Albert-Ludwigs-Universität Freiburg

MASTERARBEIT

ARE STORMWATER INFILTRATION SYSTEMS COMPROMISING THE QUALITY OF OUR GROUNDWATER?

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an~der

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Dezember 2015

Declaration of Authorship

I, Manuel SAROOS, declare that this thesis titled, 'Are stormwater infiltration systems compromising the quality of our groundwater?' and the work presented in it are my own. I confirm that:

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"In the face of overwhelming odds, I'm left with only one option, I'm gonna have to science the shit out of this."

Matt Damon in 'The Martian'

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Abstract

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Are stormwater infiltration systems compromising the quality of our groundwater?

by Manuel SAROOS

Biocide depositions from urban areas are a growing exposure for today's ecosystems, as they are extensively applied for weather protection of external walls and on flat roofs in housing construction. Therefore, storm runoff can have high loads of biocides and other contaminants. Stormwater infiltration systems (SIS), as part of modern urban water management should, besides increasing the groundwater recharge in urban areas, also prevent these pollutant loads from reaching the natural water cycle, especially for surface water. However, this study investigated the risks of groundwater contamination with biocides due to the infiltration of loaded stormwater runoff. For that, a field study was performed to research a SIS in a southern district of Freiburg. A combination of reactive (resazurin/resorufin, sulforhodamine b) and quasi-conservative tracers (uranine, sodium bromide) were used as surrogates of biocidal products, to identify hydraulic, sorption and degradation characteristics. A focus was on the fluorescence tracer resazurin, reducing to resorufin under high microbial activity and therefore was used to mimic degradation/transformation processes of biocides. Water samples from the underground drain and a nearby groundwater well were analyzed to evaluate the matter transport and to model the water fluxes between the different sections of the SIS. Especially under flooded conditions, fast pulses of tracer fluxes flowed into the drain. Although, there were high concentrated tracer fluxes into the drain, it was not measured in the groundwater well. All resazurin transformed into resorufin while infiltrating through the top soil. Also, results showed that the top soil layer played a major role for biocide degradation and sorption capacity. Generally, it is assumed that the SIS is an important barrier for biocidal products, but particularly for bigger rain events, loaded water fluxes into the groundwater cannot be excluded. Further research is needed to identify the characteristics of SIS with different structures and ages.

Keywords: Stormwater infiltration system, biocides, multi-tracer-approach, resazurin, resorufin, degradation, sorption

UNIVERSITÄT FREIBURG

Zusammenfassung

Fakultät für Umwelt und Natürliche Ressourcen Professur für Hydrologie

Gefährden Regenwasserversickerungsanlagen die Qualität unseres Grundwassers?

von Manuel SAROOS

Der Eintrag von Bioziden aus urbanen Räumen ist eine zunehmende Belastung für heutige Ökosysteme. Als Schutz gegen Witterung und Schädlinge werden sie großflächig im Hausbau, auf Aussenwänden und Flachdächern eingesetzt. Darum können Regenwasserabflüsse hohe Konzentrationen an Bioziden und anderen Schadstoffen aufweisen. Regenwasserversickerungsanlagen (RVA) sollen, neben der Erhöhung der Grundwasserneubildung, außerdem insbesondere für Oberflächenwasser solche Schadstofffrachten vor dem natürlichen Wasserkreislauf zurückhalten. Dennoch untersuchte diese Arbeit die Risiken einer Grundwasserverschmutzung durch Biozide über die Versickerung von belastetem Regenwasser. Anhand einer RVA in einem südlichen Freiburger Stadtteil wurde eine Feldstudie durchgeführt. Es wurde eine Kombination aus reaktiven (Resazurin/Resorufin, Sulforhodamin B) und quasi-konservativen (Uranin, Bromid) Tracern als Ersatzmittel für Biozide eingesetzt, um Hydraulik-, Sorptions- und Abbaueigenschaften zu untersuchen. Ein Fokus lag dabei auf dem Fluoreszenztracer Resazurin, welcher bei mikrobieller Aktivität zu Resorufin reduziert und deshalb eingesetzt wurde, um Abbauund Umwandlungsprozesse von Bioziden zu imitieren. Wasserproben aus der unterirdischen Rigole und einer nahen Grundwassermessstelle wurden untersucht, um den Stofftransport auszuwerten und die Wasserflüsse zwischen den verschieden Bereichen der RVA zu modellieren. Insbesondere bei gefluteter RVA flossen impulsartig hochkonzentrierte Tracerflüsse in die Rigole. Resazurin wurde beim Durchfließen der oberen Bodenschicht komplett zu Resorufin umgewandelt. Die Ergebnisse zeigten außerdem, dass die Bodenschicht eine Hauptrolle für den Abbau und die Sorptionskapazität für Biozide einnimmt. Insgesamt wird angenommen, dass die RVA eine wichtige Barriere für Biozide darstellt. Jedoch können, gerade bei größeren Regenereignissen, belastete Wasserflüsse in das Grundwasser nicht ausgeschlossen werden. Weitere Forschung ist notwendig, um die Eigenschaften von RVA mit unterschiedlichem Aufbau und Alter zu bestimmen.

Schlagwörter: Regenwasserversickerungsanlage, Biozide, Multi-Tracer-Ansatz, Resazurin, Resorufin, Abbau, Sorption

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Abbreviations

APEG	automatic sampling device			
\mathbf{BR}	sodium \mathbf{br} omide			
\mathbf{EC}	electrical conductivity			
IC	\mathbf{i} on \mathbf{c} hromatograph			
m.a.s.l.	meters above sea level			
\mathbf{UR}	uranine			
\mathbf{R}^2	coefficient of determination			
RAZ	\mathbf{r} es \mathbf{az} urin			
RRU	\mathbf{r} eso \mathbf{r} ufin			
RSE	\mathbf{r} esidual \mathbf{s} tandard \mathbf{e} rror			
\mathbf{RSS}	${\bf r}{\rm esidual}~{\bf s}{\rm um}$ of ${\bf s}{\rm quares}$			
SIS	$\mathbf{s} tormwater \ \mathbf{i} n flitration \ \mathbf{s} y stem(s)$			
SRB	\mathbf{s} ulfo \mathbf{r} hodamine \mathbf{b}			

Chapter 1

Introduction

1.1 Motivation

The European Water Framework Directive (European Community, 2000) defines holistic future goals to improve the quality, ecology and quantity conditions of surface and groundwater. Thinking about the increasing growth of urban areas and the gaining relevance of cities as a place to work and live for the current and future population results in a demand for modern concepts of urban water management. There are various challenges like falling groundwater tables and increasing surface runoff due to surface sealing. Additionally, the quality of stormwater runoff can be strongly affected by numerous forms of contaminants. In Switzerland alone around 7,400 tons of biocides are used every year, thereof 25 % for protection of construction materials (Bürgi et al., 2009). The growing application of biocides in facades and for roof insulation, used to protect it from decomposition, lead to a strengthened focus in the hydrological research on leaching and transportation characteristics of these contaminants. When biocides reach the hydrological cycle they can be a thread to human beings, animals and the environment.

Different approaches to improve the infiltration efficiency of urban areas and to reduce the transport of contaminants into surface waters are executed. Although artificial stormwater infiltration systems (SIS) should improve the retention capacity of contaminants, additional research is essential to investigate the contamination risks of the soil and groundwater due to stormwater inflow. Therefore, multi-tracer approaches can be applied to evaluate the hydraulic conditions of SIS and to quantify transportation and degradation processes of biocides.

This study is part of the MutRewa project, which investigates ecological and chemical conditions in surface and groundwater focusing on pesticides and biocides. Its goal is to define approaches for a sustainable exposure with pesticides/biocides and their transformation products for the regional water management.

1.2 State of the art

Biocides and rainwater infiltration systems

The European Biocidal Product Directive defines biocides as "substances, with the intention of destroying, deterring, rendering harmless, preventing the action of, or otherwise exerting a controlling effect on, any harmful organism by any means other than mere physical or mechanical action, (...)" (The European Paliament and the Council of the European Union, 2012). Its application for material preservation plays an important role, especially for house constructions. Todays construction of buildings accelerates the algae and fungi growth on facades (Burkhardt et al., 2005). Therefore, biocides are used in urban areas to protect the coating of thermal insulation systems, as well as walls of wooden houses against fungal attack. They are mixed in renders and paints as In-can preservatives (Paulus, 2005) and as root inhibitors in bitumen sheets on flat roofs. The most common biocide products for building protection are fungicides (e.g. triazoles and carbamates), algaecides (e.g. triazines and phenylureas), bactericides (e.g. isothiazolinones) and insecticides. For a long time, the role of urban areas as a contributor of pesticides/biocides was highly underestimated, with agriculture being responsible for the most pesticide losses in the surface water (Wittmer et al., 2011). But studies showed that the urban input can be as big as the agricultural (Gerecke et al., 2002), or even exceed them (Wittmer et al., 2011).

The large-scale use of biocides for buildings results to be the most important contributor of biocide contamination in urban water (Burkhardt et al., 2007). Considering that nowadays rainwater from urban areas often flows directly in receiving water courses or drains in rainwater infiltration systems, shows how important the investigation of rainwater runoff is. Stormwater infiltration systems were built to reduce the water level depression in urban areas, due to large-scale surface sealing, and to decrease surface runoff (Pitt et al., 1999). Additionally they can be seen as a contaminants retention construction. Nevertheless, the lack of research and long-term experience calls for indepth investigation of soil and groundwater contamination potential for these systems, as an important environmental issue (Pitt et al., 1999). For this reason many studies investigated the leaching capacity of contaminants, especially biocides.

Dechesne et al. (2004) examined nutrients, heavy metals and hydrocarbons in soil samples from stormwater infiltration systems. They determined decreasing concentrations of these substances with soil depth and therefore concluded good efficiency in trapping these contaminants in the top soil layer. Additionally, Birch et al. (2004) showed high contaminant retention for total phosphorous, total Kjeldahl nitrogen and for the heavy metals Cu, Pb and Zn. An increase of the compound concentration between stormwater runoff and the outflow of the RIS could be observed for total oxidisable nitrogen. Burkhardt et al. (2007) sampled a separated stormwater system, which drained the surface runoff from buildings with known biocide applications. They stated high variable leaching rates between different biocide products. The concentration peaks were found during first flush events and elevated values during tailing for several days. Lab studies with a weathering chamber from Burkhardt et al. (2011) also showed a strong concentration decrease during rain events. Unlike these results, Bollmann et al. (2014) declared a continuing emissions input during one rain event, instead of a first flush peak. They found a high correlation between the contaminants input and the amount of rainwater, but no relationship to the rain intensity or the time-span between two events. Burkhardt et al. (2011) determined that emission concentrations decreased strictly with each rain event.

Another important factor with a high impact on contaminants leaching is the age of the buildings and of the separated sewer network. (Burkhardt et al., 2011, 2012) state strongly decreasing concentrations with growing age of the coating. Also the exposure of the buildings to weather plays an important role for the leaching rate of biocides (Burkhardt et al., 2012, Wangler et al., 2012). Thus, rainwater runoff from the weather side of buildings shows higher contaminant leaching rates. Artificial irrigation experiments of Burkhardt et al. (2009) showed loss rates for several pesticides ranging between 7 and 25 % in the facades runoff. However, it has to be considered that the experiment rainfall amount exceeded the natural mean amount for this region five-fold. Results from a field study showed a high variability for the loss rates of biocides from urban areas ranging between 0.6 and 15 % and exceeded the loss rates of agricultural compounds by an order of magnitude.

Calculations for Switzerland show, that under consideration that approximately 0.5 % of outside wall paint and renders are biocides, and around 8 million sqm wall area get painted per year, circa 50 to 100 tons of biocides are applied per year (Burkhardt et al., 2011). This impressive amount of emissions, the leaching characters of the different biocides and its possible impact on contamination of soils, groundwater and surface water emphasize the importance of a comprehensive approach to research biocides for stormwater infiltration systems. The determination of degradation processes, which result in differences between the estimated leached biocide mass and the measured mass, are a central part (Burkhardt et al., 2012).

Resazurin/Resorufin system

Long before resazurin was used in environmental sciences, the redox reaction of resazurin (RAZ) to resorufin (RRU) was already applied in the industry as a bioreactive tracer to identify bacterial reduction of milk (Moyer and Campbell, 1963) and in medical laboratories to test the quality of semen (Zrimšek et al., 2004). It was also an often used tool to identify living bacteria (e.g. Liu (1983) and O'Brien et al. (2000)). Under reducing conditions the reaction leads to a color change from the blue low-fluorescent RAZ to the pink high-fluorescent RRU. The reaction from RAZ to RRU is irreversible, whereas the further reduction of RRU to the non-fluorescent hydroresorufin is only stable under the absence of dissolved oxygen (O'Brien et al., 2000). O'Brien et al. (2000) state that due to its low toxicity, the RAZ/RRU reaction is used for toxicity tests to count living bacteria cells. McNicholl et al. (2007) determined that the reduction process correlates with cell biomass and the respiration rate and that it can be a tool to measure microbial activity. These reports of RAZ as a tracer for biological reactions showed that the reduction depends on oxygen, as it is done by aerobe and facultative anaerobe organisms, but not under anaerobe conditions.

The resazurin/resorufin system as a tool for hydrological sciences was primarily introduced by Haggerty et al. (2008). They defined resazurin as a 'smart' tracer which gives additional information about the system trough which it percolates compared to a conservative tracer. This can be distinguished by an irreversible change in its chemical structure under the presence of a process of interest. As Haggerty et al. (2008) showed in batch experiments, reduction of RAZ can be used to identify metabolic activity. They also investigated chemical and physical interactions as sorption processes, light decay, reduction processes and transport mechanisms of this system within batch experiments. They determined that RAZ and RRU are stable in pure water for weeks. However, the reduction rate of RAZ increases three orders of magnitude under the presence of sediment in the water. A significant photochemical decay was observed under the exposure of intensive solar radiation after tens of hours for RRU and hundreds of hours for RAZ. They also expected weak absorption processes, given that the organic carbon content in the sediment is low. Lemke et al. (2014) focused on different sorption processes and pointed out its important role for mass transport studies. Thereby, kinetic sorption had major influence on tracer retention, which resulted in delayed tracer breaktrough curves, tailing and incomplete mass balances, compared to non reactive tracers. They also determined that linear sorption can be accepted to model these processes for regular field experiments.

Using the RAZ/RRU system as a successful tool to detect aerobic respiration was confirmed by Haggerty et al. (2009) and González-Pinzón et al. (2012). In field experiments they showed a high correlation of the reduction of RAZ under deoxidized conditions within the stream ecosystem. They pointed out in particular, that metabolically high active hyporheic sediments have a high effect on the reaction rate of RAZ to RRU. Lemke et al. (2013) used the RAZ/RRU system to quantify the hyporheic exchange and metabolic activity to identify in stream interactions of ground- and surface water. They successfully introduced an on-line fluorometry system to measure the breaktrough curves of RAZ, its reduction product RRU and the conservative tracer Uranine. The automatic measurement inhibited the influence of degradation processes on the results. Yet, they also declared, unlike their results of the lab experiment, that field tracer tests can show fractional outliers. It has also been used in anthropogenically influenced streams as an quantifiable indicator of ecosystem functions (Stanaway et al., 2012). RAZ indicated respiration rates of microbiological organisms in hyporheic sediments from several heavy metal contaminated sites. Different respiration rates along a contamination gradient were identified. Stanaway et al. (2012) stated that the RAZ/RRU can be used to get continuous data about biotic processes which are influenced by a changing environment.

Multi-tracer approach

The studies about the hydrological use of RAZ/RRU show the applicability of this system as a 'smart' tracer. In combination with conservative tracers it provides the ability to investigate microbiological activity in water ecosystems. The application of several tracers in hydrological experiments is an important tool to examine hydraulic or even reactive processes. In the last years, several studies, which used a combination of artificial or natural tracers as a mimicry of contaminants to examine their pathways and transformations in ecosystems, were realized. Passeport et al. (2010), Lange et al. (2011) and Schuetz et al. (2012) investigated the behaviour of a combination of tracers in surface flow wetlands. Lange et al. (2011) used sodium bromide and sodium chloride to research the hydraulic conditions and uranine (UR) and sulforhodamine-b (SRB), two fluorescence tracers, as surrogates for photolytic decomposition and sorption properties of contaminants, respectively. The results showed an increase of sorption in vegetated areas, compared to degraded areas and UR being an adequate tracer to represent light decay. The detection of sorption processes plays an important role assessing the contaminants retention capability of ecosystems. Passeport et al. (2010) showed differences in sorption dynamics between a wetland and a forest buffer zone by using SRB as a surrogate for pesticides. Schuetz et al. (2012) implemented a similar multi tracer approach to examine changes of sorption, light decay and hydraulic conditions in a wetland during succession. A direct comparison of transport mechanism of pesticides with conservative (UR) and reactive tracers (SRB) in artificial wetlands was executed by Durst et al. (2013). They concluded, that depending on the type of pesticide, there are correlations with the tracer transport characteristics. The studies pointed out, that the tracers UR and SRB can be used to estimate different aspects of pesticide transport processes. The combination of conservative and non-reactive tracers represent a tool to have insights in chemical processes of solutions (Schuetz et al., 2012). However, Durst et al. (2013) also indicated, that since UR and SRB are persistent to degradation, there are still gaps to mimic transformation or decomposition of contaminants.

Previous studies

Several bachelor theses, master theses and research studies examined SIS in the Vauban district. Opferkuch (2012) examined the hydraulic conductivity and analyzed soil samples at different sites along two SIS in the Vauban. The infiltration efficiency and the contaminant retention were both estimated to be high. Still, it was indicated that sedimentation of fine material from inflow water can reduce the hydraulic conductivity. Additionally, Helbig (2013) executed a grain size analysis of soil samples from different SIS to examine the physical properties of the soils towards pollutant retention and hydraulic conductivity. Claußner (2013) investigated the SIS in regard to its technical construction, hydraulic conductivity and soil layer. He concluded that both, soil properties and the structure of the systems, showed distinct deviations from the requirements in technical worksheets. Santa Maria (2013) examined the influences of SIS on the groundwater by measuring natural isotope signatures of soil water profiles. Due to high groundwater tables, the evaluation of the isotopes data was insufficient. By monitoring precipitation, river water levels and storm runoff discharge over 1.5 years, Jackisch and Weiler (2012) estimated the performance of the two major SIS towards water balance, flood mitigation and reduction of the runoff. Altogether, the expectations about the volume reduction and the water balance were fulfilled. Jackisch et al. (2013) evaluated the rain water management in the Vauban district and concluded that the SIS distinctly increase water retention in the district. They stated additionally that small rain or first flush events, which usually contain the highest pollutant load, were kept back.

1.3 Problem and ambition

The main objective of this work is to improve knowledge about contaminant transport, with a strong focus on biocides, through stormwater infiltration systems. Direct measurements of biocides are expensive and require very specific laboratory equipment. Therefore, different tracers are used as surrogates to investigate their physical and chemical behavior while infiltrating through a SIS. The results of the conservative tracers UR and BR should improve the understanding about hydraulics of this system, whereas the reactive tracer SRB should provide information about sorption characteristics. The application of the RAZ/RRU should indicate the usability of smart tracers in closing the gap of degradation or transformation processes in SIS. Furthermore, it is of interest if the physical and chemical characteristics change over space and time. In-situ measurements in a field study may directly help to evaluate the hydraulic conditions and matter transport of a longer existing SIS. By comparing the hydraulic characteristics from this work with those from the tracer experiment in 2011, potential changes which occur during that time should be identified. The primary research questions of this work are presented in the following:

Research questions

- Is the multi-tracer approach suitable to estimate biocide retention in stormwater infiltration systems?
- Are there contamination impacts on soil and/or groundwater conditions?
- Is RAZ/RRU a suitable tracer to estimate degradation processes?
- Are there important sorption and degradation processes in the soil and do they change with depth?
- Is the investigated stormwater infiltration system appropriate to serve as a runoff retention basin and does it reduce contaminant leaching into surface water and groundwater?

Chapter 2

Study area

The study site is located at the urban district Vauban of the city of Freiburg im Breisgau. The city is situated in the southwest of the federal state Baden-Württemberg in Germany. The urban district lies at the mouth of the Hexental and is part of the region "Freiburger Bucht". It is bordered by the Schlierberg in the East, by the Dorfbach in the South, by the railway line and Wiesentalstraße in the North and by the Insbrucker-Straße in western direction (see figure 2.1). The district area is slightly sloped in western direction. Therefore, the ground level elevation increases from ca. 254 meters above sea level (m.a.s.l.) (northwest) up to ca. 263 m.a.s.l (southeast).

Historically, from 1936 till 1992, the area was under military use for barracks. After the Second World War it was taken over by the French armed forces. In 1992, the withdrawal of the troops resulted in the end of the military use of the area (Wagenmann-Gaiser, 2004). The redevelopment as a residential area started in 1996 (Jackisch and Weiler, 2012).

2.1 Soils and Geology

The geological facts in this subsection rely mainly on the diploma thesis of Wagenmann-Gaiser (2004). The Freiburger Bucht lies at the edge of the Oberrheingraben, which is part of the European rift system. It counts along the ditch-margin-fault, which divides the Oberrheingraben and the eastern Black Forest. The geology of this area is exclusively



FIGURE 2.1: The Vauban district and the location of the study site.

characterized by sediments from the Pleistocene and Quartary, transported by erosion or from the Dreisam river (figure 2.2).

The Vauban district lies at the southeastern border zone of the Freiburger Bucht. The upper two meters of the sediments consist mainly of limy, fine erosion sediments in the eastern part of the Vauban district and high tide clay in the northern and central part. These high tide sediments consist of clayey, sandy silt with an underlying layer of silty sand. Next to the Dorfbach there is a narrow stripe with floodplain sediments. In many parts of the Vauban district there are anthropogenic fillings crossing through the natural sediments (Scherzinger, 2002).

The sediments between two and five meters below ground can be differentiated between gravel from the Dreisam in the north and high weathered gravel from the Hexental in the south. Additionally in the very east there is a clay pit and the soils have a high clay content. The thickness of the Dreisam gravel layer decreases from northwest to southeast. The Dreisam gravel consists mainly of fine to coarse gravel and has a low sand content. The Hexental gravel is finer and more weathered.



Geologische Übersichtskarte des Oberrheingrabens

FIGURE 2.2: General map of the geology of the Oberrheingraben (Röhr, 2006).

2.2 Hydrogeology

The facts about the hydrogeological conditions of the Vauban district are mainly from results of Wagenmann-Gaiser (2004) and reports of Beller Consult GmbH (1996). The groundwater conditions, which are discussed here, apply only to groundwater from the Quaternary sediments. Deeper aquifers are not mentioned here. The Dreisam gravel in the north and the southern weathered gravel are the most important aquifers in the study area. The hydraulic conductivities (k_f) range between 10^{-2} m/s and 10^{-4} m/s for the Dreisam gravel. Higher silt portions can result in k_f -values below $5*10^{-6}$ m/s for the weathered gravel, which is unsuitable for rainwater percolation (ATV-Arbeitsblatt A 138, 1999). The gravel layer is overlain by high tide sediments, erosion material or floodplain sediments, which build a compact layer with very low conductivities $(k_f = 10^{-7} - 10^{-8} \text{ m/s})$. Therefore it acts as an aquiclude. With raising ground water levels it leads to confined aquifer conditions (Beller Consult GmbH, 1996).

The groundwater from the study site comes from the Hexental and flows in the direction

of a deep well in Merzhausen, a local cummunity adjacent to the Vauban district, which is used by the municipal utility of Freiburg. Due to the sedimentation of the dreisam gravel, the groundwater flow changes to a northwestern direction, with an average hydraulic gradient of 8 ‰. The groundwater gradient has an average between 1.4 and 1.5 ‰, but raises up to 1.7 ‰southeast of the Merhausener Straße due to the influence of the deep well Merzhausen. Estimating an effective porosity of circa 0.15, Wagenmann-Gaiser (2004) state a groundwater distance velocity of about 0.8 m/day, which exceeds in the area that is affected by the deep well. In his work the groundwater depths until 2004 are specified to range between about 2.5 and 3.5 meters for relative high water in the northwestern part of the study area and raises up to a range between about 3.5 and 4.5 meters southeast of the Merzhausener Straße. The study also describes rising groundwater tables during the last years and expected highest water tables of about 0.2 and 0.5 meters below ground level. Due to its historical military use of the Vauban district, the results of hydrogeological reports show increased concentrations of halogenated hydrocarbons.

2.3 Stormwater management

When in 1996 the planning for the redevelopment of the new district Vauban occurred, several boundary conditions for the stormwater infiltration had to be considered. The hydraulic conductivity of the overlaying soil layers is very low, and the groundwater table distance to the surface can be very low. The soil layer is partly contaminated, due to the military history of the area, and the use of the Dorfbach as a draining ditch is limited.

The primary goals were to establish an innovative drainage system which separates residential wastewater from stormwater runoff and to build trough-drain systems. Additionally, a decentralized stormwater management, including for example rainwater use for irrigation, green roofs and -areas, should be applied. All these actions should result in reducing the surface runoff. Finally a conventional mixed water system was applied In the north of the Vauban district, whereas for a 16 hectares area in the southern part the modern surface drainage approach was implemented.

2.3.1 Study site - Trough-drain system

The multi-trough-drain system of the Vauban district is built up of two parallel systems, which in each case consist of several strung together trough-drains. The troughs are separated by spillover barriers and connected with inlet pipes, through which the surface runoff of the adjacent urban area enters (see figure A.9). Cobbled channels collect the stormwater runoff from houses and streets and carry the water to the inlet pipes. An exception is stormwater from the main street, which drains in a mixed water system due to contamination risks. If the collected stormwater exceeds the retention volume of the multi-trough-drain system, it flows across a spillover, directly into the receiving water course Dorfbach.

The researched trough for this study was the trough 914/3, which is the third in a row of the cascadian rowed multi-trough drain system Boulevardgraben. It is a trapezoidal ditch and about 48 meters long and 1.1 meters wide. The escarpment is grassed and has a steep angled at about 56°. Big Linden trees are rowed at the northern side of the trough which shadows the area during noontime. The measured ground height of the trough in 2011 was 256.8 meters and has a slight slope in the northwestern direction. Its total catchment area is around 8600 m² (figure 2.3). All buildings have flat roofs whereof most is greened. Additionally there are tiled and tin roofs. Besides the buildings area there are a road, smaller trails, gardens and green areas.

layer	area	${ m thickness}$	total vol.	porosity	retention vol.
dimension	$[m^2]$	[m]	$[m^3]$	-	$[m^3]$
trough	53.2	-	-	-	5.95
top soil	61.75	0.7	43.23	0.3	12.97
sand	61.75	0.2	12.35	0.4	4.94
drain	61.75	0.7	43.23	0.35	15.13
sum	-	1.6	98.81	-	38.99

TABLE 2.1: Dimensions of the trough-and-drain system.

The retention volume of the trough is about 5.95 m³, which implies a water storage level of about 10 centimeters. Additional water inflow passes the spillover barriers and enters the next trough. For the maximum retention volume the watered area, including the flanks, averages about 53.2 m². Infiltration experiments from 2011 resulted in a



FIGURE 2.3: The study site 'Trough 914/3' and its catchment. The purple rectangle shows the dimensions of the drain.

hydraulic conductivity of $2.93 * 10^{-5}$ for the trough, which gives an infiltration rate of about 1.58 liters per second for the whole area.

In the longitudinal cut of figure 2.4 and the cross section of figure 2.5, the structure of the trough-drain system is shown. The top soil layer is about 70 cm thick, which gives a retention volume of circa 12.35 m³ under an estimated porosity of n = 0.3. The underlying sand layer acts as a barrier between the drain and the top soil layer. Its retention volume is about 4.3 m³, with an estimated porosity of n = 0.4. The drain underneath is about 0.7 m thick and has a retention volume of 16.1 m³. This results in a total retention volume of about 38.99 m³.

2.3.2 Study site structures

In 2012 an observation well as illustrated in figure 2.6 was built next to the trough 914/3. The 4.15 meters long tube is filtered for 3.72 meters. The drill log shows the thickness of the different layers. As already discussed in chapter 2.1, there is a thick layer of high flood sediments which strongly decreases the percolation rate of rainwater



FIGURE 2.4: A longitudinal cut through the study site.



FIGURE 2.5: Cross section of the trough-drain system. Changed after Jackisch et al. 2013



FIGURE 2.6: Drill log of the observation well (changed after Santa Maria (2013)).

and disconnects the underlying aquifer of weathered gravel.

Another important structure of the through is the overflow pit (figure 2.7). Besides, they act as an additional outflow if the water filling of the trough is above the threshold, overflow spills have a direct connection to the drain. The connection is through a screened pipe on the bottom of the overflow pit which "passes" the drain. Therefore, as long as the drain is partly saturated with water, there is a water level inside of the overflow pit. The monitoring tube is used for protecting of the measuring probes. The groundwater pit at the end of the trough has a very similar function as the overflow pit. The difference is that the bottom of the pit is connected with the aquifer, so that the water inflow directly percolates into the groundwater.

2.4 Experimental setup

For the realization of the tracer experiment, several measurement and sampling devices had to be installed.



FIGURE 2.7: Overflow pit with a monitoring tube.

2.4.1 Soil moisture devices

To measure the soil moisture 5TE soil moisture probes purchased from UMS (Umwelt-Monitoring-Systeme) were used. 5TE probes measure volumetric moisture content, temperature and electrical conductivity. The measurement accuracy averages ± 3 % and the vertical measuring range is 10 cm. Due to the length of the probe cables, the moisture probes were installed in 1.5 meters distance from the monitoring tube. Therefore, two 30 cm deep holes were dug with a spade, to avoid destroying the soil texture or the sod and in each case the probes were put vertically in 5 and 15 cm depth (figure 2.8). After that the pit was refilled with the soil. Between application of the soil moisture probes and the implementation of the tracer experiment there was a time difference of three weeks, so the natural soil texture could restore. To protect the probes, the cables were buried till the monitoring tube, then staked along the tube and put through the inlet of the overflow pit. In the overflow pit an EM50 digital data logger (Decagon Devices) was applied to save the measurement data of the soil moisture probes. The logger storage has 5 megabytes lasting for 36,000 scans of all input channels. The logger case is



FIGURE 2.8: Installation of the soil moisture probes.

weatherproof and impact resistant.

2.4.2 Pressure devices

Three OTT Orpheus Mini WaterLevel Logger were used for measuring the water levels in the trough, the drain and in the observation well. It has a ceramic-capacitive measuring cell to detect pressure of the water depth and a temperature sensor. The pressure probe is connected with the communication unit by cable, containing a four megabyte data logger, capable of recalling approximately 500,000 measurements. At the top of the communication unit is an infrared interface to readout the data. The measuring resolution is 0.01 % and 0.1 °C for the pressure and the temperature sensor, respectively. The accuracy is ± 0.05 % and ± 0.5 °C, respectively.

One of the pressure probes was put at the bottom end of the monitoring tube to measure the water level of the dammed water in the trough. The second probe was put in the observation well to monitor the groundwater level and the third was put in the tube which gains access to the drain.
2.4.3 Automatic sampling devices

To collect water probes from the observation well and the drain, two automatic sampling devices (APEG) were used (figure A.1 and A.2 in the appendix). Each can hold 42 samples and is controlled by an analog timer. The minimum time between two samples is 15 minutes and the maximum is one sample each day. The sampling tube was put together with the diver probe of the observation well and the drain to collect probes from both systems.

2.4.4 Tracer

As already introduced three different types of tracers have been applied for this study. Table 2.2 lists all relevant physical properties and information of these substances. According to this, one can see that UR and BR have a very high solubility, compared to very small values of RAZ and RRU. The soil retention of RRU and SRB is about two dimensions bigger than of UR. Big differences are also between the detection limit of the tracers. By a factor of 50.000 the limit for BR is greater compared to UR. It has to be considered that the detection limits are usually determined in pure, deionized water and increase for stream and especially for soil water samples.

2.4.5 Jackisch tracer experiment

The experimental setup of the multi-tracer experiment from Nicole Jackisch was similar to the one of this work. She buried two 5TE soil moisture probes from UMS in 5 and 40 centimeters soil depth and also used an APEG for automatic sampling of water from the drain. Additionally, CTD-diver from UIT were used to measure the water level, temperature and electrical conductivity in the drain and the monitoring tube at the trough. As the adjacent groundwater well was built one year after that, there was no sampling of the groundwater.

property	\mathbf{UR}^{-1}	\mathbf{RAZ} ²	\mathbf{RRU} ²	\mathbf{SRB}^{-1}	Bromide ¹
chemical formula	$C_{20}H_{10}O_5Na_2$	$NaC_{12}H_6NO_4$	$NaC_{12}H_6NO_3$	$NaC_{27}H_{29}N_2O_3$	NaBr
excitation	491 nm	602 nm	$570 \ \mathrm{nm}$	561 nm	ı
emission	516 nm	616 nm	585 nm	586 nm	
relative fluorescence intensity $[\%]$	100	0.11 ³	0.74^{-3}	7	ı
delta lambda	$25 \ \mathrm{nm}$	14 nm	$15 \ \mathrm{nm}$	$25 \ \mathrm{nm}$	
detection limit	$0.001~{ m mg/m^3}$	depends on RRU-Conc. ⁴	$0.036~{ m mg/m^3}~^4$	$0.03~{ m mg/m^3}$	$50~{ m mg/m^3}$
solubility	$> 600 \text{ g/l} (20 ^{\circ}\text{C})^{5}$	$18.4 \text{ g/l} (25 ^{\circ}\text{C})$	$20.0 \text{ g/l} (25 ^{\circ}\text{C})$	$3-20.0 \text{ g/l} (25 ^{\circ}\text{C})$	$850 \text{ g/l} (10 ^{\circ}\text{C})$
soil retention (K_d)	0-0.4 ml/g	6.63 ml/g	33.2 ml/g	36.6 ml/g	
sorption processes	negligible	possible	possible	important	negligible
light sensitivity	high	${ m small/medium}$	medium	low	no
photolytic stability (DT_{50})	11h	> 100 h	$> 10 \ h$	820 h	ı
method	FS	FS	\mathbf{FS}	\mathbf{FS}	IC
¹ If not cited differently all values o	f column from Leibund	lgut et al. (2009).			

² If not cited differently all values of column from Haggerty et al. (2008). ³ For RAZ and RRU values of the quantum yield, from Bueno et al. (2002).

⁴ Haggerty et al. (2008), detection limit approximately three times higher than limit of quantification (for RRU= 0.012 mg/m³). ⁵ Käss (2004).

Chapter 3

Experimental procedure and methods

This chapter explains the procedure of the tracer experiment including the methods which have been used either in field, lab or to analyze the measurements data. The open source software R and the commercial software Excel from Microsoft were used for the analysis, evaluation and presentation of the data in this study. For the development of maps, the commercial software Arc GIS version 10.2 was used.

3.1 Field methods

The tracer experiment occured on the 9th of July in 2015. The experiment can be roughly divided in three different steps:

1st: Saturation of the trough-and-drain system.2nd: Injection of the tracers3rd: Rewetting of the trough-and-drain-system

3.1.1 Saturation

As shown in table 2.1, the total retention volume is expected to be around 39 m^3 . Therefore, the goal for the whole tracer experiment was to inject this amount of water, in order to have a good vertical water flow and approximately saturated conditions for the system. A mobile hydrant and fountain was borrowed from the local public services and installed next to the trough, where it could be connected with the drinking water pipeline. It had an analog water meter which helped to determine the flow rate. A fire hose was plugged with the hydrant and fountain and placed until the upper end of the trough. Next all data logger were turned on and adjusted to a storage interval of 2 minutes.

From 14:30 until 16:00 h, the hydrant and fountain was turned on and the saturation of the trough-and-drain system began. The mean water flow of the hydrant was around five liters per second (table 3.1). During the saturation, the flooding height at the end of the trough was measured manually. It exceeded from 3 centimeters at 15:40 h, to 5 centimeters at 15:47 h and up to 8 centimeters at 16:00 h. (As already mentioned, the trough has a small slope and therefore the flooding height had its maximum at the end of it). At 16:00 the hydrant was turned off and the water height decreased slowly.

work step dimensions	time	water meter $[m^3]$	\mathbf{Qmean} $[1/s]$	$Vtot$ $[m^3]$
	LJ	L]	L / J	L J
1. saturation-start	14:36	939.71	-	-
saturation-end	16:00	964.03	4.8	24.3
2. tracer injection-start	20:10			
tracer injection-end	20:16			
3. rewetting-start	20:23	964.03	-	_
rewetting-end	22:02	981.44	2.9	17.4

TABLE 3.1: Water and tracer injection schedule.

3.1.2 Tracer injection

The estimation of the required tracer mass resulted from the set-up of the last experiment at this study site. In 2012, Jackisch used 6.4 g of UR and 1000 g of Sodium bromide (BR). The fluorescence intensity of UR was higher than the measuring range during peak flow, hence these samples had to be diluted. To avoid this, only about 1 g of UR was used for this study. The amount of BR was maintained. The assessment of the RAZ/RRU tracer mass was more challenging. In a student tracer experiment at a wetland in 2014, 0.25 g of UR and 4 g of RAZ/RRU were injected. Transferring the ratio



FIGURE 3.1: Flooded water at the end of the trough during saturation.

between the masses of 1:16 would result in 16 g of RAZ/RRU for this experiment. Since the investigated systems are very different and the amount of RAZ/RRU was limited, the actual used mass for this study was decreased to 10 g of RAZ/RRU. Table 3.2 shows all tracer masses which were used for this experiment.

tracer	injection mass
dimensions	[g]
Uranine	1.04
RAZ/RRU	10.0
Bromide 1	777.3

TABLE 3.2: Tracer injection masses.

¹ Bromide mass from sodium bromide

Three hours after the saturation phase, the preparation of the tracer injection started (figure A.4 in the appendix). BR and UR were already dissolved in the lab. UR was mixed with 100 ml of water and BR was dissolved in two liters of water. Both bottles were put fifty-fifty in two 10 liter watering cans. RAZ/RRU was purchased in powder

form 5 g vials. Due to a very low solubility of RAZ/RRU, one vial was put in each of the cans directly, which then were made up to 10 liters with water. After that the tracers were mixed for about twenty minutes, assuring that all of RAZ/RRU gets dissolved. Immediately after mixing, the tracer injection on the trough started. Both cans were spilled out, meandering along the whole length of the trough (figure A.6 in the appendix). Only at the inlet pipe where the ground is cobbled, an action against erosion processes, and next to the probes it was spared. The empty cans were filled again with water for further two times and spilled out along the trough to ensure that the whole tracer solution was out.

3.1.3 Rewetting

A few minutes after tracer injection all automatic samplers and the hydrant and fountain were turned on (figure A.7 in the appendix). The mean water flow into the trough was circa 2.9 liters per second which resulted in a total volume of 17.4 cubic meters (see also table 3.1). Summed up around 44 cubic meters water have been flowed into the trough-trench system for the whole time of the experiment. The time schedule of the auto samplers is shown in table 3.3. The samples were stored dark and cooled in the refrigerator until they were measured.

sample interval	end	start
$0.5 \ h$	$10.7.15\ 20:30$	$9.7.15\ 22{:}00$
1 h	$11.7.15\ 12:30$	10.7.15 21:30
2 h	$23.7.15\ 10:30$	11.7.15 14:30

24 h

28.8.15 08:00

TABLE 3.3: Sample time schedule.

3.1.4 Jackisch tracer experiment

24.7.15 08:00

Nicole Jackisch conducted a multi-tracer experiment between July and October in 2011. The injected tracer masses are listed in table 3.4. Due to a much higher soil retention and and a lower fluorescence intensity the injected SRB mass is distinctly higher than the UR mass (see table 2.2). The tracers were each diluted in two 8 liters watering cans and spilled out along the trough. Compared to the experiment of this study there was no intensive rewetting phase. Instead, with a mean flow rate of about 1.6 liters, they injected the same water flow in the trough for about 6 hours. The sample interval increased with time from half an hour up to one sample a day. The measured data from this tracer experiment is analyzed and evaluated in this study.

TABLE 3.4: Jackisch tracer injection masses.

tracer	injection mass
dimensions	[g]
Uranine	6.4
Sulforhodamine B	64.9
Sodium bromide	906.1

TABLE 3.5: Water and tracer injection schedule of the Jackisch experiment.

work step	time
BR-application	20.07.2011 $22:10$
UR-application	20.07.2011 $23:05$
SRB-application	20.07.2011 $23:05$
Start flooding	20.07.2011 $23:05$
Start sampling	20.07.2011 $23:05$
End flooding	$21.07.2011 \ 05:15$
End sampling	08.10.2011 23:01

3.2 Lab methods

3.2.1 Flurometer spectrometry

The fluorescence spectrometer LS 50B from Perkin Elmer was used to measure the concentration of the fluorescence tracers. The measurement principle is a pulsed light from a xenon lamp which excites the molecules of the sample. After the stimulation the molecules energy level falls back, which results in an energy emission in terms of fluorescence radiation. Both intensities of the excitation radiation and the emission radiation are measured, with a molecule specific maximum. The synchronous scan technique, used for this work, does not separate between the scans of the excitation and the emission spectra. It uses the distance between the emission and excitation wavelength ($\Delta\lambda$) and



FIGURE 3.2: Example for the result of a synchronous scan. (Leibundgut et al., 2009).

scans the given spectrum (Leibundgut et al., 2009). For the result it overlies the intensities of both spectra (figure 3.2). The adjustments for the analysis of each tracer are shown in table 3.6. Due to the same $\Delta\lambda$ of RAZ and RRU they can be measured at once. All measurement results could be found within the measuring range, so no dilution had to be applied. Also the pH value of the randomly measured samples varied only between 7.6 and 8.0, hence no alkalinization was executed. The fluorescence intensity of RRU is almost unaffected within this pH range (Bueno et al., 2002) and also for UR the changes of intensity are minimal.

tracer	$\Delta\lambda$	scan speed	wavelength of peak
dimensions	[nm]	[nm/min]	[nm]
UR	25	300	488.77
RAZ	15	300	606.97
RRU	15	300	567.71

TABLE 3.6: Spectrometer adjustments.

To determine the tracer concentrations by the fluorescence intensity, calibration curves were fitted. Therefore, standards with water from the hydrant at the study site and known tracer concentrations were measured. The results of the calibration are shown in table 3.7. Due to self shadowing effects, higher concentrations of RAZ and RRU left the linearity. Therefore an exponential regression line has been applied for higher values. Plots of all calibration curves are in the appendix (figure B.3).

tracer	calibration curve	units	max. I	\mathbf{R}^2	RSS
UR	c = 0.006 * I - 0.0531	$\mu { m g/l}$	813	0.9998	0.0038
RRU	c = 0.129 * I -0.0795	$\mu { m g/l}$	53	0.9987	0.0434
RRU	$c = 3.646 * e^{0.0141*I}$	$\mu { m g/l}$	53 <i<160< td=""><td>-</td><td>1.438</td></i<160<>	-	1.438
RAZ	c = 2.656 * I -1.6957	$\mu { m g/l}$	72	0.9981	51.01165
RAZ	$c = 100.012 * e^{0.0103*I}$	$\mu { m g/l}$	72 <i<220< td=""><td>-</td><td>925.8</td></i<220<>	-	925.8

TABLE 3.7: Fluorescence tracer calibration.

Due to suspended material, humins or air bubbles, water samples from surface, soil or unclear groundwater can have high background signals while measuring its fluorescence activity. This is particularly true for lower wavelength ranges. Leibundgut et al. (2009) therefore recommends to allow the samples to stand for one night. In case of very turbid water, the samples can additionally be filtered or centrifuged. However, if background signals are still present during measurements, the background signal has to be interpolated as shown in figure 3.3. The consequential intensity of the peak ($I_{peakresult}$) after removing the background signal was calculated as shown in equation 3.1 and figure 3.4.

$$I_{peakresult} = I_{peak} - I_{start} - \left(\frac{(I_{start} - I_{end})}{(\lambda_{end} - \lambda_{start})} * (\lambda_{peak} - \lambda_{start})\right)$$
(3.1)

Therefore the different wavelength (λ) values of the start and end of the peak have to be identified. They can distinguish between peaks.

3.2.2 Ion chromatography

The Dionex ICS-1100 Ion Chromatography System from Thermo Fisher Scientific was used to measure the BR concentration in the water samples. Therefore, the sample gets injected into an eluent, a liquid of constant concentration and composition, which assists to separate the ions of the sample. Next it flows through two different columns,



FIGURE 3.3: Interpolation of the background signal from the fluorescence peak.



FIGURE 3.4: Terms of the equation to calculate the resulting peak intensity.

which first remove possible contaminants and then separate the ions. After passing the suppressor, which improves the detection of the sample ions but suppresses the conductivity of the eluent, the sample enters the detection cell. Here, a conductivity cell measures the electrical conductance of the ions. The resulting data is compared to standard solutions to quantify the ion concentrations of the sample (Thermo Fisher Scientific, 2012). The standard solutions are renewed every month and the results are

stored for the data collection software.

The experimentally determinated detection limit of Bromide is about 0.088 mg/l. That is why the amount of injected mass must be considerably higher compared to fluorescence tracers. For preparation of the injection vials, each water sample had to be filtered with 0.45 μ m paper, in order to avoid contamination or jamming the injection.

3.2.3 Soil analysis

One objective of this work was to investigate if there are sorption processes in the top soil layer, which delay or even reduce the tracer flow. Thus, soil samples were taken before the tracer experiment was applied to get background values and additionally two weeks after the experiment was conducted. Every 5 meters along the trough, an auger was hammered until 50 cm depth and pulled out. It was sampled over the entire width of the bottom trough. The soil samples were differentiated between 0-25 cm and 25-50 cm depth and put in different bags. Subsequently, the samples were air-dried for two days under shaded conditions. Afterwards, they were stored in the refrigerator. The holes in the trough were refilled to generate its former conditions.

For the UR and RAZ/RRU analysis, the soil samples were executed under the instructions for activated carbon as a medium for determination of fluorescence tracer following Wernli (2011). Instead of activated carbon, there were soil samples. At first 2 g of soil were weighed three times for each depth zone and also for the blank soil sample of previous conditions (before tracer application). The weighed soil was put into lockable test-glass. To extract the tracer from the soil, a solution of 60 % ethanol and 40 % of a 20 % - ammonia dissolution was prepared. 11 ml of this extraction solution was pipetted into each test-glass. Every half hour each locked test-glass was shaken carefully for a minute. After two hours it was shaken one last time and was allowed to stand for one night. During that time all visible soil fractions sedimented. The next day, 3 ml of solution was pipetted out of each test-glass, put in beaker glasses and diluted with 20 ml of de-ionized water. In addition, one sample exclusively filled with the extraction solution was added to scan for fluorescence activity. Finally, these solutions could be measured with the fluorescence spectrometer.

Due to the dilution, the results had to be calculated as shown in equation 3.2 and 3.3a. c_{soil} is the resulting tracer concentration per gram soil, f_{dil} the dilution factor and f_{calib} the calibration factor from the tracer calibration. These factors had to be multiplicated with the measured intensity ($Int_{solution}$), the volume of the pipetted solution ($V_{pipette}$) and divided through the exact mass of the soil sample (m_{soil}) to finally get the tracer concentration.

$$c_{soil} = \frac{Int_{solution} * f_{calib} * f_{dil} * V_{pipette}}{m_{soil}} = \left[\frac{\mu g}{g_{soil}}\right]$$
(3.2)

$$f_{dil} = \frac{V_{dilution}}{V_{pipette}} = \frac{23ml}{3ml} = -7.67 \tag{3.3a}$$

$$f_{calib} \rightarrow calibration \ curve$$
 (3.3b)

Due to the very high ammonia concentrations, the tracer extraction method of Wernli (2011) could not be used for analyzing the BR concentrations in the IC. The measurement cell and the flow columns would be too high loaded. Thus a different method was used similar to Leistra and Boesten (2010). At first, 5 g soil samples were shaken with 20 ml de-ionized water for one hour and then centrifugated for 2 minutes at 3000 revolutions per minute. After centrifugation, the clear supernatant was filtered with 0.45 μ m filter paper and then measured with the IC.

The resulting tracer concentration in the soil is calculated as in equation 3.4. As shown, the given concentration of the solution has to be multiplicated with the volume of the added water (20 ml) and then divided through the mass of the soil sample.

$$c_{soil} = \frac{c_{solution} * V_{pipette}}{m_{soil}} = \left[\frac{\mu g}{g_{soil}}\right]$$
(3.4)

3.3 Soil model

An important part of this work was to get a better understanding of the hydraulic characteristics of the trough-trench system. Therefore a conceptional model of this system was the basis of further calculations. As it is shown in figure 3.5 the major part of this system are three different storages. Each storage has a specified water volume. The trough volume (V_{trough}) is determined by the soil moisture content, which is measured by the soil moisture probes. The water volume of the drain (V_{drain}) and the groundwater (V_{gw}) are both determined by the water table which is measured by the pressure probes. It is assumed that in case of a water table or a soil moisture content equal zero that the storage is empty.

Between the storages there are different fluxes. The water flow from the trough to the drain storage is stated by Q_{trough} , and from the drain to the groundwater storage by Q_{drain} . The water flux which leaves the groundwater storage of the system is stated by Q_{gw} . The only flux which flows against gravity is the evapotranspiration-powered water flow E_{pot} , which affects the trough soil water storage. The units of all fluxes and water volumes in the following equations are mm.

3.3.1 Calculate evapotranspiration

Whereas all storage units of the model are known, the fluxes between them have to be calculated. E_{pot} was calculated with data from the climate station next to the study site. To get daily values of evapotranspiration, the empirical method after Turc (1961) was used. For that, mean daily values of temperature (T) and relative humidity (U) plus the daily sums of the global radiation (R_G) had to be calculated from the available minute values. Using the equations after Turc (1961), as shown in equation 3.5 and 3.6, results in an evapotranspiration rate for each day ($E_{potturc}$). In case of relative humidity values higher than 50 %, the factor C is 1 (equation 3.6b); otherwise it is calculated after equation 3.6a. For further calculations the daily values were divided into 30 minutes values.

$$E_{pot_{turc}} = 0.0031 * C * (R_G + 209) * \left(\frac{T}{T + 15}\right)$$
(3.5)

$$C = 1 + \left(\frac{50 - U}{70}\right) \Leftarrow for U \leqslant 50\%$$
(3.6a)

$$C = 1 \Leftarrow for U > 50\% \tag{3.6b}$$

During days of high solar radiation, the soil moisture data showed diurnal variations. They were independent of the trend of the moisture content. It was assumed that these variations were powered by evapotranspiration processes. That is why these curve characteristics were separated by linear interpolation from the continuing soil moisture content trend. The moisture variations from different days were normalized by dividing each value through the sum of all values (equation 3.7). Calculating the mean of all normalized variation curves resulted in a density function ($f_{density}$), which describes the diurnal variations of the soil moisture content (equation 3.8). This function was then multiplied with $E_{pot_{distributed}}$) (equation 3.9).

$$M_{variation_{norm(i)}} = M_{variation_i} / \sum_{i}^{n} M_{variation_i}$$
(3.7)

$$f_{density} = \frac{\sum_{i}^{n} M_{variation_i}}{n} \tag{3.8}$$

$$E_{pot_{distributed}} = f_{density} * E_{pot_{turc}}$$
(3.9)

3.3.2 Calculate water fluxes

The next step was to determine Q_{trough} . The assumption was, that in times during the measurement period where no water input in the system occurred, the soil moisture content is continuously decreasing. Additionally, it was assumed that the only factors which would change the soil moisture content during these times were E_{pot} and Q_{trough} . This means that after subtraction of E_{pot} , the resulting change in water volume of the soil moisture content per time step (ΔV_{trough}) is due to the output Q_{trough} (equation 3.10 and 3.11).

$$Q_{trough_i} = \Delta V_{trough_i} - E_{pot_i} \tag{3.10}$$

$$\Delta V_{trough_i} = V_{trough_i} - V_{trough_{i-1}} \tag{3.11}$$

Therefore it was crucial to have a longer rain-free period. Luckily, after the tracer input there was no precipitation for several days. The soil moisture recession curve of that time was the basis to define a functional relationship between soil moisture content and Q_{trough} . Therefore, V_{trough_i} of the rain-free period was plotted against ΔV_{trough_i} to perform a regression. The function of this regression was furthermore applied to the whole measurement period to calculate ΔV_{trough_i} depending on V_{trough_i} , but independent on any water input in the trough. After subtracting Epot_i, Q_{trough} was calculated for the whole measurement range. Then the other fluxes Q_{drain} and Q_{gw} could be computed with the equations 3.12 and 3.13.

$$Q_{drain_i} = \Delta V_{drain_i} - Q_{trough_i} \tag{3.12}$$

$$Q_{gw_i} = \Delta V_{gw_i} - Q_{drain_i} \tag{3.13}$$

3.3.3 Calculate matter transport

After assessing the water transport of this model, the next step was to determine the matter transport. As illustrated in figure 3.6, the measured tracer concentrations are from the water samples of the drain and the groundwater, differing from its former concentration in the trough soil. The reason is that incoming tracer fluxes get diluted by the water volume in each storage. To remove this dilution factor and to calculate the actual tracer concentration entering the drain, the following equations 3.14 and 3.15 had to be computed. With the given concentrations of the drain water samples, equation 3.14 provides the tracer concentration of the trough soil (C_{trough}) for each time step. For the groundwater samples, the tracer concentration for the drain storage had to be calculated beforehand. The results could then be filled in equation 3.14. The mass balance underlying these equations is shown in equation 3.16.

$$C_{trough_i} = \frac{(C_{drain_i} * V_{drain_i}) - (C_{drain_{i-1}} * Q_{drain_i}) - (C_{drain_{i-1}} * V_{drain_{i-1}})}{Q_{trough_i}}$$
(3.14)

$$C_{drain_{i}} = \frac{(C_{gw_{i}} * V_{gw_{i}}) - (C_{gw_{i-1}} * Q_{gw_{i}}) - (C_{gw_{i-1}} * V_{gw_{i-1}})}{Q_{drain_{i}}}$$
(3.15)

$$(C_{drain_{i-1}} * V_{drain_{i-1}}) + (C_{trough_i} * Q_{trough_i}) = (C_{drain_i} * V_{drain_i}) + (C_{drain_{i-1}} * Q_{drain_{i-1}})$$

$$(3.16)$$

To compare those results, the tracer concentrations of the time series were normalized by dividing the concentration through the tracer injection mass (see equation 3.17). $m_{injection}$ is the injection mass and $C_{tracer_{norm(i)}}$ stands for the normalized tracer concentration.

$$C_{tracer_{norm(i)}} = \frac{\sum_{i=0}^{n} C_{tracer_i}}{m_{injection}}$$
(3.17)

$$R_{tracer} = \frac{\sum_{i=0}^{n} C_{tracer_i} * Q_{trough_i} * A}{10^6 * m_{injection}} * 100\%$$
(3.18)

The tracer mass retention (R_{tracer}) for the trough soil system was calculated in the following steps: First, multiplying the tracer concentrations with the trough outflow and the area (A) of the trough-and-drain system; second, dividing it through the tracer injection mass and a factor which depends on the input units. The equation 3.18 is for tracer concentrations in μ g/l and the trough outflow in mm. Working with concentrations im mg/l reduces the factor from 10⁶ to 10³.



FIGURE 3.5: Conceptional model of the hydraulic structure of the SIS.



FIGURE 3.6: Conceptional model to determine matter concentrations in the SIS.

Chapter 4

Results

4.1 Hydraulics

Soil moisture

Figure 4.1 illustrates the soil moisture content of the probes in the trough soil. The brownish lines represent the time series for the probes in 5 cm soil depth, whereas the greenish lines stand for 15 cm soil depth. One of the deeper moisture probes died during the time of observations. Climate data was available until the 23rd of August.

Four main peaks are visible during the measurement period. The first represents the soil moisture change due to the flooding during the tracer experiment. The other peaks can be related to bigger rainfall events. The reaction to the main peak events is similar for all probes, but the peak values of the deeper soil probes are smaller. The curves of the deeper soil depth flatten earlier after the big events show less variations between the main peaks. The shallow probes show fluctuations due to smaller rain events, and partly show diurnal variations in the soil moisture content. The shallow soil usually drained stronger, however one of the probes in 5 cm depth showed a higher soil moisture content and dried for the second half of measurements, similar to the deeper soil layer. It seems that 30 to 35 % are the highest value for the soil moisture content. Therefore it can be an estimate for soil porosity.

Drain water and groundwater

Figure 4.2 and 4.3 show the measurements of the groundwater and drain water pressure probes. The red horizontal lines represent the limits of periods where the drain was dry.



FIGURE 4.1: Time series measurements of the soil moisture probe.

Both figures show three main peak events in their water tables. The first comes from the flooding of the tracer experiment, the other from bigger rain events. Temperature and electrical conductivity (EC) data of the drain probe also show clear reactions on infiltrating water, visible by collapsing values at events. For the first two peaks, it takes approximately four days until the conductivity ranges between pre-event values again (900 - 1000 μ S/cm). Both peak events lead to a minimum in the EC of about 650 μ S/cm. There are very strong fluctuations between the second and third peak. Shortly after the drain dries out, the conductivity measurements stop.

Looking at the temperature time series, the reaction on infiltrating water is a sharp peak, followed by a fast drop back and a slower increase with a maximum at the same time as the EC has its minimum. Usually, the temperature then decreases slowly. For the whole measurement time a slight increase of the temperature could be detected.

The water table of the groundwater data (figure 4.3) displays the same three main peaks. The time difference of the peak maxima between the drain and the groundwater is 35 minutes for the first, 25 minutes for the second and around 30 minutes for the third



FIGURE 4.2: Time series measurements of the pressure probe in the drain water. The red horizontal lines show the time period where the drain was dry.



FIGURE 4.3: Time series measurements of the pressure probe in the groundwater. The red horizontal lines show the time period where the drain was dry.

peak. This leads to an estimated hydraulic time lag of about 30 minutes between the two systems. The increase of water level during the peak event for both systems is the same for the third event (15 cm), but differs for the other two bigger peaks. For the first peak, the rise of water table amounts 74 cm for the drain, 47 cm for the ground water and for the second peak 68 cm and 44 cm, respectively. For both events the water table rise reduces about 35 % from the drain to the groundwater system.

The EC shows only little reaction on the bigger peak events with a little drop during the maxima of the peaks. Otherwise, there are only little fluctuations and a slight increase of the EC during the measurement period. The temperature displays no reaction on the peak events. A constant increase of the groundwater temperature from about 14 to 16 °C is recognizable.



FIGURE 4.4: Correlation between the groundwater table and the drain water table. The dashed black line is a 1:1 line.

Figure 4.4 illustrates the correlation of the drain water table against the groundwater table. The color shift represents the time of the measurement period. Several hysteresis

like loops, which proceed in an anticlockwise direction, are visible. The dashed black line is a 1:1 line. Both systems correlate similar to that line for lower water tables. The different roots are related to the individual maximum peaks due to rain events and the flooding experiment. The sudden drop down of the curve results from the drying out of the drain.

4.2 Major ions

The drain and groundwater samples depict very different major ions compositions and behavior during time. In figure 4.5, major anions from the drain samples are displayed. The sample interval increased with time, so that the measurement resolution strongly decreased. The curve shapes show distinct changes of the ion concentrations during bigger rain events and the flooding event at the beginning. The chloride and sulfate concentrations drop during rain events, indicating a dilution by the infiltrating water. In comparison, the nitrate concentration progression is horizontally flipped. It illustrates an increase during rain events up to 14 mg/l, whereby concentrations range between between 0 and 3 mg/l during longer times of no precipitation.

For the groundwater samples there is almost no variation for the ion concentration of nitrate, sulfate and chloride (figure 4.6). Only the first sample shows higher values for chloride and nitrate. Otherwise, nitrate concentrations range around 1 mg/l, sulfate concentrations around 40 mg/l and chloride concentrations around 25 mg/l. Correlations to rain events and infiltrating water are not identifiable.

Additionally to the main anions, the main cations of the groundwater and drain water samples are listed in table 4.1. The cations were measured very infrequently (around every tenth sample). The results display, that the mean ions concentrations of both sample types are in the same range. However, the standard deviation (sd) points out that the variation of the concentration was higher in the drain water samples.



FIGURE 4.5: Anions concentration in the drain water.



FIGURE 4.6: Anions concentration in the groundwater.

ion co	drain water ncentration	drain water sd	groundwater concentration	groundwater sd
dimensions	$[\mu { m g}/{ m l}]$	$[\mu { m g}/{ m l}]$	$[\mu { m g/l}]$	$[\mu \mathrm{g}/\mathrm{l}]$
Ammonium	0	0	0.3	0.2
Calcium	92.3	7.8	85.6	0.8
Magnesium	7.5	2.5	11.1	0.1
Potassium	2.5	0.7	1.2	0.1
Sodium	16.7	6.3	20.2	0.3

TABLE 4.1: Mean cations concentration of groundwater and drain water samples.

4.3 Tracer in the drain water

As an example for a measured tracer breakthrough in the Flurometer, the displayed curves in figure 4.7 show the different intensities due to RRU concentrations as a function of time. The first increase of intensity can be recognized at 22:00 h. At this time, UR and BR can also be measured in the water samples. Assuming that the infiltration of the tracer started with the starting point (20:23 h) of the rewetting stage, one can conclude that it took around 1.5 hours to infiltrate through circa 1.6 m. Assuming then that saturated conditions existed, results in a hydraulic conductivity of about 2.96 * 10^{-4} m/s. It is important to consider, that this is only valid for these special flooded conditions.

The tracer breakthrough curves in figure 4.8 show the evaluation of the Flurometer measurements in the drain water samples. All curves have a very sharp peak with high peak concentrations from 9.10.15 22:00 h till 10.10.15 01:30 h. After that, concentrations remain zero until 10.10.15 07:00 h for BR and until 10.10.15 08:30 h for UR and RRU. Hence, a second broader peak shows up with a longer recession of the concentrations. The peak concentration for all tracers is at the same time. However, compared to the conservative tracers, the RRU concentrations show a faster recession. The normalized and focused tracer breakthrough curves in figure 4.9 additionally display that for these first two peaks the concentration of RRU, compared to its input mass, is considerably



FIGURE 4.7: Breakthrough of the first RRU peak in the drain water since tracer injection. The results are from the Flurometer measurements.

higher than of UR and BR. From 15.10.15 8:35 h on, the normalized RRU concentrations are smaller than the BR concentrations, due to its faster recession. Only at the time of four small rain events (17.07, 18.07, 19.07 and 02.08), the normalized tracer concentration of RRU exceeds the one of BR.

The third significant peak follows a big rain event around the 22nd and 23rd of July. Due to bigger sample intervals, the shapes of the curves are very rough. Unlike the other tracers, the maximum of this peak is for BR also the maximum of the normalized tracer concentrations for the whole sampling time. After this peak, except for the little RRU peak at the 2nd of August, the RRU and UR concentrations remain zero.

Figure 4.8 illustrates the last measurement of BR on August 30th. The measurements of the fluorescence tracers were stopped at the 17th of August, as no concentrations could be measured in the samples for about two weeks. RAZ was never measured in the drain water. Tracer concentrations in the groundwater samples could not be measured.

The normalized tracer breakthrough curves from the Jackisch data are depicted in figure 4.10. For normalization in this work, the concentrations (in μ g/l) are divided through their input masses (in g). The first peak at the very beginning can be linked to the flood-ing experiment. For a better presentation, the RRU peak is truncated. The normalized peak concentration is around 180 1/l. The others are at times of bigger rain events. It can be seen that the ratio between SRB and the conservative tracers change with time.



FIGURE 4.8: Time series of the tracer concentrations in the drain water.



FIGURE 4.9: Tracer breakthrough with normalized concentrations in the drain water. The first peak is clipped off and the displayed sample time is shortened with a focus on the RRU breakthrough curve.



FIGURE 4.10: Tracer breakthrough from the Jackisch data with normalized concentrations in the drain water.

For the first peak and the following recession of the curves, the normalized concentration of SRB is generally lower, compared to the conservative tracers. This changes with the second main peak, where the concentrations of SRB raise distinctly sharper. The SRB curve shows subsequently sharper rises of peaks.

Figure 4.11 displays correlations between the tracer concentrations in the drain water samples. The corresponding functions are listed in the appendix (table B.1). The color scheme of the data points reflects the sampling time. Displayed is the same time range as for the normalized plot in figure 4.9. The solid lines are linear and non-linear regressions for concentrations of a specific period. The same color of the line is a regression for the same sample period. The red line shows the linear regression for the first tracer peak, the green line is the linear model for the remaining samples concentrations. The dashed black line is the 1:1 line. The dashed colored lines in the left plot are lines with a specific slope.

The left plot shows the correlation between the two conservative tracers UR and BR. The BR/UR relation almost triples after the first peak and then decreases slightly after



FIGURE 4.11: Mutual comparison of the the normalized tracer concentrations in the drain water. The color scheme reflects the number of water samples. The different curves are functional adaptions to different types of correlations depending on the sampling time.

the second main peak. Except for three samples at the beginning of sampling time, all other samples have a greater proportion of BR.

The central and the right plot show both the relation of RRU against one of the conservative tracers. The red lines of both plots show a non-linear regression for the normalized tracer concentrations of the first main peak. Most of the remaining points indicate a linear relationship pointed out by the green linear regression line. The proportion of RRU is considerably higher compared to UR and BR.

4.4 Soil samples

Figure 4.12 and table 4.2 illustrate the results of the soil samples analysis. The left barplot in figure 4.12 presents the measured tracer concentrations of BR and RRU for different soil depths. The error bars show the standard deviation of the measurements. The BR concentrations are considerably higher than the RRU concentrations. For both



FIGURE 4.12: Tracer extraction from soil samples.

tracers, there is also a strong decrease of the concentration in the deeper soil layer. The central plot shows the tracer mass per cubic meter soil. The barplot on the right represents the normalized tracer mass (or tracer recovery (1/100 %)). It shows bigger portions of RRU, compared to its input mass. The precise value for each bar in the plot is listed in table 4.2.

tracer	${ m soil} { m depth}$	soil concentration	standard deviation	tracer mass	tracer recovery
dimensions	[cm]	$[\mu { m g}/{ m g}_{soil}]$	$[\mu { m g}/{ m g}_{soil}]$	$[g/m^3]$	$[1/100 \ \%]$
Br	0-25	6.36	0.597	8.90	0.15
Br	25-50	3.82	0.613	5.35	0.09
RRU	0-25	0.86	0.067	1.2	47.69
RRU	25-50	0.019	0.0013	0.03	1.05

TABLE 4.2: Tracer extraction from soil samples.

4.5 Hydraulic model

Figure 4.13 displays the diurnal variations and calculated mean of the soil moisture for three different days and for the four different probes. The upper probes have sharp diurnal variations, whereas the lower probes only show slight variations in the left plot. The peak is always at 16:00 h. The different plots also indicate that the pattern of the different soil moisture measurements is not always the same. Except for the light green curve, all curves are close together in the left plot. In the other plots the different soil depths of the probes can be better distinguished, as the deeper probes have a greater volumetric soil moisture content.



FIGURE 4.13: The diurnal variations of the volumetric soil moisture content for the four different probes and the calculated mean. Each plot shows the variations for a specific day.

A section of the mean diurnal variations of the soil moisture content is illustrated in figure 4.14. The single diurnal variations, which were used to determine the distribution of soil moisture variations, are highlighted with colored dots. The selection is reduced to sunny days. The peaks are mainly characterized by a very sharp rise and a steady decrease.

The following work steps generating the evapotranspiration density distribution are illustrated in figure 4.15. The left plot presents one example of the soil moisture variation



FIGURE 4.14: Selection of the diurnal variations of the soil moisture.



FIGURE 4.15: Work steps from the diurnal soil moisture variations to the evapotranspiration density distribution curve (from left to right).

during the day. To extract the variations, the background was cut by linear interpolation (central plot). The rise of the peak begins around 9:00 h and ends around 4:00 h. The

highest values are around 14:00 until 16:00 h. The right plot results from the mean of all background-removed soil moisture variation curves. It is a clear peak with its maximum around 16:00 h and its minimum around 8:00 and 9:00 h. The integral adds up to 100 %.

The functions which describe the relationship between soil moisture content and Q_{trough} are shown in figure 4.16. The results of this study are in the left plot. The Jackisch data can be found in the right plot. The soil moisture difference for these data points is assumed to be equal to the water flow from the trough soil into the drain (Q_{trough}). The corresponding functions are stated in equation 4.1 and 4.2, respectively. In both plots, the most values for Δ soil moisture differ between 0 and 1 mm. In case of the Jackisch data, the highest Δ soil moisture value of the fitting period is around 3 mm, whereas for this experiment accounts for around 8 mm. The corresponding soil moisture is generally lower for the data of this work.



FIGURE 4.16: Correlation of the soil moisture with the change of the soil moisture within each time step. Data points are for both plots from a period of soil moisture recession without any rainfall. The left plot is from the data of this work, the right plot from the Jackisch data. The green line is the regression line for each plot.

$$Q_{trough_i} = e^{\frac{V_{trough_i} - 152.83}{18.73}} \tag{4.1}$$

$$Q_{trough_i} = 2.5 * 10^{-7} e^{V_{trough_i} * 0.07614}$$
(4.2)

Using the fitted model for the whole measurement period of this work gives values of Q_{trough} for each time step. This is illustrated in figure 4.17. It correlates significantly with the trough soil moisture content. The log scale of Q_{trough} has to be considered. The highest values of Q_{trough} are around 50 mm for a half hour time step. After high peaks, the recession of the outflow is very quick and reduces to less than 1 mm within a few days.



FIGURE 4.17: Calculated water flow from the trough soil layer into the drain (middle plot). The Water volume of the trough soil is imaged in the upper plot and the watertable of the drain in the lower plot.

Furthermore, the calculated outflow from the drain into the groundwater (Q_{drain}) is illustrated in figure 4.18. The upper plot shows the water table of the drain and the lower plot shows the groundwater table. The middle figure displays Q_{drain} for the whole measurement period. Some of the distinct outliers indicate even negative values. The outliers are mostly in the field of high peaks. Beside that, the outflow ranges between around 40 mm (maximum peak value) and 0 mm. The outflow amounts between 2 and 0.5 mm five days after high peaks . Compared to Q_{trough} , Q_{drain} shows less variations in the outflow and the reaction to smaller rain events is also extenuated.



FIGURE 4.18: Calculated water flow from the infiltration drain into the groundwater (middle plot). The water table of the drain is imaged in the upper plot and of the groundwater in the lower plot.

Finally, the groundwater outflow Q_{gw} is shown in the lower plot of figure 4.19. The upper plot presents the groundwater table. Outliers are more frequently compared to the calculations of Q_{drain} and additionally, more negative values are present. The curve

progression is very ragged. The highest values are around 40 mm. After peaks, the values range between the same amounts as they are for Q_{drain} . For further calculations, all outliers and negative values of the calculated outflow from the drain and the groundwater have been removed.



FIGURE 4.19: Calculated groundwater outflow (lower plot). The groundwater table is imaged in the upper plot.

4.6 Matter transport

Based on the calculated fluxes between the different storages, the tracer mass transport trough the trough soil layer was calculated. The results are presented in figure 4.20, 4.21 and 4.22. It has to be considered that the time distance between the bars is not linear as the sampling period changed during the time of measurements. Negative outliers have been removed from these figures.

Figure 4.20 presents the calculated normalized tracer concentrations in the trough soil based on drain water samples. According to that, the tracers show different flux patterns. It seems that tracer fluxes from the trough soil are rather pulsed than floating. Where some drain water samples show a definite tracer concentration, the calculated


FIGURE 4.20: Normalized concentrations of tracer fluxes through the trough soil layer.

values for the soil water concentrations account for zero. Normalized RRU concentrations are higher than the BR and UR concentrations. All tracers show a first pulse after the tracer injection, but strongly differ in their extent. For RRU the highest value is reached, whereas for the conservative tracers the normalized concentrations are small, compared to other fluxes. Also a second smaller, yet broader and a third more flat and broader pulse with partly elevated concentrations is displayed. Looking at the whole pattern, it looks like there are three different partly disconnected peaks. The main pulses consist of several single and often disconnected fluxes.

The results for UR show great gaps with no UR concentrations. The highest values occurred in the same period as the second RRU pulse occurs. They are more than four times bigger than the concentrations of the first pulse. Furthermore, the UR plot shows



FIGURE 4.21: Normalized concentrations of tracer fluxes from the Jackisch data through the trough soil layer.

the smallest number of bars. After one week of no calculated UR in the trough outflow, the last UR flux is at the 23rd of August.

At this time, the BR plot illustrates one of the highest concentrations. The pattern of the BR bars indicates one main pulse at the same time as the UR plot has its main pulse and the second main pulse of RRU. After that, the concentrations vary in the same range, except for two extreme values.

The tracer fluxes of the Jackisch data in figure 4.21 have a different pattern. One notices that the number of bars is distinctly lesser compared to figure 4.20. Often there are big gaps between the bars. The first pulses after the tracer input show very small



FIGURE 4.22: Nitrate concentrations of soil water fluxes through the trough soil layer.

normalized tracer concentrations compared to the following values. For SRB two main pulses can be seen. Between them there are a few days with very little or even no tracer concentration. The patterns of the UR and BR plot are very similar. There are a few fluxes with very high tracer concentrations at the first days after tracer injection and after that a few isolated fluxes with low concentrations. A second main pulse, as it can be seen for SRB, does not exist.

Beside the modeled tracer fluxes, the nitrate outflow from the trough soil layer was also calculated for the generated data of this work (figure 4.22). The pattern of the nitrate fluxes is very different compared to the tracer fluxes. Generally, there are higher values towards the end of the measurement period. Therefore, the pattern differs strongly from the tracer fluxes. The highest concentration of 5250 mg/l is calculated for the last flux in the plot. For a better presentation of the data, the bar is truncated at 2500 mg/l. Unfortunately, there were no nitrate data for the Jackisch experiment to compare.

Based on the modeled tracer concentrations for the trough soil water fluxes, the tracer recovery was calculated. The results are represented in figure 4.23. The results for the data of this work are in the left plot are and the calculated recovery rates for the Jackisch data are in the right plot. The results of this work show distinct differences in the tracer mass recovery between the tracers. Whereas for RRU the recovery rate is clearly over 100 %, the UR rate is considerably under it. The absolute value of the RRU recovery is around 3 g. Additionally, the recovery rates of both conservative tracers differ sharply from each other. All values from the Jackisch data are above 100 %. BR shows the highest recovery rate, followed by UR. SRB shows the lowest rate. The BR recovery



rate is around three times higher than the SRB rate.

FIGURE 4.23: Modeled tracer mass recovery. Left plot is from the data of this work, right plot is from the Jackisch data.

Chapter 5

Discussion

5.1 Experimental setup and methods

Generally, the setup of the flooding experiment was successful. The measurement devices worked well and data failure only existed for the groundwater sampling. This was caused by problems with the filling valve and a squeezed off sampling tube. The estimation of the tracers input masses was good, as tracer fluxes could be measured over a long time and additionally, the samples did not have to be diluted for the fluorometer. It is supposed that due to a very dry summer over the time of measuring, the number of bigger tracer fluxes was strongly decreased leaving a reduced data set to examine the SIS. But on the other side, it gives insights in the behavior of these systems for future summers, which are predicted to take turns between longer dry periods and intensive rain events.

A greater problem exists for the soil moisture probes in general. If one involves the measurement accuracy of \pm 3 % soil moisture content, the applicability would be strongly limited. With a maximum measuring range between approximately 10 and 35 %, this failure would have a massive effect on the soil moisture data, especially considering the observed diurnal variations. Here, it even exceeds the measured signal. However, by reason of a generally logical pattern of the data curves and even little changes in soil moisture are mostly similar between the probes in the different soil depths, the accuracy was not involved for further calculations. Nevertheless, it can not be neglected and it should be discussed how useful these probes are for hydrological applications and research. The analysis of the tracer measurements was challenging. The background signal often varied strongly between the samples. Hence, each had to be removed to get the tracer induced signal. This is very time consuming and requires a precise examination of each fluorescence peak in order to define the borders of the tracer peaks. It can not be excluded that high background peaks overlay small tracer peaks. Leibundgut et al. (2009) states that suspended sediments can be responsible for these high background signals. It seems to be very likely that this is increased for the samples of this work as the water percolated through a deep soil layer. Figure B.1 also points out that there were high differences between the background signals of the drain water and the groundwater samples. Especially for the groundwater samples, the background signals varied very much and often even exceeded for certain wavelength ranges the measurement range. Using a 0.45 μ m filter partly decreased the strength of these signals. The reason for the higher background in the groundwater samples is not clear. Pollution of the well tube

is thinkable, as the measurement devices where covered by a black, oily layer when they were pulled out after the end of the measurement period. The IC measurements were steady and without any bigger trouble.

5.2 Hydraulics

The hydraulic situation of the SIS was an important part of the research in this study. To understand matter transport processes, it is critical first to examine the water fluxes of the system of interest. As the water injection for the field experiment were conducted, it could be observed that the water table in the trough increased more slowly during the saturation phase, compared to the subsequent rewetting phase. Additionally, the period, in which the water injection stopped and the water in the trough infiltrated, was considerably greater for the rewetting phase. Both indicates that the saturation phase could already highly raise the saturated soil content. Therefore it seems that the saturation phase was quite successful.

The soil moisture time series of the trough soil in figure 4.1 shows distinct reactions of the moisture content to rain events or infiltrating water, respectively. Especially the increases are fast and high, indicating soil structures with high infiltration rates. It is important to consider, that the probes are in the upper part of the soil layer. Lower lying probes would probably measure a slower increase. The determined soil porosity from the probes data of around 35 % matches well with the assumed value from previous studies. Also, the assessed hydraulic conductivity from the tracer flow time of about 2.96×10^{-4} m/s seems to be comprehensible. Thereby, it is around one dimension greater than it was determined by infiltrometer experiments in 2011. But on the one hand, the flooded conditions must be taken into account and on the other hand, the hydraulic conductivity is calculated for the whole trough-and-drain system and not only for the soil layer. The underlying sand and gravel layer and the pressure from the trough water table should increase the infiltration rate. Therefore, it can be seen better as a maximum hydraulic conductivity. But as SIS are constructed to storage storm runoff and infiltrate slowly, these flooded settings are desired after bigger rain events. This could be more relevant for the determination of the hydraulic conductivity of a SIS, especially when thinking about matter transport. Also retardation processes of the tracers cannot be completely excluded, but this would result in an actually higher infiltration rate.

Both drain and groundwater table (figure 4.2 and 4.3) show distinct reactions on infiltrating water. The time lag between the peaks of the drain and the groundwater indicates, that at least under the conditions of this experiment, the water flows around half an hour from the drain into the groundwater. Additionally, the reduced rise of the groundwater table for the high peaks can be assumed to point out the size of this system. Unlike the drain system, there are no clear lateral borders, so that a local elevated groundwater table can drain off to several sides.

The correlation plot between the drain and the groundwater table shows the hydraulic relationship of both systems (figure 4.4). The curve progression points out the hydraulic time lag and size difference between both systems. For each big event, the water table increase of the drain is stronger. However, during the recession, the ratio adapts continuously to an equal decrease. This inertia of the groundwater is due to its substantially bigger size of the system and the time water needs to flow from the drain to the groundwater.

5.3 Water chemistry and main ions

The EC time series in the drain (figure 4.2) shows clear reactions of infiltrating water. It can be seen that the drinking water from the infiltration experiment and the rainwater

both have lower EC values and therefore have a diluting effect on drain water. Compared to that, the EC signals from these events in the groundwater are strongly alleviated. A reason for that could be, that during these events the EC of the drain water is around the same as it is in the groundwater. This is different for the EC of the pre-event drain water, which is usually between 800 and 1000 μ S/cm. Another reason could lie in the groundwater system being much bigger, so that a dilution effect is strongly decreased when the water finally reaches the probe in the groundwater well. By looking at the temperature time series, this seems more obvious. In contrast to the drain, there is no temperature effect visible in the groundwater, although it is higher in the drain. The increasing trend in the groundwater temperature is due to the extraordinary warm and dry summer during the measurement period.

The outliers of the temperature and EC at the beginning of high peak events could result from soil water, which flows into the drain and is driven by the pressure of the infiltrating water from the trough. This would explain that these outliers persist only for a short time and then fall back to the initial value. The EC time series also shows many outliers in the middle of measurement period. At this time, the water table in the trough was very low and drying out. It is possible, that small rain events during that time therefore had a bigger effect on the EC, as there was a lower mixing with the drain water.

The major ions composition of the groundwater and the drain water samples (figure 4.5 and 4.6) show very different patterns. There is almost no variation of the ions in the groundwater, whereas in the drain water changes can be linked to infiltrating water from rain events or the flooding experiment of this work.

An interesting fact is that changes of the nitrate concentration are mirrored to changes of the sulfate and chloride concentrations. It seems that infiltrating water dilutes sulfate and chloride, but increases nitrate concentrations in the drain water. It is possible that the nitrate concentration in the drinking water is responsible for the increase during the flooding experiment. Yet, it does not explain the peaks at rain events. An assumption is that nitrate is formed in the through soil and leaches with the infiltrating rain. It is also possible that it gets deposited by the storm runoff, which flows into the trough. Although the maximum nitrate concentration is distinctly smaller than the threshold value for drinking water, the characteristics of nitrate leaching and transport in SIS can be interesting to research and model.

5.4 Soil samples

The results for the tracer measurements in the soil samples show that significant amounts of conservative and reactive tracers can be detected. Although BR is known to be very low-sorptive, adsorption can be of importance in humic soils (Leibundgut et al., 2009). However, Opferkuch (2012) shows that the humus content from neighboring troughs is mostly low and decreases strongly with depth. Exceptions could result from soil sedimentation due to storm runoff. Furthermore, it can not be clarified if the detected tracer is chemically or physically adsorbed in the soil, or if it is retained in the remaining soil water at the time of sampling. A contrary indication to the tracer retention is that the samples were taken more than two weeks after tracer application. But since then, it was dry and no rainfall occurred, so that it would be possible that tracer containing soil water evaporated and the tracer was left in the soil. Nevertheless, sorption processes seem to be a more probable explanation for the tracer masses in the soil.

The normalized concentration of RRU is much higher than it is for BR. It is assumed that the transformation of RAZ to RRU is responsible for that, as it increases the mass of RRU compared to the tracer input mass. Haggerty et al. (2008) states that sorption of RAZ and RRU depends on the size of the organic carbon fraction. Haggerty et al. (2009) determine that the reaction of RAZ to RRU indicates microbial activity. Therefore it can be assumed that high microbial activity is responsible for the high recovery rate of RRU. This would also explain that no RAZ is found in the soil. Haggerty et al. (2008) also stated that the reduction to RRU is slow in pure water, but increases strongly when sediment is available. Hence, it seems logical that the transformation rates are distinctly higher compared to common stream tracer tests.

The strong decrease of RRU mass in the lower soil layer could indicate that the reduction processes vary with the soil depth. Assuming that the RAZ/RRU system can be used as a surrogate to identify degradation or transformation processes of biocides, this would conclude a distinct higher degradation potential in the lower soil layer compared to deeper soil depths. Furthermore, the high recovery rate in the soil would declare the important role of the soil layer in SIS for sorption, degradation and transformation of biocides. But it has to be considered that the calculations for the tracer mass implicated the whole volume of the soil layer in the SIS. Nevertheless, a complete mixing of the tracers in the soil seems unlikely. For this reason, the tracer masses are probably overestimated. However it is clear, that the tracer mass reduces on its way through the soil by adsorption and therefore it is less mass remaining for deeper soil layers. Anyway, it can be determined that important degradation or transformation processes in the soil layer are very likely and that they change with depth.

The absence of UR in the soil samples could result from several assumptions. The little tracer input mass could be a reason. An argument against this is the low detection limit of UR (see table 2.2). Degradation processes could play a role. Fluorescence scan peaks beside the usual UR spectrum, as they are described in Sweeney et al. (n.d.) referring to transformation products of UR (Gutowski et al., 2015), were present. But these peaks also existed in the blank soil samples, hence this approach was longer pursued. Maybe it is just as simple as that the low sorption capacity of UR leads to no retention in the soil.

Unfortunately, for the Jackisch experiment there was no measuring of SRB in soil samples, so that an evaluation of the sorption capacity is difficult. But as the soil retention factors of RRU and SRB are very similar (see table 2.2), an estimation is made by the RRU retention in the soil. Looking at that, it is assumed that there are important sorption processes in the soil, especially for the upper layer. A big portion of the RAZ/RRU input mass is found in the soil samples. Therefore it can be concluded that the soil layer in this SIS has a good efficiency for biocides retention. Nevertheless, this work cannot clarify how suitable this tracer is to imitate sorption of biocides.

5.5 Water samples

Like for the soil samples, there was no RAZ in the drain water samples. It is assumed that all RAZ transformed to RRU on its way through the soil and into the drain. This would explain the high normalized tracer concentration of RRU. As it could be observed in the temperature and the EC time series, there is also a short and very strong pulse visible in the beginning of the measured tracer time series (figure 4.9). RRU even has the highest normalized concentration for this peak compared to the other tracers. This very sharp peak, which drops back to almost 0 one hour after its maximum, looks like a short pressured tracer wave through preferential flow paths in the soil. This just being an assumption, it could explain the fast rise and drop back and the following slower increase of the tracer concentrations. However, it is a phenomenon that was also observed for the drain temperature and EC and therefore is an interesting fact about flow dynamics in this SIS. The correlations of tracers (figure 4.11) also show a very different pattern for this first pulse. The correlations of RRU with the conservative tracers are defined by an exponential function at this time and differ distinctly from a linear relationship, which represents the other sample points. The exponential relationship implies that the portion of RRU against the other tracers increased with the rise of the first pulse. It can be summarized, that there is a high concentrated flux shortly after tracer application, showing a different behavior of the reactive tracer RRU compared to the conservative tracers.

Apart from that first pulse, the relationship is more or less linear. Therefore, there are no dramatic changes of the tracer fluxes compared to each other. The reactive tracer behaves similar as UR and BR. The biggest rain event caused another big tracer wave through the SIS. It shows how long these fluxes remain in the system, until they percolate through it. All tracer curves showed, that the fluxes are driven by rain events, especially when there are big events and the trough is flooded by the incoming stormwater runoff. The longer measurement period of BR can be due to its much bigger input mass. The artificial flooding experiment does not represent the usual flow in rate into the trough. It should better be considered as an extreme event.

The absence of any tracer in the groundwater samples leaves some questions. The water table clearly shows a fast hydraulic connection between the observation well and the drain. Additionally, measurements of the groundwater height in the observation well showed, that for the most of the measurement time the water table was higher than the underline of the drain. Therefore, there is a direct connection of the SIS and the groundwater. Nevertheless, there could be some reasons why no tracer is detected. It is possible that the tracer cloud did not flow in the direction of the well. But the well position is directly next to the trough and also lies in the groundwater flow direction. It is also possible that the groundwater mixing in the well tube is insufficient, so that the water samples are all from the stagnant water within the tube. This would also explain that there were almost no changes in the water chemistry and ions composition, which would be an indication of infiltrating water. Due to the high groundwater table it is not possible that there was generally no tracer flow into the groundwater. Also, there is only gravel between drain and groundwater, which usually does not strongly increase the retention capacity. It is assumed that all fluxes, which pass the drain, directly flow into the groundwater. That is why it is supposed that the tracers flowed into the groundwater, but could not be measured for a not definite known reason.

The Jackisch data breakthrough curve points out, that SRB fluxes, compared to conservative tracers, change over time. The stronger decrease for the first peak followed by a stronger increase for the second peak could be indications of initial sorption processes and gaining influence of resorption with time. Assuming that SRB can be a surrogate for sorption behavior of biocides, this gives much information about the ability of the SIS to withhold contaminants. It must be taken in consideration, that sorbed substances can solute after events at a future time.

5.6 Modeled results

The development of an evaporation driven density distribution curve was the first step to build the hydraulic model. The period of the maximum day temperatures seems to have an increasing effect on the soil moisture. It might be, that these high temperatures support the capillary rise and therefore water from the deeper and more wet soil gets up to the surface. In principal, the application of a diurnal evaporation curve helped to improve the performance of the hydraulic model, as it removed soil moisture variations which could not be linked to tracer fluxes from the soil into the drain. Nevertheless, especially for cloudy and colder days, the reality can differ from the density distribution curve. It can be seen as a first approach to improve the accuracy of daily values of evaporation and therefore to improve the soil moisture model.

Thy hydraulic model is the basis to calculate the matter transport. The calculated drain fluxes (figure 4.18) show strong outliers which are mostly due to different changes in the water balance of the drain that cannot be explained by the change of the soil moisture content. These exist mainly during high peaks and are the result of short intensive changes in the drain water table which immediately drop back to its original value. It is assumed that these changes are due to short time pressure variations. The same effect can also be observed in the results of the groundwater fluxes (figure 4.19). As already said, these outliers were removed for further calculations. It is the reason for some gaps in the matter transport modeling.

The trough soil water fluxes are the key process for the model. Therefore it is important to get a good fit between the soil moisture and its change for each time step. But the small selection of recessions where no rainfall occurred, makes it challenging. Besides, there are only few data points with higher soil moisture contents, which makes it difficult to find a suitable non-linear base regression function. It has to be considered, that this approach to model the soil water fluxes is a simplification. To improve it, there should be more soil moisture probes along the trough and in at least one additional deeper soil depth to represent the heterogeneity. Calculation of the additional water flow due to flooded conditions in the trough pointed out, that it increases the outflow distinctly. It brings out how important this process is for SIS, where the flooded conditions are desired after bigger rain events.

The modeled recovery rates for the soil water vary strongly between the different tracers. The calculated high portion of RRU is due to the RAZ to RRU reduction processes in the soil. The differences between the conservative tracers cannot be completely explained. It is possible that the tracer's different chemistry has an effect. Often for stream tracer tests the BR recovery rate is the highest. Sorption and degradation can have an important influence. Regarding the big differences between both conservative tracers, it is possible that the injected UR mass was too little and therefore was partly diluted under the detection limit. Photolytic degradation should be excluded due to the tracer injection late in the evening and the following soil infiltration. Nevertheless, it is also possible that the modeling approach is not sufficient and should be improved. Outliers due to an incomplete mass balance should be observed to identify the driving factors.

Compared to each other, the recovery rates of the tracers from the Jackisch data seems reasonable. Again the BR recovery is the highest, followed by UR and with the lowest rate SRB. Sorption processes are probably responsible for the lower recovery of the reactive tracer SRB. But it cannot be explained why all rates distinctly exceed 100 %. As the modeling procedure for both data sets was similar, a general mistake of the model is not very likely. But errors during the evaluation of the model cannot be excluded completely. It is known that for the fluorescence measuring from 2012 an individual removing of the background signals was not executed which could explain the overestimating of the UR and SRB recovery rate. But since BR is measured with the IC it does not explain its strong overestimation.

5.7 Hypotheses

Finally, to close the discussion the research questions of this study are highlighted in the following:

Is the multi-tracer approach suitable to estimate biocide retention in stormwater infiltration systems? The application of the reactive tracers SRB and RAZ/RRU and its comparison with the conservative tracers UR and BR gave quantitative insights in degradation and sorption processes for the investigated SIS. Beside difficulties in evaluating the measurement results from the flurometer and in modeling the soil tracer fluxes, the application of this method was quite successful. But it has to be considered, that the usage of RAZ/RRU as a surrogate for degradation processes of definite biocides is limited. Differences in chemical and physical behavior of the numerous types of biocides must be respected.

Are there contamination impacts on soil and/or groundwater? Are there important sorption and degradation processes in the soil and do they change with depth? The soil sample results showed, that there are significant RRU concentrations in the top soil layer. Including the determined sorption capacity of the soil, it is assumed that there are important transformation and degradation processes for biocides and other contaminants. But this implies also, that big portions are refrained in the soil and therefore could lead to contaminated conditions in the long term. Additionally, the soil results showed that the retention rate decreases with depth. Also, the groundwater could be affected by pollutant fluxes. Although it was not measured in the well, the drain samples and the modeling results are signs of significant matter transport into the groundwater. Whether these fluxes contain harmful contaminants, respectively harmful transformation products, or are degraded into harmless substances cannot be answered here. Particularly the high groundwater table illustrates an increased contamination potential, as it intercepts the drain and reduces the length of the contaminants pathways. Is RAZ/RRU a suitable tracer to estimate degradation processes? In principle, the RAZ/RRU system can be well used in SIS to determine the microbial activity and therefore act as a tool to determine degradation/transformation processes. However it is recognized that all RAZ transformed into RRU, so that quantitative calculations as reaction rates are not possible.

Is the investigated stormwater infiltration system appropriate to serve as a runoff retention basin and to reduce contaminant leaching into surface water and groundwater? Combining the experiences from the flooding experiment, the hydraulic characteristics and the sorption and degradation behavior, it can be concluded that the SIS still fulfills its requirements as part of a sustainable water management. It is still working as a retention basin for incoming storm runoff and improves the infiltration capacity of the urban district. It therefore reduces the surface runoff into local creeks or into the drainage system. For this reason it should also decrease the contamination load into surface waters. Compared to the infiltration tests in 2011 the hydraulic conductivity increased. This could be due to the calculation for the flooded conditions. The deposition of sediments from storm runoff could decrease the hydraulic conditions of the SIS but this was not observed until these days.

Chapter 6

Conclusion

Generally, the multi-tracer experiment was successfully. Sorption and degradation characteristics of the SIS could be detected, which helped to estimate the risk potential of a groundwater contamination due to biocides from storm runoff. Analyzing soil and water samples showed, that there is a high microbial activity in the trough soil layer, which strongly decreases the leaching potential. Therefore this points out the importance of the top soil in a SIS to be well structured and thick enough for a sufficient hydraulic and matter transport resistance. However, it cannot be excluded that there are significant fluxes into the groundwater, especially at bigger rain events when there is a high storm runoff rate into the trough. Fast vertical pressure waves through the SIS could lead to high concentrated pollutant pulses. Unfortunately, all RAZ reduced to RRU on its way through the soil, which limited the evaluation of absolute transformation rates. Yet, it was possible to identify soil zones with a high impact on degradation. This study could also point out, that due to dilution and retention of incoming tracers into the drain, it is critical to model the soil tracer fluxes.

Discrepancies in the hydraulic signals between the trough soil, the drain and the groundwater lead to problems for the model evaluation. Due to this, an improvement of the model approach is recommended. Several studies determined the applicability of reactive and conservative tracers to mimic tracer characteristics. However, field studies, which directly compare tracer and biocide fluxes in SIS, are recommended to identify correlations between them and to identify biocide/pesticide types which behave similar or not. For future studies an extension of the experimental approach for different SIS would also help to compare their characteristics with structure and age. Although this study could not prove greater changes of the hydraulic conditions within several years it cannot be excluded in principal. Furthermore, it is recommended for future studies to take soil samples at several times, to investigate the variation of the tracer retention with depth and time. Additionally, it would be interesting to compare different approaches to solute and examine the tracer from soil samples. This would help to identify the most effective method and possible impacts on the results due to the method.

Future research is needed to make reasonable long-term assumptions about biocide leaching from urban area and deposition in groundwater, surface water and other ecosystems. This will improve urban water management and contribute to reach the goals of natural conditions for these systems.

Appendix A

Photos



FIGURE A.1: Interior view of an APEG. Top right is the control unit, bottom right is the battery. Bottle places are vacant.



FIGURE A.2: Exterior view of the APEGs. On the left side the groundwater APEG. On the right side the drain APEG.



FIGURE A.3: Diver logger head and APEG tube in the observation well.



FIGURE A.4: Preparation of the tracer experiment.



FIGURE A.5: Mixing of the tracers in the field.



FIGURE A.6: Tracer injection.



FIGURE A.7: Left: Flooding. Right: Water hose in action.



FIGURE A.8: Left: Water hose in action II. Right: Hydrant and fountain.



FIGURE A.9: Inlet pipe.





Appendix B

Tables and Figures

TABLE B.1: Line functions from the tracer correlations plot (figure 4.)	11	L)).
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Line style	UR vs BR	UR vs RRU	BR vs RRU
red	2.31*x - 0.34	$45.05^* e^{0.6045x} - 45.89$	$96.67^* e^{0.1736x} - 95.09$
quality criterion	$R^2 = 0.98$	RSE= 5.5 $(5)^1$	RSE= $8.21 \ (5)^1$
green	-	$12.09^*x + 0.44$	2.07*x - 0.37
quality criterion	-	$R^2 = 0.93$	$R^2 = 0.78$
green dashed	5*x	-	-
blue dashed	$5^*x + 1.5$	-	-

 1 Degrees of freedom.



FIGURE B.1: Comparison between the measured fluorescence signals from the groundwater (left plot) and the drain water (right plot) samples for the same period (10.07.15 12:30 - 15:00h). The dashed line is located at UR maximum.



FIGURE B.2: Comparison between the measured fluorescence signals from the groundwater (left plot) and the drain water (right plot) samples for the same period (15.07.15 10:30 - 20:30h). The dashed line is located at UR maximum.



intensity [W/m^2]

FIGURE B.3: Calibration curves for the fluorescence measurements.

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