d$ (mg L$^{-1}$ g$^{-1}$)</td>
<td>$\beta$ (-)</td>
</tr>
<tr>
<td>Batch study</td>
<td>0.87</td>
<td>0.25</td>
</tr>
<tr>
<td>Column study</td>
<td>2.12</td>
<td>0.08</td>
</tr>
</tbody>
</table>

4.4.4.3 Application of chemical non-equilibrium model (CNEM)

The 2-site CNEM parameters, the first-order rate coefficient ($\omega$) and the fraction of sorption sites in equilibrium ($f_e$) were initially inversely calibrated to fit the experimental data. However, the results showed a very small value of $f_e$ (~ 0.001) for the zinc transport, thereby reducing to the 1-site CNEM, considering ($f_e = 0.0$). The 1-site CNEM described the early tailing effect of the asymmetrical portion of zinc BTCs better than the equilibrium model (FIGURE 4.6(a-f)). Due to the heterogeneous nature
of the natural soil, sorption to some surfaces may not be in equilibrium. This reflects that zinc sorption is a kinetic process, described by a first-order rate equation (Van Genuchten & Cleary, 1979). The $\omega$ values for the soil increased (0.015-0.056 h$^{-1}$) with increasing initial concentrations (10-100 mg L$^{-1}$). Higher values of the first-order rate, $\omega$, at higher concentrations represented a relatively faster equilibration process between zinc in the liquid and solid phases, and vice versa (Šimůnek et al., 2008).

In line with the analysis, smaller RMSE and higher $r^2$ values (TABLE 4.5) estimated for the 1-site CNEM provided better agreement with the experimental results than those of the equilibrium model. It is clear that the 1-site CNEM can predict the experimental BTCs without needing to fit the batch sorption parameters, $K_d$ and $\eta$.

TABLE 4.5: Values of root mean squared error (RMSE), and the correlation coefficient ($r^2$) as the indicators of simulation accuracy for the equilibrium model and the 1-site chemical non-equilibrium model.

<table>
<thead>
<tr>
<th>Zn(II) (mg L$^{-1}$)</th>
<th>Equilibrium model using batch sorption data</th>
<th>1-site CNEM using column sorption data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RMSE</td>
<td>$r^2$</td>
</tr>
<tr>
<td>10.78</td>
<td>1.27E-06</td>
<td>0.924</td>
</tr>
<tr>
<td>21.87</td>
<td>2.73E-06</td>
<td>0.917</td>
</tr>
<tr>
<td>41.83</td>
<td>6.09E-06</td>
<td>0.909</td>
</tr>
<tr>
<td>62.12</td>
<td>1.10E-05</td>
<td>0.893</td>
</tr>
<tr>
<td>82.63</td>
<td>1.43E-05</td>
<td>0.888</td>
</tr>
<tr>
<td>102.67</td>
<td>1.76E-05</td>
<td>0.868</td>
</tr>
</tbody>
</table>
FIGURE 4.6: Fitted and observed BTCs of zinc transport experiments at a temperature of 22 ± 2 ºC and a flow rate of 50 μL min⁻¹. (a) 100 mg L⁻¹, (b) 80 mg L⁻¹, (c) 60 mg L⁻¹, (d) 40 mg L⁻¹, (e) 20 mg L⁻¹, (f) 10 mg L⁻¹.
4.4.5 Simulation and Sensitivity of zinc transport and reaction parameters

In the simulation of zinc transport, the main parameters affecting the results were $K_d$, $\eta$, and $\alpha_L$ in the equilibrium model; and $K_d$, $\eta$, $\alpha_L$, and $\omega$ in the 1-site CNEM. The simulation sensitivity results for a zinc initial concentration of 10.78 mg L$^{-1}$ were quantified through the sensitivity coefficient using Eq. (4.12).

The zinc BTCs for different $K_d$ values using both models indicated a noticeable hysteresis, indicating that the zinc BTC was lagged with increasing $K_d$. At any specific time, the zinc relative concentration decreased as $K_d$ increased, showing an increase in the amount of the zinc sorbed due to a decrease in the rate of zinc sorption (Hou et al., 2018). The sensitivity of zinc BTCs to changes in the $\eta$ values was in the other direction (FIGURE 4.7 and FIGURE 4.8). Increasing $\eta$ resulted in a leftward shift of the BTC. This means that the zinc relative concentration increased as $\eta$ increased at a given time, leading to a decrease of the zinc sorbed to the soil.

The lower the value of $\alpha_L$, the steeper the zinc BTC as expected, and therefore the greater sorption rate due to a decrease in the diffusion rate. As a result, the time required to reach equilibration between the solution and solid phases was reduced. However, the influence of $\alpha_L$ on the zinc BTC slope was negligible. For the 1-site CNEM, the higher the value of $\omega$, the steeper the zinc BTC, the higher the zinc sorption rate in the soil and thus the shorter the time for zinc to reach equilibrium (FIGURE 4.8). The effects of $\omega$ on zinc transport was negligible. The simulated results for zinc transport at a given time (e.g. $T = 720$ h) were selected to show the impacts of different sorption and reaction parameters on the BTCs (TABLE 4.6). Analysis of $X_k$ values
indicated that the soil-water distribution coefficient ($K_d$), followed by the Langmuir coefficient ($\eta$), play pivotal roles in zinc transport, both in the equilibrium model or 1-site CNEM. For the two models, the sensitivity of the 1-site CNEM to $K_d$ and $\eta$ was lower than that of the equilibrium model. The results were least sensitive to changes in $\alpha_L$ for the equilibrium model and to both $\alpha_L$ and $\omega$ for the 1-site CNEM.
TABLE 4.6: Results of parameter sensitivity analyses for zinc transport into the soil. Initial concentration: 10.78 mg L⁻¹; Base case values - $\alpha_L$: 0.31 cm; $\omega$: 0.015 h⁻¹; C/C₀: Zn(II) outlet / Zn(II) inlet; $X_k$: sensitivity coefficient.

<table>
<thead>
<tr>
<th>Parameter Variation</th>
<th>Equilibrium model using batch sorption parameters</th>
<th>1-site CNEM using column sorption parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_d$ (L g⁻¹)</td>
<td>$\eta$ (L mg⁻¹)</td>
</tr>
<tr>
<td>%</td>
<td>C/C₀</td>
<td>$X_k$</td>
</tr>
<tr>
<td>-20</td>
<td>0.99</td>
<td>-1.26</td>
</tr>
<tr>
<td>0</td>
<td>0.79</td>
<td>-</td>
</tr>
<tr>
<td>+20</td>
<td>0.02</td>
<td>-4.87</td>
</tr>
</tbody>
</table>

FIGURE 4.7: Influence of changes in (a) the soil–water distribution coefficient ($K_d$) (b) the Langmuir coefficient ($\eta$) (c) the longitudinal dispersivity ($\alpha_L$) on zinc transport (initial concentration: 10.78 mg L⁻¹) using the equilibrium model. $K_d$ and $\eta$ values derived from batch experiments.
FIGURE 4.8: Influence of changes in (a) the soil–water distribution coefficient ($K_d$) (b) the Langmuir coefficient ($\eta$) (c) the longitudinal dispersivity ($\alpha_L$) and (d) first-order rate coefficient ($\omega$) on zinc transport (initial concentration: 10.78 mg L$^{-1}$) using the 1-site CNEM. $K_d$ and $\eta$ values derived from column experiments.
4.5 Conclusions

4.5.1 Summary

We undertook laboratory batch and column experiments to explore the amount of zinc sorption onto the soil and determine the dispersion coefficient for a non-reactive tracer using chloride. The data collected in the laboratory were then used to set up and parametrize the HYDRUS-1D model using Advection-Dispersion-Reaction Equation (ADRE). From the batch sorption data, the transport of zinc could be ascribed to non-linear sorption on the soil. The use of the batch-determined sorption parameters, however, did not adequately predict zinc transport when the residence time in the soil is not sufficiently long. Alternatively, we found that the sorption parameters derived from column experiments performed better in approximating the non-equilibrium sorption behavior of zinc during its transport in real systems. The asymmetrical shape of the zinc BTCs with long tailing may be attributed to the chemical non-equilibrium conditions during zinc transport through the soil. We thus concluded that heavy metal transport can be considered as non-linear and non-equilibrium across a wide range of metal concentrations.

4.5.2 Current limitations and recommendations for future research

This research was an attempt to assess the efficacy of column tests versus batch tests for understanding solute movement through soils. Column tests provide a more realistic analogue of conditions in the field, but there were some experimental limitations. The measured hydraulic conductivity of soil was found to be very low, leading to a long duration of tests. To overcome this issue, the options were either to
increase the flow rate or decrease the size of columns. We used very small columns without replication in order to finish the multiple experiments within a reasonable time frame. However, using small columns could potentially increase the head pressure exerted from the peristaltic pump to the inlet of the columns. Therefore, we used a very low flow rate to avoid the generation of preferential flow paths in the columns. It is clear that the experiments conducted in this research are site-specific (based on the soil type used) and the results will vary somewhat with experimental conditions. However, we believe that the complementarity of batch and column experiments for assessing solute transport in soils will also be seen elsewhere. Our approach could potentially be expanded, using longer columns with more flow rates and multiple replicates. In addition, using different soils with varied clay content would enhance further understanding of heavy metal transport in the subsurface.

4.5.3 Recommendation for infiltration-based stormwater management

Given the widespread use of infiltration systems as a stormwater management strategy, recent research showing that complete pollutant removal is unlikely in these systems (e.g., Li et al., 2018) and thus should be of concern to stormwater managers. Stormwater pollutants (e.g., heavy metals) may travel with the plume of infiltrated stormwater, percolating through the filtration media and being introduced into the surrounding soils. If the local soil itself (e.g., the soil lacking clay content) is unable to act as an extended filter to capture the pollutants leaching from the filtration media, safety nets must be considered in designing biofilters of infiltration systems. Our current lack of understanding to accurately quantify pollutant sorption during its transport through the soil makes it difficult to optimize the benefits of stormwater
infiltration in protecting and restoring urban streams. We recommend that during the
design of stormwater infiltration systems, managers assess the heterogeneity of the
surrounding soils between the infiltration system and receiving waters to estimate the
extent to which metals and other pollutants will be treated and the extent to which they may percolate back into receiving waters.
4.6 Bibliography

Alloway, B. J. (2013). Sources of heavy metals and metalloids in soils *Heavy metals in soils* (pp. 11-50): Springer.


Chapter 5 – Transport of reactive solutes through the urban karst
Chapter 5 – Transport of reactive solutes through the urban karst

5.1 Chapter perspective

The literature suggests that the urban karst (i.e., the network of subsurface trenches supporting urban infrastructure) leads to preferential flow pathways that impact on the transport of solutes. A preferential flow cell was used in the laboratory to study the movement and fate of zinc due to such shortcuts. The column was packed with a low permeability soil (same natural soil used in previous experiments) surrounding a high-permeability gravel core (excavated from the field) through which the majority of water and zinc are convected. The zinc breakthrough is plotted and compared with that of the single porosity medium with no gravel core (see Chapter 4). The results of this chapter provide evidence that the fate and transport of reactive solutes along subsurface infrastructure trenches is complex and needs to be accurately assessed to ensure that the use of stormwater infiltration does not further degrade urban stream ecosystems due to bypassing of the soil and rapid transmission of solutes into the streams.
5.2 Introduction

Urbanization greatly changes hydrology compared with natural landscapes as permeable surfaces are replaced with impervious areas such as roads, parking lots, and roofs. The change in the impervious-pervious surface balance results in reduced infiltration and increased stormwater runoff. Urban stormwater is a major source of pollutants from road and construction materials, atmospheric deposition, vehicle wear, and animal faeces (Folkeson et al., 2009; Hwang et al., 2016) which, in combination with changes to flow regimes, leads to the widespread degradation of urban stream ecosystems and their associated biodiversity (King et al., 2011; Roy et al., 2008). The most recognized pollutants of concern in stormwater are nutrients, pesticides, heavy metals, organics, pathogens, and dissolved salts (Ingvertsen et al., 2012; Pitt et al., 1999).

In response to the increasing amount of stormwater and the contamination of receiving waters, stormwater managers are increasingly advocating the use of stormwater control measures (SCMs) to protect or improve stream health by mimicking the pre-development hydrology and reducing pollutants (Fletcher et al., 2013). Among the many SCMs, stormwater infiltration systems are a promising retrofit option worldwide to reduce pollutant concentrations before water infiltrates into the surrounding soils, either through unvegetated sand or gravel media or through vegetated loamy-sand media (Campisano et al., 2011). A wealth of literature has been written regarding the water quality treatment performance of infiltration systems (Bratieres et al., 2008; Tedoldi et al., 2016; Trenouth & Gharabaghi, 2015). The consensus is that infiltrated pollutants are deposited in the top few centimeters of the systems (Kluge et al., 2018) by mechanical and physicochemical filtration. Despite the widespread application of stormwater infiltration as a strategy, some studies have raised the issue that infiltrated pollutants accumulated in the filtration media may be transported into the surrounding soils (Li et al., 2018), or to receiving waters (Hatt et al., 2007), thereby contaminating underlying soil and water resources.
An important question remains about the fate of locally infiltrated water and the pollutants it carries. The routes taken by infiltrated water are particularly complex in urban landscapes, where there are potential interactions with subsurface infrastructure and their surrounding high-permeability trenches, referred to as the ‘urban karst’ (Kaushal & Belt, 2012). The urban karst is defined as the network of pipelines conveying water flow along with highly permeable gravel-filled trenches surrounding these pipelines (Bonneau et al., 2017). This extensive network of large voids creates preferential flow paths through which infiltrated water, and its pollutants can move quickly towards the receiving waters (White, 2002). Understanding the potential mobilization and fate of pollutants when interacting with the urban karst is thus an essential prerequisite to help better predict the impacts of stormwater infiltration on the water quality of receiving waters.

Observational examples of the urban karst affecting the fate of infiltrated water and pollutants in the subsurface are emerging. Sharp (2003) found that gravel trenches around pipes (e.g., sewer and water supply) formed networks of hyper-permeability paths for groundwater and its pollutants. The measured hydraulic conductivities of gravel trenches were two to three orders of magnitude greater than the local soil. In a recent study, Bonneau et al. (2018) examined whether the high-permeability gravel trench around the sewer line could intercept infiltrated stormwater. The groundwater table in a monitoring bore upgradient of a sewer line fluctuated during summer; however, a bore downgradient of it was totally dry, providing evidence of potential diversion of infiltrated stormwater from its topographical pathway by the urban karst. The existing, albeit incomplete, knowledge suggests a risk that the application of infiltration systems in the proximity of other infrastructure could undermine efforts to restore the health of urban streams.

In preferential column transport approaches, solutes are mobilized by the effect of advection through the central core and radial diffusion through the low-permeability soil matrix (Young & Ball, 1998). Solute diffusion in soil refers to the movement of a dissolved
substance in a liquid phase from an area of higher concentration toward an area where is less concentrated (Fetter et al., 1999). This process in the soil thus determines the rate by which a solute is transported. Diffusion is commonly regarded as the dominant mode of solute transport in low-permeability material (Chou et al., 2012).

While papers to date have shown field-based evidence of the impact of the urban karst on the potential diversion of infiltrated stormwater and its associated pollutants (e.g., Perera et al., 2013), few experimental attempts have been made to explicitly examine the transport behavior of reactive pollutants in urban karst-like environments. In this study, we aim to evaluate the degree to which high-permeability trenches affect pollutant transport (exemplified by zinc) in a more controlled environment. In doing so, we applied a preferential flow cell, packed with two media with distinct hydraulic conductivities. We tracked the movement of zinc in the presence of a central gravel core surrounded by the low-permeability soil. Soil samples were also taken at various cross-sections from the gravel core and surrounding soil matrix for evaluating radial diffusion of zinc from the central permeable core to the low-permeability soil. Finally, a semi-analytical solution was used to model the radial diffusion.

5.3 Materials and methods

5.3.1 Soil sample and reagent

The natural soil was collected from a peri-urban catchment (-37°51’23”S and 145°19’16”E) located in the eastern suburbs of Melbourne, Australia. Soil samples were oven-dried, crushed, and sieved through a 2 mm mesh prior to characterization. We characterized the texture and hydraulic conductivity of soil using a Beckman-Coulter LS13320 Laser Particle Size Analyzer and falling head test (ASTM D5084-03). The physicochemical properties of the natural soil are shown in TABLE 5.1. We measured cation exchange capacity using an NH₄Cl solution extraction at pH 7.0 (Rayment & Lyons, 2011). The specific surface area of the soil was estimated using BET⁴ (Brunauer et al., 1938) with

⁴ Brunauer, Emmett, and Teller
nitrogen (N2) as the sorbate. The mineralogical composition was determined using a Bruker D8 Advance X-ray diffractometer with Ni-filtered Cu Kα radiation (Warren, 1990). The diffraction data were obtained between 5° and 85° with a step size of 0.02° 2θ and a scan rate of 1 s per step. We prepared the stock solutions by dissolving ZnSO4·7H2O in deionized water to make a 100 mg L⁻¹ zinc solution. A Hach HQ40D portable multi-meter was used to measure solution pH which was adjusted with buffer solutions. The concentrations of zinc in the liquid phase were measured using an inductively coupled plasma-optical emission spectrometer (ICP-OES) (Optima 4400, Perkin Elmer, USA).

TABLE 5.1: Physicochemical properties of the local soil.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand fraction (0.02 – 2 mm) (%)</td>
<td>56.38</td>
</tr>
<tr>
<td>Silt fraction (0.002 – 0.02 mm) (%)</td>
<td>19.16</td>
</tr>
<tr>
<td>Clay fraction (&lt; 0.002 mm) (%)</td>
<td>24.46</td>
</tr>
<tr>
<td>Soil texture (International)</td>
<td>Sandy clay loam</td>
</tr>
<tr>
<td>Abundant clay mineral(s)</td>
<td>Kaolinite and Muscovite</td>
</tr>
<tr>
<td>Permeability (cm²)</td>
<td>5.86 e⁻¹²</td>
</tr>
<tr>
<td>Hydraulic conductivity (cm h⁻¹)</td>
<td>3.6 e⁻³</td>
</tr>
<tr>
<td>CEC (meq/100g)</td>
<td>13</td>
</tr>
<tr>
<td>BET surface area (m² g⁻¹)</td>
<td>49.04</td>
</tr>
<tr>
<td>Bulk density (g cm⁻³)</td>
<td>1.55</td>
</tr>
<tr>
<td>Mean porosity (cm³ cm⁻³)</td>
<td>0.41</td>
</tr>
</tbody>
</table>

5.3.2 Experimental setup

We used a cast acrylic flow cell (Soil Measurement Systems Co., Arizona, USA) with a length of 50 cm and an internal diameter of 5 cm (FIGURE 5.1). A 1.5 cm plastic tube was backfilled with gravel (2.8 < dₚ < 4.75 mm) in the middle core of the flow cell. The rest of the flow cell was then packed with the local soil to closely mimic the porosity and dry bulk density of the in-situ material (see TABLE 5.1). To begin, the soil in the flow cell was saturated from the bottom with deionized water using a peristaltic pump (Precision Pump Co., Baoding, China) to eliminate trapped air. The bottom cap consisted of a flat round plate with a perforated aluminum support disk, as well as a porous nylon membrane to evenly distribute the inflow. Once the soil was fully saturated, deionized water containing 100 mg L⁻¹ of zinc was injected from the bottom. Two experiments were run with flow rates of 1 and 2 mL min⁻¹ and the core was repacked with fresh material.
between the two experiments. 5 mL effluent samples were periodically collected, filtered through 0.45 µm syringe filters, and then analyzed for zinc using ICP-OES\(^5\) (Optima 4400, Perkin Elmer, USA). During the experiments, samples were randomly taken from the stock solution to monitor the influent zinc concentration and pH. Zinc breakthrough curves (BTCs hereafter) described as the relative concentration versus time, were then plotted and compared with that estimated for a single medium (the lower permeability field soil).

![Photo of the studied preferential column experiment. A 1.5 cm core was backfilled with highly permeable gravel through which zinc is advected.](image)

**FIGURE 5.1**: Photo of the studied preferential column experiment. A 1.5 cm core was backfilled with highly permeable gravel through which zinc is advected.

5.3.3 Modeling

We showed that HYDRUS-1D was able to simulate BTCs for the homogeneous column experiments with small errors (see details in Chapter 4). Therefore, we used HYDRUS-1D to predict zinc BTCs through the low-permeability field soil (single medium) in the larger flow cell. This was carried out because the low-permeability of the field soil renders

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\(^5\) Inductively Coupled Plasma-Mass Spectrometry
experiments with homogeneous conditions in the flow cell non-feasible. We compared modeled zinc BTC within the homogeneous condition in the large flow cell with observed BTCs in the preferential flow case. The preferential flow cell comprises two regions: a medium of low hydraulic conductivity and a central gravel core of comparatively higher hydraulic conductivity (FIGURE 5.2). To determine how much zinc was diffused radially in the preferential flow cell, we used a semi-analytical solution (Van Genuchten et al., 1984) using equation (5.1). It was applied assuming radial diffusion from the gravel boundary into the surrounding soil matrix.

\[
R_{sm} \frac{\partial C_{sm}}{\partial t} = D_{sm} \frac{\partial}{\partial r} \left( r \frac{\partial C_{sm}}{\partial r} \right) \tag{5.1}
\]

where \( R_{sm} \) is the retardation factor for soil matrix, \( C_{sm} \) (M L^{-3}) is the zinc concentration in the soil matrix solution, \( t \) (T) is time, \( r \) (L) is the radial coordinate, and \( D_{sm} \) (L^2 T^{-1}) is the zinc diffusion coefficient in the soil matrix. \( D_{sm} \) can be expressed as:

\[
D_{sm} = \xi D_w \tag{5.2}
\]

where \( \xi \) is a tortuosity factor, and \( D_w \) is the zinc diffusion coefficient in water (L^2 T^{-1}). The tortuosity factor accounts for the impact of the shape of the flow path that tends to mitigate solute diffusion through the porous media (Young & Ball, 1998). The semi-analytical solution to Eq. (5.1) was given by:

\[
C_{sm}(z, r, t) = C_m(z, t) B(r, t_1) \tag{5.3}
\]

\[
B(r, t_1) = 1 - \pi \sum_{n=1}^{\infty} \exp \left( D_{sm} \alpha_n^2 t_1 / R_{sm} \right) J_0^2(\alpha_n b) \\
\times \left[ J_0(\alpha_n a) Y_1(\alpha_n b) - Y_0(\alpha_n a) J_1(\alpha_n b) \right] / J_1^2(\alpha_n a) \tag{5.4}
\]

\[
J_0(\alpha_n, a) Y_1(\alpha_n, b) - J_1(\alpha_n, b) Y_0(\alpha_n, a) = 0 \tag{5.5}
\]

where \( C_m \) (M L^{-3}) is the zinc concentration in the macropore solution, \( z \) (L) is distance, \( t_1 \) (T) is the adjusted time \((t - z R_m / v_m)\), \( R_m \) is the retardation factor for macropore region, \( v_m \) (L T^{-1}) is the average fluid velocity through macropores, \( a \) (L) is the radius of cylindrical core, \( b \) (L) is the radius of soil mantle surrounding the cylindrical core, \( B \) is the
Bessel function, $J_0$ and $J_1$ are the Bessel functions of the first kind, $Y_0$ and $Y_1$ are the Bessel functions of the second kind, and $\alpha_n$ are the roots of (Eq. (5.5)). $C_m$ can be expressed as:

$$C_m (z,t) = \exp \left(-\frac{\theta_m D_{am} z}{a^2 \theta_m v_m}\right) \text{erfc} \left[\frac{\theta_m z}{a \theta_m v_m} \left(\frac{D_{am} R_{am}}{t - R_m z/v_m}\right)^{1/2}\right]$$

(5.6)

where $\theta_m$ and $\theta_m (L^3 L^{-3})$ are the water contents of the soil matrix and macropore regions, respectively.

FIGURE 5.2: Schematic representation of the cylindrical core (gravel medium) from which zinc diffuses into the adjacent low-permeability soil matrix, ‘a’ is the radius of cylindrical core, ‘b’ is the radius of soil mantle surrounding the cylindrical core.

5.3.4 Soil dissection for chemical analysis

Soil samples (gravel and the local low-permeability soil) were collected at five cross-sections along the flow cell to give information on how zinc was propagated spatially through the core. At all cross-sections except the mid-section, we took a 2 cm slice through the core and sampled three concentric rings from it ~ 0.6 cm thick. At the middle cross-section, we took a 4 cm slice and divided the concentric rings into four quadrants (FIGURE 5.3). The high-permeability gravel was also sampled at each cross-section to quantify the amount of zinc retained on the gravel surfaces. We sent the soil samples to a commercial laboratory for chemical analysis. Samples were initially digested using a ‘reverse aqua regia’ solution of nitric and hydrochloric acid. The resultant water extracted
from the soil samples was injected into an ICP-MS where hot plasma atomized the samples. This gave off radiation characteristic of zinc, which can be quantified. Results were corrected to give mg g\(^{-1}\) dry weight results. For the mid cross-section (section 3), we bulked the samples and the mean dry weight was computed. Once zinc concentrations in the soil samples (solid-phase) were obtained, we used the best-fitted isotherm (see FIGURE 3.8) to calculate zinc concentrations in the soil matrix solution.

![Diagram](image)

FIGURE 5.3: Soil sample collection along the column. The left cross-section is a 2 cm soil slice taken from the intervals 3-5, 13-15, 33-35, 43-45 cm from the bottom of the column (sections 1-5 except 3) while the right is a 4 cm soil slice of the mid-section (section 3) taken from the interval 22-26 cm from the bottom of the column. R stands for the ring, the first subscript is the number of a ring, and the second subscript is the number of the quadrant.

5.4 Results and discussion

5.4.1 Zinc BTC behavior

5.4.1.1 Homogeneous condition

The value of dispersion coefficient (\(D_L\)) was calculated to be 1.32 cm\(^2\) h\(^{-1}\) (see TABLE 5.2) for a small column through fitting the chloride median BTC to the analytical solution of the advection-dispersion equation (Fetter et al., 1999). The chloride median BTC displayed a sharp front (see Chapter 4), which featured the very early appearance of chloride in effluent solution after half an hour of running the experiment (around 0.6 pore
volume). The BTC then approached relative concentration \((C/C_0)\) of 1 in about two hours (less than three pore volumes). Unlike the chloride BTC, a large number of pore volume was required to feed the column to observe the adsorption front in the zinc BTC (initial concentration: 100 mg L\(^{-1}\)). The zinc retardation factor in the small column, calculated from the area under the curve of \((1-C/C_0)\) vs. pore volume was equal to 95.21.

The values of sorption parameters, \(\eta\), and \(q_m\) and the first-order rate, \(\omega\), are shown in TABLE 5.2 (see Chapter 4 for details). These parameters were used to simulate zinc BTC in the large preferential flow cell. However, the value of the dispersion coefficient determined for the small column cannot be used in the case of the large preferential flow cell. This is because dispersivity is highly sensitive to the transport distance and velocity, scale of the experiment, and flow rate (see a review; Vanderborght & Vereecken, (2007)). Hence, we used the value of the dispersion coefficient (37.2 cm\(^2\) h\(^{-1}\)) taken from similar experimental conditions reported in the above-mentioned review.

TABLE 5.2: Physicochemical and sorption parameters of the single medium (a low-permeability soil) used for zinc transport study (L: column length; d: column diameter; q: Darcy’s velocity; \(D_L\): dispersion coefficient; \(B_d\): soil bulk density; \(\theta_s\): soil porosity in saturated media; \(\omega\): first-order rate coefficient; \(\eta\): the Langmuir coefficient; \(q_m\): maximum sorption capacity; \(R\): retardation factor).

<table>
<thead>
<tr>
<th>(L \times d) (cm)</th>
<th>(q) (cm h(^{-1}))</th>
<th>(D_L) (cm(^2) h(^{-1}))</th>
<th>(B_d) (g cm(^{-3}))</th>
<th>(\theta_s) (cm cm(^{-3}))</th>
<th>(\omega) (h(^{-1}))</th>
<th>(\eta) (L mg(^{-1}))</th>
<th>(q_m) (mg g(^{-1}))</th>
<th>(R) (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 \times 1.2</td>
<td>2.02</td>
<td>1.32</td>
<td>1.51</td>
<td>0.43</td>
<td>0.05</td>
<td>0.23</td>
<td>3.20</td>
<td>95.21</td>
</tr>
</tbody>
</table>

As shown in FIGURE 5.4, the curve-fitted BTC using the column-determined Langmuir parameters through the non-equilibrium model (best-fit model; see Chapter 4) showed a very good agreement with the experimental data (RMSE: 4.75E-06 and \(r^2\): 0.993). For the large preferential flow cell, the center of zinc mass predicted using the non-equilibrium model broke through much later (after 630 h) than the small column (around 95 h).
FIGURE 5.4: Transport of zinc predicted through a single low-permeability soil matrix in the large flow cell (dimensions: 50 × 5 cm). The model was initially validated based on the results obtained for the small column. Zinc concentration: 100 mg L\(^{-1}\); used flow rates: 0.05 mL min\(^{-1}\) in the small column and 1 mL min\(^{-1}\) in the large flow cell.

5.4.1.2 Preferential flow condition

A remarkable difference in breakthrough response to zinc introduction with the same concentration (100 mg L\(^{-1}\)) was observed using two flow rates in the preferential flow cell (FIGURE 5.5). We found that zinc retention was significantly enhanced with decreasing flow rate from 2 to 1 mL min\(^{-1}\). As flow rate increased, the time needed for zinc to breakthrough (C/C\(_0\) = 0.05) decreased an order of magnitude, changing from 10 h at a flow rate of 1 mL min\(^{-1}\) to about 1 h at 2 mL min\(^{-1}\). Thus, the larger flow rate resulted in lower retention of zinc ions, likely because of the higher rate of advection, which leads to lower contact time for the establishment of equilibrium between the zinc ions and adsorption sites of the two media in the flow cell.
5.4.2 Zinc BTC comparison of homogeneous and preferential flow case

Unlike the modeled zinc BTC in the low-permeability single medium, the BTC was immediate and the shape was completely different due to the preferential flow paths (FIGURE 5.6). It is obvious from these results that the zinc bypassed the soil matrix and passed through the centralized gravel core. After an initially steep slope up to C/C₀ = 0.5 (approx. 3 days), the decline in slope characterized by the long recession, was a new behavioral feature, likely indicating the interaction between soil matrix and gravel core. The diffusion of zinc into the soil matrix and seeping back into the gravel core during flushing could be the reason for the long tail of the breakthrough (Mahmood-ul-Hassan et al., 2006).
5.4.3 Soil zinc patterns

Results from the chemical analysis showed no systematic variations in the pattern of zinc accumulated along the flow cell. The soil matrix was completely exhausted in the first 5 cm of column depth (red region, FIGURE 5.7) and then concentrations of zinc in the soil matrix fluctuated longitudinally. Chemical analysis on gravel samples also showed that a portion of the zinc ions can be adsorbed by gravel particles but to a lesser extent compared to the soil matrix particles (vertical green belt in the middle of the core, FIGURE 5.7). This is confirmed by the results obtained from the batch test on gravel particles (maximum sorption capacity: 0.25 mg g\(^{-1}\)). In section 5 (close to the outlet of the column), however, we found higher concentrations of zinc in gravel samples relative to its maximum capacity in adsorbing zinc. This can be attributed to the fact that some parts of the low-permeability soil matrix were clung to the surfaces of gravel samples in the collecting process.
Results also showed a significant movement of zinc into the low-permeability medium, despite orders of magnitude differences in hydraulic conductivity. I expected that zinc would rapidly flow through the high-permeability gravel core with no significant portion of the total water volume and zinc to move through the soil matrix (almost zero advection in soil matrix). However, zinc substantially spread out into the surrounding soil matrix either side of the gravel core (FIGURE 5.7), indicating that the water in the soil matrix is mobile. This implies that even in the presence of the preferential flow path, zinc yet interacts with the soil active sites due to the radial diffusion with a decrease in the concentration found as it approached the column sidewalls (FIGURE 5.7).

FIGURE 5.7: Spatial distribution of solid-phase zinc concentration in the preferential flow cell, zinc concentration: 100 mg L\(^{-1}\), time: 50 d. Detailed results of zinc concentrations in soil samples (solid-phase) measured along the column and at different radii were given.
5.4.4 Modeled zinc radial distribution

To determine how far zinc was propagated radially into the soil matrix, the diffusion coefficient of zinc in the soil matrix, $D_{sm}$, was evaluated to be $10^{-6}$ cm$^2$ s$^{-1}$ from Eq. 5.2. In doing so, we used the value of $0.708 \times 10^{-5}$ cm$^2$ s$^{-1}$ for the diffusion coefficient of zinc sulfate (ZnSO$_4$) in water, $D_w$, as reported in the literature (see e.g., Harned & Hudson, 1951). The predicted tortuosity factor, $\xi$, of the low-permeability soil (sandy clay loam soil) was also estimated to be 0.15 from a quadratic function of soil water content (Chou et al., 2012).

An approximate semi-analytical solution for zinc transport through two media with distinct hydraulic conductivities highly overestimated the radial diffusion of zinc from the larger pores into the surrounding soil matrix (FIGURE 5.8). One possible reason for this discrepancy could be the assumption of a linear sorption isotherm. In reality, sorption non-linearity is likely to be important in our case given the wide range of zinc concentrations (see Chapter 4). In addition, our quantitative estimation of tortuosity reported in the literature and further calculation of soil matrix diffusion coefficient may deviate from lab-scale values due to the repacking of the material.

FIGURE 5.8: Radial diffusion of zinc in the vicinity of the outlet of the preferential flow cell (section 5), zinc concentration: 100 mg L$^{-1}$, time: 50 d.
5.5 Conclusions

5.5.1 Summary

We used a column-type method to evaluate the extent to which a reactive solute (exemplified by zinc) is advected through a gravel core and radially diffused through the low-permeability soil matrix surrounding the permeable core. The preferential flow considerably varied in nature and magnitude, with an early breakthrough of zinc through the central permeable channel. We observed a far more gradual slope thereafter due to the radial diffusion of zinc into the binding sites of the soil matrix, showing an intimate contact between the percolating water and the soil matrix, which led to sufficiently large contact time for zinc sorption. Predicted radial diffusion of zinc from an approximate solution in the literature was, however, inaccurate, as it considerably overestimated the movement of zinc into the low-permeability zone.

5.5.2 Current limitations and recommendations for future research

In this research, we described the application of a semi-analytical solution to trace the diffusion of a reactive solute from a permeable central core into the surrounded low-permeability materials. There were, however, some limitations in this study. First is the assumption of the linearity of sorption isotherm for both the gravel core and soil matrix regions. Second is the lack of data to account for the tortuosity factor, meaning that estimates from many of those reported in the literature may substantially vary from lab-scale values due to repacking issues. It is obvious that the diffusion rate in the low-permeability soil matrix is hard to accurately predict without direct measurement in the laboratory; therefore we recommend further laboratory experiments in the future. In addition, numerical evaluations using a 3D model against experimentally-measured radial diffusion of a solute into the soil mantle could also help to resolve this issue. We note that all measurements here were made on repacked materials. This has brought benefits, such as the ability to measure physicochemical and sorption parameters for each medium independently. However, using repacked columns may not fully reflect aspects
of the in-situ behavior of reactive solute transport. We thus agree that preferential column experiments using intact cores could also be an option for future extension of this method.

5.5.3 Management implications

To date, the potential for highly permeable trenches around underground infrastructure (the urban karst) to affect the transport of reactive solutes from the infiltrated stormwater into the surrounding soil matrix has received very little attention. Preferential flow plays a pivotal role in mobilizing reactive solutes such as metals through bypassing the soil media and leaching them quickly from the soil matrix, thus undermining the objectives of stormwater infiltration systems. While we now understand that preferential flow paths would make a significant difference in the fate and transport of reactive solutes and infiltrated water, our lack of understanding to accurately predict how a reactive solute is propagated radially into the surrounding soil mantle makes it difficult to characterize preferential flow paths. Therefore, we suggest that managers need to locate stormwater infiltration systems with a view to minimizing interactions with existing subsurface infrastructure. This requires examination of spatial databases of existing subsurface infrastructure in the surrounding area. This should be taken into account as a criterion for design purposes to better predict the movement of reactive solutes within the soil profile and the extent to which they may mobilize back into receiving waters.


Chapter 6 – Summary, discussion and conclusion
Chapter 6 – Summary, discussion, and conclusion

6.1 Chapter perspective

The main objective of my thesis was to examine, through laboratory studies, the transport of a reactive solute in situations where complex networks of high-permeability pathways associated with subsurface infrastructure dominate, such as in urban areas. To achieve this, the movement of a reactive solute through the soil was studied with and without the interference of the gravel core as a representation of subsurface infrastructure. This work is described in four chapters: a literature review (Chapter 2) and three results chapters (Chapters 3-5) presented as a draft or submitted journal articles. In this chapter, I present a summary of research findings, review experimental constraints, describe practical implications, draw some conclusions from the analysis, and provide recommendations for future studies.
6.2 Summary

Stormwater infiltration systems are among the most widely applied stormwater control measures across the world, given their ability to reduce the volume of stormwater, and the water quality benefits by filtering water through the soil matrix. However, the long-term benefit of implementing such systems is still uncertain, since very little is known about the fate of infiltrated water and pollutants in complex urban subsurfaces. The role of different flow paths on pollutant transport and removal capacity in natural catchments has been well studied, but this knowledge cannot be directly transferred to highly altered urban environments. Urban landscapes pose a particular challenge due to the complex network of gravel trenches associated with subsurface infrastructure. That network likely creates strong preferential flow pathways, potentially short-circuiting the soil and rapidly transmitting water and pollutants to streams. In Chapter 2 (literature review), I identified a need for experimental studies to investigate the fate of the reactive solutes through the urban karst. Clues to the importance of field-scale preferential flow pathways impacting the transport of solutes have been mentioned in the literature, but few experimental studies have been conducted in the laboratory to properly understand the mechanisms involved. This gap in the existing literature led to research question 2 regarding the influence of the urban karst on the transport of reactive solutes. I considered this as an overarching gap and the details of the reactive solute transport in such environments then led to the consideration of the role of soil characteristics in solute transport. This led to research question 1, through which I investigated the role of soil type characteristics (e.g., clay mineralogy) on the movement of reactive solutes, for which the literature is covered in Chapter 2. Overall, this thesis aimed to use understanding from experimental investigations to underpin knowledge to inform better location and design of stormwater infiltration systems in urban areas. That will protect urban streams from degradation caused by the likely transport of infiltrated reactive solutes. To achieve this overall aim, the present work addressed the following objectives:
Objective 1 - Understanding the role of soil clay mineralogy on the fate of reactive solutes

In Chapter 3, I tested the potential adsorptive capacities of two soils (one natural soil and one synthetic soil) in removing zinc, a representative solute due to its ubiquitougsness in groundwater, through single solute batch tests. The soils had similar clay content but were different in clay mineralogy. The natural soil was a mixture of quartz-kaolinite-muscovite, while the synthetic soil lacked the muscovite. I calculated the Langmuir maximum sorption capacity of each soil and found that the natural soil sorbed far more zinc ions than the synthetic soil. This was attributed to the presence of the 2:1 clay mineral, muscovite, in the natural soil. I also compared the observed sorption capacity of the natural soil with its sorption capacity predicted (based on sorption values that are widely reported in the literature). I showed that the values of sorption capacities of individual-sized clay minerals cannot be linearly extrapolated to estimate the overall sorption capacity of soil that contains mixtures of clay minerals.

Objective 2 - Evaluating the transport of reactive solutes in porous media

To better mimic what happens to the transport of reactive solutes such as zinc within the porous media, I used flow-through systems using column tests covered in Chapter 4. The use of sorption parameters from batch studies obtained in Chapter 3, failed to suitably describe the zinc breakthrough curves simulated with the HYDRUS-1D numerical model. While a sharp breakthrough curve front was expected due to the non-linear nature of the batch sorption isotherms, I observed a more dispersed asymmetrical front in the columns. This demonstrated the existence of chemical non-equilibrium sorption in zinc transport. I concluded that (1) zinc was highly retarded in the natural soil due to relatively high clay content and its mineralogy including a significant fraction of muscovite, (2) batch tests overpredicted the travel time in transport behavior of zinc in the natural soil, and (3) column tests better approximated non-equilibrium sorption behavior of zinc during its transport through the natural soil. These results suggest that column tests should be carried out to better predict the solute transport behavior in the surrounding soils.
Objective 3 - Assessing the role of highly permeable trenches on the transport of reactive solutes

Following the investigation of the transport of zinc through homogeneous porous media using dynamic tests in Chapter 4, the impact of preferential flow paths on the transport of zinc in more altered urban areas was investigated. In Chapter 5, I used a preferential flow cell in which I packed a column with an annulus of low-permeability natural soil surrounding the central core (1.5 cm diameter), which was filled with highly permeable gravel. Zinc tracer tests were run through the core. I found that the zinc breakthrough curve (BTC) greatly differed in shape and timing compared with that predicted by the HYDRUS-1D model (in Chapter 4) for a single low-permeability medium. I observed that the breakthrough time reduced by an order of magnitude in the presence of the gravel core. I dissected the preferential flow cell and sent soil samples taken from different points along the column and at different radii for analysis. The results from the chemical analysis showed no systematic variations along the core. Despite this, I observed higher concentrations of zinc in the soil matrix next to the gravel core, with declines towards the outer edge of the core. I used an approximate semi-analytical solution to estimate how zinc is diffused into the surrounding soil matrix. However, the solution overestimated the radial diffusion of zinc due to the simplified assumptions made. As an alternative solution, I tried to solve this problem through a numerical 3D model (HYDRUS-3D) but was unable to predict zinc radial pattern successfully. It is because HYDRUS-3D was very time-consuming to run each trial and mostly failed to converge due to an unknown reason. I also used multiple pairs of dispersivity (both longitudinal and transverse) but never found a good pair to get promising results. Moreover, the inverse mode previously used for model calibration in HYDRUS-1D was inactive in the 3D package, so that it did not allow me to find a good pair of dispersivity through calibration. Therefore, this was identified as unresolved issue in chapter 6 that require further research in future.
6.3 Current limitations and recommendations for future studies

From my literature review, I found many stormwater pollutants with the potential to contaminate groundwater via infiltration systems e.g., pesticides, metals and non-metals, organics, along with pathogens (Clark & Pitt, 2007). I selected heavy metals (zinc as the solute of interest) since they are normally toxic, non-degradable and detrimental to a variety of biota (Salman et al., 2015). Throughout my thesis, I used a single-component system in batch mode to remove zinc ions from synthetic solutions under optimized experimental conditions. However, about 24 metals have been observed in groundwater in literature. Therefore, I recommend using more realistic multi-component batch modes (binary or ternary for instance) to include the competitive effects of metals for adsorption sites. This would be expected to result in a decrease in the sorption capacity of soil in removing a particular metal. I also did not examine the impact of organic matter content on the metal sorption capacity in batch modes because the chosen site had no to very little organic matter content in the soil. Thus, I recommend considering the effect of organic matter content on the metal sorption that is expected to reduce its sorption capacity (Wong et al., 2007). In addition, I used synthetic stormwater in experiments because it is difficult to maintain the consistency of solute concentrations in natural stormwater (Hatt et al., 2007). I recommend using real stormwater for future laboratory works. Finally, using more soil types with different clay content and mineralogy to test their effectiveness in sorbing reactive solutes such as metals would be a useful future extension of this work.

In Chapter 4, I assessed the transport of zinc in porous media using column experiments. There were, however, some constraints. The measured hydraulic conductivity of soil was in the order of $10^{-8}$ m s$^{-1}$ due to the high clay fraction. This made the experiments harder and more time-consuming, due to the low flow rates and high affinity of the clay surfaces to the solutes especially metals. To resolve this problem, I had to design a column that was a compromise between sufficient physical scale and experimental run time. I also used the same range of zinc concentrations (5-100 mg L$^{-1}$) in column experiments as used in batch modes. This range is far superior to zinc concentrations that can be expected in
urban stormwater or in percolation from infiltration systems. This is because using lower concentrations of zinc was not possible due to several reasons. For example, 1200 pore volumes (around two months) were required to end up the experiment ($C/C_0 = 1.0$) for 10 mg L$^{-1}$ of zinc concentration in the stock solution. For more realistic concentrations of zinc (say 5 mg L$^{-1}$ and lower), the time would have been doubled (approx. four months) and so forth. Given the limitations in performing column experiments in laboratory e.g., faulty test due to the leakage, tubes lifetime, etc., I was unable to run experiments that take so long. In addition, the detection limit of the ICP-MS constrained me to use very low but more realistic concentrations of zinc in my experiments. Thus, the outcomes of this research will change somehow with varied experimental conditions. To expand our approach for future studies, I thus recommend using longer columns with more flow rates and multiple replicates.

In Chapter 5, I used a preferential flow cell to create a low-permeability material of repacked natural soil (used in the previous experiments) with a central core of gravel. While using repacked materials has some benefits in terms of our ability to independently measure physicochemical and sorption parameters for each medium, this approach may not reflect some of the aspects of the transport of solutes as the soil structure is destroyed. It is recommended that future preferential-flow column experiments could be conducted using intact cores to better mimic what happens to the transport of solutes in urban karst-like environments. The modeling of the preferential flow core that I undertook was limited to a semi-analytical solution for which there was a large discrepancy between the model and experimental results. This could be initially attributed to the assumptions made by the solution for simplification. Adsorption effects were included using linear isotherms (Van Genuchten et al., 1984) for both regions, while non-linearity governed in our case. Further modeling, likely through running a 3D solute transport model to better predict radial diffusion of a reactive solute into the surrounding soil matrix would help further interpret and generalize experimental results.
6.4 Management implications

Stormwater infiltration systems are widely applied as a management technique for mitigating the impacts of stormwater runoff from impervious surfaces drained directly to streams in urban landscapes (Burns et al., 2012). Recent studies have recognized that stormwater solutes cannot be completely removed by infiltration systems (e.g., Li et al., 2018), leading to concerns about long-term legacy effects. Leaching of metals from the infiltration system filter media into the underlying soil over time can be detrimental to ecosystems of receiving waters (Aryal et al., 2006; Hossain et al., 2007). However, not much is known about the extent to which metals can be mobilized through the soils and regolith between the infiltration systems and receiving waters. The data presented in Chapters 3-4 suggest that the potential removal of metals by surrounding soils largely depends on the clay mineralogy of the soil. Once stormwater solutes such as metals are remobilized into the local soil via infiltration systems, soil and its clay content and mineralogy play a significant role in solute removal as an extra filter. One might question the long-term sustainability of the pollutant-retention role of local soil, if it is unable to provide extended filtration due to low clay content and low 2:1 clay mineral fraction. In that case, it is a must to over-design the filtration media of infiltration systems, likely with regard to increasing filter depth or using materials with higher affinity to heavy metals. Alternatively, regular replacement of the filtration media may be required, to maintain its own sorption capacity.

The interaction between groundwater flows and preferential flow paths or shortcuts impacts where and how quickly infiltrated stormwater solutes move. There is a risk for pollutants to reach water bodies through human-made subsurface pathways in urban landscapes, analogously to the role of macropores in natural environments. Chapter 5 demonstrated that the preferential flow results in a rapid and accelerated breakthrough of solutes, therefore undermining the objective of using stormwater infiltration to protect and improve the health of waterways. This is obviously an area where further research is
required so that stormwater managers can more accurately anticipate the degree to which infiltration-based systems will meet their stated goal of restoring water quality regime.

Given the insights from this thesis, stormwater managers should ideally first test the heterogeneity of the soils, that is, potential sorption characteristics of the underlying soil, their purity, and composition, before implementing stormwater infiltration strategies. In addition, they need to carefully examine spatial data of existing subsurface infrastructure in the surrounding area, to identify the risk of preferential flow paths for mobilized pollutants. These two criteria must be taken into account to better design and particularly locate the infiltration-based techniques in the landscape, in order to minimize the risk of contamination of water resources.
6.5 Bibliography


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Behroozi, Amir

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