Groundwater contamination from urban line sources - monitoring and evaluation approach with integral pumping tests

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by

Sebastian Leschik

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Ph. D. Thesis Evaluation Committee:

Prof. Dr. Daniel Hunkeler, University of Neuchâtel (directeur de thèse)

Prof. Dr. Mario Schirmer, University of Neuchâtel (co-directeur de thèse)

Prof. Dr. Rudolf Liedl, Technical University of Dresden, Germany

Université de Neuchâtel

FACULTE DES SCIENCES
Secrétariat-Décanat de la faculté
- Rue Emile-Argand 11
- CP 158
- CH-2009 Neuchâtel

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Groundwater contamination from urban line sources – monitoring and evaluation approach with integral pumping tests

Sebastian LESCHIK

UNIVERSITE DE NEUCHATEL

FACULTE DES SCIENCES

La Faculté des sciences de l'Université de Neuchâtel,
sur le rapport des membres du jury

MM. D. Hunkeler (co-directeur de thèse), M. Schirmer (co-directeur de thèse)
et R. Liedl (Dresden, D)

autorise l'impression de la présente thèse.

Neuchâtel, le 2 septembre 2010

Le doyen :
P. Kropf

■ Téléphone : +41 32 718 21 00 ■ E-mail : secretariat.sciences@unine.ch ■ www.unine.ch/sciences

Abstract

Urban areas can affect groundwater quality by releasing wastewater-borne contaminants including inorganic compounds and micropollutants. Sewer networks and urban streams that receive effluent from wastewater treatment plants, for example, act as wastewater transport pathways, while potentially losing treated or untreated wastewater to groundwater. Collectively, these pathways are known as urban line sources, which are characterized by human-dominated variations of the wastewater composition in sewers and by temporally higher loads of wastewater constituents in urban streams during combined sewer overflows. In combination with exfiltration via randomly distributed sewer leaks or heterogeneous streambeds, this leads to extremely heterogeneous concentration patterns which complicate the investigation of groundwater contamination originating from these types of urban line sources.

This study investigates the influence of urban line sources on groundwater quality with a new monitoring approach that overcomes the problem of heterogeneous concentrations by using large volume sampling with the integral pumping test (IPT) method. In the evaluation of the monitoring approach, wastewater compound mass flow rates of IPT applications up- and downstream of line source sections are compared to quantify exfiltration mass flow rates per unit length M_{ex}.

The monitoring approach was operated at a leaky sewer and a temporally losing stream for the inorganic compounds B, Cl^-, K^+, NO_3^-, NH_4^+ and SO_4^{2-} as well as for the micropollutants bisphenol-a, caffeine, technical-nonylphenol and tonalide. The concentration-time series of the IPTs at the two sites revealed an influence of the line sources on the groundwater quality. The observed variability of the concentration values was higher for micropollutants than for inorganic compounds.

At the leaky sewer site, higher mass flow rates downstream of the sewer section were observed for B, Cl^- and total nitrogen N_{tot}. Therefore, values of M_{ex} could be calculated for these compounds. Reduced or unaltered mass flow rates of the most reactive wastewater constituents, including micropollutants downstream of the leaky sewer, indicate that mass reduction processes occurred on the passage from the sewer to the pumping wells. The water exfiltration rate Q_{ex} from the sewer was calculated with concentrations of the conservative ion Cl^-. The comparison of these Q_{ex} values with alternative measurements shows that the line source monitoring approach can provide reliable data.

Results from the losing stream site show higher mass flow rates downstream of the two target sections for Cl^-, K^+, NO_3^-, SO_4^{2-} but for caffeine only downstream of one target section. The calculated M_{ex} values of these compounds were higher than those from the leaky sewer site. Reduced mass flow rates of technical-nonylphenol downstream of the target sections suggest that this compound was partially eliminated in the groundwater. Additional concentration measurements in the losing stream and in a connected sewer at the test site were performed to identify relevant processes that influence the concentrations at the downstream IPT wells.

The IPT method is a well accepted approach for the estimation of mass flow rates in groundwater. However, no substantiated guidelines are yet available for the design of IPT sampling schedules with an optimal number of samples and optimal sampling times. Therefore, in the last part of this study, 30 high-frequency concentration-time series from the IPT applications of the line source monitoring approach were used to derive principles for an optimal design of IPT sampling schedules. Different sampling schedules were tested by modifying the original concentration-time series. The results show that the number of samples depends on the required accuracy. Concerning the sampling time, a sampling scheme relying on constant time intervals Δt between different samples yielded the highest accuracy.

This study shows that the quantification of groundwater contamination from urban line sources can be realized with a new monitoring approach based on the application of IPTs. The line source monitoring approach also yields reliable results in urban aquifers with heterogeneous concentration patterns.

Additional research is needed to investigate the exfiltration process from line sources in detail. Further, more studies are required to extend the developed evaluation procedure for reactive compounds and to implement the results from the line source monitoring approach into complex numerical groundwater models at the city-scale or for regional catchments.

Kurzfassung

Urbane Gebiete können die Grundwasserqualität durch den Eintrag von abwasserbürtigen Schadstoffen einschließlich anorganischer Verbindungen und Mikroverunreinigungen, beeinträchtigen. Abwasserkanalnetze und urbane Fließgewässer, in die zum Beispiel der Abfluss von Abwasserreinigungsanlagen eingeleitet wird, fungieren als Abwassertransportwege und können dabei gereinigtes oder ungereinigtes Abwasser ins Grundwasser abgeben. Diese Transportwege sind allgemein bekannt als urbane Linienquellen, die durch den Menschen verursachte Variationen der Abwasserzusammensetzung in Abwasserkanälen und temporär erhöhten Frachten von Abwasserinhaltsstoffen in urbanen Fließgewässern bei Kanalisationsüberläufen gekennzeichnet sind. Zusammen mit der Exfiltration durch zufällig verteilte Kanallecks oder ein heterogenes Gewässerbett, verursacht dies extrem heterogene Konzentrationsmuster in urbanen Gebieten, welche die Erkundung von Grundwasserverschmutzungen durch urbane Linienquellen erschweren.

Diese Arbeit untersucht den Einfluss von urbanen Linienquellen auf die Grundwasserqualität mit einem neuen Monitoringansatz, der das Problem von heterogenen Konzentrationen durch die Beprobung von großen Volumina mit der Immissionspumpversuchsmethode (IPV) überwindet. Die Auswertung des Monitoringansatzes basiert auf dem Vergleich der Massenflüsse von Abwasserinhaltsstoffen zwischen IPV-Anwendungen stromauf- und abwärts von Linienquellenabschnitten um Exfiltrationsmassenflussraten pro Längeneinheit M_{ex} zu quantifizieren.

Der Monitoringansatz wurde an einem undichten Abwasserkanal und einem temporär exfiltrierendem Fließgewässer für die anorganischen Verbindungen B, Cl^-, K^+, NO_3^-, NH_4^+ und SO_4^{2-} sowie für die Mikroverunreinigungen Bisphenol-a, Koffein, technisches Nonylphenol und Tonalid durchgeführt. Die Konzentrations-Zeit-Serien von den IPVs an den beiden Standorten zeigen, dass die Linienquellen die Grundwasserqualität beeinflussen. Die beobachtete Variabilität der Konzentrationswerte war für die Mikroverunreinigungen höher als für die anorganischen Verbindungen.

An dem Standort mit dem undichten Abwasserkanal wurden für B, Cl^- und Gesamtstickstoff N_{tot} erhöhte Massenflussraten stromabwärts des Kanalabschnittes beobachtet. Demzufolge konnten für diese Verbindungen M_{ex} Werte berechnet werden. Geringere oder unveränderte Massenflussraten stromabwärts des Kanalabschnittes deuten für die meisten reaktiven Abwasserinhaltsstoffe, inklusive Mikroverunreinigungen, auf Massenreduzierungsprozesse auf dem Weg vom Abwasserkanal zu den Pumpbrunnen hin. Die Wasserexfiltrationsraten Q_{ex} vom Abwasserkanal wurden mit Hilfe des konservativen Ions Cl^- berechnet. Der Vergleich dieser Werte mit alternativen Messungen zeigt, dass der Linienquellenmonitoringansatz zuverlässige Daten liefern kann.

Die Ergebnisse des Standortes mit dem exfiltrierenden Fließgewässer ergaben erhöhte Massenflussraten für Cl^-, K^+, NO_3^-, SO_4^{2-} stromabwärts der beiden untersuchten Abschnitte und für Koffein jedoch nur stromabwärts eines Abschnittes. Die berechneten M_{ex}-Werte für diese Verbindungen waren höher als die von dem Standort mit dem undichten Abwasserkanal. Geringere Massenflussraten stromabwärts der Zielabschnitte für technisches Nonylphenol deuten auf eine teilweise Eliminierung dieser Verbindung im Grundwasser hin. Zusätzliche Konzentrationsmessungen im Fließgewässer und einem verbundenem Abwasserkanal am Standort wurden durchgeführt um relevante Prozesse zu identifizieren, welche die Konzentrationen an den IPV Brunnen stromabwärts beeinflussen.

Die IPV Methode ist ein anerkannter Ansatz für die Abschätzung von Massenflussraten im Grundwasser. Trotzdem sind derzeit keine fundierten Richtlinien für die Konzeption von IPV-Probenahmeplänen mit optimaler Probenanzahl und optimalen Probezeitpunkten verfügbar. Im letzten Teil dieser Arbeit wurden aus diesem Grunde 30 Hochfrequenz-Konzentrations-Zeit-Serien von den IPV Anwendungen genutzt, um Prinzipien für die Gestaltung von optimalen IPV-Probenahmeplänen abzuleiten. Verschiedene Probenahmepläne wurden durch die Modifikation der originalen Konzentrations-Zeit-Serien getestet. Die Ergebnisse zeigen, dass die Anzahl der Proben von der benötigten Genauigkeit abhängt. Bezüglich des Probenahmezeitpunktes lieferte ein Probeschema mit konstanten Zeitabschnitten Δt zwischen verschiedenen Proben die höchste Genauigkeit.

Diese Arbeit zeigt, dass die Quantifizierung von Grundwasserverschmutzungen durch urbane Linienquellen mit einem neuen IPV-basierten Monitoringansatz durchgeführt werden kann. Der Linienquellenmonitoringansatz liefert auch für heterogene Konzentrationsmuster in urbanen Aquiferen zuverlässige Ergebnisse.

Zusätzliche Forschung wird benötigt, um den Exfiltrationsprozess von Linienquellen im Detail zu untersuchen. Darüber hinaus ist weitere Arbeit nötig, um die entwickelte Auswertungsprozedur auf reaktive Verbindungen zu erweitern und um die Ergebnisse vom Linienquellenmonitoringansatz in komplexe numerische Grundwassermodelle auf Stadt- oder Regionaleinzugsgebietsebene zu implementieren.

Résumé

Les zones urbaines peuvent affecter la qualité des eaux souterraines en libérant des contaminants transportés par les eaux usées, incluant des composés inorganiques et des micropolluants. Les réseaux d'égouts et les cours d'eau urbains qui reçoivent par exemple les effluents des stations d'épuration, se comportent comme des chemins de transport d'eaux usées, qui potentiellement perdent ces eaux usées traités ou non traités vers les eaux souterraines. Collectivement, ces chemins de transport sont connus comme des sources urbaines linéaires qui sont caractérisées par des variations de la composition des eaux usées dans les égouts dominés par l'influence des activités humaines et par des charges temporairement plus hautes des constituants provenant des eaux usées, dans les cours d'eau urbains lorsque les égouts unitaires débordent. En combinaison avec des exfiltrations via des fuites d'égouts distribués de façon aléatoire ou via des lits de rivières hétérogènes, cela conduit a des motifs de concentration extrêmement hétérogènes, ce qui complique les investigations sur la contamination des eaux souterraines de ces types de sources linéaires urbaines.

Cette étude examine l'influence des sources linéaires urbaines sur la qualité des eaux souterraines avec une nouvelle approche de monitoring qui résout le problème des concentrations hétérogènes en utilisant d'importants volumes d'échantillonnage grâce à la méthode du test de pompage intégral (TPI). Pour évaluer l'approche de monitoring, les débits massiques des composés des eaux usées mesurés par le TPI en amont et en aval de la section de source linéaire, sont comparés afin de quantifier les débits massiques d'exfiltration par unité de longueur M_{ex}.

L'approche de monitoring a été opérée sur des égouts fuyants et sur un cours d'eau temporairement exfiltrant, pour les composés B, Cl^-, K^+, NO_3^-, NH_4^+ et SO_4^{2-} mais également pour les micropolluants bisphénol-a, caféine, nonylphénol technique et tonalide. Les séries de concentration-temps des TPIs au niveau des deux sites révèlent une influence des sources linéaires sur la qualité des eaux souterraines. La variabilité des concentrations observée était plus haute pour les micropolluants que pour les composés inorganiques.

Au niveau du site de l'égout fuyant, de plus hauts débits massiques ont été observés pour B, Cl^- et le total d'azote N_{tot} en aval de la section d'égout. Par conséquent, les valeurs de M_{ex} ont été calculées pour ces composés. Les débits massiques réduits ou non altérés des constituants les plus réactifs des eaux usées, incluant les micropolluants, en aval de l'égout fuyant, indiquent que le processus de réduction de masse se produit lors du passage de l'égout vers les puit de pompage. Le taux d'exfiltration d'eau Q_{ex} depuis l'égout a été calculé grâce aux concentrations de l'ion conservatif Cl^-. La comparaison de ces valeurs Q_{ex} avec des mesures alternatives montre que l'approche de monitoring de source linéaire peut fournir des données fiables.

Les résultats sur le site du cours d'eau exfiltrant montrent des débits massiques plus hauts en aval des deux sections ciblées pour les Cl^-, K^+, NO_3^-, SO_4^{2-} et pour la caféine en aval seulement d'une des sections ciblées. Les valeurs M_{ex} calculées pour ces composés étaient plus hautes que celles pour le site de l'égout fuyant. Les débits massiques réduits pour le nonylphénol-technique, en aval des sections ciblées, suggèrent que ce composé était partiellement éliminé des eaux souterraines. Des mesures additionnelles de concentrations dans le cours d'eau exfiltrant et dans un égout connecté au niveau du site de test ont été réalisées pour identifier des processus pertinents qui influencent les concentrations des puits de TPI en aval.

La méthode de TPI est également une approche bien acceptée pour l'estimation des débits massiques dans les eaux souterraines. Cependant, aucune directive confirmée n'est disponible à l'heure actuelle concernant le design des programmes d'échantillonnage des TPI, avec un nombre optimal d'échantillons et des temps d'échantillonnage optimaux. Par conséquent, dans la dernière partie de cette étude, 30 séries de concentration-temps à haute fréquence, provenant de l'utilisation du TPI lors l'approche de monitoring de la source linéaire, ont été employées pour dériver des principes pour un design optimal des programmes d'échantillonnage du TPI. Différents programmes d'échantillonnages ont été testés en modifiant la série de concentration-temps originale. Les résultats montrent que le nombre d'échantillons dépend de la précision nécessaire. Concernant le temps d'échantillonnage, un plan d'échantillonnage reposant sur des intervalles constants de temps Δt entre différents échantillons, a fournit la plus haute précision.

Cette étude montre que la quantification de la contamination des eaux souterraines provenant de sources linéaires urbaines peut être effectuée avec une nouvelle approche de monitoring qui repose sur l'utilisation des TPI. L'approche de monitoring de la source linéaire fournit également des résultats fiables dans les aquifères urbains qui ont des motifs de concentration hétérogènes. Des recherches additionnelles sont nécessaires pour examiner en détail les processus d'exfiltration de la source linéaire. De plus, des efforts sont requis pour étendre la procédure d'évaluation développée à des composés réactifs et pour implémenter les résultats de l'approche de monitoring de la source linéaire dans des modèles numérique complexes des eaux souterraines, à l'échelle des villes ou pour des bassins versant régionaux.

Table of contents

List of figures

List of tables

List of annexes

Annex:	Concentration-time-series of the IPT applications

List of abbreviations

B	Boron
BPA	Bisphenol-a
CAF	Caffeine
CC	Connection crack
CCTV	Closed circuit television inspection
Cl^-	Chloride
CP	Control plane
CSO	Combined sewer overflow
CV	Coefficient of variation
GW	Groundwater
IPT	Integral pumping test
K^+	Potassium
KWL	Kommunale Wasserwerke Leipzig (Municipal Waterworks Leipzig)
LOD	Limit of detection
NO_3^-	Nitrate
NON	Technical-nonylphenol
NH_4^+	Ammonium
N_{tot}	Total dissolved nitrogen
PPCP	Pharmaceuticals and personal care products
RI	Root intrusion
SIM	Selected ion monitoring
SO_4^{2-}	Sulfate
SPE	Solid phase extraction
SW	Surface water
TON	Tonalide
WW	Wastewater
WWI	Wastewater indicator
WWTP	Wastewater treatment plant

List of variables

b	Aquifer thickness [m]
b_x	Width of an IPT streamtube [m]
C_{av}	Average concentration along an IPT control plane [mg L^{-1}]
$C_{best\ case}$	Average concentration of original concentration-time series [mg L^{-1}]
$C_{downstream}$	Concentration in the groundwater downstream of line sources [mg L^{-1}]
$C_{surface\ water}$	Concentration in the surface water [mg L^{-1}]
$C_{upstream}$	Concentration in the groundwater upstream of line sources [mg L^{-1}]
CV	Coefficient of variation [%]
$C_{wastewater}$	Concentration in the wastewater [mg L^{-1}]
C_x	Average concentration of modified concentration-time series [mg L^{-1}]
i	Gradient [-]
J_{CP}	Mass flux through a control plane [g m^{-2} d^{-1}]
K	Hydraulic conductivity [m s^{-1}]
K_{OW}	Octanol-water partitioning coefficient [-]
L	Affected line source length [m]
L_{CP}	Control plane length [m]
M	Arithmetic mean [-]
M_{CP}	Mass flow rate through a control plane [g d^{-1}]
M_{ex}	Exfiltration mass flow rate per unit length from line sources [g m^{-1} d^{-1}]
n	Number of samples [-]
n_e	Effective porosity [-]
q_0	Specific discharge / Darcy velocity [m s^{-1}]
Q_{CP}	Water flow through a control plane [m^3 d^{-1}]
Q_{ex}	Exfiltration rate from line sources [L m^{-1} d^{-1}]
Q_w	Pumping rate of the IPT well [m^3 s^{-1}]
S	Standard deviation [-]
t	Pumping time [h]
Δt	Sampling time interval during IPTs [h]
t_D	Dimensionless time [-]
U	Uncertainty of a specific IPT sampling schedule [%]
V_P	Pumped aquifer volume during IPTs [m^3]
Δx	Distance between isochrones of IPTs [m]

1 Introduction

1.1 Groundwater contamination from urban line sources

Urban areas affect groundwater quantity and quality by disturbing the natural water cycle (Vazquez-Sune et al., 2005). Roads, sewers and other surface and subsurface infrastructures lead to more complex flow patterns in urban areas in comparison to rural areas. The estimation of urban groundwater recharge needs to account for this complexity (Lerner, 2002). On the one hand recharge is reduced by extensive surface sealing but on the other hand additional recharge occurs below leaky water mains or leaky sewers. The reliable quantification of this additional recharge (or leakage) is a challenging task that is described by several studies (e.g., Eiswirth et al., 2004; Wolf et al., 2007).

Leakage from urban infrastructure may also affect groundwater quality if the exfiltration water has a lower grade than the groundwater (Ellis and Revitt, 2002; Wolf et al., 2004; Musolff, 2009). Leaky infrastructures that contaminate the groundwater can be defined as urban line sources. This definition focuses mainly on sewers and urban streams that transport treated or untreated wastewater and are characterized by hydraulic conditions allowing temporal or permanent exfiltration. In detail, exfiltration depends on gradients to groundwater levels and on the sediments in the vicinity of the urban line sources.

In case of leaky sewers also the size and position of possible leaks and the self-sealing process of the leaks have an important influence on the exfiltration (Wolf et al., 2006; Ellis et al., 2009). Closed circuit television inspection (CCTV) data can be used to obtain indications about the state of a sewer section and therefore help to assess sewer exfiltration. However, CCTV databases seldom cover the entire sewer network and, due to the formation of colmation layers around the leaks, not all detected leaks cause exfiltration.

Several approaches for the estimation of sewer exfiltration rates Q_{ex} exist for the laboratory scale (Ellis et al., 2003; Vollertsen and Hvitved-Jacobsen, 2003; Blackwood et al., 2005), sewer sections (Rieckermann et al., 2005; Revitt et al., 2006) or complete sewer catchments (Karpf and Krebs, 2005). The overview about actual methods for the quantification of sewer exfiltration in Rutsch et al. (2006) shows that the majority of these methods estimate Q_{ex} as percentages of dry-weather flow or as exfiltration volume per cm^2 leak size. Assessments of the exfiltration influence on the groundwater quality also require considering the wastewater composition. In this context the simple combination of exfiltration volumes with wastewater concentrations may yield unreliable exfiltration mass flow rates M_{ex} because attenuation processes occur in the colmation layers of leaks as well as in the sediments below the sewer (Fuchs et al., 2004).

More dependable information about the influence of sewer exfiltration on the groundwater can be obtained by holistic approaches which consider wastewater and groundwater compositions at the same time (Wolf et al., 2004; Fenz et al., 2005). The accuracy of these approaches depends on a reasonable monitoring in wastewater and groundwater.

The wastewater flow and composition in sewers varies due to the human-dominated activity of wastewater production (households or industries) with a mainly diurnal pattern (Ort et al., 2005). Randomly distributed leaks possibly clogged by the deposition of particles and biological activity generate an extremely heterogeneous concentration distribution in the groundwater of urban areas. Monitoring strategies in wastewater and groundwater need therefore to be adapted to the temporal and spatial variability in urban areas (Musolff et al., 2007; Schirmer et al., 2007; Musolff et al., 2009).

Beside leaky sewers, also losing streams that are in contact with treated or untreated wastewater can be included in the term urban line source because of their potential release of contaminants. Although natural losing streams are rare under climatic conditions of central Europe, temporally losing streams occur frequently in urban agglomeration because stream courses are altered and groundwater levels can be lowered by anthropogenic influences.

Urban streams receive effluents from wastewater treatment plants (WWTPs) containing wastewater compounds that were not completely eliminated during the treatment process (Kim et al., 2007; Strauch et al., 2008). The continuous inflow of treated wastewater from WWTP causes increased wastewater compound concentrations in urban streams. During rain events also untreated wastewater can be discharged to urban streams via combined sewer overflows (CSOs) if the capacity of the sewers or the WWTP is exceeded (Rose, 2007). Thus CSOs can lead to a significant increase of wastewater compound loads in urban streams (Mulliss et al., 1996).

Owing to dilution with the natural water flow, the wastewater compound concentrations in urban streams are mostly lower than in sewers that transport mainly wastewater (and infiltrating groundwater). In contrast, streams often possess a permeable bed with a connection to the underlying sediments. Water exfiltration from a losing stream section may therefore be higher in comparison to a sewer section with the same length that loses water only via leaks. Exfiltration mass flow rates from line sources depend strongly on the specific field conditions and must be considered for a reliable estimation of M_{ex} values.

Regarding the exfiltration induced concentration pattern in groundwater downstream of urban line sources, losing streams also cause heterogeneous concentration distributions. Temporal variations in the stream water composition caused by CSOs and variable effluents from WWTPs, as well as heterogeneities in streambeds (Schmidt et al., 2006), support the formation of zones with different wastewater compound concentrations in the groundwater downstream of losing streams.

Due to heterogeneous concentration patterns in the groundwater of urban areas, the assessment of groundwater contamination from urban line sources is difficult to achieve. Thus, monitoring of the contamination from urban line sources is a challenge and need to account for the heterogeneity.

1.2 Wastewater-borne compounds originating from urban line sources

Wastewater poses a possible threat to groundwater resources because it can be discharged from urban line sources. Wastewater-borne compounds are released from damaged sewers and from losing streams that are fed by continuous effluents from WWTPs and discontinuous effluents from CSOs during rain events.

Groundwater pollution by wastewater from urban line sources concerns different chemical species. Beside inorganic species such as major ions and heavy metals, research recently focuses on a new group of contaminants. Micropollutants are defined as synthetic and natural trace contaminants (Schwarzenbach et al., 2006) occurring in water in low concentrations (pg L^{-1} to ng L^{-1}). Pharmaceuticals and personal care products (PPCP), endocrine disrupters as well as other ecotoxicological relevant substances can be combined in the expression “micropollutants” (Schirmer and Schirmer, 2008). Recent studies also use the term “xenobiotics” for a similar group of contaminants which also include industrial chemicals (Strauch et al., 2008).

Although occurring mostly in low concentrations, micropollutants affect the aquatic environment (Heberer, 2002). In this context, acute toxicity for aquatic life is seldom given in consequence of dilution. Pharmaceuticals are designed to be bioactive. Different modes of action of pharmaceuticals indicate that they are relevant for ecotoxicology (Fent et al., 2006). A remarkable number of micropollutants imitate hormones and act as endocrine disrupters (Sumpter, 2005). The feminization of fish (Jobling et al., 1998) is an important example for the impact of micropollutants on the aquatic environment.

Micropollutants are contaminants but can also be used as an indicator for wastewater influence in urban areas because wastewater is the main source of micropollutants. Fenz et al. (2005) used the anti-epileptic drug carbamazepine for the estimation of sewer exfiltration in the city of Linz (Austria). Due to the high consumption of caffeine in urban areas, it can be used as a wastewater indicator in surface waters (Buerge et al., 2003) and for the quantification of CSOs (Buerge et al., 2006).

In the framework of the research platform WASSER Leipzig – Water and Sewershed Study of Environmental Risk in Leipzig (Schirmer et al., 2007) this thesis investigates a variety of wastewater-borne compounds which are relevant as wastewater indicators and as contaminants. The wastewater compounds were chosen according to preliminary studies (Musolff et al., 2007; Reinstorf et al., 2008; Strauch et al., 2008) and a literature research. Major and minor ions (B, K^+, Cl^- and SO_4^{2-}) were selected because of their low-cost and precise chemical analysis, as well as their relevance as wastewater indicators. In particular, Cl^- and SO_4^{2-} are useful marker because of their reasonable conservative character (Barrett et al., 1999).

Investigated individual nitrogen species (NO_3^- and NH_4^+) which are important groundwater contaminants and total dissolved nitrogen N_{tot} have potential as indicators. However, the interpretation of nitrogen concentrations is difficult to achieve due to different sources (NO_3^- mainly from agricultural fertilizers and NH_4^+ mainly from wastewater) and the redox-sensitive transformation between NO_3^- and NH_4^+.

The investigated micropollutants bisphenol-a (BPA), caffeine (CAF), technical-nonylphenol (NON) and tonalide (TON) are characterized by different transport properties (retardation and degradation) in the groundwater and therefore suitable for the identification of wastewater sources (Musolff et al., 2007). BPA, NON and TON with a relatively high octanol-water partition-coefficients ($\log K_{OW}$) are, in contrast to CAF ($\log K_{OW} \approx 0$), influenced by sorption processes. Biodegradation of CAF was reported in Buerge et al. (2003), whereas BPA and TON appear to be quite resistant against degradation processes in groundwater (Heberer, 2003; Ying et al., 2003).

Effects of the investigated micropollutants on the aquatic environment were identified for early life stages of medaka fishes for BPA (Pastva et al., 2001), standard freshwater organisms for CAF (Moore et al., 2008), crustaceans as well as zebrafishes for NON (Correa-Reyes et al., 2007) and early life stages of zebrafishes as well as marine mussels for TON (Carlsson and Norrgren, 2004; Luckenbach and Epel, 2005).

1.3 Integral pumping test method

The integral pumping test (IPT) method was developed at the University of Tübingen in Germany (Teutsch et al., 2000; Ptak et al., 2000) for the estimation of average concentrations C_{av} and mass flow rates M_{CP} of target compounds in aquifers. Fig.1 shows the concept of IPTs for the investigation of contamination from urban line sources.

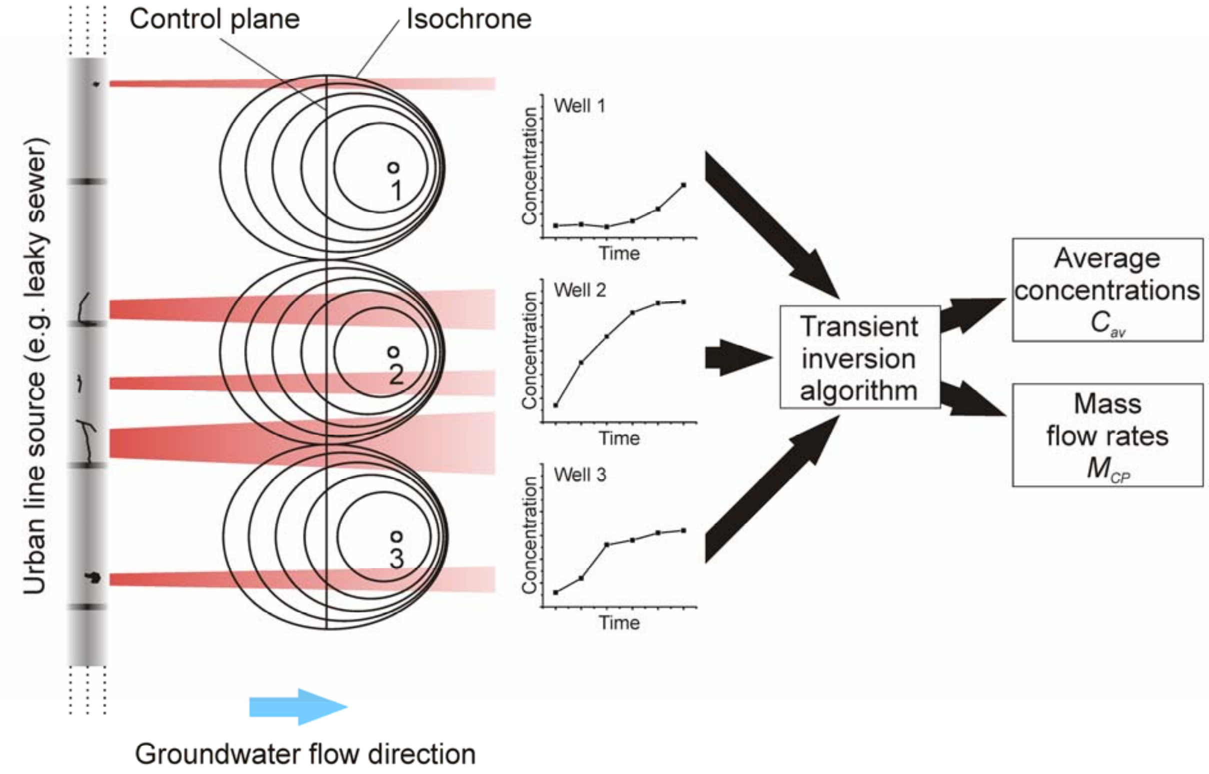

Fig. 1. Integral pumping test with pumping wells 1, 2 and 3 downstream of an urban line source. The IPT evaluation in this thesis bases on the transient inversion algorithm. Average concentrations C_{av} and mass flow rates M_{CP} through a control plane are obtained for each well.

The method consists of one or more pumping wells that are pumped sequentially or simultaneously for a long duration (e.g., several days). During pumping, samples are taken following a predefined sampling schedule. The isochrones for the IPT evaluation (Fig. 1) correspond to the sampling times. The last isochrone (maximum extent of the capture zone) defines the control plane lying perpendicular to the natural groundwater flow direction. The shape of the obtained concentration-time series depends on the concentration distribution in the capture zone of the pumping wells (concentration-time diagrams in Fig. 1).

The IPT evaluation relies on a transient inversion algorithm that estimates the concentration distribution before the start of pumping from the measured concentration-time series. The evaluation of the observed concentration-time signal can be performed using an analytical solution for homogeneous aquifers or a numerical algorithm based on particle back-tracking that considers heterogeneous aquifers with a numerical groundwater model (Schwarz, 2002; Bayer-Raich et al., 2004). The equations for the IPT evaluation are implemented in the CSTREAM code (Bayer-Raich, 2004) which was used for the IPT evaluations in this thesis.

Values of C_{av} and M_{CP} from IPTs are more reliable than those from conventional point samplings because large volume sampling reduces the risk of missing contaminant plumes. Therefore IPTs were applied in several studies for the quantification of natural attenuation at contaminated sites (Bockelmann et al., 2001; Peter et al., 2004; Rügner et al., 2004; Schirmer et al., 2006). In addition, Kalbus et al. (2007) showed by the application of IPTs for the estimation of mass fluxes at the stream-aquifer interface that IPTs are not limited to field sites with a distinct plume.

Results from IPTs can be biased by different factors. Jarsjö et al. (2005) investigated the influence of different settings for flow and transport properties of the aquifer on the well capture zone and streamlines of the natural flow field. Moreover, the transport properties of the investigated compounds affect the results of IPTs. Former IPT applications assume conservative target compounds within the capture zone (e.g., Bauer et al., 2004). Recently published studies (Bayer-Raich et al., 2006; Jarsjö and Bayer-Raich, 2008; Bayer-Raich et al., 2009) extend the IPT evaluation procedures to sorptive or degradable compounds.

Also the IPT dimensioning has an important influence on the accuracy of the IPT results. Positioning of wells, pumping rate and pumping duration are crucial points regarding cost effective applications of IPTs. In this context, a reasonable dimensioning of the IPT sampling schedule is necessary. No substantiated guideline for the dimensioning of IPT sampling schedules is presently available. Therefore, the design of sampling schedules between different IPT applications shows large variations. The majority of IPT studies (e.g., Bockelmann et al., 2001) use sampling schedules with a constant spatial resolution of maximal 5 m between the isochrones along the control plane (Ptak et al., 2000). In contrast, IPT operations in Kalbus et al. (2007) with a simplified sampling schedule based on constant time intervals also provided reliable results. This indicates that suggestions about the optimal design of IPT sampling schedules are required.

1.4 Objectives and structure of the thesis

The main goal of this study is the reliable quantification of exfiltration mass flow rates per length unit M_{ex} of wastewater-borne compounds from urban line sources with a monitoring approach that can be applied to various line sources and various hydrological settings. The monitoring and evaluation approach overcomes the problem of heterogeneous concentrations by averaging concentrations from large aquifer volumes with the IPT method. The investigated compounds are inorganic wastewater indicators and micropollutants. The study focuses on the groundwater as a receiving body of wastewater-borne compounds. The obtained M_{ex} values can be used for the assessment of groundwater contamination from urban line sources. After the operation of the monitoring approach, the obtained concentration-time series are used to adapt the sampling schedules of IPTs (number of samples and sampling times) to the specific conditions of line sources that generate concentration patterns without distinct plumes.

This thesis is divided into 5 chapters. After this introduction (*Chapter 1*), the following *Chapter 2* describes the application of the line source monitoring approach at a leaky sewer. The monitoring approach consists of four IPTs, two were conducted upstream and two downstream of a leaky sewer section in Leipzig (Germany). The comparison of mass flow rates M_{CP} between up- and downstream control planes yielded M_{ex} values from the leaky sewer.

A similar line source monitoring approach at a wastewater influenced losing stream is described in *Chapter 3.* The approach uses four IPT wells two up- and two downstream of the stream. The field measurements and the IPT evaluation were adapted to the specific conditions at a losing stream.

Presently, no profound guidelines for the dimensioning of IPT sampling schedules exist. In order to derive principles for the design of optimal IPT sampling schedules, a detailed analysis of the concentration-time series from the IPTs at the leaky sewer and the losing stream is presented in *Chapter 4*. The original high-frequency concentration-time series were modified by systematically omitting several concentration values. The modified concentration-time series represent different IPT sampling schedules. The comparison of the results from the original with the modified concentration-time series yielded uncertainties that were used to rank the different sampling schedules.

In *Chapter 5* a summary is provided. The main outcomes and an outlook for future research are presented.

2 Investigation of sewer exfiltration using integral pumping tests and wastewater indicators

This chapter is published as:

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Abstract:

Leaky sewers affect urban groundwater by the exfiltration of untreated wastewater. However, the impact of sewer exfiltration on the groundwater is poorly understood. Most studies on sewer exfiltration focus on water exfiltration, but not on the impact on groundwater quality. In this paper we present a new monitoring approach to estimate mass flow rates M_{ex} of different wastewater indicators (WWIs) from leaky sewers by applying integral pumping tests (IPTs). The problem of detecting and assessing heterogeneous concentrations in the vicinity of leaky sewers can be overcome with the IPT approach by the investigation of large groundwater volumes up- and downstream of leaky sewers. The increase in concentrations downstream of a leaky sewer section can be used to calculate M_{ex} with a numerical groundwater model. The new monitoring approach was first applied using four IPT wells in Leipzig (Germany). Over a pumping period of five days we sampled five inorganic WWIs: B , Cl^-, K^+, NO_3^-, NH_4^+ and three xenobiotics: bisphenol-a, caffeine and tonalide. The resulting concentration-time series indicated an influence of wastewater at one IPT well downstream of the leaky sewer. We defined ranges of M_{ex} by implementing the uncertainty of chemical analyses. The results showed a M_{ex} of 0 - 10.9 g m^{-1} d^{-1}. The combination of M_{ex} with wastewater concentrations from the target sewer yielded an exfiltration rate Q_{ex} of 28.0 - 63.9 L m^{-1} d^{-1} for the conservative ion Cl^-. Most non-conservative WWIs showed reduced mass flow rates in the groundwater downstream of the leaky sewer that indicate a mass depletion during their passage from the sewer to the pumping well. Application of the IPT methodology at other field sites is possible. The IPT monitoring approach provides reliable M_{ex} values that can help to assess the impact of leaky sewers on groundwater.

2.1 Introduction

The impact of urban areas on groundwater has become an emerging field of hydrogeological research. Eiswirth et al. (2004) and Vazquez-Sune et al. (2005), for example give overviews on water and contaminant flows in urban water systems. According to these studies, urban subsurface infrastructures like sewer networks may lose wastewater to the groundwater. Lerner (2002) defined water from leaky sewers as urban groundwater recharge. Urban groundwater pollution by leaky sewers was also identified by Ellis and Revitt (2002). In order to assess urban groundwater pollution an accurate estimation of sewer exfiltration is necessary. Leak sizes, leak positions, leak self-sealing processes and the sewer flow regime as well as the groundwater level and the aquifer material which surrounds the sewers are the major factors controlling the exfiltration from sewers (Wolf et al., 2006). As a result, sewer exfiltration shows a large temporal and spatial variability (Schirmer et al., 2007). Leak sizes and leak positions can be monitored via closed circuit television inspection (CCTV), however these databases are seldom complete and sewer exfiltration estimation is therefore a challenging task. Rutsch et al. (2006) gave an overview on exfiltration estimation methods. Studies at the laboratory scale (Blackwood et al., 2005; Ellis et al., 2003; Vollertsen and Hvitved-Jacobsen, 2003) are rarely transferable to operational sewers (Rutsch et al., 2007). On the other hand studies at the catchment scale (Karpf and Krebs, 2005) are often not focused on the impact on groundwater quality. Revitt et al. (2006) and Rieckermann et al. (2005) used in-sewer responses of artificial tracers to estimate exfiltration on the operational sewer scale, however an impact on groundwater quality was not addressed. Common units of exfiltration rates Q_{ex} from leaky sewers are water flow per cm² leak size or percentage of dry weather flow. These units are helpful for water balance estimations, but are less meaningful for groundwater quality investigations. Sewer exfiltration measurements that focus on groundwater quality must consider the wastewater composition that depends on the connected household (Wilkie et al., 1996). Diurnal and seasonal variations can also occur depending on the activity of the inhabitants in the sewer catchment, thus the use of Q_{ex} to assess the impact of leaky sewers on the groundwater quality may provide unrealistic values.

Only a few studies (e.g., Barrett et al., 1999; Wolf et al., 2006) use wastewater indicators (WWIs) to estimate the impact of leaky sewers on the groundwater quality. The most common WWIs are major and minor ions as well as nitrogen species and metals because of their simple and accurate chemical analysis. Besides inorganic WWIs, also organic substances called “xenobiotics” such as pharmaceuticals, personal care products (PPCP) and other ecotoxicological relevant substances are used as WWIs (Musolff et al., 2007). In this context

Fenz et al. (2005) applied the pharmaceutical carbamazepine as a indicator species for sewer exfiltration. The described WWIs are helpful indicators, but also represent an important impact on groundwater quality. For example nitrate (NO_3^-) pollution poses a major threat to groundwater based drinking water supplies (Appelo and Postma, 1999). The impact of xenobiotics on groundwater quality is investigated by a large number of recent studies. Schwarzenbach et al. (2006) and Schirmer and Schirmer (2008) show the relevance of xenobiotic micropollutants for aquatic systems. An increasing body of information about the transport behaviour of xenobiotics in the aquatic environment is becoming available (Heberer, 2002; Heberer et al. 2002; Scheytt et al., 2006; Ternes et al. 2007). Biodegradation and sorption of WWIs at leak-sealing zones and in unsaturated soil beneath sewer leaks (Fuchs et al., 2004) will reduce the concentrations of WWIs before reaching the groundwater. Thus, the impact of leaky sewer on the groundwater should be investigated by estimating the mass flow that reaches the groundwater and not only by the estimation of water exfiltration from leaky sewers.

In this study, a monitoring approach is presented with which mass flow rates M_{ex} of WWIs from leaky sewers into the groundwater can be estimated. In the following M_{ex} can be used to assess the influence of the leaky sewer on the groundwater composition. Concentration measurements in the groundwater up- and downstream of a leaky sewer section are used to quantify a WWI mass flow increase downstream of the target sewer section. Due to spatially heterogeneous WWI concentrations in the groundwater surrounding leaky sewers, the estimation of M_{ex} is difficult to perform. The monitoring approach overcomes the problem of spatially heterogeneous WWI concentration patterns in the vicinity of leaky sewers by using the integral pumping test method (IPT), which was developed in the University of Tuebingen (Germany) to estimate mass fluxes in an aquifer (Teutsch et al., 2000; Ptak et al., 2000). Multiple leaks and household-related fluctuating outflow from these leaks create the formation of small WWI plumes. Conventional point sampling may miss these small WWI plumes in the groundwater. Large volume sampling with an IPT avoids this problem by giving average concentrations along a control plane perpendicular to the mean groundwater flow direction. In the framework of the research platform WASSER Leipzig (Water and Sewershed Study of Environmental Risk in Leipzig – Germany (Schirmer et al., 2007; Musolff et al., 2007) we operated IPTs with different WWIs at an operational sewer. This is the first application of an IPT that focuses on a leaky sewer as a contaminant source zone. The estimation of xenobiotic mass flow rates with an IPT has not previously been attempted. In order to apply the new monitoring approach, we operated four IPT wells up- and downstream of a significantly damaged sewer in Leipzig (Germany). The resulting concentration-time series were used to calculate mass flow rates of WWIs with a numerical groundwater flow model. The comparison of up- and downstream mass flow rates yields M_{ex}. In this study we present results of five inorganic compounds: B, Cl^-, K^+, NO_3^- and NH_4^+ as well as three xenobiotics: bisphenol-a (BPA), caffeine (CAF), tonalide (TON). Supplementary measurements of WWI concentrations in the wastewater of the target sewer were used to calculate Q_{ex}. An alternative measurement of Q_{ex} was derived and compared to the results from the IPT monitoring approach.

2.2 Materials and methods

2.2.1 Leaky sewer field site

In order to find a sewer with a significant exfiltration rate Q_{ex} for the application of the IPT monitoring approach, we surveyed CCTV data from the local sewer network operator "Kommunale Wasserwerke Leipzig" (KWL) to identify sewer defects. Due to sealing processes caused by biological activity and sedimentation of wastewater particles, not all defects may cause wastewater exfiltration. A field site with large Q_{ex} was therefore sought to ensure a sufficiently high WWI concentration after dilution in the groundwater. The leaky sewer field site was chosen to meet the following conditions:

- Combined sewer type (most common sewer system in Germany; Berger and Lohaus, 2004)
- Sewer with substantial defects and a diameter larger than 0.3 m
- Sewer bottom above the groundwater level
- High hydraulic conductivity of the sediments in the vicinity of the sewer
- Sewer draining a large sewer catchment (sewershed) to maintain sufficient flow even during dry-weather conditions

The limited number of accessible areas within the urban agglomeration of Leipzig rapidly narrowed the choice of leaky sewer field sites. The selected leaky sewer field site in Leipzig (Germany) is shown in Fig. 2. In the vicinity of this sewer no other source of WWIs existed. The 0.6 m diameter sewer was built in 1934. Over the last few decades tree roots have intruded into the pipe connections and have caused significant leaks. Wastewater from more than 1 km² of urban areas passes through this sewer which generates a minimum night-time wastewater level in the sewer of 0.11 m.

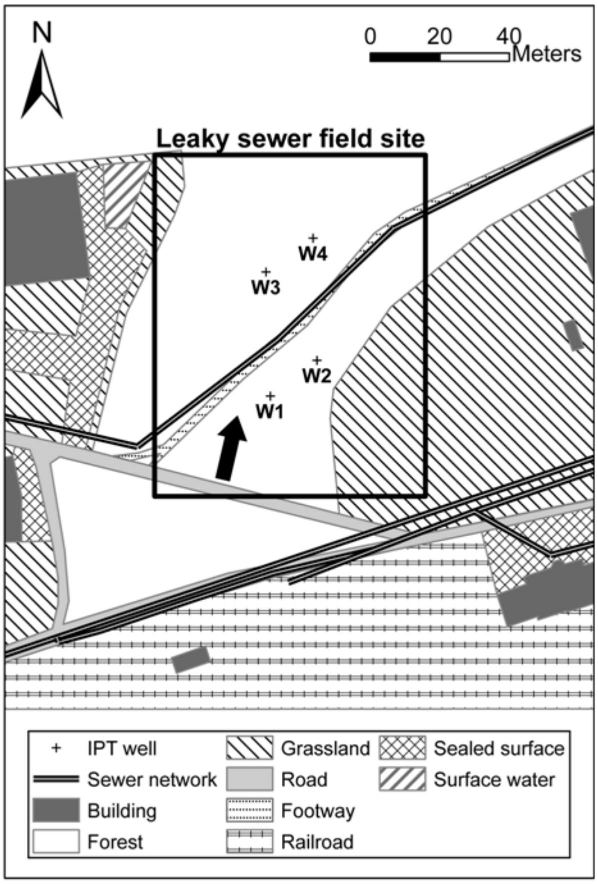

Fig. 2. Leaky sewer field site with land use cover and sewer network. The black arrow indicates the mean groundwater flow direction.

The geologic structure at the leaky sewer field site consists of Tertiary fine sands, which are overlain by Quaternary sands and gravels. The latter sediments form a highly permeable aquifer with an average thickness of 6 m. The aquifer is covered by a heterogeneous floodplain loam of up to 1.5 m thickness. Ram sounding, pumping tests and sieve analyses were applied to obtain fundamental hydraulic aquifer properties. The estimation of the hydraulic conductivity *K* yields values of 3×10^{-4} to 4×10^{-3} m s^{-1} in the investigated aquifer. A consistent spatial distribution pattern of the obtained *K* could not be identified from the data. The base of the sewer is located 1.7 m below the surface at the top of the partially confined quaternary aquifer. Observation wells near the sewer show variable groundwater levels throughout the year, which are in summer below and in winter above the sewer bottom. Thus, exfiltration of wastewater and infiltration of groundwater seasonally alternate at the leaky sewer field site. The IPTs were therefore applied at the end of summer to guarantee that exfiltration had occurred for a sufficiently long time before the start of pumping.

2.2.2 Wastewater indicators

According to preliminary studies (Osenbrück et al., 2007; Reinstorf et al., 2008; Strauch et al., 2008) and a literature survey we chose eight different WWIs in the groundwater. Tab. 1 shows the investigated WWIs with their limit of detection (LOD). All selected WWIs have already been used in other studies to trace wastewater impact in the aquatic environment. Five inorganics (B, Cl^-, K^+, NO_3^- and NH_4^+) that are highly concentrated in wastewater were used for this study. Groundwater analyses described in other studies from the Leipzig urban area (Musolff et al., 2007) gave information about detectable xenobiotics in the groundwater of Leipzig. The endocrine disrupting chemical bisphenol-a (BPA), the psychoactive stimulant caffeine (CAF) and the musk fragrance tonalide (TON) were chosen. Negative effects on the aquatic environment are known for these substances (Pastva et al., 2001; Carlsson and Norrgren, 2004; Moore et al., 2008).

The investigated WWIs are characterized by different transport behaviour. Cations like K^+ and NH_4^+ are depleted by sorption on clay minerals, whereas sorption processes do not affect anions like Cl^-. The octanol-water partitioning coefficient log K_{OW} in Tab. 1 has a direct relation to the potential of sorption to organic substances. Thus, BPA and TON with coefficients of 3.3 and 5.7 may tend to be depleted via sorption. The negative log K_{OW} of CAF indicates a low sorption potential of this WWI. The process of biodegradation affects most of the investigated WWIs. Important biodegradation processes of NH_4^+ and NO_3^- are explained by Freeze and Cherry (1979). In the following estimations NH_4^+ and NO_3^- were combined to N_{tot}, because nitrification can convert NH_4^+ to NO_3^-. Clara et al. (2005) and Buerge et al. (2003) show degradation of BPA, CAF and TON in wastewater treatment plants.

2.2.3 Integral pumping test method

Average concentrations C_{av} and mass fluxes M_{CP} of target substances in an aquifer can be estimated by using IPTs (Teutsch et al., 2000; Ptak et al., 2000; Schwarz, 2002). The method consists of one or more pumping wells, which form a control plane perpendicular to the natural groundwater flow direction. The pumping wells are operated for several days and the samples are taken following a predefined schedule during pumping. The obtained concentration-time series can be evaluated with multiple wells using the program code

CSTREAM (Bayer-Raich, 2004). Control planes that are formed by several wells must have small overlapping zones between their individual control planes to guarantee that no plume can pass between the wells. The control plane length ℓ_{CP} depends primarily on the pumping rate, but also on the aquifer properties that influence the shape of the capture zones. The proper placement of the pumping wells is the most crucial step during implementation of IPTs. In comparison to conventional point sampling, the IPT method provides more reliable results, because of the large sampled aquifer volume. Various applications of IPTs are described in Bockelmann et al. (2001), Rügner et al. (2004), Schirmer et al. (2006) and Brooks et al. (2008). The versatility of the IPT method is shown by Kalbus et al. (2007) who estimate contaminant mass fluxes from the groundwater towards a stream by using data from an IPT within the adjoining aquifer, and by Ptak et al. (2004) who use the approach to estimate depth-orientated contaminant mass fluxes. Although these studies are focus on classical groundwater contaminants like BTEX or NO_3^-, the IPT can also be applied to other substances in the groundwater. The effect of sorption and degradation of target substances (Bayer-Raich et al., 2006; Jarsjö and Bayer-Raich, 2008; Bayer-Raich et al., 2009), however, is not currently implemented in the numerical solution of the CSTREAM code used for IPT interpretation.

The formulation for solving the average concentration for each IPT test on the basis of the measured concentration-time series $C_w(t)$ is given in Bayer-Raich (2004). In order to clarify the assumptions required to apply the method, we provide here the basic equations used within the code CSTREAM. The contaminant mass flux at the control plane, M_{CP} [kg s^{-1}], is defined as:

$$M_{CP}(t) = \int_{\ell_{CP}(t)} C_0(x,y) q_{0y}(x,y) b(x,y) dx \tag{1}$$

where $\ell_{CP}(t)$ is the control plane extent at pumping time t, $C_0(x,y)$ the initial (i. e. when pumping starts) concentration distribution, $q_{0y}(x,y)$ the Darcy velocity in the y-direction and $b(x,y)$ the thickness of the aquifer. The equation relating the concentration-time series $C_w(t)$ and the concentration distribution prior to pumping $C_0(x,y)$ is given through the mass balance (Bayer-Raich et al., 2004):

$$Q_w C_w(t) = -\oint_{\ell_I(t)} C_0(x,y)\vec{q}_w(x,y)\vec{n}b(x,y)d\ell \tag{2}$$

where $\vec{q}_w(x,y)$ [m s^{-1}] is the Darcy velocity during pumping, $\ell_I(t)$ the isochrone at time t (i. e. the boundary of the capture zone), $\vec{n}$ an outward unit vector perpendicular to the isochrone $\ell_I(t)$, $b(x,y)$ [m] the saturated aquifer thickness, and $Q_w = -\int_{\ell_I(t)} \vec{q}_w(x,y)\vec{n}b(x,y)d\ell$ [m^3 s^{-1}] the pumping rate at the well.

Equations (1) and (2) are mass conservation equations valid for any conservative compound. For obtaining the concentration distribution $C_0(x,y)$ on the basis of $C_w(t)$, the aquifer is discretized into $2n-1$ streamtubes, with n the total number of samples. We now introduce the assumption that the concentration is constant in the flow direction within the capture zone volume. Then $C_0(x,y)$ is expressed as

$$C_0(x,y) = C_0(x_j)\xi_j(x,y) \tag{3}$$

Where $\xi_j(x,y)$ is an indicator function defined as

$$\xi_j(x,y) = \begin{cases} 1 & \text{if } (x,y) \text{ belongs to streamtube } j \\ 0 & \text{otherwise} \end{cases} \tag{4}$$

Using (3) it is assumed that initial concentrations are constant and equal to $C_0(x_j)$ within each streamtube j.

Inserting (3) into (2) we obtain n equations, one for each sampling time, as

$$C_w(t_i) = \sum_{j=n-i+1}^{n+i-1} C_0(x_i)g_{ij} \tag{5}$$

where the matrix g_{ij} is defined as

$$g_{ij} = \frac{-1}{Q_w}\oint_{\ell_I(t_i)} C_0(x,y)\xi_j(x,y)\vec{q}_w(x,y)\vec{n}b(x,y)d\ell\,. \tag{6}$$

This matrix can be physically interpreted as the water volume of sample i, initially located within streamtube j, divided by the total water volume of sample i. Written in matrix notation, equations in (5) can be expressed for 4 samples, i. e. with $n = 4$, as (e. g. Bayer-Raich, 2004; Jarsjö et al., 2005)

$$\begin{bmatrix} 0 & 0 & 0 & g_{14} & 0 & 0 & 0 \\ 0 & 0 & g_{23} & g_{24} & g_{25} & 0 & 0 \\ 0 & g_{32} & g_{33} & g_{34} & g_{35} & g_{36} & 0 \\ g_{41} & g_{42} & g_{43} & g_{44} & g_{45} & g_{46} & g_{47} \end{bmatrix} \begin{bmatrix} C_0(x_1) \\ C_0(x_2) \\ C_0(x_3) \\ C_0(x_4) \\ C_0(x_5) \\ C_0(x_6) \\ C_0(x_7) \end{bmatrix} = \begin{bmatrix} C_w(t_1) \\ C_w(t_2) \\ C_w(t_3) \\ C_w(t_4) \end{bmatrix} \tag{7}$$

Since equation (7) contains $2n-1$ unknowns and only n equations, the solution to the system is non-unique. In previous work, e. g. Bauer et al. (2004) and Jarsjö et al. (2005), the non uniqueness of equation (7) is dealt with by computing total mass flow rates for 3 different extreme situations: (a) all contaminant mass is located to the left hand side of the well (in the flow direction); (b) contaminant concentration is symmetrical with respect to the streamtube containing the first isochrone and (c) all contaminant mass is located to the right hand side of the well. Further, Herold et al., (2009) implements a methodology to condition equation (7) to independent data obtained from Direct Push measurements. Depending on the restrictions, negative concentrations may arise from the inversion; in these cases a non-negative constraint should be implemented in equation (7) to avoid non physical results. Since the aquifer here considered is not highly heterogeneous (see analyses given in Jarsjö et al., 2005) we consider here the solutions (b) above for quantifying mass flow rates and average concentrations. As discussed in previous work (see e.g., Bayer-Raich et al., 2009) using option (b) does not mean that the contaminant plume is symmetrical: the average concentration and mass flow rate can be computed regardless of the left-right contaminant distribution. This approach can be expressed as solving the following system of equations:

$$\begin{bmatrix} 0 & 0 & 0 & g_{14} & 0 & 0 & 0 \\ 0 & 0 & g_{23} & g_{24} & g_{25} & 0 & 0 \\ 0 & g_{32} & g_{33} & g_{34} & g_{35} & g_{36} & 0 \\ g_{41} & g_{42} & g_{43} & g_{44} & g_{45} & g_{46} & g_{47} \\ 0 & 0 & 1 & 0 & -1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & -1 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} C_0(x_1) \\ C_0(x_2) \\ C_0(x_3) \\ C_0(x_4) \\ C_0(x_5) \\ C_0(x_6) \\ C_0(x_7) \end{bmatrix} = \begin{bmatrix} C_w(t_1) \\ C_w(t_2) \\ C_w(t_3) \\ C_w(t_4) \\ 0 \\ 0 \\ 0 \end{bmatrix} \tag{8}$$

After solving equation (8), the average concentration C_{av} is obtained in discretized form as

$$C_{av} = \frac{\sum_{i=1}^{2n-1} C_0(x_i) q_0(x_i)}{\sum_{j=1}^{2n-1} q_0(x_j)} \tag{9}$$

Where $q_0(x_i)$ is the water discharge associated to streamtube i, defined as

$$q_0(x_i) = \int_{\ell_{CP}(t)} q_{0y}(x,y) b(x,y) \xi_i(x,y) dx \tag{10}$$

2.2.4 Integral pumping test setup at the leaky sewer field site

The IPT setup was conducted with four IPT wells. The exact positioning of the IPT wells (Fig. 2) along the sewer was chosen according to significant leaks observed by CCTV data and the requested overlap between the multiple individual control planes. Two wells pump the groundwater upstream of the sewer and two other wells were installed downstream of the leaky sewer. All IPT wells were screened along the complete Quaternary sand-gravel aquifer with a 12.7 cm inner diameter HDPE-tube. The IPT wells were pumped simultaneously for five days from September 2 to 7, 2007 with a pumping rate of 1 L s^{-1} each. Due to a pronounced drawdown at well W4 the pumping rate of this well was reduced to 0.3 L s^{-1} during the IPT. Ram sounding in the vicinity of well W4 did not indicate a difference in the aquifer formation. Therefore no explanation can be given for the pronounced drawdown at well W4. We measured electrical conductivity, pH, redox potential, oxygen content and temperature at the IPT wells and the water level in all existing observation wells at the leaky sewer field site, including the pumping wells and the sewer.

2.2.5 Sampling and chemical analyses during field programs

Groundwater sampling during IPT

During pumping, a high sampling frequency was applied in order to detect also small variations in WWI concentrations variability in the groundwater. The inorganic species were sampled every 4h. Due to a higher effort required in the xenobiotic analyses the sampling frequency of the xenobiotics was reduced to once every 8 h. Constant sampling intervals for all WWIs instead of different sampling schedules for the different WWIs reduced the possibility of errors during field works of IPTs. The samples were taken from a bypass valve directly from the pumping well. Samples were stored cooled in 60 ml HDPE bottles and 1 L glass bottles for inorganic and xenobiotic analyses, respectively.

Wastewater sampling program

The daily variation of wastewater flow and WWI concentrations in the investigated sewer was observed during a 24h-sampling program in February 2008. During the sampling program wastewater samples were taken as grab samples with a sampling frequency of 2 h. The resulting 12 xenobiotic samples were mixed into one sample to obtain average WWI concentrations $c_{wastewater}$. The 12 inorganic samples were analyzed separately. All wastewater samples were stored similarly to groundwater samples until chemical analyses.

Chemical analysis of samples

The B, Cl^- and K^+ concentrations were analyzed by ion chromatography. The components NH_4^+ and NO_3^- were analyzed by photometry. The analysis of BPA, CAF and TON was performed by the method of Braun et al. (2003) using the solid-phase microextraction method and gas chromatography-mass spectrometry. The LOD's are given in Tab. 1.

2.2.6 Calculation of mass flow rates and exfiltration rates

Average concentrations from IPT

The first step of interpreting the results from the IPTs was the estimation of average concentrations c_{av1}, c_{av2}, c_{av3} and c_{av4} at the individual control planes of the four IPT wells with the CSTREAM code (Fig. 3). The groundwater modeling system Processing Modflow (Chiang and Kinzelbach, 1998) was used to set up a numerical groundwater model of the leaky sewer field site with an extent of 200 m × 300 m. This homogenous one-layer model represents the sand-gravel aquifer. The Tertiary fine sand layer below the aquifer is not included. The cell size of the modeling grid ranges from 2 m at the boundaries to refined cells of 0.25 m in the vicinity of the pumping wells. Data from field programs were used to estimate hydraulic properties of the aquifer. Water flow calculations were made using the following aquifer properties: average saturated thickness $b = 6.2$ m and effective porosity $n_e = 0.2$. Constant flow and fixed head boundary conditions were compared in the numerical model and revealed that both can achieve reliable groundwater surfaces during steady state and transient conditions. Finally, fixed head cells were implemented as constant boundary conditions. A constant gradient of 0.002, which was derived from the evaluation of water level measurements at the study site, was achieved by entering a head of 101.35 m amsl at the north and of 102 m amsl at the south of the modeling domain.

Tab. 1. Investigated wastewater indicators (WWIs) with limit of detection (LOD) and analysis uncertainty from the laboratory. The octanol-water partitioning coefficient log K_{OW} was obtained from the PhysProp database of the Syracuse Research Corporation.

WWI	**Application as WWI**	**LOD**	**Analysis uncertainty**	**log K_{OW}**
Inorganic substances		[mg L^{-1}]	[%]	[-]
B	Wolf et al. (2004); Musolff et al. (2007)	0.03	5	0.23
Cl^-	Musolff et al. (2007); Rose (2007)	0.1	5	-0.46 (NaCl)
K^+	Wolf et al. (2007); Rose (2007)	1.0	5	-0.77
NO_3^-	Garnier et al. (2007)	0.5	5	0.21
NH_4^+	Garnier et al. (2007)	0.1	5	-4.37
Xenobiotics		[ng L^{-1}]		
BPA	Clara et al. (2005); Reinstorf et al. (2008)	10	66	3.32
CAF	Buerge et al. (2003); Kim et al. (2007)	3	63	-0.07
TON	Peck et al. (2006); Strauch et al. (2008)	2	56	5.70

The calibration of the numerical flow model was performed using the hydraulic conductivity K as a fitting parameter. Simulated water levels were fitted to observed water levels before and during pumping of the IPT wells. The best fit of simulated to observed water levels was achieved for a hydraulic conductivity K of 5×10^{-4} m s^{-1}. The sewer as a water source was not implemented in the numerical model due to expected low Q_{ex}. Isochrones of the IPT wells during pumping (Fig. 3) were calculated using the particle tracking tool Modpath (Pollock, 1988). Each isochrone represents one sampling time. Combining the isochrone shape with the groundwater flow direction, the numerical solution of the CSTREAM code determined streamtubes with a concentration c (Bayer-Raich, 2004). The number of streamtubes depends on the sampling frequency and the streamtube width is defined by the distance between neighboring isochrones. The evaluation with the CSTREAM code was achieved individually for each well. No concentration values were exchanged between the different well evaluations, although hydraulic influences between the wells are still possible due to the same underlying flow model. The calculation included 31 concentration values for each inorganic compound and 12 - 14 concentration values for each xenobiotic per well. Accounting for a worst case scenario, the concentrations below the LOD were set equal to the LOD. The weighted average of the several c values from the different streamtubes gave the average concentration c_{av} along the individual control plane of an IPT well.

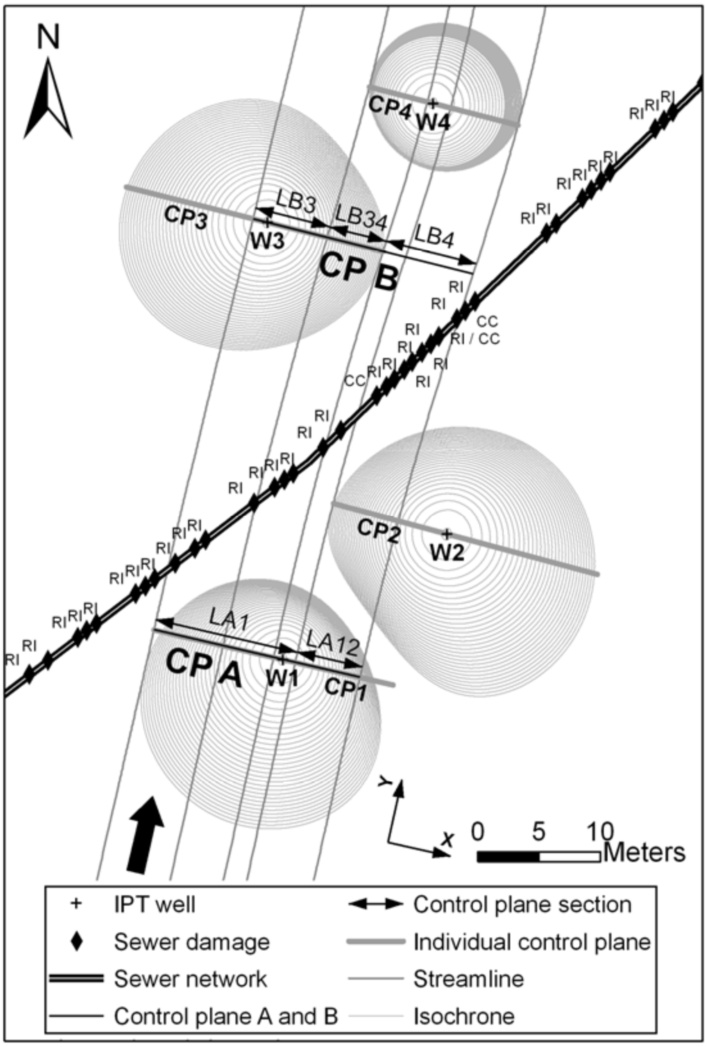

Fig. 3. IPT wells and resulting isochrones for a 4 h-sampling frequency. Individual control planes of the IPT wells W1 to W4 are shown. The merged control planes CP A and CP B are defined by the simulated streamlines. The black arrow indicates the mean groundwater flow direction. Sewer defects are marked by RI (root intrusion) and CC (connection crack).

Specific mass flow rate from the sewer

In order to compare c_{av} and M_{cp} of the individual control planes up- and downstream of the leaky sewer we merged the individual control planes of well W1 and W2 to CP A and well W3 and W4 to CP B (Fig. 3). The numerical groundwater flow model was used to compute the corresponding streamlines in Fig. 3. Average concentrations c_A and c_B of the merged control planes CP A and CP B are calculated by equations:

$$c_A = \frac{c_{av1} L_{A1} + \left(\frac{c_{av1} + c_{av2}}{2} \right) L_{A12}}{L_{A1} + L_{A12}} \tag{11}$$

$$c_B = \frac{c_{av3} L_{B3} + \left(\frac{c_{av3} + c_{av4}}{2} \right) L_{B34} + c_{av4} L_{B4}}{L_{B3} + L_{B34} + L_{B4}} \tag{12}$$

using the average concentrations c_{av1}, c_{av2}, c_{av3} and c_{av4} of the four individual control planes and the indicated control plane sections L in Fig. 3. The mass flow rate from the sewer M_{ex} is calculated from the following equation:

$$M_{ex} = \frac{M_B - M_A}{L_{sewer}} \tag{13}$$

The mass flow rates M_A and M_B were obtained by multiplying c_A and c_B with a water flow rate Q_{av} of 11.7 m³ d^{-1}. Q_{av} was obtained from the numerical groundwater model for an average control plane length of 17.9 m for CP A and CP B. The sewer length between the outer streamline in the west to the outer streamline in the east is the affected sewer length L_{sewer} of 31.50 m (Fig. 3). Using M_{ex} from equation (13) gives the Q_{ex} using:

$$Q_{ex} = \frac{M_{ex}}{c_{wastewater}} \tag{14}$$

The concentration $c_{wastewater}$ is the average concentration over the 24h-sampling period in the sewer. The estimation of Q_{ex} with equation 14 is only valid for conservative target substances.

2.2.7 Exfiltration measurement by sewer blocking

In September 2008 an alternative exfiltration measurement was conducted in three adjacent sewer sections at the field site (Fig. 2). The sewer was blocked with pressurized balloons and the falling water level was logged over a period of two hours. The estimation of the water volume difference between the beginning and the end of the blocking yields the exfiltration rate.

2.3 Results and discussion

2.3.1 Groundwater sampling during the IPT

In-situ field parameters are useful to characterize the groundwater at the field site and to compare the groundwater at the different pumping wells. The in-situ parameters that were measured during pumping show variations between the four IPT wells for electrical conductivity (1160 - 1320 µS cm^{-1}), pH (6.4 - 6.6), redox potential (140 - 210 mV), oxygen content (0 - 1 mg L^{-1}) and temperature (11.0 - 12.1 °C). Highest electrical conductivity of 1277 - 1320 µScm^{-1} at well W4 indicates highest concentrations of ions in comparison to the other wells and suggests an influence of wastewater at this well.

The following section presents and discusses the obtained concentration-time series from the different IPT wells. The comparison of concentration-time series of wells W1 and W2 upstream of the sewer with the concentration-time series of wells W3 and W4 downstream of the sewer was performed in order to show a possible WWI concentration increase downstream of the sewer. A significant increase between WWI concentrations must exceed the chemical analysis uncertainty.

Concentration-time series of wells W1, W2 and W3 (Fig. 4) show similar stable inorganic concentrations during IPT with small ranges of 0.33 - 0.41 mg L^{-1} for B, 65.8 - 99.0 mg L^{-1} for Cl^-, 11.7 - 13.8 mg L^{-1} for K^+ and 16.3 - 27.0 mg L^{-1} for NO_3^-. NH_4^+ was at these wells mostly below or near the LOD. Well W4 reveals increased concentration ranges of B (0.34 - 0.42 mg L^{-1}), Cl^- (86.4 - 122.0 mg L^{-1}), K^+ (12.4 - 14.4 mg L^{-1}), NO_3^- (15.2 - 28.2 mg L^{-1}) and NH_4^+ (0.2 - 1.0 mg L^{-1}). A slight increase of the concentration-time series during the pumping period series was observed for Cl^- and NO_3^- at well W4. Xenobiotic concentration-time series show higher concentration variability than inorganic concentrations during pumping with ranges of 10 - 450 ng L^{-1} for BPA, 3 - 49 ng L^{-1} for CAF and 2 - 24 ng L^{-1} for TON. Increased concentrations at well W4 were not observed for xenobiotics. The concentration variability decreased during pumping for BPA and CAF. Several TON concentrations at the end of pumping are below the LOD.

The chemical analyses of 124 inorganic samples and 64 xenobiotic samples from the four IPT wells were derived in the laboratory. Electro-neutrality balances of the inorganic samples reveal deviations of less than 6 %. The uncertainty of the xenobiotic analysis was evaluated by averaging the concentration deviations from the internal standards. Large amounts of humic substances in the groundwater interacted with the solid-phase sorbent and caused a high variability of the extraction during the laboratory work. Thus, analysis uncertainties of 66 %, 63 % and 56 % were obtained for BPA, CAF and TON, respectively. The xenobiotic concentrations of 11 samples were removed from the IPT calculations, due to low measured internal standards.

The inorganic concentration-time series indicate an influence of wastewater at well W4 whereas the xenobiotic concentrations did not prove this. Cl^- and NH_4^+ yielded the most significant concentration difference between W4 and the other three wells that exceeded the analysis uncertainty. Well W3 did not reveal any influence of wastewater although it is located downstream of the sewer. Leak sealing in the sewer upstream of this well may have prevented exfiltration of wastewater. The large variability of measured xenobiotic concentrations is primarily an effect of the large analysis uncertainty, but also of spatially heterogeneous concentrations in the aquifer. For BPA and CAF the concentration variability at the end of the pumping period after 50 h was reduced. This indicated the presence of a heterogeneous concentration pattern in the capture zone of the IPT wells. Due to mixing of different aquifer zones with different concentrations at the end of the IPT, this variability must decrease while analysis uncertainty stays constant. Concentration values below the LOD for TON at the end of the pumping time seemed to be unrealistic, because of more intensive mixing of different concentration zones in the aquifer at the end of pumping.

Following the characteristic plume scenarios in Bockelmann et al. (2001), the rising concentration-time series of Cl^- and NO_3^- at well W4 may indicate a wastewater plume in the vicinity of this well. A reliable estimation of the plume position was not an aim of this study and was not possible with only two wells per merged control plane due to the ambiguity of the spatial concentration resolution obtained from the IPT (Ptak et al., 2000).

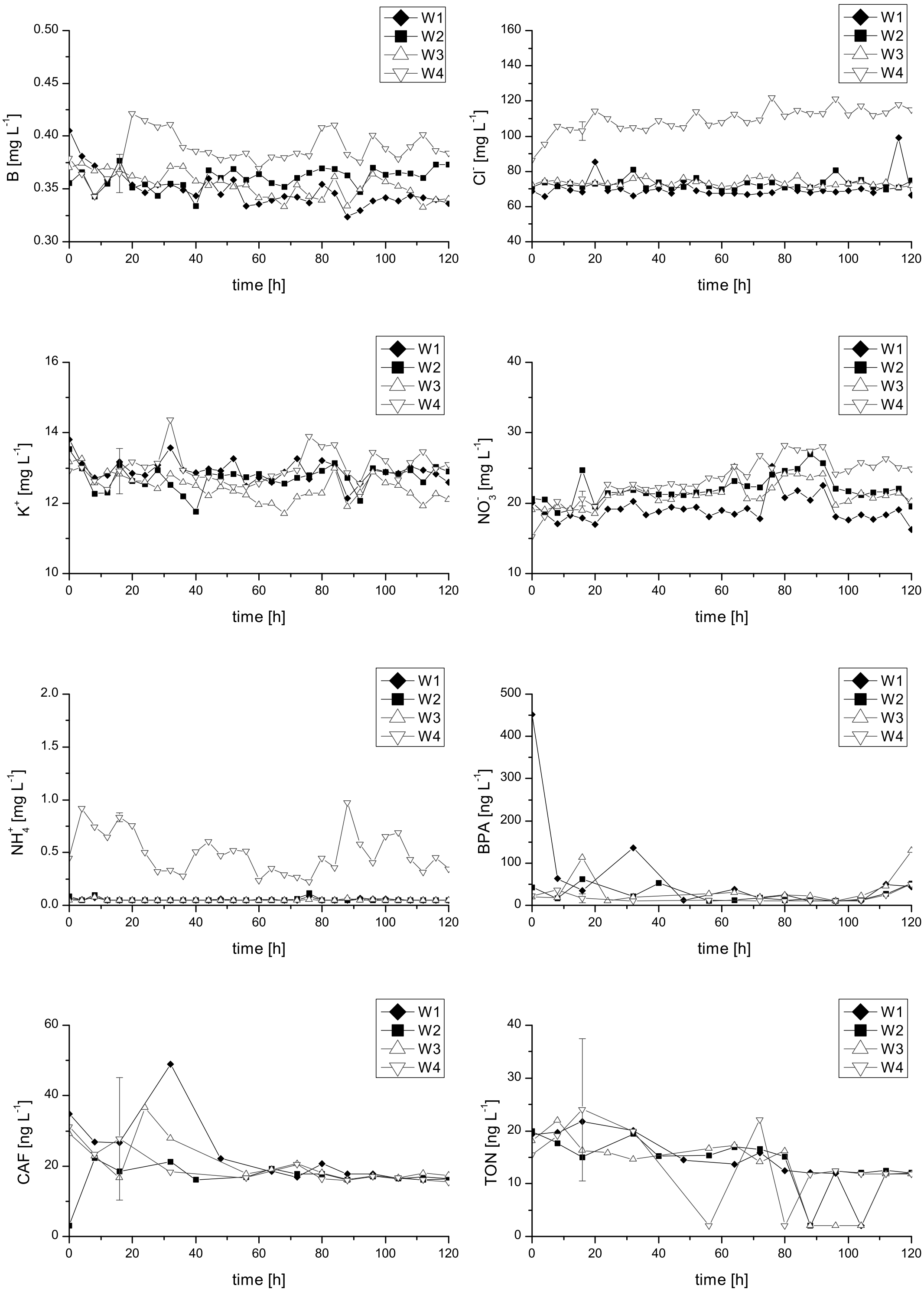

Fig. 4. Concentration-time series of WWIs during the five days of IPT duration. Well W1 and W2 are situated upstream where W3 and W4 are situated downstream of the leaky sewer. Error bars are only added for the 16h-value of well W4.

2.3.2 Wastewater sampling program

Concentrations of B (0.2 - 0.6 mg L^{-1}), Cl^- (106 - 450 mg L^{-1}), K^+ (18 - 28 mg L^{-1}), NO_3^- (5 - 13 mg L^{-1}), NH_4^+ (29 - 64 mg L^{-1}), BPA, CAF and TON were obtained from the 24h-sampling program. Mixing of 12 wastewater samples yielded average WWI concentrations $c_{wastewater}$ (Tab. 2). NH_4^+ and NO_3^- were combined to N_{tot}. Fig. 5 shows the concentration variation of inorganic WWIs during the sampling day. Low concentrations during the night hours 04:00 am to 06:00 am for B, Cl^-, K^+ and NH_4^+ and peak concentrations of NH_4^+ at 10:00 am and of B as well as Cl^- at 20:00 pm indicate that the wastewater composition in the observed sewer is related to the activity of the inhabitants in the connected sewershed. Therefore a diurnal variation of the wastewater inflow can be expected. Former studies in the same area reported similar wastewater concentration ranges (Musolff et al., 2007). A comparison of WWI concentrations in the groundwater (Fig. 4) with $c_{wastewater}$ (Tab. 2) reveals higher concentration in the wastewater. The exception of B shows only peak concentrations in the wastewater that are higher than in the groundwater.

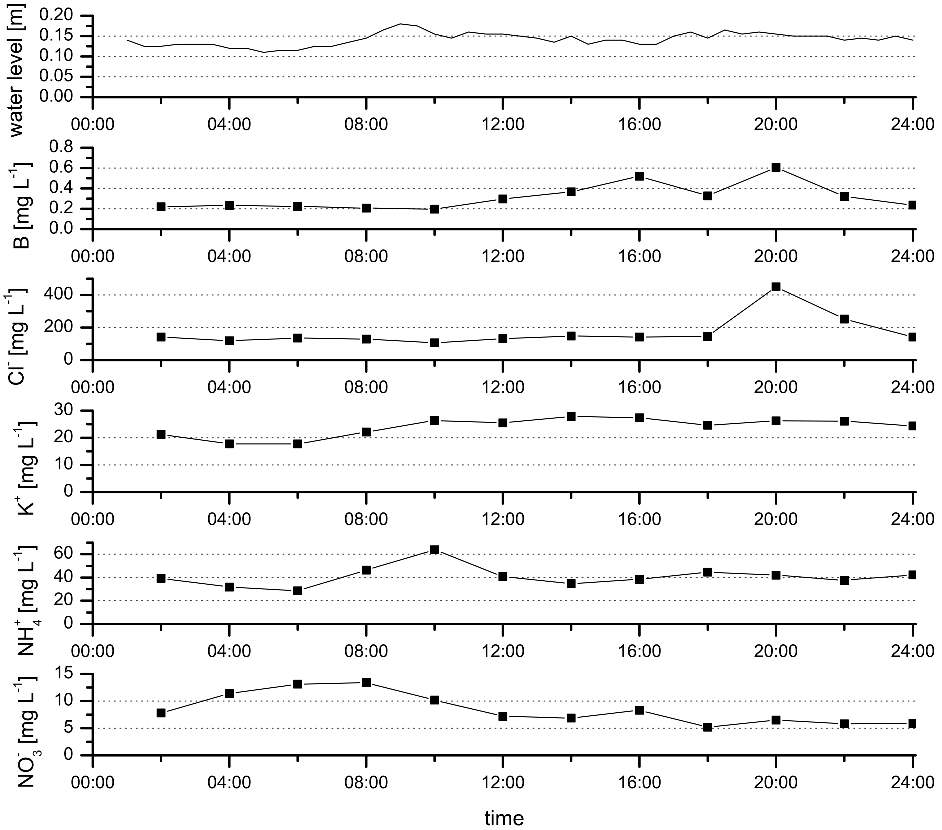

Fig. 5. Water level and inorganic WWI concentrations in the target sewer during 24h-sampling program in February 2008.

Tab. 2. Mass flow rates M_A and M_B with resulting M_{ex} from the sewer. Average concentrations $c_{wastewater}$ are obtained by the 24h-sampling in February 2008. The value of Q_{ex} of Cl^- was derived from M_{ex} and $c_{wastewater}$. Exfiltration measurements in September 2008 by sewer blocking and simultaneous water level logging in the sewer yielded an alternative Q_{ex}.

WWI	M_A	M_B	M_{ex}	$c_{wastewater}$	Q_{ex}
Inorganic substances	[g d^{-1}]	[g d^{-1}]	[g m^{-1} d^{-1}]	[mg L^{-1}]	[L m^{-1} d^{-1}]
B	4.1 ± 0.2	4.3 ± 0.2	0 - 0.02	0.31	
Cl^-	839 ± 42	1086 ± 55	4.8 - 10.9	170	28.0 - 63.9
K^+	149 ± 8	148 ± 8		24	
N_{tot}	51 ± 3	61 ± 3	0.14 - 0.5	34	
Xenobiotics	[µg d^{-1}]	[µg d^{-1}]	[µg m^{-1} d^{-1}]	[ng L^{-1}]	
BPA	496 ± 329	410 ± 272		1767	
CAF	246 ± 155	221 ± 139		13006	
TON	157 ± 88	147 ± 82		170	
Exfiltration measurement in September 2008					28.8 - 40.8

2.3.3 Mass flow rates and exfiltration rates

Average concentrations c_A and c_B of the merged control planes CP A and CP B obtained from the concentration-time series via the CSTREAM code are presented in Fig. 6. The concentration uncertainty of inorganic components is lower than concentration uncertainty of xenobiotics. The most significant concentration increase at the downstream control plane CP B can be observed for Cl^- and N_{tot}, indicating that even the upper limit of the c_A error bar is lower than the lower limit of the c_B error bar. Concentrations of B show a slightly increased concentration downstream of the sewer whereas K^+ and all xenobiotics decrease downstream of the sewer. This decrease is not significant, because c_B still lies in the range of the c_A error bars, indicating that the analysis uncertainty is not exceeded. However, the obtained differences between average concentrations c_A and c_B are more meaningful than the differences between single point measurements because they base on several concentration measurements from similar groundwater regions.

The values of M_A and M_B in Tab. 2 were calculated for concentrations in Fig. 6. The obtained mass flow ranges were included in the calculation of M_{ex}. Negative values of M_{ex} were set to 0 for the calculation, because an infiltration of groundwater into the sewer can not be investigated with the presented approach. In case of non conservative WWIs the values of M_{ex}

represent only minimum mass flow rates that were released from the sewer. Due to the applied IPT setup that yields only integral mass flow rates, mass depletion on the pathway from the sewer to the downstream control plane can not be quantified. If M_B is equal or lower than M_A it can only be stated that the exfiltration mass is completely or partly depleted. Thus, only M_A as well as M_B and no M_{ex} are given in this case. Higher M_B than M_A indicate that the additional mass flow must originate from the sewer as no other sources are known. It can be that even more mass flow reached the aquifer, but was depleted on the pathway from the sewer to the downstream control plane. Therefore, we define M_{ex} as minimum mass flow from the sewer for non conservative WWIs.

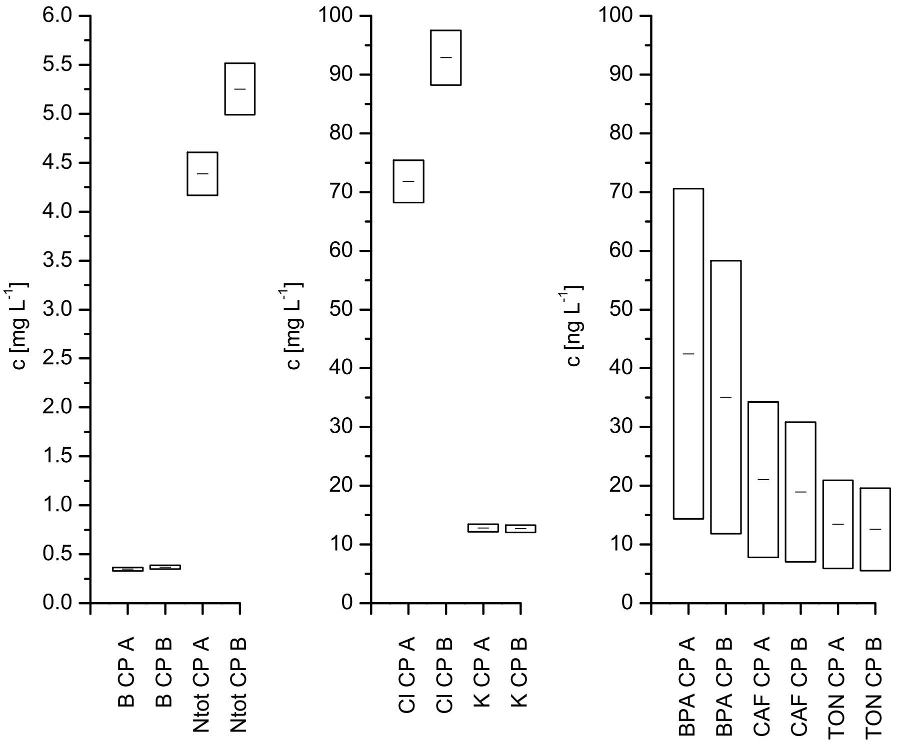

Fig. 6. Resulting concentrations of WWIs (black dashes) with the laboratory analysis uncertainty (black error bars). CP A is situated upstream and CP B downstream of the sewer. N_{tot} includes concentrations of NH_4^+ and NO_3^-.

Regarding the results in Tab. 2 higher downstream mass flow rates M_B were identified significantly for Cl^- as well as for N_{tot} and not significantly with overlapping of the error ranges between M_A and M_B for B. Consequently, M_{ex} was given for these three WWIs. The highest M_{ex} was identified for Cl^- followed by N_{tot} and B. All other WWIs show lower M_B that are in the range of the analysis error of M_A. The obtained M values depend on different transport behaviour of the target WWIs. Lower M_B than M_A were observed for WWIs that are affected by sorption (K^+, BPA and TON) or degradation (BPA, CAF and TON). Mass depletion processes of WWIs may take place at three different compartments on the pathway between the sewer and downstream control plane: in the clogging zone of sewer leaks, in the unsaturated zone beneath the sewer and in the groundwater. A detailed interpretation of depletion processes with the measured data is not feasible, because no sampling was conducted in the three different compartments and the sampling analysis uncertainty, especially for the xenobiotics, was too high. However, reduced M downstream of the sewer and high wastewater concentrations for K^+, BPA, CAF as well as for TON indicate that only low or no mass of these WWIs reach the groundwater via sewer leakage at the field site.

Due to the conservative transport behaviour of Cl^- (Appelo and Postma, 1999), it can be used to estimate Q_{ex} with equation (14) (see Tab. 2). The estimation of Q_{ex} by using $c_{wastewater}$ may cause errors, because the 24h-sampling was not derived during the IPT. A difference of the wastewater composition between September 2007 and February 2008 in the sewer is possible, but we assume that the day-night variation of wastewater components is more important, due to the seasonally stable household-dominated wastewater inflow pattern. The seasonal variation in the wastewater composition is neglected for the calculation of Q_{ex}, but the daily variation was included by using average WWI concentrations of one day. A verification of the presented IPT monitoring approach was derived by comparing the Q_{ex} of Cl^- with the Q_{ex} of the alternative exfiltration measurement via sewer blocking (Tab. 2). Similar Q_{ex} ranges for both measurements indicate that the IPT monitoring approach can provide reliable data. Rutsch et al. (2008) reported a Q_{ex} with a lower range of 8.6 to 38 L m^{-1} d^{-1} derived from a study based on conservative marker species in the groundwater. Different field site properties can explain the discrepancy to our own measurements.

The obtained c_{av} and mass flow rates M depend on the evaluation procedure that is described in section 2.6. The basis of the evaluation is the numerical model that represents the aquifer as one homogenous layer. The model structure and the parameterization of the model have a direct influence on the obtained results. Especially the isochrone shape is important for the evaluation of the IPTs. For example unrealistically high values for the hydraulic conductivity K and for the gradient i will lead to elongated isochrones with relatively short control planes. In this the estimation of c_{av} will be biased and the affected sewer length L_{sewer} will be too short. The parameters for the model in this study were derived from common field methods and represent the properties of the investigated aquifer. The use of a one-layer homogenous model may produce errors because spatial heterogeneities can not be included. So far the evaluation of IPT with the CSTREAM code does not allow a model with several layers. However, relative low deviations between observed and simulated water levels show that the applied model setup is able to reproduce the conditions at the field site. The definition of the model boundary conditions has to be achieved carefully in order to get realistic groundwater flow directions that allow a reliable interpretation of the overlapping between control planes up- and downstream of the sewer. We checked the output groundwater surface from the model with Kriging-interpolated groundwater surfaces that contain water levels from observation wells all over the study area and revealed a good agreement between them. Another source of uncertainty in the applied model may arise from not including Q_{ex} for the groundwater flow estimations. The influence of the additional flow Q_{ex} must be limited because no deflection of isolines in the vicinity of the sewer could be identified from the Kriging-interpolated groundwater surfaces. Overall the applied numerical model is not very sophisticated, but the parameterization is easily comprehensible and represents the relevant flow processes.

2.4 Conclusions

This study presents a new monitoring approach that applied integral pumping tests (IPTs) to obtain mass exfiltration rates M_{ex} of different wastewater indicators (WWIs) from leaky sewers. The IPT monitoring approach accounts for heterogeneous WWI concentration patterns in the vicinity of leaky sewer by giving average concentrations along control planes in the aquifer up- and downstream of leaky sewers. Large volume sampling overcomes the problem of missing wastewater plumes in the aquifer downstream of leaky sewers. A first application of the IPT monitoring approach at the leaky sewer field site in Leipzig (Germany) was performed for five ions and three xenobiotics. Large chemical analysis uncertainty for the xenobiotics caused large variability of the average concentrations c_{av} for xenobiotics. By including the average concentration $c_{wastewater}$ of the wastewater at the leaky sewer field site, the estimation of Q_{ex} was possible. The comparison of Q_{ex} of Cl^- from the IPT application with alternative measurements and other studies revealed that the IPT monitoring approach provides reliable data. Depletion of non-conservative WWIs during their passage from the sewer to the pumping well was identified by reduced mass flow rates in the groundwater downstream of the sewer. Due to the significant effort required for IPT operations, a complete survey of the sewer network is not possible. Dilution of exfiltrating wastewater with groundwater and dilution during pumping limits the applicability of the IPT monitoring approach to field sites with strong sewer exfiltration. The impact of leaky sewers on the groundwater can be assessed by using M_{ex}. Transfer of M_{ex} values to other sewers need to account for different field conditions, which influence Q_{ex} (e.g., groundwater level, sediments in the vicinity of the sewer). The new IPT monitoring approach can be applied to other leaky sewer locations.

3 Application of integral pumping tests to investigate the influence of a losing stream on groundwater quality

This chapter is published as:

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Abstract:

Losing streams that are influenced by wastewater treatment plant effluents and combined sewer overflows (CSOs) can be a source of groundwater contamination. Released micropollutants such as pharmaceuticals, endocrine disrupters and other ecotoxicologically relevant substances as well as inorganic wastewater constituents can reach the groundwater, where they may deteriorate groundwater quality. This paper presents a method to quantify exfiltration mass flow rates per stream length unit M_{ex} of wastewater constituents from losing streams by the operation of integral pumping tests (IPTs) up- and downstream of a target section. Due to the large sampled water volume during IPTs, the results are more reliable than those from conventional point sampling. We applied the method at a test site in Leipzig (Germany). Wastewater constituents K^+ and NO_3^- showed M_{ex} values of 1241 to 4315 and 749 to 924 mg $m_{stream}^{-1}d^{-1}$, respectively, while Cl^- (16.8 to 47.3 g $m_{stream}^{-1}d^{-1}$) and SO_4^{2-} (20.3 to 32.2 g $m_{stream}^{-1}d^{-1}$) revealed the highest observed M_{ex} values at the test site. The micropollutants caffeine and technical-nonylphenol were dominated by elimination processes in the groundwater between upstream and downstream wells. Additional concentration measurements in the stream and a connected sewer at the test site were performed to identify relevant processes that influence the concentrations at the IPT wells.

3.1 Introduction

Contamination of streams and groundwater by substances that originate from wastewater have been reported in many studies (Eiswirth et al., 2004; Vazquez-Sune et al., 2005; Ellis, 2006). Streams can become contaminated, for example, from wastewater treatment plant discharge containing contaminants that are not completely eliminated during the treatment process. Untreated wastewater is discharged to streams during combined sewer overflows (CSOs) where it leads to increased loadings of wastewater constituents (Mulliss et al., 1996). Mendoza et al. (2008) demonstrated that contaminated streams with alternating conditions between losing and gaining may pose a threat to groundwater quality. Micropollutants such as persistent pharmaceuticals, originating primarily from wastewater, have become emerging contaminants in surface water and groundwater (Fenz et al., 2005; Schwarzenbach et al., 2006; Schirmer et al., 2007; Schirmer and Schirmer, 2008). Various groundwater studies have focused on the occurrence of these substances during bank filtration (e.g., Heberer, 2002), but few studies exist on the transport of wastewater constituents from losing streams to the groundwater under natural conditions.

This paper aims to improve the knowledge on the influence of temporally losing streams on groundwater quality by presenting a method to estimate exfiltration mass flow rates per stream length unit M_{ex} of wastewater constituents from a stream during losing conditions. In this context the water flow from the stream to the groundwater is defined as exfiltration form the stream. The approach of Kalbus et al. (2007) that uses integral pumping tests (IPTs; Bayer-Raich et al., 2004) for the estimation of mass fluxes J at the stream-aquifer interface of gaining streams was extended to the application to losing streams. The study was performed in 2008 at a test site in Leipzig, Germany (Strauch et al., 2008). The analysis was derived for four inorganic substances (K^+, Cl^-, NO_3^- and SO_4^{2-}) as well as for the micropollutants caffeine (CAF) and technical-nonylphenol (NON). We operated IPTs up- and downstream of the investigated target section to account for heterogeneous concentration patterns in the vicinity of the stream. On the one hand, we faced varying concentrations resulting from heterogeneities in the aquifer and the fluctuating household-related input of wastewater to the stream during dry- and wet-weather conditions. Under these conditions, sampling during long-time pumping with IPTs yields more reliable average concentrations c_{av} than conventional point sampling in space and time. On the other hand, natural hydraulic gradients between stream and groundwater are disturbed by pumping. The dimensioning of the IPT needs to account for this by increasing the distance between the pumping well and the stream so that the capture zone of the pumping well does not reach the groundwater that is influenced by the intensified exfiltration from the stream. The mass flow increase ΔM downstream of the investigated stream yields M_{ex}.

In order to interpret the concentrations and mass flow rate data from IPTs, processes that influence the concentration pattern in the groundwater need to be defined. We assume that the following processes (a) to (h) may occur at the test site. Exfiltration water concentrations from the stream are influenced by (a) temporally high concentrations in the stream as a result of variable wastewater treatment plant effluents and CSOs in the upper catchment of the stream, (b) retardation in the streambed, (c) degradation in the streambed and (d) exchange with storage pools in the pore water of the streambed and the stream banks that are fed during times of high water levels in the stream. Concentrations of target substances in the groundwater increase or decrease along the flow path from the upstream to the downstream wells due to (e) mixing of groundwater with exfiltration water from the stream, (f) hydrodynamic dispersion and mixing with groundwater recharge, (g) retardation in groundwater and (h) degradation in groundwater. Additional concentration measurements in the stream and in a connected sewer at the test site were performed to identify these processes.

3.2 Materials and methods

3.2.1 Test site

The investigated stream "*Bauerngraben*" (Fig. 7) is located in the urban area of the city of Leipzig (Germany). The small, artificial watercourse is constructed of cobbled pavement, whose joints are filled with sand. It has an average width of 1 m in the study area. The inflow to the *Bauerngraben* originates from a flood protection reservoir and is controlled by a weir. Under dry-weather conditions the *Bauerngraben* has a discharge of 0.01 to 0.03 m^3s^{-1}. The *Bauerngraben* is strongly influenced by three outlet pipes for CSOs that are located in the east of the test site (only one is shown in Fig. 7). Due to the controlled inflow to the *Bauerngraben*, water level fluctuations in the stream are mainly an effect of CSOs. In the period from April 2006 to April 2007 43 CSOs were detected by water level logging in the *Bauerngraben* with water level fluctuations between 10 and 105 cm. Observation wells near the *Bauerngraben* show variable groundwater levels that are above the streambed in winter and below it in summer. The IPTs were performed during losing conditions of the *Bauerngraben*.

The stratigraphy below the study area consists of Tertiary fine sands overlain by a Quaternary sand and gravel layer. The Quaternary sediments form a highly permeable aquifer with a hydraulic conductivity *K* of 3×10^{-4} to 4×10^{-3} ms^{-1}. Heterogeneous floodplain loams with an average thickness of 1.5 m cover the aquifer. Ram sounding in the streambed of the *Bauerngraben* indicated no floodplain loam below the investigated reach.

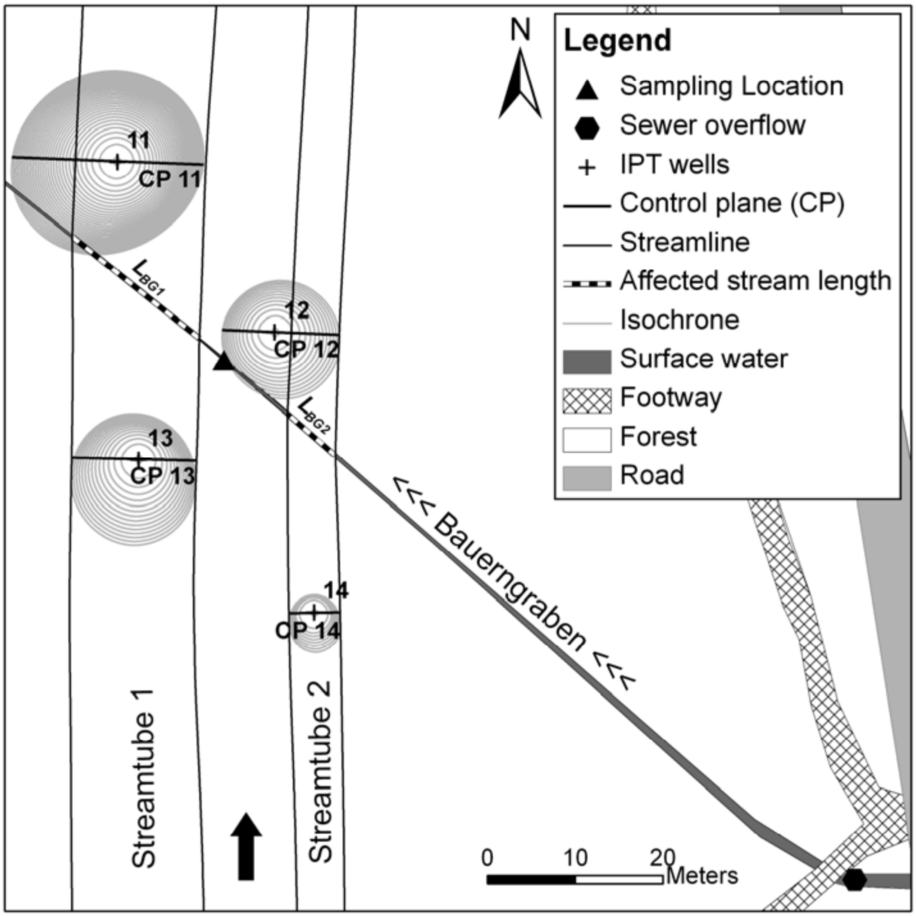

Fig. 7. Test site showing the temporally losing stream *Bauerngraben*, IPT wells and isochrones at sampling times. Streamlines define streamtube 1 (wells 11 and 13) and streamtube 2 (wells 12 and 14). The mean groundwater flow direction is indicated by the black arrow. Isochrones are for the 4h sampling interval.

3.2.2 Observed wastewater constituents

The four inorganic substances (K^+, Cl^-, NO_3^- and SO_4^{2-}) and two micropollutants (CAF and NON) were chosen according to preliminary studies (Musolff et al., 2007; Reinstorf et al., 2008) in which these substances had already been used as wastewater indicators. Regarding possible sources of the chosen wastewater constituents, K^+ originates from laundry discharge (Wolf et al., 2007). Large amounts of Cl^- are washed from roads during the winter period when road salting occurs (Mayer et al., 1999), but other sources are also known (e.g., dishwashers). Nitrification of NH_4^+, which can originate from urine, is a common source of NO_3^-. Industrial wastewater represents a source of SO_4^{2-} (Barrett et al., 1999). CAF is a constituent of different beverages such as coffee or tea and of numerous food products (Buerge et al., 2003). Technical-nonylphenol (NON) is used for the production of non-ionic tensides, thus it originates mainly from industrial wastewater and laundry (Bradley et al., 2008).

3.2.3 IPT method background

Average concentrations c_{av} and mass flow rates M_{CP} along control planes (CP) in an aquifer can be reliably estimated by the IPT method (Bayer-Raich et al., 2004). The CPs are oriented perpendicular to the natural groundwater flow direction and contain one or more pumping wells. Long-time pumping (several days) of the wells and simultaneous sampling gives more reliable information about c_{av} and M_{CP} at the predefined CP than conventional point sampling, because the sampled volume is larger and small-scale plumes cannot be missed. The code CSTREAM (Bayer-Raich, 2004) can be used to estimate c_{av} and M_{CP} by performing a weighted average with the values from the obtained concentration-time series. The weights base on spatial distances between isochrones that were calculated by a particle tracking tool (Modpath) in combination with a one-layer Modflow model. The resulting isochrones define the boundary of the capture zone for the respective sample at this time. Successful operations of IPTs are reported in Bockelmann et al. (2003), Bayer-Raich et al. (2006) and Kalbus et al. (2007).

3.2.4 IPT design at the study area

Four IPT wells (11, 12, 13 and 14), two upstream and two downstream of the *Bauerngraben*, were drilled in the study area (Fig. 7) and screened along the Quaternary aquifer with HDPE-tubes. Over a period of five days (May 28 to June 2, 2008), wells 11, 12 and 13 were operated with a pumping rate of 1 Ls^{-1}. Due to operational problems at well 14, pumping was reduced to 0.5 Ls^{-1} and stopped already after 32 h. The standard parameters of pH, electrical conductivity, oxygen content and temperature were measured in the pumping wells during the entire pumping period. The drawdown in 12 observation wells was measured at least every 2 h (with shorter intervals directly after the beginning of pumping) using a water level logging device in the pumping wells.

3.2.5 IPT evaluation

A groundwater model of the Quaternary aquifer was built with the software model Processing Modflow. The homogeneous, semi-confined model covers an extent of 200 × 300 m with an average aquifer thickness of 5.8 m at the wells. In the model grid cell sizes vary from 1 m at model boundaries to 0.25 m in the pumping area. Fixed head cells were implemented at the north and south boundaries of the model domain. The parameters of hydraulic conductivity $K = 4.5 \times 10^{-4}$ ms^{-1}, gradient $i = 4.1 \times 10^{-3}$ and effective porosity $n_e = 0.2$ were estimated from various field measurements and set for water flow calculations. Water levels in groundwater on May 25 before the start of pumping were measured to be 20 cm below the streambed of the *Bauerngraben*, indicating that water was flowing from the *Bauerngraben* to the groundwater. For that reason it was assumed that pumping-induced drawdown would not increase the leakage from the *Bauerngraben*. Therefore, the leakage was implemented as a constant discharge rate per stream length unit Q_{ex}. Best fitting of observed to simulated water levels at the observation wells was obtained for a Q_{ex} of 85 L $\mathrm{m_{stream}}^{-1}$ d^{-1}. The average deviation between the simulated and observed water levels was 3 cm. Isochrones for the respective sampling schedule and streamlines (Fig. 7) were obtained by the particle tracking code Modpath. In order to get a complete overlapping of the upstream CPs (13, 14) by the downstream CPs (11, 12), the considered volume was reduced by neglecting samples of wells 12 and 13 at the end of the pumping period (Fig. 7). Streamtubes 1 and 2 are defined by streamlines from the groundwater model before pumping and by the CP extents of wells 13 and 14 that determine the width b. These streamtubes were used for mass balance calculations between the up- and downstream wells of the *Bauerngraben*. The estimation of c_{av} for the different CPs was derived with the code CSTREAM in combination with the groundwater model. Corresponding M_{CP} values were obtained by multiplying c_{av} with the respective water flow Q_{CP}. Thus M_{CP} specifies only the part of the CP at wells 11 and 12 that is located in the respective streamtube. Values of Q_{CP} were derived from the groundwater model. Differences of M_{CP} values between upstream and downstream wells depend on concentrations differences Δc and on different water flows Q_{CP}. For the comparison of the two streamtubes the mass fluxes J_{CP} at each CP were included. Values of M_{ex} were calculated by

$$M_{ex} = \frac{M_{CP\,Y} - M_{CP\,X}}{L_{BG}} \tag{15}$$

where $M_{CP\,X}$ and $M_{CP\,Y}$ are the mass flow rates up- and downstream of the *Bauerngraben* and L_{BG} is the affected stream length, which is marked in Fig. 7. The estimation of M_{ex} was only possible for substances that show a downstream mass flow rate increase (positive ΔM_{CP}).

3.2.6 Sampling in groundwater, surface water and wastewater

Groundwater samples were taken during the pumping period 28 May to 2 June 2008 from a tap at the IPT wells following a predefined schedule: samples for inorganic analyses every 4 h and samples for organic analyses every 8 h. After 56 h the sampling frequency for organic substances was reduced to 16 h. Surface water sampling was completed with an automatic sampling device that pumped surface water from the *Bauerngraben* (location in Fig. 7) to storage bottles every 5 minutes during the period 17 May to 2 June 2008. A reduction of the sample number from the surface water was achieved by mixing all 5 minutes samples from one day in one bottle. The obtained 17 mix-samples were analyzed for the target substances. In a former study (Leschik et al., 2009), grab samples of wastewater were taken from a sewer that was connected to the overflow pipe which discharges into the *Bauerngraben* (Fig. 7). These samples were picked during a 24 h period in February 2008 at an interval of 2 h for inorganic analysis and 8 h for organic analysis to quantify daily concentration variations of target substances.

3.2.7 Sample preparation and chemical analysis

Samples were stored cooled in 60 mL HDPE bottles for inorganic analysis and 1 L amber glass bottles for organic analysis. Ion chromatography was applied to analyze K^+, Cl^- and SO_4^{2-} with limits of detection (LOD) of 1, 0.1 and 1 mgL^{-1}, respectively. NO_3^- was analyzed by the photometric salicylic acid method (LOD of 0.5 mgL^{-1}).

The sample preparation for micropollutant analysis was derived by solid phase extraction (SPE) to enrich the target compounds from the water samples. Before they were concentrated, samples (1L, pH at about 7) were filtered through a glass fiber filter and spiked with the internal standards (100ng 4-n-nonylphenol). The filtrates were adjusted to pH 2 and concentrated by SPE using a sorbent mixture (C18 and Lichrolut®EN) preconditioned with methanol and water. After application of the water sample, the sorbent was dried under inert gas and finally eluted with methanol and acetone. After evaporation of the solvent to a final volume of 300 µL a cleanup with silica gel was accomplished using a mixture of acetone and hexane. Evaporation of the solvent to a volume of 200 µL gives the sample for GC-MS analysis.

The GC-MS analyses of the micropollutants were performed using a Varian GC/MS (CP 3800, MS 1200) equipped with a temperature-programmable injection port. The gas chromatographic separation was carried out on a 60 m long Zebron ZB1 capillary column of 0.25 mm internal diameter and 0.25 µm film thickness (Phenomenex). The samples (5 to 10 µL each) were injected at 50°C by large volume injection. The GC oven program started at an initial temperature of 50 °C. Helium was used as the carrier gas in a constant flow mode at 1 mL min^{-1}. The mass spectrometer operated at positive electron impact ionization mode with 70 eV. The GC-MS interface temperature was set at 270 °C and the source temperature at 200 °C. A solvent delay of 8 min was used to fade out the solvent signal. The investigations utilized selected ion monitoring (SIM) for sensitive detection of the target analytes (target ions caffeine -194,149,109; nonylphenols -220,149,107). All sample extracts were twice analyzed and after every fourth analysis blank analysis was carried out to check carryover and memories of previous analyses. The standard mixture was measured repeatedly within every sample series.

3.3 Results and discussion

3.3.1 Concentrations of wastewater constituents in groundwater

Concentration-time series and standard parameters of the IPT wells were evaluated in order to derive concentration differences Δc between the wells, especially downstream of the *Bauerngraben*. These Δc identify how the inflow from the *Bauerngraben* influences the groundwater quality at the test site.

The measured pH of 6.2 to 6.4, an oxygen content of 0 to 1 mgL^{-1} and temperatures of 9 to 10 °C obtained from the wells during the pumping period did not indicate a large difference between the pumped water from different locations, whereas the electrical conductivity in well 12 of 1360 to 1450 μScm^{-1} in comparison to the other wells (1260 to 1370 μScm^{-1}) points to a difference in the ion composition of the groundwater.

The influence of the *Bauerngraben* can be identified by higher concentrations of Cl^- and lower concentrations of SO_4^{2-} at the downstream wells 11 and 12 (Fig. 8). The concentration comparison between up- and downstream wells has to focus mainly on average concentrations that include all observed concentration values at one well. The comparison of single concentration values between two wells for a specific time (e.g., after 8 h) is not useful because shortly after start of pumping the control plane extents of up- and downstream wells (see isochrones in Fig. 7) do not or only in small parts overlap. Hence for K^+ higher concentrations can be identified at downstream well 12 whereas wells 11 and 13 show K^+ concentrations in a similar range. NO_3^- shows a similar concentration pattern between upstream and downstream wells with mostly increased concentrations downstream of the *Bauerngraben* in both streamtubes, but concentrations in streamtube 2 are generally higher than in streamtube 1. This is caused by heterogeneous inflows of wastewater constituents to the groundwater upstream of the test site where parts of the urban area of Leipzig are located.

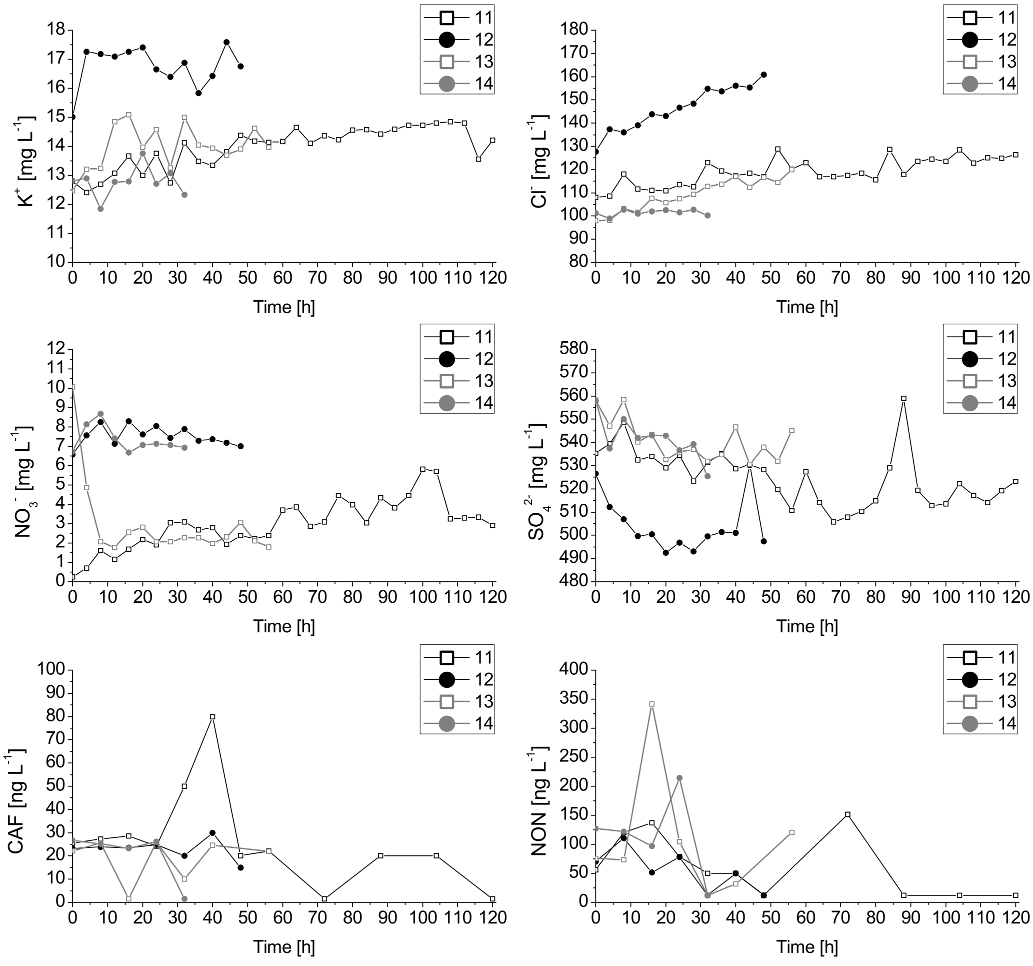

Fig. 8. Concentration-time series for the estimation of M_{CP} with the CSTREAM code. Concentrations are given for inorganic wastewater constituents as well as for caffeine (CAF) and technical-nonylphenol (NON) at the four IPT wells 11, 12, 13 and 14. Concentrations below the LOD were set to half of the LOD.

The comparison of the obtained ion concentrations at the test site with other studies of urban groundwater (e.g., Choi et al., 2005) reveals high ion concentrations in the urban aquifer of Leipzig. This indicates a strong influence of the urban area of Leipzig on the groundwater composition, but also shows that additional sources of the investigated ions (unassociated with wastewater) exist upstream of the test site. Examples of these additional sources are abandoned metalworking and chemical industries that act as point sources of the investigated substances.

A higher variability in the concentration-time series for micropollutants in comparison to inorganic substances points to a more heterogeneous concentration pattern of micropollutants in the groundwater. Due to these high variations, the identification of micropollutant Δc values between IPT wells from concentration-time series alone is not feasible. A more reliable comparison of the average concentration c_{av} at the IPT wells was conducted using M_{CP} and J_{CP} values from the CSTREAM code calculations.

3.3.2 Mass flow rates of wastewater constituents

Values of M_{CP} from IPTs depend on the estimated water flow through the CP. Since the CP length L_{CP} is defined by the isochrone shape, in this section we will briefly discuss these isochrones. The isochrone shape in Fig. 7 is influenced by pumping-induced interaction between wells and natural groundwater flow, which shifts the isochrones upstream. At the end of the pumping period, the capture zones of wells 11 and 12 reach areas of the aquifer that are upstream of the *Bauerngraben*, thus measured concentrations at this time are mixed between up- and downstream groundwater. As the concentration-time series did not show a significant change in the water composition at this time, and the pumped upstream volume is small compared to the pumped downstream volume, this was neglected for the evaluation of the IPTs.

The obtained M_{CP} and J_{CP} (Tab. 3) mainly confirm the differences in the groundwater composition between the IPT wells from the concentration-time series. K^+, Cl^- and NO_3^- show higher M_{CP} downstream of the *Bauerngraben*. Due to increased Q_{CP} at the downstream CPs, M_{CP} of SO_4^{2-} are higher downstream even if the concentrations are higher at the upstream CPs. Micropollutant M_{CP} are lower at the downstream wells for NON whereas M_{CP} of CAF increase (streamtube 2) or remain unaltered (streamtube 1) at the downstream wells. The major ions Cl^- and SO_4^{2-} show the highest J_{CP} at the test site. Differences of one order of magnitude in J_{CP} between both streamtubes for NO_3^- indicate a more heterogeneous concentration pattern of NO_3^- in the groundwater upstream of the test site in comparison to the other wastewater constituents. Higher values of ΔM_{CP} in streamtube 2 for the majority of substances can be explained by higher Q_{ex} from the affected stream section L_{BG2}. The reasonably conservative ion SO_4^{2-} (reasons for the conservative behavior at the test site are given in the next section) can be used for the estimation of Q_{ex} by

$$Q_{ex} = \frac{Q_{CP\,upstream}}{L_{BG}} \times \frac{c_{downstream} - c_{upstream}}{c_{surface\,water} - c_{downstream}} \tag{16}$$

with the average concentration in the *Bauerngraben* $c_{surface\,water}$, at the upstream CP $c_{upstream}$ and at the downstream CP $c_{downstream}$. The affected stream length L_{BG} and the water flow Q_{CP} are given in Tab. 3. The application of equation (16) with the measured data yields Q_{ex} values of 52 and 104 L $m_{stream}^{-1}d^{-1}$ for streamtube 1 and 2, respectively.

Tab. 3. Mass flow rates M_{CP}, mass fluxes J_{CP} of the different control planes and exfiltration mass flow rates M_{ex} for two streamtubes. The water flow Q_{CP} through the respective control planes, the width of the streamtubes b_1 and b_2 as well as the affected stream length L_{BG1} and L_{BG2} of the two streamtubes are given.

	Streamtube 1 **b_1 = 14.25 m L_{BG1} = 18.55 m**						**Streamtube 2** **b_2 = 5.84 m L_{BG2} = 7.23 m**					
	Upstream Well **$Q_{CP\,13}$ = 13.72 m^3d^{-1}**		**Downstream Well** **$Q_{CP\,11}$ = 15.30 m^3d^{-1}**				**Upstream Well** **$Q_{CP\,14}$ = 5.00 m^3d^{-1}**		**Downstream Well** **$Q_{CP\,12}$ = 5.61 m^3d^{-1}**			
	$M_{CP\,13}$	**$J_{CP\,13}$**	**$M_{CP\,11}$**	**$J_{CP\,11}$**	**ΔM_{CP1}**	**M_{ex1}**	**$M_{CP\,14}$**	**$J_{CP\,14}$**	**$M_{CP\,12}$**	**$J_{CP\,12}$**	**ΔM_{CP2}**	**M_{ex2}**
	$\left[\frac{mg}{s}\right]$	$\left[\frac{mg}{m^2s}\right]$	$\left[\frac{mg}{s}\right]$	$\left[\frac{mg}{m^2s}\right]$	$[\%]$	$\left[\frac{mg}{m\,d}\right]$	$\left[\frac{mg}{s}\right]$	$\left[\frac{mg}{m^2s}\right]$	$\left[\frac{mg}{s}\right]$	$\left[\frac{mg}{m^2s}\right]$	$[\%]$	$\left[\frac{mg}{m\,d}\right]$
K^+	2.24	0.026	2.50	0.029	11.9	1241	0.73	0.023	1.10	0.034	49.2	4315
Cl^-	17.90	0.206	21.50	0.248	20.1	16750	5.85	0.184	9.81	0.308	67.6	47261
NO_3^-	0.37	0.004	0.57	0.007	53.3	924	0.42	0.013	0.48	0.015	14.9	749
SO_4^{2-}	85.70	0.987	92.62	1.066	8.1	32204	31.03	0.975	32.73	1.029	5.5	20321
	$\left[\frac{ng}{s}\right]$	$\left[\frac{ng}{m^2s}\right]$	$\left[\frac{ng}{s}\right]$	$\left[\frac{ng}{m^2s}\right]$	$[\%]$	$\left[\frac{ng}{m\,d}\right]$	$\left[\frac{ng}{s}\right]$	$\left[\frac{ng}{m^2s}\right]$	$\left[\frac{ng}{s}\right]$	$\left[\frac{ng}{m^2s}\right]$	$[\%]$	$\left[\frac{ng}{m\,d}\right]$
CAF	3.17	0.036	3.15	0.036	-0.5	-	0.86	0.027	1.40	0.044	63.8	6528
NON	17.01	0.196	8.58	0.099	-49.6	-	5.30	0.167	2.83	0.089	-46.7	-

Therefore less dissolved wastewater constituents infiltrate the groundwater from the *Bauerngraben* in streamtube 1. Due to the increased Q_{ex} to streamtube 2, the M_{ex} values of K^+, Cl^- and CAF (Tab. 3) are higher in this streamtube than in streamtube 1. NO_3^- shows an inverse pattern with a higher M_{ex} in streamtube 1. The calculated Q_{ex} from SO_4^{2-} are in the same magnitude of the Q_{ex} value (85 L $m_{stream}^{-1}d^{-1}$) that was implemented in the groundwater model. A spatially variable Q_{ex} as a boundary condition for the groundwater model was not assigned because the influence of the stream on the groundwater flow is limited. The streamlines that define streamtubes 1 and 2 (Fig. 7) were only marginally deflected by the stream.

3.3.3 Identification of processes that influence concentrations in the groundwater

The sampled concentrations in the wastewater in February 2008, those in the *Bauerngraben* from 17 May to 2 June 2008 and from the IPT wells from 28 May to 2 June 2008 are summarized in the boxplot in Fig. 9. The wastewater concentrations were included to show how CSOs from the connected sewer can affect the water composition in the *Bauerngraben*. The resulting concentrations of wastewater constituents in the *Bauerngraben* during CSOs may be lower than in the wastewater due to dilution from precipitation and mixing with water from the *Bauerngraben*, but can still be higher than in the groundwater. Gasperi et al. (2008) compared wastewater concentrations during wet-weather and dry-weather conditions and found out that concentrations during wet-weather conditions are not strictly reduced. The erosion of in-sewer deposits formed within sewer during dry periods was identified as a potential reason for this. However, measurements in the wastewater during precipitation events were not undertaken to prove this. Thus the shown wastewater concentrations can be helpful to identify CSOs as a cause of temporally high concentrations of the investigated substances in the *Bauerngraben*. Temporally high concentrations during CSOs are accompanied by high water levels in the *Bauerngraben* that induce bank storage. In this context Li et al. (2008) defined bank storage as the storage of water in stream banks during the rise of stream level due to a flood. The outflow from the stream banks can also influence the groundwater composition following the CSO event. Concentrations of the three water compartments in Fig. 9 are used to identify processes (a) to (h) that influence the observed M_{CP} depending on the components' transport properties. In the following section we thus discuss M_{CP}, J_{CP} and M_{ex} substance by substance. Process (f) hydrodynamic dispersion and mixing with groundwater recharge was not included in the detailed discussion because the short flow path of approximately 32 m between the up- and downstream wells and the floodplain loam cover of the observed aquifer reduce the influence of this process.

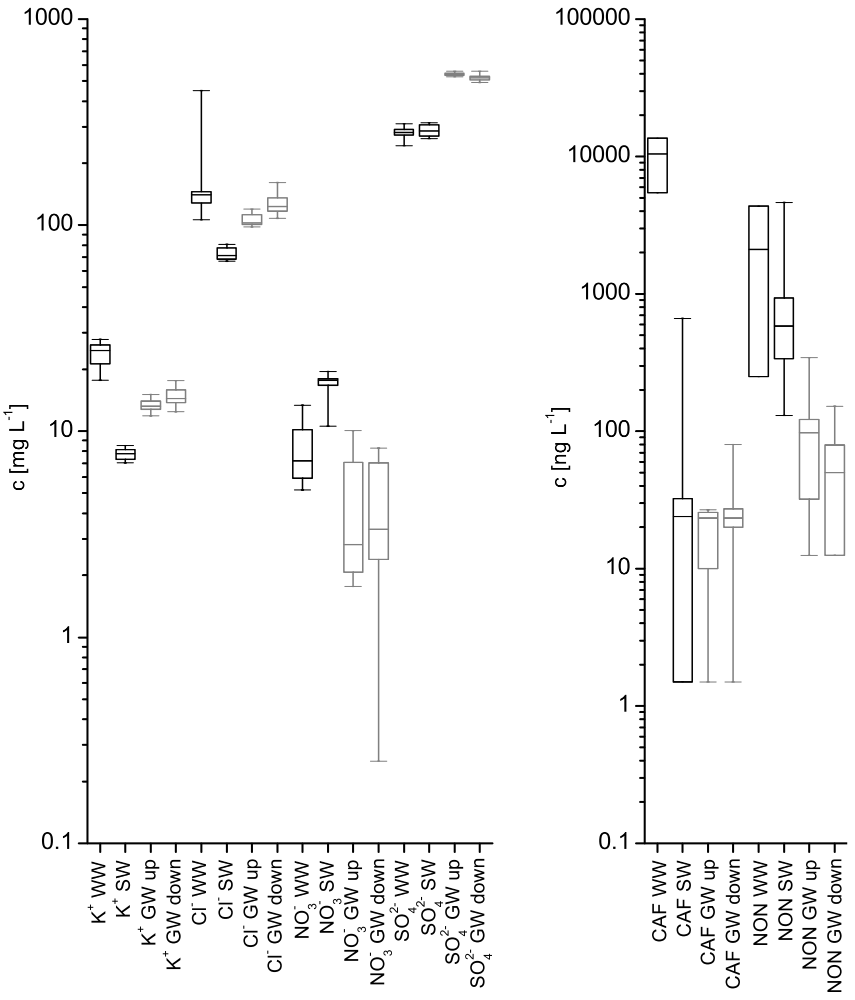

Fig. 9. Boxplot of measured concentrations in the wastewater (WW), surface water (SW) *Bauerngraben* and groundwater (GW). Black boxplots mark WW and SW. Grey boxplots mark GW. The boxes show the 25th and 75th percentile and the median. The whiskers mark the lowest and the highest concentrations. Boxplots of CAF WW and NON WW include no whiskers, because only three values were considered. The lowermost concentration limit for all samples was half of LOD.

K^+

Higher M_{CP} downstream of the *Bauerngraben* point to an exfiltration of K^+ from the *Bauerngraben*. Measured concentrations of K^+ in the *Bauerngraben* are below concentrations in groundwater. Positive M_{CP} may partly derive from process (a) temporally high concentrations in the stream. Reversible sorption of K^+ on streambed materials ((b) retardation in the streambed) and (d) exchange with storage pools in the streambed may lead to an accumulation of K^+ in the streambed. High K^+ concentrations in the wastewater indicate that this temporal storage may be supplied by (a). Leaching of the streambed and the stream banks can lead to the observed M_{ex}. A reduction of K^+ via (g) retardation in groundwater is possible, but is likely less important because ΔM_{CP} is still positive.

Cl^-

Cl^- behaves conservatively in the groundwater (Barrett et al., 1999), thus processes (b) retardation in the streambed, (c) degradation in the streambed, (g) retardation in groundwater and (h) degradation in groundwater do not occur. Concentrations in the groundwater lie above those in the *Bauerngraben*, therefore exfiltration from the *Bauerngraben* must reduce concentrations of Cl^- downstream of the *Bauerngraben*, but the opposite was observed. The calculated ΔM_{CP} were positive in both streamtubes. Mayer et al. (1999) reported an accumulation of Cl^- in the pore water of benthic sediments of surface waters. Process (d) exchange with storage pools in the streambed can thus be an explanation of the increased Cl^- concentrations downstream of the *Bauerngraben*. Temporally high concentrations of Cl^- in the *Bauerngraben* (a) can originate from CSOs, because concentrations in the wastewater are higher than in the groundwater. Because a high ΔM_{CP} (especially in streamtube 2) cannot be explained by exfiltration from the *Bauerngraben* alone, we thus assume an additional Cl^- source in the groundwater or in the streambed that could not be identified with the observed concentrations.

NO_3^-

Fig. 9 shows higher NO_3^- concentrations in the *Bauerngraben* than in groundwater. Positive ΔM_{CP} as a result of (e) mixing of groundwater with exfiltration water seem to be reasonable due to the high mobility of NO_3^- in groundwater that is not affected by sorption processes (b) retardation in the streambed and (g) retardation in groundwater (Freeze and Cherry, 1979). Measured low oxygen concentrations at the test site indicate that denitrification may cause (c) degradation in the streambed and (h) degradation in groundwater. NO_3^- concentrations in wastewater are considerably low, but will be increased if enough oxygen is available to nitrify dissolved NH_4^+ to NO_3^-, thus (a) temporally high concentrations in the stream may increase NO_3^- concentrations in the *Bauerngraben*. During the wastewater sampling program NH_4^+ concentrations of 41 to 64 mgL^{-1} were observed, whereas concentrations in the *Bauerngraben* and groundwater were mostly below 1 mgL^{-1}.

SO_4^{2-}

We identify (e) mixing of groundwater with exfiltration water as the most important process at the field site which is affecting SO_4^{2-} concentrations. Similar SO_4^{2-} concentrations in wastewater and the *Bauerngraben* indicate that CSOs will not increase concentrations of

SO_4^{2-} in the *Bauerngraben*. Concentration gradients between the *Bauerngraben* and groundwater point to a dilution of groundwater with exfiltrating water from the *Bauerngraben* (e). Anions such as SO_4^{2-} are not affected by sorption thus (b) retardation in the streambed and (g) retardation in groundwater can be excluded for SO_4^{2-}. Sulfate reduction ((c) degradation in the streambed and (h) degradation in groundwater) is not relevant because alternative electron donors (O_2 or NO_3^-) are available at the test site.

CAF

A gradient between surface water and groundwater concentrations points to a possible input of CAF into the groundwater via (e) mixing of groundwater with exfiltration water. Higher concentrations in the wastewater than in the *Bauerngraben* indicate that (a) temporally high concentrations in the stream may occur. Lower limits of CAF concentrations that are below the LOD in surface water and groundwater can be explained by natural elimination processes. Buerge et al. (2003) reported biodegradation as an important elimination process of CAF in surface water. In contrast, sorption was identified to be negligible by the same authors, due to a low octanol-water partition-coefficient $p_{OW} \approx 0$. Attenuation of organic contaminants in streambeds was reported by Höhn et al. (2007). Thus we assume that CAF loadings are reduced by (c) degradation in the streambed and (h) degradation in groundwater, but not by (b) retardation in the streambed and (g) retardation in groundwater. The reduction processes lead to a negative ΔM_{CP} in streamtube 1. Parts of the CAF input from the *Bauerngraben* must be degraded in the streambed because the input does not increase $M_{CP\ 11}$ above the level of $M_{CP\ 13}$. In contrast, streamtube 2 revealed a positive ΔM_{CP}. Assuming similar degradation conditions in the groundwater of both streamtubes, the additional mass flow of CAF in streamtube 2 must originate from the *Bauerngraben*. Whether this is an effect of reduced degradation in the streambed of streamtube 2 or of the increased Q_{ex} in streamtube 2 cannot be distinguished with the applied method. An influence of process (d) exchange with storage pools in the streambed may increase or decrease concentrations in the groundwater depending on the degradation rate in the pore water of the streambed.

NON

Process (e) mixing of groundwater with exfiltration water may lead to positive ΔM_{CP}, but observed negative ΔM_{CP} in both streamtubes reveal that ΔM_{CP} is dominated by (g) retardation in groundwater and (h) degradation in groundwater. Due to the hydrophobic character of NON (Ying et al., 2008), its concentration may be affected by sorption onto streambed sediments. Degradation in streambeds was reported in Bradley et al. (2008). Considering these studies, the outflow concentrations from the *Bauerngraben* are strongly reduced by (b) retardation in the streambed and (c) degradation in the streambed. Therefore (a) temporally high concentrations in the stream and (d) exchange with storage pools in the streambed show only a small influence on the observed M_{CP}. A reliable quantification of degradation and sorption processes in the groundwater and in the streambed using the NON data is not possible. However, the calculated M_{CP} indicate that NON has only a low mobility in the groundwater at the test site.

3.4 Conclusion

This study shows that the application of integral pumping tests (IPTs) can provide detailed information about the influence of losing streams on the groundwater composition. The operation of IPTs up- and downstream of a wastewater affected target section yields reliable mass flow rates M_{CP} in groundwater that are not based on conventional point measurements. Exfiltration mass flow rates per stream length unit M_{ex} from the investigated stream can be estimated for substances that show increased M_{CP} downstream of the stream. The evaluation of the M_{CP} was derived for two streamtubes that are defined by two IPT wells per streamtube. The observed four inorganic and two organic wastewater constituents reveal different influences on groundwater quality. Concentrations of major ions K^+, Cl^- and NO_3^- increased, whereas the concentration of SO_4^{2-} was diluted by exfiltration from the stream at the test site. The application of IPT was reasonable, especially for micropollutants, because high variability of concentration-time series during pumping points to high concentration heterogeneity in groundwater. Lower M_{CP} of technical-nonylphenol (NON) downstream of the target section were primarily caused by elimination processes in groundwater. Similar M_{CP} patterns were observed for caffeine (CAF) in one streamtube. Higher downstream values of M_{CP} for CAF in the other streamtube can be a result of stronger exfiltration Q_{ex} from the stream section in this streamtube or can be due to degradation processes in the streambed. Consequently, M_{ex} was only given for CAF in one streamtube as well as for K^+, Cl^-, NO_3^- and SO_4^{2-}. The comparison of the concentrations in the groundwater with additional concentration measurements in wastewater and surface water at the test site were used to identify processes that influence the concentrations at the IPT wells downstream. Accordingly, the streambed was recognized as an important storage area, but also as an important area where degradation processes of the wastewater constituents occurs. Wastewater concentrations indicate that combined sewer overflows (CSOs) can induce temporally high concentrations of wastewater constituents in the target stream and thus can influence the groundwater composition at the test site. The results show that losing streams can be a relevant source of inorganic wastewater constituents. For the micropollutants, investigated here, losing streams seem a less important source due to the degradation potential of the streambed. The proposed IPT method can be operated at other field sites to investigate the influence of small streams on groundwater quality. Due to the significant effort required to carry out an IPT, a complete survey of a stream is impossible. Another limitation is that the method gives only integral ΔM values, therefore the distinction between different sources (groundwater or surface water) or processes (retardation or degradation) is difficult. Despite these limitations, this study shows that IPTs can be a powerful tool to quantify the influence of losing streams on groundwater quality.

4 Optimal dimensioning of sampling schedules for integral pumping tests

This chapter is submitted to the Journal of Contaminant Hydrology as:

Leschik, S., Bayer-Raich, M., Musolff, A. and Schirmer, M., Optimal dimensioning of sampling schedules for integral pumping tests. Journal of Contaminant Hydrology. (submitted October, 23., 2009)

Abstract

Conventional point sampling may miss plumes in groundwater due to insufficient spacing of the sampling locations. The integral pumping test method (IPT) overcomes this problem by increasing the sampled volume. One or more wells are pumped for a long duration (several days) and samples are taken during pumping. The obtained concentration-time series are used for the estimation of average concentrations C_{av} and mass flow rates M_{CP}. Although the IPT method is a well accepted approach for the characterization of contaminated sites, no substantiated guideline for the design of IPT sampling schedules (optimal number and optimal sampling times) is available. In this study, the principles for an optimal design of IPT sampling schedules are derived from a detailed investigation of 30 high-frequency concentration-time series. Different sampling schedules were tested by modifying the original concentration-time series. The results reveal that the uncertainty of the C_{av} estimation increases with a reduced number of samples and higher variability of the investigated concentration-time series. Maximum uncertainties of up to 22 % were observed for sampling schedules with the lowest number of samples of 3. The sampling scheme that relies on constant time intervals Δt between different samples yielded the lowest uncertainties.

4.1 Introduction

Reliable characterization methods for contaminant plumes in groundwater downstream of source zones are necessary to protect water resources. More specially, groundwater remediation strategies at contaminated sites need dependable estimates of concentrations and mass fluxes (Schirmer et al., 2006). A powerful tool for this task is the Integral Pumping Test (IPT) method that was first proposed by Teutsch et al. (2000) and Ptak et al. (2000). Conventional point measurements may misinterpret average concentrations C_{av} and mass flow rates M_{CP} in aquifers because plumes can be missed due to an insufficient spacing of the sampling locations. The IPT method overcomes this problem by increasing the sampled volume and is therefore more reliable than conventional point measurements. IPT operations contain one or more sampling wells that are pumped for several days during which time the water is sampled. The evaluation of the measured concentration-time series from IPTs yields an integrated picture of the concentrations in the capture zone of the pumping wells. Values of M_{CP} are defined as mass flow through a control plane perpendicular to the natural flow direction. The control plane length is defined by the maximum extent of the capture zone, which is congruent with the last isochrone of the IPT. The basic equations of the evaluation procedure are given in Schwarz (2002), Bayer-Raich (2004) and Bayer-Raich et al. (2004). Various field studies (Bockelmann et al., 2001; Bauer et al., 2004; Ptak et al., 2004) have verified that IPTs provide helpful data for decision support at contaminated sites. In this context the quantification of natural attenuation is an important application area of IPTs (Bockelmann et al., 2003; Peter et al., 2004; Rügner et al., 2004; Schirmer et al., 2006). Moreover, the IPT method is limited neither to contaminated sites with a distinct plume nor to specific contaminants. An example of the versatility of the IPT method was demonstrated in Kalbus et al. (2007), where IPTs were utilized to estimate contaminant mass fluxes from an aquifer to a gaining stream and in Leschik et al. (2009a, b), where IPTs were used to estimate mass fluxes of so-called xenobiotics originating from wastewater in urban areas. The given studies clarify that especially under conditions of heterogeneous concentration in groundwater, IPT operations are highly useful.

Values of C_{av} and M_{CP} from IPTs are more reliable than those from point samples but still contain uncertainty. Jarsjö et al. (2005) investigated uncertainties in the estimation of the well capture zone and of the streamlines for the natural flow field (before and after pumping of IPT wells) by applying different settings for the flow and transport properties of the aquifer. As a result of this work Bayer-Raich et al. (2006), Jarsjö and Bayer-Raich (2008) and Bayer-Raich et al. (2009) provided equations for the IPT evaluation of target compounds that are affected by sorption and/or degradation including procedures for uncertainty quantification.

Besides uncertainties from IPT evaluation procedures, uncertainties in the dimensioning of the IPT may also bias the results. The most crucial point during IPT dimensioning is a careful placement of the pumping wells or, in the case of existing pumping wells at the site, a reasonable choice of the wells which are used for IPT operations. Optimally situated pumping wells in combination with an optimal pumping rate leads to limited overlap of neighboring control planes that guarantees a complete survey of an aquifer cross-section without gaps. Even under these optimal conditions, the results depend on the applied sampling schedule, and more precisely on the number of samples as well as on the sampling time. A high spatial resolution of the IPT, which requires a high number of samples, also increases the effort for the sample analyses, which is an important cost factor of IPTs.

In order to reduce the cost of IPTs without losing accuracy, IPT operations should aim for an optimal number of samples. In contrast, optimizing the sampling times does not increase the cost, but may provide more accurate results. To date, however, no substantiated guidelines for the dimensioning of the sampling schedule of IPTs are available. Former IPT studies mainly rely on Ptak et al. (2000) who stated that for most practical applications of IPTs a constant spatial resolution of 5 m between the isochrones along the control plane is sufficient. More recent studies (Kalbus et al., 2007; Leschik et al., 2009a, b) used a sampling schedule where samples were taken at constant time intervals of 3 to 16 h during pumping. The disagreement of different sampling strategies and the lack of studies about sampling strategies of IPTs indicate that the current practice of IPT sampling needs guidance on the design of optimal sampling schedules that yield accurate C_{av} and M_{CP} values with a low number of samples.

In this study, principles for an optimal design of IPT sampling schedules are derived by comparing the uncertainty of IPT evaluations between different sampling schedules. In detail, we try to provide guidance for determining: A) what is the optimal number of samples and B) when these samples must be taken during IPT operations. The study is based on 30 high-frequency concentration-time series of IPTs that were realized in the urban area of Leipzig (Germany) in 2007 (Leschik et al., 2009b) and in 2008 (Leschik et al., 2009a).

The chosen target compounds K^+, B, Cl^-, NO_3^- and SO_4^{2-} are common wastewater indicators (Barrett et al., 1999) that require only a low effort for chemical analyses. The evaluation of the 30 frequency concentration-time series yield reliable C_{av} values that can be defined as “best cases”. In the following, the original high-frequency concentration-time series are modified by systematically omitting data points. The modified concentration-time series represent different sampling schedules. The comparison of C_{av} values from the modified concentration-time series with the best case C_{av} values provides uncertainty values that are a measure of the accuracy of a specific sampling schedule.

The investigation focuses on C_{av} because we assume a homogeneous aquifer in which constant water flow Q_{CP} and mass flow rates M_{CP} through the control plane depend linearly on C_{av} ($M_{CP} = C_{av}Q_{CP}$). Therefore uncertainty values that derive from the sampling schedule are the same for C_{av} and M_{CP}. Complex IPT evaluations regard beside the estimation C_{av} and M_{CP} also on the delineation of possible source zones (Jarsjö et al., 2005). This specific issue was not considered for the design of optimal sampling schedules because this study focuses exclusively on an accurate estimation of C_{av}. Concerning the sampling time, we investigate two fundamentally different sampling schemes that are based on former IPT applications. One relies on constant time intervals Δt between different samples whereas the other relies on constant distances Δx along the control plane between isochrones at the sampling times. In order to study the influence of the number of samples, we apply the two sampling schemes during the reduction of the number of samples. A comparison of the uncertainties provides the principles on which to base the optimal design of IPT sampling schedules.

4.2 Methods and data sets

4.2.1 IPT background

The estimation of C_{av} from an IPT is obtained by performing a weighted average of the concentration-time series C_p measured at the pumping well through the equation (Bayer-Raich et al., 2004):

$$C_{av}(t) = \frac{1}{2t}\int_0^t \frac{C_p(\tau)}{\sqrt{1-\tau/t}}\,d\tau \tag{17}$$

where t is the total pumping time and τ is the integration variable. A generalized form of this equation (which may account for heterogeneous conditions) is implemented in the code CSTREAM (Bayer-Raich, 2004), which was used in this study for the evaluation of IPTs.

4.2.2 High-frequency concentration-time series

This study is based on 30 high-frequency concentration-time series from 6 IPTs that were operated within the framework of the research platform WASSER Leipzig (Water and Sewershed Study of Environmental Risk in Leipzig – Germany; Musolff et al., 2007). As part of an investigation into the release of wastewater indicators from line sources (leaky sewers or losing streams) into urban aquifers, average concentrations C_{av} and mass flow rates M_{CP} were estimated from these concentration-time series by Leschik et al. (2009b) (wells 1, 2 and 3) and by Leschik et al. (2009a) (wells 11, 12 and 13). The wells were installed within the city of Leipzig (Germany) investigating a leaky sewer (wells 1, 2 and 3) and a losing stream (wells 11, 12 and 13).

Both sites are underlain by a Quaternary sand and gravel aquifer and are separated by about 200 m. All wells at one site were operated simultaneously for a pumping period of 5 days with a constant pumping rate of 1 L s^{-1}. Due to the expected highly variable concentration patterns at these urban sites, a high-frequency sampling approach was chosen with a period of 4 h. Thus, all concentration-time series consist of 31 data points. The five target compounds K^+, B, Cl^-, NO_3^- and SO_4^{2-} were chosen based on their function as relevant wastewater indicators in urban areas (Barrett et al., 1999) and their chemical analysis requires only a relatively low effort in comparison to more selective wastewater indicators (e.g., pharmaceuticals). Details on the sample handling in the field and in the laboratory can be obtained from Leschik et al. (2009a, b).

Tab. 4 gives an overview of the high-frequency concentration-time series and their concentration ranges during the IPTs. The coefficient of variation (CV) is used as a measure of the concentration variability in the capture zone of an IPT well and is calculated by CV [%] = $S \times M^{-1} \times 100$ with the standard deviation S and the arithmetic mean M. CV values in the range of 1.7 to 77.3 % indicate that different degrees of heterogeneity are covered by the observed concentration-time series.

Tab. 4. Minimum, maximum and average concentrations as well as coefficients of variation (CV) for the high-frequency concentration-time series. Each concentration-time series consists of 31 data points.

Number	Compound	Well	Min [mg L^{-1}]	Max [mg L^{-1}]	Average [mg L^{-1}]	CV [%]
1	K^+	1	12.6	14.4	13.5	3.1
2	K^+	2	11.6	13.7	12.6	3.2
3	K^+	3	11.5	13.5	12.4	3.4
4	K^+	11	12.4	14.9	14.0	5.1
5	K^+	12	15.0	18.2	16.8	3.4
6	K^+	13	12.5	16.5	14.5	5.4
7	B	1	0.32	0.41	0.35	4.6
8	B	2	0.33	0.38	0.36	2.7
9	B	3	0.33	0.37	0.35	3.5
10	B	11	0.33	0.37	0.34	2.6
11	B	12	0.29	0.32	0.30	2.7
12	B	13	0.32	0.37	0.34	3.6
13	Cl^-	1	65.8	99.0	70.3	9.1
14	Cl^-	2	69.8	81.0	72.7	3.7
15	Cl^-	3	70.7	77.2	73.6	2.6
16	Cl^-	11	108.1	128.9	119.1	4.9
17	Cl^-	12	127.6	161.5	152.6	5.5
18	Cl^-	13	98.0	127.8	115.5	7.1
19	NO_3^-	1	16.3	25.3	19.1	9.2
20	NO_3^-	2	18.6	27.0	22.0	8.6
21	NO_3^-	3	18.6	25.1	21.2	7.9
22	NO_3^-	11	0.3	5.8	3.0	43.0
23	NO_3^-	12	4.9	8.3	6.6	15.3
24	NO_3^-	13	0.5	10.1	2.2	77.3
25	SO_4^{2-}	1	334.3	363.7	347.7	2.0
26	SO_4^{2-}	2	375.3	401.3	387.8	1.8

27	SO_4^{2-}	3	372.5	421.8	391.0	3.3
28	SO_4^{2-}	11	505.8	558.9	524.9	2.3
29	SO_4^{2-}	12	492.5	530.3	504.6	1.7
30	SO_4^{2-}	13	517.4	558.5	538.9	1.8

4.2.3 Design of sampling schedules

Two different sampling schemes were applied for the modification of the original concentration-time series to reduce the number of samples taken into account. In sampling scheme A, samples are taken following a constant time interval Δt and sampling scheme B is based on constant distances Δx along the control plane between isochrones for the specific sampling times. The definition of Δt and Δx for sampling schemes A and B is clarified in Fig. 10 by showing the principle isochrone shape and the corresponding concentration-time series for the two sampling schemes. For constant Δt (sampling scheme A), the distances Δx along the control plane vary and for constant Δx (sampling scheme B), the values of Δt vary. This indicates that only constant Δt or constant Δx can be achieved in one sampling schedule. A comparison of the two different sampling schemes was derived by implementing the sampling schemes during the sample reduction of the original concentration-time series.

The most accurate sampling schedule was then identified by the comparison to the best case C_{av} that originates from the evaluation of the original concentration-time series which contains all available information. An overview of the modified concentration-time series, which represent the different sampling schedules, is given in Fig. 11 for the example of concentration-time series 19. The number of samples of the original concentration-time series was reduced stepwise from 31 to 3 samples following the two different sampling schemes A and B. Thus one sampling schedule is defined by a specific number of samples and an applied sampling scheme (A or B). The variable Δx in the sampling scheme A schedules and constant Δx in sampling scheme B schedules can be recognized by the supplementary isochrones (Fig. 11), which correspond to the respective sampling times of the concentration-time series.

A direct comparison between different sampling schedules is only possible if the estimation of C_{av} is based on the same capture zone. It was therefore necessary to always keep the last sample of the original concentration-time series, because it defines the final capture zone size. A further constraint for the modification of the concentration-time series was the conservative handling of the original concentration values. Concentration values were not shifted to another time or interpolated between different concentration values to get new values for specific times. All concentration values that are used in the different sampling schedules originate from the original concentration-time series. Due to these restrictions it was not always possible to achieve a constant Δt or Δx in all sampling schedules. Thus, in sampling scheme A for the case of 9 samples, Δt between the last two samples is smaller than in the rest of this sampling schedule.

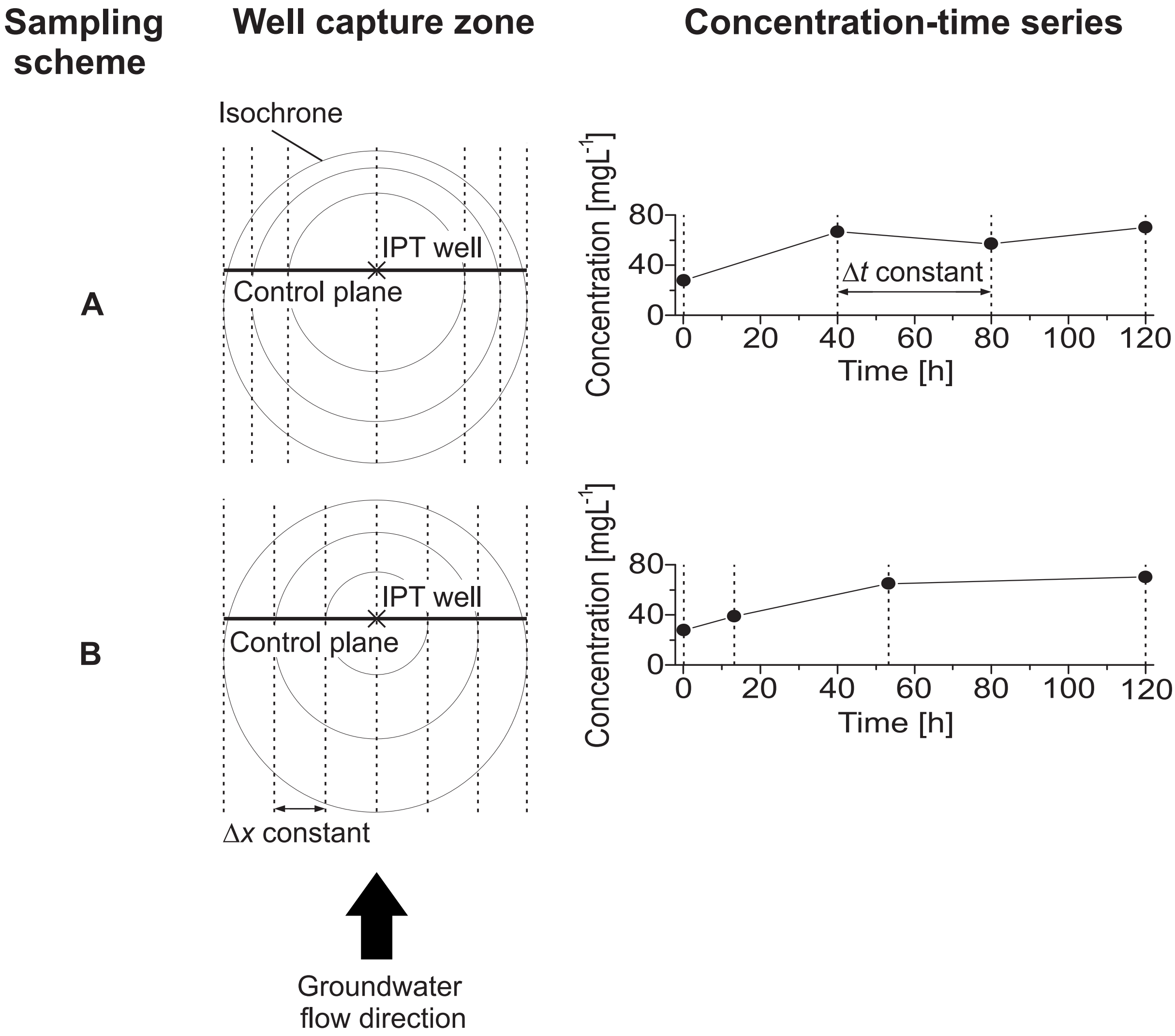

Fig. 10. Different IPT sampling schemes A and B with isochrones and corresponding concentration-time series. Sampling scheme A relies on constant time intervals Δt between different samples whereas sampling scheme B relies on constant distances Δx between isochrones along the control plane.

The definition of sampling schedules with a constant Δx was difficult to accomplish because the original sampling was derived with a constant Δt. However, a quite satisfying distribution of isochrones (Fig. 11) was obtained in sampling scheme B even if values of Δx show slight variations among the sampling schedules. In order to allow a comparison of the results from this study to other field sites with other operational parameters (e.g., pumping rate) a generalized parameter is introduced for the characterization of IPT sampling schedules. Thus, for each sampling schedule, the pumped volume V_P divided by the total number of samples n is shown ($V_P n^{-1}$).

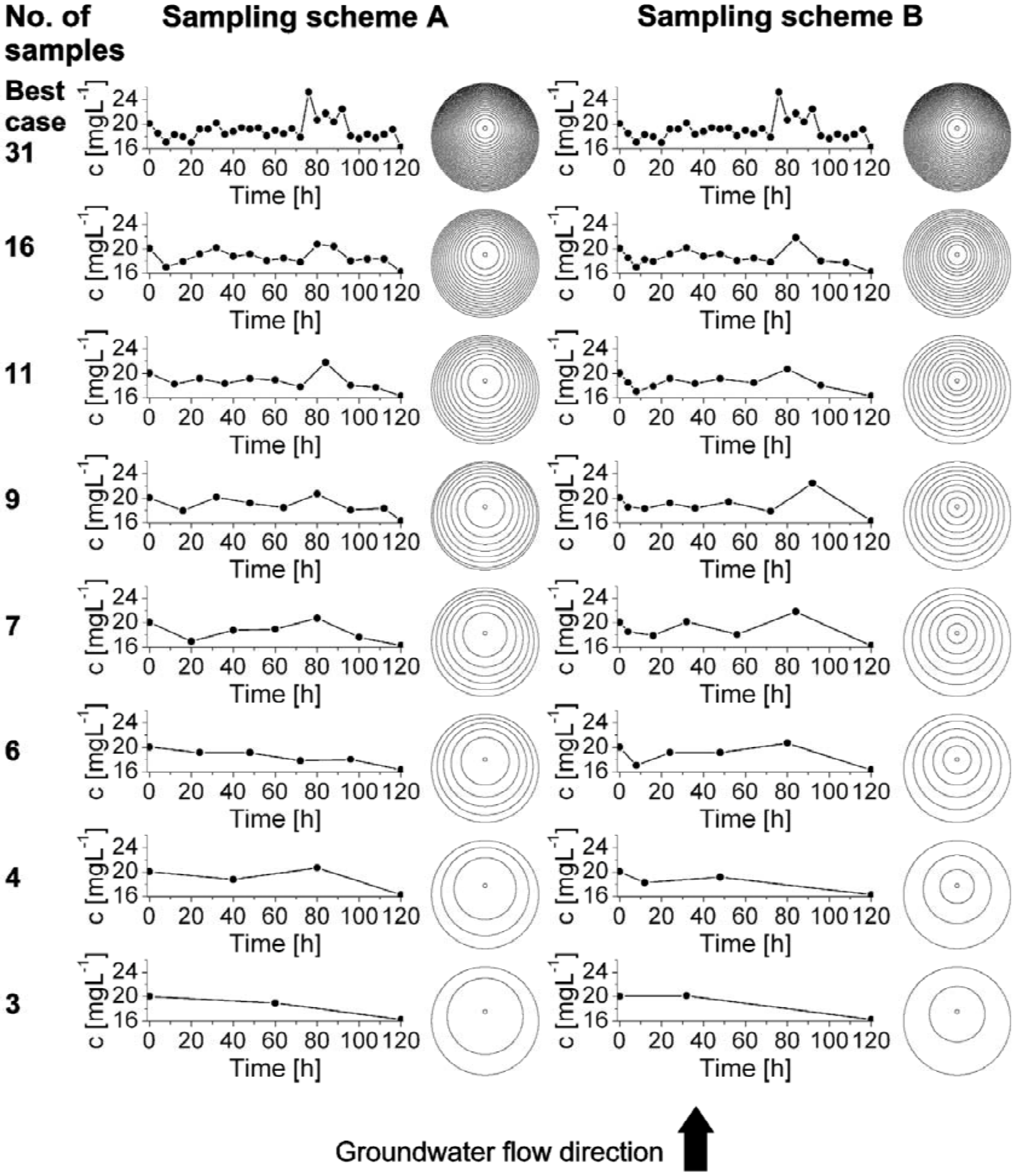

Fig. 11. Overview of the modified concentration-time series that result from the 14 applied sampling schedules for the example of concentration-time series 19 with relatively high fluctuations of the concentration values. Each sampling schedule is characterized by a specific number of samples and a sampling scheme (A or B) for the determination of the sampling times. The additional isochrones show how the isochrone position is influenced by the respective sampling schedule. The example was chosen to clarify that the modified concentration-time series may miss peak concentrations that were detected with the high-frequency concentration-time series.

4.2.4 Estimation of average concentration from concentration-time series

The estimation of C_{av} from the original and modified concentration-time series was realized by applying equation (1), which has been implemented in the CSTREAM code (Bayer-Raich, 2004). This analytical solution was applied instead of the more sophisticated numerical evaluation used in Leschik et al. (2009a, b) to reduce the computing time. However, the IPT evaluation remains based on the original field data set, which contains slight parameter variations between the 6 IPT wells. An aquifer thickness of 5.8 to 6.8 m, a hydraulic conductivity of 5×10^{-4} m s^{-1}, a gradient of 0.002 to 0.004 and a porosity of 0.2 were used in combination with the CSTREAM code to obtain C_{av} for each of the IPT wells.

Identical capture zones for the IPT evaluations of different sampling schedules were obtained by the application of the same parameter set for the original and the modified concentration-time series at each well. The resulting control plane lengths are therefore constant at each specific well, but range from 20.0 to 21.5 m among the different wells. The consideration of transport properties (sorption or degradation) for specific compounds was not achieved in the IPT evaluation. A total of 450 computation runs was necessary for the evaluation of the 14 different sampling schedules in Fig. 11. The obtained 450 C_{av} values include 30 C_{av} values from the original concentration-time series and 420 C_{av} values (6 wells, 5 compounds and 14 sampling schedules) from the modified concentration-time series. In the following, uncertainties U are estimated for the respective sampling schedules by

$$U[\%] = \left| \frac{C_{best\,case}[mg\,L^{-1}] - C_x[mg\,L^{-1}]}{C_{best\,case}[mg\,L^{-1}]} \right| \times 100 \tag{18}$$

with the average concentrations $C_{best\ case}$ from the original concentration-time series and the average concentration C_x for sampling schedule x. The calculated uncertainties represent deviations of C_{av} from a sampling schedule to $C_{best\ case}$ and can therefore be used to evaluate the accuracy of a specific sampling schedule.

4.3 Results and discussion

4.3.1 Uncertainties for different sampling schedules

The uncertainties of the respective sampling schedules are presented and summarized in Tab. 5. Minimum, maximum and average uncertainties of the specific sampling schedules were derived from 30 C_{av} realizations (6 wells with 5 compounds each) per sampling schedule. The observed uncertainties of all sampling schedules range from 0 to 22.1 %. Most of the uncertainty ranges were higher for those sampling schedules with fewer samples. Regarding the average uncertainties, a similar trend can be observed in uncertainties that increase from sampling schedule 16A to 3A and from 16B to 3B with exceptions to sampling schedules 4A, 9A and 6B where the uncertainties slightly decrease.

Tab. 5. Minimum, maximum and average uncertainties for the investigated sampling schedules. Values of $V_P n^{-1}$ define the pumped volume V_P divided by the number of samples n. Uncertainty values for each sampling schedule base on 30 C_{av} values from the 30 concentration-time series.

Sampling scheme	No. of samples [-]	Sampling schedule	$V_P n^{-1}$ [m^3]	Minimum uncertainty [%]	Maximum uncertainty [%]	Average uncertainty [%]
A	16	16A	27.0	0.00	3.47	0.71
A	11	11A	39.3	0.02	8.95	1.11
A	9	9A	48.0	0.04	6.48	0.99
A	7	7A	61.7	0.03	10.06	1.28
A	6	6A	72.0	0.01	9.77	1.78
A	4	4A	108.0	0.01	11.02	1.55
A	3	3A	144.0	0.03	22.10	2.59
B	16	16B	27.0	0.07	8.95	1.09
B	11	11B	39.3	0.01	5.56	1.11
B	9	9B	48.0	0.04	13.90	1.46
B	7	7B	61.7	0.11	16.79	1.63
B	6	6B	72.0	0.03	10.94	1.34
B	4	4B	108.0	0.07	20.69	2.78
B	3	3B	144.0	0.01	21.92	3.27

Another finding is that the majority of sampling schedules with sampling scheme B yield higher average uncertainty than those with sampling scheme A although the number of samples is the same. Only for a $V_P n^{-1}$ of 72 m^3 sampling scheme B yields lower average uncertainty than sampling scheme A. Consequently, all sampling schedules with sampling scheme A yield an average uncertainty of 1.4 % whereas those with sampling scheme B yield an increased value of 1.8 %. Furthermore, sampling schedules with sampling scheme B revealed for the same $V_P n^{-1}$ up to 17.1 % higher uncertainty than sampling scheme A.

For a more detailed interpretation, the compound-specific results were plotted in diagrams that show the dependency of average *U* to $V_P n^{-1}$ (Fig. 12). All compounds reveal an often non-continuous rise of *U* for increased $V_P n^{-1}$ values. The lowest levels of uncertainty were observed for SO_4^{2-} followed by B, K^+, Cl^- and NO_3^- with *U* values below 1, 2, 2, 4 and 10 %, respectively. Differences between sampling schemes A and B are visible for all compounds, but are more pronounced for compounds with a higher *U* such as NO_3^-. The plot of average uncertainty shown in Fig. 12 shows that especially for data points with high values of $V_P n^{-1}$ sampling scheme A yields lower *U* values than B.

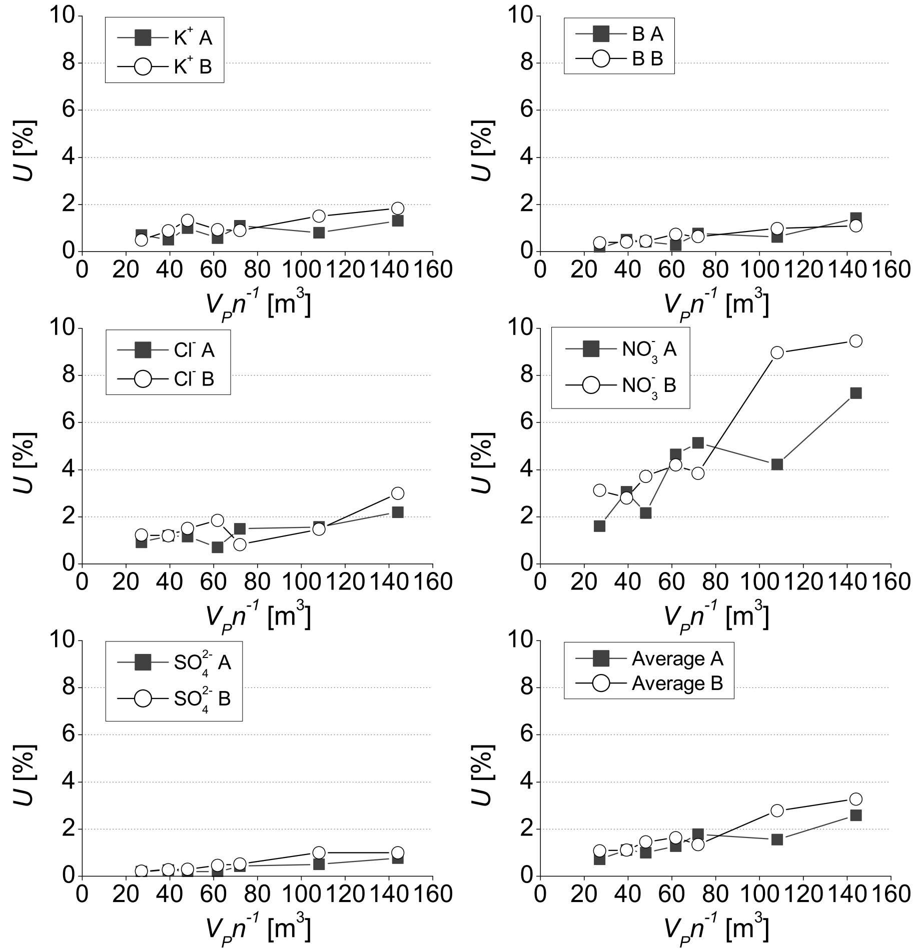

Fig. 12. Compound-specific and average uncertainties *U* against $V_P n^{-1}$ for sampling schemes A and B. Each data point represents the average of 6 C_{av} values (from 6 wells). Average values were also presented in Tab. 5.

Concentration-time series from IPTs depend on the concentration distribution in the capture zone. Variable levels of uncertainty between specific compounds suggest differences in the concentration distribution in the capture zone for these compounds. Complex target compound distributions within the capture zone yield concentration-time series with highly variable concentrations. Using the CV values in Tab. 4 as a measure of the concentration distribution heterogeneity, it can be stated that high uncertainty values are obtained for compounds that are characterized by highly heterogeneous concentration distributions such as NO_3^- with a maximum CV value of 77.3 %.

In comparison, the concentration-time series of SO_4^{2-}, which have the lowest CV values (1.7 to 3.3 %), yield the lowest average uncertainty (below 1 %) of all investigated compounds. Large CV ranges for Cl^- (2.6 to 9.1 %) and NO_3^- (7.9 to 77.3 %) indicate that the concentration distribution heterogeneity of these compounds varies between different IPT locations. In order to show the dependency between the uncertainty and the concentration distribution heterogeneity, the 30 concentrations-time series were divided into 3 CV classes (Fig. 13). The CV classes were defined by a minimum class width of 5 % and a minimum class size of 3 CV values.

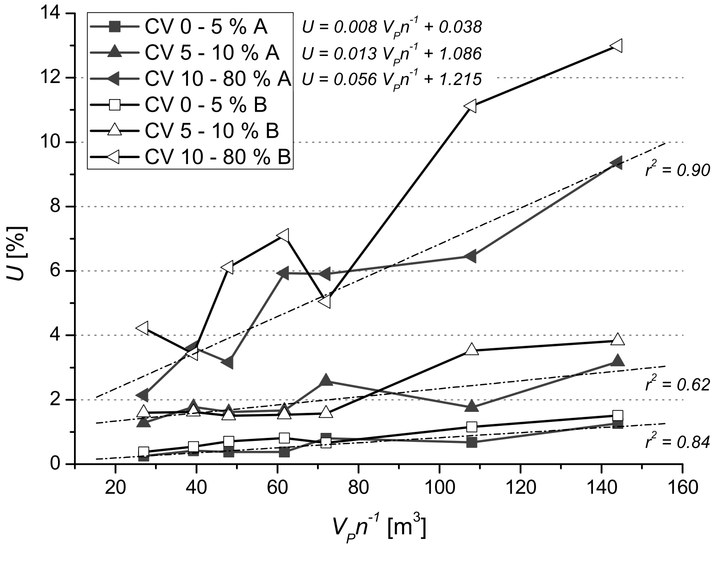

Fig. 13. Plot of average uncertainties U against V_Pn^{-1} for different classes of coefficients of variation (CV). The classes include 19, 8 and 3 concentration-time series for the classes 0 to 5 %, 5 to 10 % and 10 to 80 %, respectively.

Plotting the uncertainties versus V_Pn^{-1} reveals a strong influence of the concentration distribution heterogeneity. For CV values below 5 % the average uncertainties were always below 2 % whereas sampling schedules from concentration-time series with CV values of 10 to 80 % yield average uncertainties between 2.1 and 13.0 %. The uncertainty differences between sampling scheme A and B are highest for CV values of 10 to 80 % with mostly higher uncertainty values for sampling scheme B.

4.3.2 Discussion

The interpretation of the uncertainties for C_{av} needs to account for the fact that the best-case C_{av} values represent only an approximation of the "real" C_{av} in the aquifer. Even the high-frequency concentration-time series with 31 data points may miss concentration peaks or lows during the IPTs. Therefore, the best-case C_{av} values may also over- or underestimate the "real" C_{av} values. Inaccuracies in the calculation of the uncertainties were reduced by averaging the results of several concentration-time series.

The detailed analysis of 30 high-frequency concentration-time series shows that the IPT sampling schedule has an important influence on the accuracy of C_{av} and M_{CP} from the IPTs. Fig. 12 and Fig. 13 reveal a dependency between the uncertainty and the number of samples for sampling schemes A and B where sampling schedules with a high number of samples (and low $V_P n^{-1}$ values) yield more reliable results than those with a lower number of samples (and high $V_P n^{-1}$ values). The general rise of the uncertainty curves in Fig. 12 is disturbed by small fluctuations. The comparison of average uncertainty curves to curves of the specific compounds (Fig. 12) indicates that the implementation of additional concentration-time series leads to average uncertainty curves with less fluctuation.

In the presented study we only focus on 30 concentration-time series because they were obtained under comparable conditions concerning the IPT operation (pumping rate and pumping duration) and therefore the calculation of average uncertainty values for specific values of $V_P n^{-1}$ was possible. Even if a higher number of concentration-time series is preferable, the uncertainty curves show that 30 concentration-time series are adequate to obtain dependencies between $V_P n^{-1}$ and U.

In this context it could be shown that the optimal number of samples (issue A) depends on the required accuracy and the concentration distribution heterogeneity of the target compounds in the investigated aquifer. The concentration distribution heterogeneity is difficult to assess before the start of IPT operations. We therefore advise to base the dimensioning of the number of samples for IPTs on the uncertainty curves that represents the worst of all investigated cases (curves CV 10 to 80 % in Fig. 13).

The determination of the optimal sampling time for IPTs (issue B) is mainly related to determining which sampling scheme (A or B) yields the most reliable C_{av}. For the majority of investigated sampling schedules, the uncertainties reveal more reliable results for sampling scheme A. These results can be justified mathematically. The function used for estimation of C_{av} is a weighted average of the measured concentration-time series and the weighting function used in the averaging is monotonically increasing (Fig. 14). This indicates that "late" samples are more important than "early" samples, since the weighting factor is larger for increasing pumping time. Sampling scheme A distributes the samples evenly while for scheme B sampling frequency is higher at the beginning of the pumping test. This implies that sampling scheme A has more samples for late pumping times, and therefore is expected to provide more dependable estimates of C_{av}. In other words it is obvious that late samples are more representative than early samples, because they are related to a much larger aquifer volume.

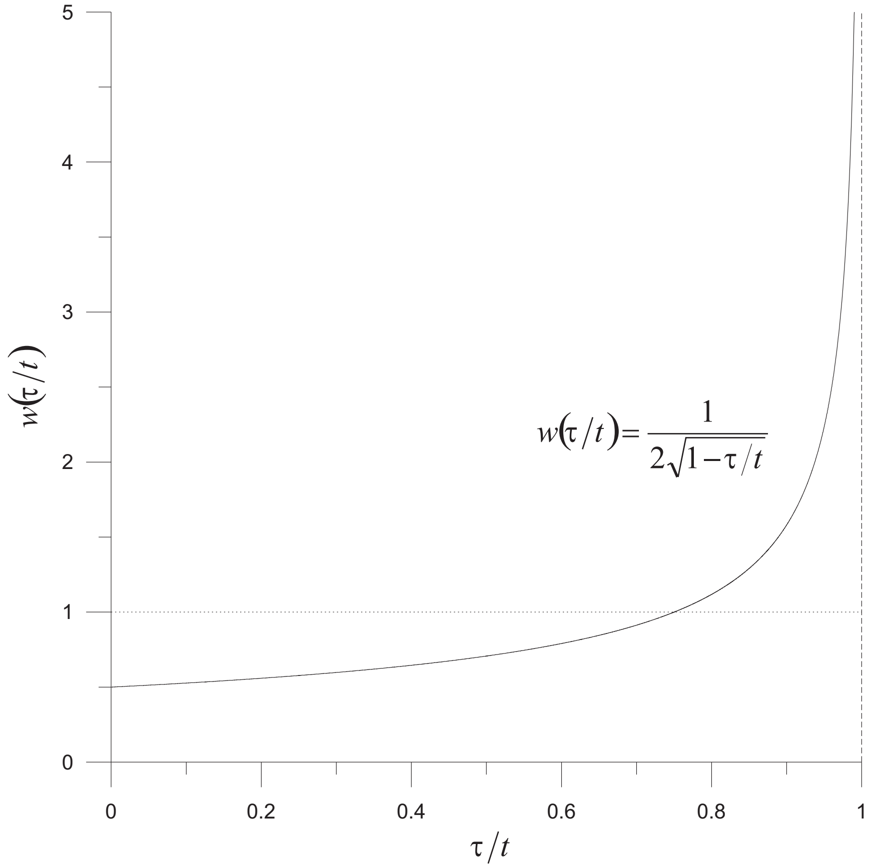

Fig. 14. Weighting function w for the estimation of C_{av} from IPT concentration-time series with the total pumping time t and the integration variable τ . The area under the function w above the x axis equals 1.

Another important point in the discussion of the obtained results is whether the results can be used to derive principles for optimal IPT sampling schedules at other sites. A detailed analysis of the influence of aquifer properties and IPT operation parameters at other potential sites on the C_{av} estimation uncertainty with different sampling schedules cannot be performed with the given data set because only slight variations of these parameters are covered. The 6 IPTs in this study were realized in one aquifer by applying the same pumping rate and the same pumping duration. However, it can be shown that the investigated aquifer properties and the applied IPT operation parameters are in a range that is relevant for common IPT applications. Bayer-Raich et al. (2004) defined the dimensionless time $t_D = 2\pi b q_0^2 Q^{-1} n_e^{-1} t$ with the aquifer thickness b, the specific discharge q_0, the pumping rate Q, the effective porosity n_e and the pumping time t. Values of t_D are used as an IPT characterization parameter that combines the aquifer properties and IPT operation parameters. According to Bayer-Raich et al. (2004) the majority of completed IPTs show t_D values between 0.001 and 5. The investigated 6 IPTs reveal t_D values (0.1 to 0.4) within this range. Furthermore the concentration distribution heterogeneity between different sites and compounds may vary significantly and therefore may hamper the transferability of the results from this study to other sites. Comparing CV values (2 to 77 %) from the concentration-time series of the urban indicators in this study to those from former IPT applications with other target compounds (Bockelmann et al., 2001: 1 to 103 %; Bauer et al., 2004: 5 to 34 %; Rügner et al., 2004: 1 to 77 %) reveals similar ranges for CV. Thus, the investigated concentration-time series are representative for the majority of IPT applications even if they do not stem from a site with a distinct plume as in most former IPT studies.

4.4 Conclusion

In this study a detailed analysis of 30 high-frequency concentration-time series was performed to lay the foundation for the optimal design of IPT sampling schedules. Omitting data points systematically from the original concentration-time series yielded modified concentration-time series that represent different sampling schedules with variable numbers of samples and variable sampling times. The comparison of average concentrations C_{av} from the original and the modified concentration-time series resulted in uncertainties U for the specific sampling schedules. According to different sampling schedule uncertainties the following suggestions for the optimization of IPT sampling schedules can be given:

A) What is the optimal number of samples?

The number of samples for IPTs depends on the required accuracy and on the concentration distribution heterogeneity of the target compounds within the capture zone. Often no information about the concentration distribution heterogeneity of a specific field site will be available. It is therefore reasonable to use the number of samples that represents the worst of all investigated cases. The curve CV 10 to 80 % A in Fig. 13 represents the case with the highest heterogeneity. For a predefined *U*, the values for $V_P n^{-1}$ (pumped volume V_P divided by the number of samples *n*) can be calculated with the corresponding linear regression equation. We hence recommend a $V_P n^{-1} \leq 67$ m^3 for an accuracy of 5 %.

Conducting preliminary IPTs with a high sampling frequency can be helpful for an improved dimensioning of the number of samples because detailed information about the concentration distribution heterogeneity at a specific field site can be given. Depending on the CV values of the concentration-time series from the preliminary IPTs, the number of samples of future IPTs at the same field site can be estimated. Thus, if the preliminary IPTs reveal CV values of 5 to 10 %, the value of $V_P n^{-1}$ for an accuracy of 5 % can be increased to the investigated maximum $V_P n^{-1} \leq 144$ m^3 (see curve CV 5 to 10 % A in Fig. 13). An estimation of *U* for $V_P n^{-1}$ values outside of the investigated range of 27 to 144 m^3 of pumped volume was not assessed in this study.

B) When must samples be taken during IPT operations?

A sampling schedule whereby samples are taken within a constant time interval Δt during pumping (sampling scheme A) is preferred to achieve a high accuracy. Another advantage of sampling schedules with constant time intervals is the simple dimensioning of the IPTs where the sampling interval can be easily obtained by dividing the planned pumping duration by the number of samples.

The given study represents a first step towards assessing sampling schedules of IPTs. The rules for the design of sampling schedules are transferable to IPTs with different operation parameters (pumping rate and time) or to other sites. However, including concentration-time series from other sites in future evaluations is necessary to substantiate the results. The proposed suggestions simplify IPT dimensioning and reduce the cost of IPTs by reducing the number of samples in cases of less heterogeneous concentration distributions in aquifers.

5 Synthesis and outlook

5.1 Synthesis

The impact of urban areas on groundwater quantity and quality has become an emerging issue in hydrological research. Urban infrastructures such as sewer networks influence the natural water flow. Depending on the hydraulic gradients to the groundwater these infrastructures may increase urban recharge by exfiltration via sewer leaks. The exfiltration water often consists of untreated and treated wastewater that may contaminate the groundwater. Therefore, leaky infrastructures can be defined as urban line sources.

The definition of urban line source includes also losing streams beside leaky sewers. Urban streams are strongly influenced by wastewater. Residues of wastewater that are not eliminated during the treatment process are released from wastewater treatment plants (WWTPs) into urban streams. Untreated wastewater contaminates urban streams by combined sewer overflows (CSOs) during rain events.

Wastewater production (households and industries) is dominated by human activity. Therefore, diurnal concentration variations occur in wastewater. The release of untreated wastewater with variable concentrations through randomly distributed sewer leaks, which may be clogged by the deposition of particles and biological activity, generates heterogeneous concentration patterns of wastewater compounds in the groundwater of urban areas.

Urban streams are also characterized by variable concentrations of wastewater compounds because CSOs release wastewater event-driven and the inflow from WWTPs is directly influenced by the variable concentrations of wastewater compounds in the sewer network. In combination with heterogeneities in the streambed, this leads to the formation of zones with different wastewater compound concentrations in the vicinity of losing streams.

The assessment of groundwater contamination in urban areas requires the consideration of line sources because they emit wastewater-borne contaminants. However, the monitoring of contaminations from urban line sources is a challenging task due to heterogeneous concentration patterns in the groundwater of urban areas and must be adapted to this specific condition.

In this study a new monitoring and evaluation approach for the estimation of exfiltration mass flow rates per length unit M_{ex} from urban line sources was tested and optimized. The problem of heterogeneous concentrations in the groundwater was overcome by averaging concentrations from large aquifer volumes with the IPT method. Focusing on the groundwater as a receiving water body, this study investigates the release of inorganic wastewater indicators and micropollutants. The results of the study are summarized and application possibilities as well as limitations of the monitoring approach are highlighted in the following sections.

The monitoring approach for urban line sources was applied for the first time at a sewer with significant defects (mainly root intrusions) in the city of Leipzig (Germany). The approach consists of four IPTs from that two were located upstream and two downstream of the leaky sewer. The IPT wells were pumped for 5 d with a pumping rate of 0.3 to 1.0 Ls^{-1}. The investigated inorganics B, K^+, Cl^-, NO_3^- and NH_4^+ were sampled every 4 h and the micropollutants bisphenol-a (BPA), caffeine (CAF), tonalide (TON) every 8 h during the pumping period. The IPT evaluation with help of the CSTREAM code and a numerical groundwater flow model yielded mass flow rates M_{CP} through the IPT control planes. Positive ΔM_{CP} downstream of the leaky sewer in comparison to upstream values represent the target value M_{ex}.

The results from the leaky sewer field site revealed high M_{ex} values for Cl^- (4.8 to 10.9 $g\ m^{-1}\ d^{-1}$) in comparison to lower values of M_{ex} for N_{tot} (0.14 to 0.5 $g\ m^{-1}\ d^{-1}$) and B (0 to 0.02 $g\ m^{-1}\ d^{-1}$). Mass flow rates of K^+ remained stable during the passage from the up- to the downstream control planes. Owing to higher chemical analysis uncertainty, the identification of mass exfiltration for micropollutants was difficult to derive. However, the obtained M_{CP} values indicate that only low or no mass of the micropollutants reach the groundwater via sewer leakages at the field site. The comparison of the estimated water exfiltration Q_{ex} with an alternative measurement and with sewer exfiltration literature indicates that the monitoring approach provides reliable results.

The second application of the line source monitoring approach was applied with a similar setup of the four IPT wells (two IPT wells upstream and two wells downstream) at a temporally losing stream that is strongly influenced by the input from three combined sewer overflow pipes. Sampling at the IPT wells was conducted with a sampling frequency of 4 h for the ions K^+, Cl^-, NO_3^- and SO_4^{2-}. Micropollutants CAF and technical-nonylphenol (NON) were sampled with a frequency of 8 h to 16 h. The numerical groundwater model for the IPT evaluation was adapted to the specific conditions of a losing stream. Additional concentration measurements in the losing stream and the connected sewer at the test site were conducted to identify relevant processes that influence the concentrations in the groundwater downstream of the losing stream.

The obtained M_{ex} values indicated a strong influence of Cl^- (16.8 to 47.3 g m^{-1} d^{-1}) and SO_4^{2-} (20.3 to 32.2 g m^{-1} d^{-1}) on the groundwater composition, whereas K^+ (1.2 to 4.3 g m^{-1} d^{-1}) and NO_3^- (0.7 to 0.9 g m^{-1} d^{-1}) revealed considerably lower M_{ex} values. In contrast, NON showed reduced M_{CP} downstream of the urban stream, therefore no M_{ex} values could be determined. CAF remained stable in one IPT streamtube and in the other a M_{ex} value of 6.5 µg m^{-1} d^{-1} was obtained. Beside the estimation of M_{ex} values the study also focuses on the identification of relevant transport processes. The concentrations in the stream and the connected sewer hint to retardation and degradation processes in the streambed and the groundwater. Also CSOs in combination with the temporal storage in the pore water of the streambed and the stream banks were identified as important processes that control the release of wastewater compounds from urban streams.

In the third step of this study the high-frequency concentration-time series from the first and second application of the line source monitoring approach are used to optimize the sampling schedules of IPTs. The optimization focuses on the number of samples and the sampling time. From the existing data set 30 high-frequency concentration-time series with a sampling interval of 4 h were chosen and systematically modified. During modification the data points of one concentration-time series were reduced stepwise from 31 to 3 samples. The reduced concentration-time series represent different sampling schedules. The evaluation of the modified concentration-time series yield average concentrations C_{av} that were compared to the best case C_{av} values from the original concentration-time series. The deviations of C_{av} from a specific sampling schedule to the best case C_{av} values were defined as uncertainties and then used to rank the different sampling schedules.

Obtained maximum uncertainties of up to 22 % showed that the sampling schedule has a relevant influence on the results from IPTs. The uncertainties of the C_{av} estimation were increased with lower number of samples and higher variability in the investigated concentration-time series. According to the uncertainties in different sampling schedules, suggestions for the optimization of IPT sampling schedules were presented. It was stated that the number of samples depends on the required accuracy. For a recommended accuracy of 5 % a value of $V_P n^{-1} \leq 67$ m^3 (pumped volume V_P divided by the number of samples n) was proposed for the dimensioning of IPTs. Concerning the sampling time, a sampling scheme where samples are taken with a constant time interval Δt during pumping is preferable in order to achieve accurate results and a simplified dimensioning of IPTs.

The studies in this thesis confirm that urban line sources have a significant influence on the groundwater quality and that heterogeneous concentration patterns in the vicinity of urban line sources occur. The concentration-time series of the wastewater compounds were characterized by variable concentrations during pumping. Higher variations for micropollutants than for inorganic compounds indicate that the occurrence of micropollutants is characterized by higher dynamics.

The comparison of the two investigated line sources revealed mainly higher M_{ex} values at the urban stream. This may be caused by the better connection of the streambed with the underlying sediments that enables higher water exfiltration Q_{ex} from urban streams than from sewers where water exfiltrates only through leaks. Although more wastewater compounds are emitted from urban streams in this study, leaky sewers seem to be more relevant for groundwater quality assessments because the sewer network length exceeds the length of streams in urban areas by many times.

To what extent the obtained M_{ex} values can be used to generalize the problem of groundwater contamination from urban line sources depends on the specific conditions of the sewer network or stream network and on the connected aquifer of the investigated area. The conditions in this study favor high mass exfiltration from line sources by numerous leaks of the sewer and intensive wastewater inflow to the stream (three CSO pipes). Therefore, the obtained results represent mainly upper limits of M_{ex}.

Furthermore, this study shows that the IPT method can be adapted to the conditions of urban line sources under which mostly not well-defined plumes occur. The implementation of more simple sampling schedules, relying on constant time intervals Δt for IPTs, yielded more accurate results.

The line source monitoring approach provides new insights into the relevance of urban line sources. However, the application of the monitoring approach is not always reasonable. Some important limitations of the monitoring approach must be taken into account:

- The applicability of the IPT method itself is strongly connected to the properties of the investigated aquifer. Under specific aquifer conditions the IPT application is not reasonable because the extraction rate is too low (in case of small aquifer thicknesses and/or low hydraulic conductivities) or because even high pumping rates can not generate the required control plane length defined by the capture zone shape (in case of high aquifer thicknesses and/or high natural flow). Bayer-Raich et al. (2004) give a more detailed overview about limiting aquifer properties for IPTs by the use of the dimensionless time t_D which combines the aquifer properties with the IPT parameters as a classification parameter for IPTs.

- The presented monitoring approach depends on pumping wells in the vicinity of the target line source. Existing wells can be included if they are well-positioned, but often new pumping wells must be installed. Because of buildings and infrastructures (e.g., roads), a high percentage of urban areas is not accessible for drilling. In combination with problems in obtaining a drilling permission on private land, the applicability of the monitoring approach may be hampered.
- The natural groundwater flow is deflected by exfiltration from urban line sources. In case of strong exfiltration the streamlines in the groundwater are nearly parallel to the line source. The positioning of the IPT wells under these conditions is difficult to achieve. It is therefore advised to exclude sites with these characteristics.
- Due to dilution of the exfiltration water from line sources with the groundwater and the mixing of different concentration zones with the IPT method, only high mass flow increases ΔM_{CP} can be detected with the line source monitoring approach. High concentrations in the exfiltration water and low background concentrations of a target compound in the groundwater are an important requirement for the determination of significant ΔM_{CP} values between up- and downstream wells. In this context also low chemical analysis uncertainties are required to significantly differentiate between up- and downstream concentrations.
- Because of the limitations, the application of the line source monitoring approach is only adequate for case studies. Owing to the high effort for drilling, pumping, sample analyses and cleaning of possibly contaminated groundwater, the surveillance of a complete sewer network is not feasible.

Despite the limitations the application of the line source monitoring approach is still beneficial because reliable M_{ex} values can hardly be obtained with other monitoring approaches. The focus on urban line source sections instead of point sources (e.g., single sewer leaks) enables the estimation of more reliable M_{ex} values because small scale concentration heterogeneities are considered by averaging concentrations of large aquifer volumes with the IPT method. Furthermore, the obtained M_{ex} values can be used for the assessment of groundwater contamination from line sources because the concentrations were measured directly in the groundwater and are not derived from measured exfiltration rates in the sewer or stream.

Possible degradation or retardation processes in the colmation layer, in the unsaturated zone below line sources and in the groundwater cannot be evaluated in detail with the presented monitoring approach. Nevertheless, the resulting M_{ex} values represent the amount of mass flow that reaches the groundwater after being affected by degradation and/or retardation. The transfer of M_{ex} values from one line source network to another must consider the different field conditions (e.g., groundwater level, sediments below the line source). However, the line source monitoring approach can be applied to sites with field properties different from this study.

The application of the line source monitoring approach requires considerable effort, but the results are unique and can hardly be obtained with alternative measurements. In combination with the newly developed and simplified dimensioning of the IPT sampling schedules, the presented monitoring approach is a helpful tool for the assessment of groundwater contamination from urban line sources.

5.2 Outlook

In this section, recommendations for further applications and optimizations of the line source monitoring approach are presented. In addition, it is discussed how the results can help to assess groundwater contamination from urban line sources.

The wastewater-borne compounds in this study represent only a small choice of contaminants and indicator substances which are emitted from urban line sources. There are a large number of relevant compounds that were not investigated in this study. Heavy metals, for example, are a substance group which is emitted in large amounts from urban line sources (Leung and Jiao, 2006). In this context, storm water drains are an important emitter because they transport heavy metals that are washed away from roads or roofs. Furthermore, the investigation of storm water drains seems to be a future application area of the line source monitoring approach.

The group of selected micropollutants can be extended by numerous compounds (Schwarzenbach et al., 2006). Preliminary samplings at the test sites revealed the presence of phthalates in the vicinity of the line sources. Pharmaceuticals pose a possible threat to aquatic life due to their bioactive design and it is therefore necessary to quantify their release from urban line sources. Including additional compounds in the monitoring programs would lead to a more detailed insight into the relevance of groundwater contamination from urban line sources.

The applications of the line source monitoring approach were conducted at two field sites in the same aquifer. For a more comprehensive assessment of the groundwater contamination from urban line sources, the application of the monitoring approach needs to be extended to other field sites with different aquifer properties. Different line source properties (sewer diameter, leak size or stream width) schould be investigated to estimate the variation of M_{ex} values. The application under different field conditions in future research also helps to define the best fitted operative range for the line source monitoring approach.

The IPT evaluation of the presented monitoring approach considers the observed wastewater constituents as conservative compounds. The results from this study indicate that sorption and degradation processes occur in the vicinity of the investigated line sources. The influences of these processes on IPTs evaluations were described in Bayer-Raich et al. (2006) and Bayer-Raich et al. (2009). Further research is required to find solutions for the implementation of sorption and degradation processes in future evaluations of the line source monitoring approach.

The optimization of IPT sampling schedules in this study can be substantiated by including additional field data. The concentration distribution of target compounds in the groundwater depends on the properties of the investigated aquifer and the inflow pattern from the sources. The optimization of IPT sampling schedules in this study is based on concentration-time series obtained from test sites that are characterized by only small variations of hydraulic conductivities, aquifer thicknesses and natural gradients. In order to gain a more widespread covering of possible aquifer properties the operation of IPTs with high-frequency sampling at additional sites is advised. For this task also concentration-time series from IPTs which were not used for the investigation of urban line sources can be included.

The monitoring approach can be used to quantify mass flow rates from line sources. Nevertheless, more detailed information about the exfiltration process itself is necessary for the assessment of groundwater contamination from line sources. It is therefore advised to measure the concentrations of wastewater compounds also on the passage from the line source to the groundwater and not only in the groundwater or the line source. Integrative modeling of the colmation layer, of the unsaturated zone and of the groundwater by using the measured concentrations in the different compartments will give new insights into the exfiltration process from urban line sources.

The assessment of groundwater contamination from entire urban line sources requires M_{ex} values on the regional catchment scale. Further research must clarify how the measured M_{ex} values from the line source monitoring approach can be implemented into complex numerical groundwater models at the city scale or for regional catchments. By using these models it can be estimated which amount of wastewater-borne compounds is emitted from an entire city.

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Annex

Concentration-time-series of the IPT applications

Leaky sewer site **Well:** **W1**

Pumping Time [h]	B [mg L^{-1}]	Cl$^-$ [mg L^{-1}]	K$^+$ [mg L^{-1}]	NO$_3^-$ [mg L^{-1}]	NH$_4^+$ [mg L^{-1}]	SO$_4^{2-}$ [mg L^{-1}]	BPA [ng L^{-1}]	CAF [ng L^{-1}]	NON [ng L^{-1}]	TON [ng L^{-1}]
0	0.41	68.55	13.81	20.09	0.06	354.52	452	35		19
4	0.38	65.78	13.12	18.53	0.06	334.26				
8	0.37	71.96	12.71	17.04	0.08	349.42	63	27		20
12	0.36	69.37	12.80	18.28	0.05	352.73				
16	0.37	68.14	13.17	17.92	0.05	341.22	35	27		22
20	0.35	85.42	12.85	16.98	0.05	342.37				
24	0.35	68.87	12.79	19.19	0.05	346.83				
28	0.35	70.27	13.09	19.18	0.05	355.32				
32	0.35	66.27	13.58	20.20	0.05	335.87	136	49		20
36	0.35	68.83	12.94	18.36	0.05	335.03				
40	0.34	69.98	12.86	18.79	0.05	344.97				
44	0.36	67.42	12.97	19.46	0.05	339.48				
48	0.34	74.54	12.91	19.17	0.06	359.85	12	22		14
52	0.36	69.11	13.26	19.39	0.05	349.22				
56	0.33	67.64	12.49	18.10	0.05	342.98				
60	0.34	67.70	12.71	18.97	0.05	344.43				
64	0.34	67.72	12.59	18.46	0.05	343.70	38	19		14
68	0.34	66.98	12.89	19.25	0.05	343.52				
72	0.34	67.02	13.26	17.83	0.05	341.71	16	17		16
76	0.34	67.78	12.68	25.26	0.08	345.92				
80	0.35	71.80	13.21	20.75	0.05	355.82	24	21		12
84	0.35	68.94	13.08	21.81	0.05	351.35				
88	0.32	67.88	12.13	20.42	0.05	347.14	10	18		12
92	0.33	69.03	12.55	22.49	0.07	350.65				
96	0.34	68.17	12.93	18.04	0.06	348.68	10	18		12
100	0.34	68.89	12.89	17.63	0.06	348.56				
104	0.34	70.15	12.84	18.35	0.06	349.74	11	16		2
108	0.34	67.84	13.03	17.73	0.05	351.47				
112	0.34	71.77	12.93	18.34	0.05	353.03	50	17		12
116	0.34	98.97	12.82	19.11	0.05	363.72				
120	0.34	66.59	12.59	16.29	0.05	356.49	44	16		12

Leaky sewer site **Well:** **W2**

Pumping Time [h]	B [mg L^{-1}]	Cl^- [mg L^{-1}]	K^+ [mg L^{-1}]	NO_3^- [mg L^{-1}]	NH_4^+ [mg L^{-1}]	SO_4^{2-} [mg L^{-1}]	BPA [ng L^{-1}]	CAF [ng L^{-1}]	NON [ng L^{-1}]	TON [ng L^{-1}]
0	0.36	71.15	13.53	20.63	0.09	392.79	43	3		20
4	0.37	73.83	12.99	20.53	0.05	401.35				
8	0.34	71.42	12.26	18.64	0.09	394.07	16	22		18
12	0.35	72.93	12.30	18.98	0.05	395.43				
16	0.38	71.24	13.09	24.70	0.05	390.96	61	19		15
20	0.35	73.05	12.62	19.53	0.05	396.96				
24	0.35	71.61	12.54	21.41	0.05	389.66				
28	0.34	74.08	12.93	21.56	0.05	390.15				
32	0.36	80.95	12.52	21.92	0.05	401.04	21	21		19
36	0.35	70.52	12.20	21.42	0.05	384.23				
40	0.33	73.54	11.76	21.25	0.05	391.11	52	16		15
44	0.37	70.52	12.87	21.22	0.05	382.45				
48	0.36	71.18	12.78	21.18	0.05	386.97				
52	0.37	76.14	12.82	21.53	0.05	390.19				
56	0.36	71.46	12.73	21.58	0.05	386.29	10	17		15
60	0.36	69.89	12.82	21.97	0.05	378.68				
64	0.36	70.16	12.63	23.14	0.05	381.22	12	19		17
68	0.35	73.67	12.56	22.38	0.05	385.93				
72	0.36	71.38	12.71	22.25	0.06	383.21	19	18		17
76	0.37	73.84	12.79	24.02	0.11	398.49				
80	0.37	70.73	12.92	24.55	0.05	381.96	12	18		15
84	0.37	71.11	13.14	24.90	0.05	383.38				
88	0.36	70.84	12.72	26.96	0.05	380.67	16	16		2
92	0.35	73.81	12.07	25.64	0.06	380.38				
96	0.37	80.74	13.00	22.03	0.05	396.03	10	17		12
100	0.36	73.01	12.88	21.66	0.05	380.32				
104	0.37	75.11	12.83	21.11	0.05	390.17	13	17		12
108	0.36	71.16	12.93	21.54	0.05	380.56				
112	0.36	69.80	12.60	21.68	0.05	375.35	27	16		12
116	0.37	70.67	13.03	22.05	0.05	381.84				
120	0.37	74.63	12.90	19.51	0.05	390.26	52	16		12

Leaky sewer site **Well:** **W3**

Pumping Time [h]	B [mg L^{-1}]	Cl^- [mg L^{-1}]	K^+ [mg L^{-1}]	NO_3^- [mg L^{-1}]	NH_4^+ [mg L^{-1}]	SO_4^{2-} [mg L^{-1}]	BPA [ng L^{-1}]	CAF [ng L^{-1}]	NON [ng L^{-1}]	TON [ng L^{-1}]
0	0.37	72.64	13.17	19.04	0.05	421.78	19	29		18
4	0.37	74.34	13.27	19.09	0.05	418.14				
8	0.37	74.88	12.57	19.51	0.08	402.36	18	23		22
12	0.37	73.46	12.90	19.17	0.05	405.11				
16	0.37	73.01	12.83	18.94	0.05	401.59	113	17		16
20	0.36	73.42	12.65	18.55	0.05	405.09				
24	0.36	73.01	12.61	21.02	0.05	396.25	10	37		16
28	0.35	72.18	12.41	21.41	0.05	392.27				
32	0.37	76.00	12.82	22.12	0.05	404.81	20	28		15
36	0.37	77.04	12.59	21.69	0.05	413.31				
40	0.36	72.10	12.50	20.36	0.05	388.20				
44	0.35	72.44	12.22	20.53	0.05	391.69				
48	0.36	76.08	12.47	21.70	0.05	400.02				
52	0.35	74.06	12.34	21.06	0.05	391.46				
56	0.35	72.89	12.23	21.35	0.05	387.47	27	18		17
60	0.34	71.72	11.95	21.47	0.05	383.63				
64	0.34	72.01	11.99	25.13	0.05	378.26	30	19		17
68	0.33	75.95	11.71	20.60	0.05	389.61				
72	0.35	76.89	12.17	20.59	0.05	385.11	20	21		14
76	0.34	76.35	12.29	22.14	0.06	390.12				
80	0.34	72.53	12.28	24.14	0.05	380.95	24	18		16
84	0.36	77.23	12.99	24.15	0.05	384.26				
88	0.33	70.70	11.91	23.62	0.07	372.49	23	16		2
92	0.35	71.06	12.31	24.11	0.05	376.10				
96	0.36	72.30	12.88	19.66	0.05	385.60	10	17		2
100	0.36	72.92	12.57	20.27	0.05	381.19				
104	0.35	74.07	12.51	21.38	0.05	382.56	23	17		2
108	0.35	72.19	12.28	20.69	0.05	379.20				
112	0.33	73.72	11.92	21.10	0.05	381.45	46	18		12
116	0.34	70.99	12.27	21.41	0.05	373.76				
120	0.34	71.89	12.11	20.27	0.05	378.55	130	17		12

Leaky sewer site **Well:** **W4**

Pumping Time [h]	B [mg L^{-1}]	Cl^- [mg L^{-1}]	K^+ [mg L^{-1}]	NO_3^- [mg L^{-1}]	NH_4^+ [mg L^{-1}]	SO_4^{2-} [mg L^{-1}]	BPA [ng L^{-1}]	CAF [ng L^{-1}]	NON [ng L^{-1}]	TON [ng L^{-1}]
0	0.38	86.39	12.91	15.22	0.45	483.69	22	31		15
4	0.36	95.48	13.01	18.09	0.92	406.47				
8	0.34	105.50	12.62	20.26	0.75	388.21	36	23		19
12	0.36	103.97	12.40	18.74	0.65	381.35				
16	0.36	102.96	12.91	20.63	0.83	374.45	16	28		24
20	0.42	114.32	13.17	19.49	0.76	395.82				
24	0.42	110.07	13.03	22.71	0.50	373.20				
28	0.41	104.59	13.14	21.75	0.32	374.13				
32	0.41	104.89	14.36	22.68	0.33	373.88	10	18		20
36	0.39	103.60	12.93	21.96	0.28	373.33				
40	0.39	108.86	12.73	22.20	0.51	379.93				
44	0.38	105.93	12.73	22.80	0.61	372.16				
48	0.38	105.04	12.62	22.41	0.47	371.46				
52	0.38	114.13	12.46	22.37	0.52	378.02				
56	0.38	106.19	12.47	23.63	0.51	366.70	12	17		2
60	0.37	107.83	12.56	23.48	0.24	374.21				
64	0.38	112.66	12.77	25.24	0.35	371.24				
68	0.38	107.70	12.86	23.78	0.29	366.05				
72	0.38	109.25	12.94	26.75	0.27	366.98	10	20		22
76	0.38	121.99	13.89	24.99	0.23	371.65				
80	0.41	111.37	13.60	28.20	0.45	376.33	10	16		2
84	0.41	114.61	13.67	27.55	0.35	373.42				
88	0.38	112.76	12.87	27.42	0.97	364.30	10	16		12
92	0.38	112.90	12.55	28.00	0.58	369.19				
96	0.40	121.03	13.45	24.16	0.41	367.04	10	17		12
100	0.39	112.22	13.21	24.57	0.65	368.22				
104	0.38	117.15	12.66	25.73	0.69	370.99	13	17		12
108	0.39	111.71	13.15	25.16	0.43	368.04				
112	0.40	113.36	13.47	26.31	0.31	368.80	24	16		12
116	0.39	118.08	12.98	25.08	0.45	378.42				
120	0.38	114.96	13.10	24.82	0.35	366.30	49	15		12

Losing stream site **Well:** **11**

Pumping Time [h]	B [mg L^{-1}]	Cl^- [mg L^{-1}]	K^+ [mg L^{-1}]	NO_3^- [mg L^{-1}]	NH_4^+ [mg L^{-1}]	SO_4^{2-} [mg L^{-1}]	BPA [ng L^{-1}]	CAF [ng L^{-1}]	NON [ng L^{-1}]	TON [ng L^{-1}]
0	0.37	108.08	12.81	0.25	1.20	535.28		26	56	
4	0.35	108.62	12.41	0.71	0.55	539.47				
8	0.35	117.99	12.70	1.60	0.61	548.62		27	120	
12	0.35	111.69	13.08	1.15	0.81	532.47				
16	0.35	111.04	13.67	1.67	1.01	534.05		29	137	
20	0.35	110.78	13.00	2.17	0.52	529.14				
24	0.35	113.58	13.75	1.92	0.61	534.64		24	79	
28	0.34	112.49	12.74	3.05	0.63	523.28				
32	0.35	123.02	14.12	3.10	0.65	531.36		50	50	
36	0.35	119.48	13.48	2.69	0.68	535.08				
40	0.35	117.26	13.35	2.80	0.63	528.73		80	50	
44	0.35	118.45	13.82	1.94	0.48	530.32				
48	0.35	116.96	14.38	2.39	0.55	528.20		20	25	
52	0.34	128.88	14.18	2.22	0.57	519.84				
56	0.34	120.06	14.13	2.38	0.58	510.69		22		
60	0.34	122.93	14.16	3.71	0.53	527.41				
64	0.34	116.87	14.66	3.87	0.68	514.05				
68	0.33	116.95	14.10	2.86	0.57	505.78				
72	0.33	117.52	14.36	3.08	0.62	507.92		3	152	
76	0.34	118.51	14.22	4.45	0.45	510.30				
80	0.33	115.58	14.56	3.98	0.74	514.92				
84	0.34	128.58	14.58	3.04	0.77	528.99				
88	0.34	117.96	14.43	4.34	0.54	558.89		20	25	
92	0.34	123.56	14.59	3.81	0.62	519.43				
96	0.33	124.49	14.73	4.46	0.52	512.72				
100	0.33	123.58	14.73	5.83	0.45	513.45				
104	0.34	128.44	14.80	5.70	0.52	522.20		20	25	
108	0.33	122.78	14.85	3.24	0.40	517.15				
112	0.33	125.10	14.80	3.30	0.67	514.05				
116	0.33	124.88	13.56	3.34	0.44	519.13				
120	0.33	126.34	14.21	2.90	0.43	523.27		3	25	

Losing stream site **Well:** **12**

Pumping Time [h]	B [mg L^{-1}]	Cl$^-$ [mg L^{-1}]	K$^+$ [mg L^{-1}]	NO$_3^-$ [mg L^{-1}]	NH$_4^+$ [mg L^{-1}]	SO$_4^{2-}$ [mg L^{-1}]	BPA [ng L^{-1}]	CAF [ng L^{-1}]	NON [ng L^{-1}]	TON [ng L^{-1}]
0	0.32	127.64	15.01	6.56	0.10	526.64		23	71	
4	0.31	137.40	17.25	7.58	0.10	512.18				
8	0.31	136.06	17.19	8.26	0.10	506.93		24	111	
12	0.31	139.04	17.09	7.14	0.10	499.76				
16	0.31	143.82	17.26	8.30	0.10	500.53		23	51	
20	0.32	143.11	17.42	7.62	0.15	492.46				
24	0.32	146.67	16.65	8.05	0.17	496.86		25	78	
28	0.31	148.29	16.40	7.43	0.37	493.06				
32	0.31	154.73	16.87	7.89	0.13	499.51		20	25	
36	0.30	153.71	15.84	7.30	0.49	501.33				
40	0.31	156.15	16.42	7.37	0.18	501.09		30	50	
44	0.30	155.31	17.59	7.18	0.10	530.28				
48	0.30	160.95	16.75	7.01	0.15	497.38		15	25	
52	0.30	153.23	16.68	6.84	0.37	496.09				
56	0.31	155.41	16.53	6.58	0.12	503.13		32	76	
60	0.30	154.70	16.91	7.17	0.10	496.61				
64	0.30	155.01	16.97	6.54	0.11	500.19				
68	0.31	156.71	16.90	5.63	0.15	506.24				
72	0.30	156.09	18.23	5.85	0.65	504.47		3	25	
76	0.30	153.93	16.89	6.01	0.18	498.96				
80	0.30	157.14	16.52	5.82	0.10	502.82				
84	0.30	158.05	16.85	5.48	0.10	504.36				
88	0.30	156.31	17.21	5.64	0.10	504.57		3	39	
92	0.29	157.71	16.77	5.99	0.10	504.21				
96	0.29	158.50	16.65	6.53	0.10	502.60				
100	0.30	157.94	16.62	5.18	0.10	504.77				
104	0.30	158.63	16.25	5.40	0.10	509.36		10	25	
108	0.30	157.60	16.30	5.47	0.10	500.81				
112	0.30	161.54	16.78	5.47	0.10	517.01				
116	0.29	158.74	16.22	5.19	0.10	511.42				
120	0.29	161.33	16.71	4.89	0.14	516.32		3	42	

Losing stream site **Well:** **13**

Pumping Time	B	Cl$^-$	K$^+$	NO$_3^-$	NH$_4^+$	SO$_4^{2-}$	BPA	CAF	NON	TON
[h]	[mg L^{-1}]	[mg L^{-1}]	[mg L^{-1}]	[mg L^{-1}]	[mg L^{-1}]	[mg L^{-1}]	[ng L^{-1}]	[ng L^{-1}]	[ng L^{-1}]	[ng L^{-1}]
0	0.34	98.01	12.47	10.06	0.26	558.21		22	76	
4	0.36	98.19	13.21	4.87	0.22	546.99				
8	0.37	103.12	13.24	2.06	0.26	558.50		26	73	
12	0.35	101.61	14.85	1.76	0.23	540.21				
16	0.35	107.59	15.09	2.57	0.25	543.41		3	342	
20	0.36	105.70	13.97	2.81	0.48	532.65				
24	0.35	107.54	14.58	2.07	0.42	535.95		26	105	
28	0.35	109.41	13.26	2.06	0.61	536.96				
32	0.34	112.80	15.01	2.27	0.58	531.88		10	25	
36	0.35	113.65	14.05	2.28	0.58	534.70				
40	0.35	117.06	13.93	1.97	0.58	546.67		25	32	
44	0.35	112.38	13.69	2.32	0.46	530.66				
48	0.35	116.68	13.91	3.07	0.45	537.88				
52	0.35	114.51	14.61	2.11	0.89	531.98				
56	0.35	120.02	13.96	1.80	0.68	545.15		22	120	
60	0.34	115.22	14.56	1.67	0.70	532.59				
64	0.35	117.50	15.17	1.28	0.64	531.02				
68	0.34	121.07	14.71	1.63	0.86	534.82				
72	0.34	117.74	14.47	1.76	0.72	532.54		109	466	
76	0.34	121.12	14.76	1.15	0.74	545.60				
80	0.34	125.13	15.02	1.72	1.20	547.80				
84	0.33	121.72	14.97	2.00	0.67	538.42				
88	0.33	125.49	16.47	1.49	0.75	548.59		3	25	
92	0.32	119.97	15.00	1.65	0.72	535.72				
96	0.33	122.51	14.98	2.06	0.72	542.80				
100	0.33	126.82	14.35	1.16	0.41	554.92				
104	0.32	122.95	14.65	1.86	0.73	537.22		5	25	
108	0.33	121.44	14.64	0.95	0.72	534.33				
112	0.33	127.81	15.18	1.05	0.55	542.27				
116	0.33	117.97	14.60	0.52	1.09	517.38				
120	0.32	119.15	15.15	0.79	0.64	519.12		3	53	

Losing stream site				**Well:**		**14**				
Pumping Time	B	Cl^-	K^+	NO_3^-	NH_4^+	SO_4^{2-}	BPA	CAF	NON	TON
[h]	[mg L^{-1}]	[mg L^{-1}]	[mg L^{-1}]	[mg L^{-1}]	[mg L^{-1}]	[mg L^{-1}]	[ng L^{-1}]	[ng L^{-1}]	[ng L^{-1}]	[ng L^{-1}]
0	0.29	101.14	12.82	6.72	0.70	557.91		27	127	
4	0.30	98.89	12.90	8.14	0.60	537.45				
8	0.29	102.66	11.84	8.68	0.80	550.02		25	122	
12	0.30	100.96	12.78	7.40	0.60	541.95				
16	0.30	102.05	12.78	6.67	0.80	543.15		23	97	
20	0.29	102.47	13.76	7.07	0.68	542.79				
24	0.29	101.58	12.72	7.15	0.83	536.54		26	215	
28	0.30	102.71	13.07	7.06	0.74	539.27				
32	0.30	100.26	12.34	6.93	0.94	525.46		3	25	