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Tracking artificial sweeteners and pharmaceuticals introduced into urban groundwater by leaking sewer networks

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ABSTRACT

There is little quantitative information on the temporal trends of pharmaceuticals and other emerging compounds, including artificial sweeteners, in urban groundwater and their suitability as tracers to inform urban water management. In this study, pharmaceuticals and artificial sweeteners were monitored over 6 years in a shallow urban groundwater body along with a range of conventional sewage tracers in a network of observation wells that were specifically constructed to assess sewer leakage. Out of the 71 substances screened, 24 were detected at above the analytical detection limit. The most frequent compounds were the iodinated X-ray contrast medium amidotrizoic acid (35.3%), the anticonvulsant carbamazepine (33.3%) and the artificial sweetener acesulfame (27.5%), while all other substances occurred in less than 10% of the screened wells. The results from the group of specifically constructed focus wells within 10 m of defective sewers confirmed sewer leaks as being a major entrance pathway into the groundwater. The spatial distribution of pharmaceuticals and artificial sweeteners corresponds well with predictions by pipeline leakage models, which operate on optical sewer condition monitoring data and hydraulic information. Correlations between the concentrations of carbamazepine, iodinated X-ray contrast media and artificial sweeteners were weak to non-existent. Peak concentrations of up to 4130 ng/l of amidotrizoic acid were found in the groundwater downstream of the local hospital. The analysis of 168 samples for amidotrizoic acid, taken at 5 different occasions, did not show significant temporal trends for the years 2002–2008, despite changed recommendations in the medical usage of amidotrizoic acid. The detailed results show that the current mass balance approaches for urban groundwater bodies must be adapted to reflect the spatially distributed leaks and the variable wastewater composition in addition to the lateral and horizontal groundwater fluxes.

1. Introduction

1.1. Motivation

The release of conventional and emerging pollutants into urban groundwater is a potential threat to the use of this groundwater in the water supply (Pomati, 2007). Knowledge of the entrance pathways and the persistence of emerging pollutants in natural systems is required for determining (i) whether these pollutants constitute a long-term threat, (ii) whether it is viable to reduce the release of these pollutants and (iii) how the use of urban groundwater is affected. Urban groundwater bodies have often been exposed to wastewater-derived pollutants over several decades, which makes them a good test bed for monitoring long-term trends. Despite the growing literature addressing pharmaceutical and micropollutant screenings in wastewater and surface water (Heberer et al., 2001; Joss, 2006; Tiehm et al., 2011; Valcárcel, 2011), few reports are available that include time series data for groundwater or interpret the data in a hydrogeological context.

To address this issue, the occurrence of pharmaceuticals and artificial sweeteners in urban groundwater has been investigated in repeated sampling campaigns over 6 years in a specifically constructed monitoring network to track wastewater exfiltration from leaky sewers. The analysis also considers data from optical sewer conditions, which monitors 164 km of sewers and draws on forward modelling of the sewer-groundwater interaction.

1.2. Sewer leakage in urban areas

The leakage from sewer systems to urban groundwater bodies remains poorly quantified despite a variety of approaches (tracer tests, direct spot measurements at test sites, mixing calculations, sewer condition monitoring, Darcy flux trough the colmation layer, and others)(DeSilva et al., 2005; Rutsch, 2008). Estimates regarding leakage rates typically span 3 orders of magnitude. The minimum

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average daily rates have been cited as being between 0.02 and 9.0 l d/cm^2 related to the standardised leak area and 0.0002 and 2.0 l/(s∗km) related to the sewer length (Ellis, 2009). The application of contemporary literature data to the Rastatt sewer system resulted in a wide range of sewer leakage estimates, between 0.02 mm/a and 1000 mm/a, whereas local sewer studies constrain the likely sewer leakage between 1 mm/a and 53 mm/a (Wolf, 2006). The uncertainties in deriving leakage estimates based on sewer conditions result from (i) the highly variable clogging of leaks with colmation layers and (ii) poorly known sewer conditions, especially for private sewers. Therefore, mass balance approaches are attractive because they can be integrated over extended periods and larger areas. The use of a mass balance approach in the context of sewer leakage using depth specific hydrochemistry resulted in a leakage rate between 0.07 and 0.12 l/s km for Doncaster, UK (Rueedi et al., 2009). However, most mass balance approaches suffer from multiple input sources of the respective tracers (e.g., nitrates, chlorides, borons). Approaches employing emerging micropollutants, such as carbamazepine, have the advantage of source uniqueness, as demonstrated in Linz (Fenz et al., 2004). These methods are only suitable for the quantification of sewer leakage if river water infiltration can be either neglected or quantified. An example for this problem is documented for the case study in Halle, in which the river water was a significant additional source (Osenbruck, 2007). In Rastatt, the Murg River is both losing to the groundwater and gaining from groundwater, as indicated by a numerical groundwater model (Wolf, 2006). None of these approaches has successfully used iodinated X-ray contrast media or artificial sweeteners nor were they able to compare urban background concentrations with systematic hot spot measurements. Artificial sweeteners were recently included in a suite of tracers to address hyporheic exchange and surface-groundwater interactions (Engelhardt et al., 2011), but the detailed analysis has not been published.

1.3. Overview of environmental tracers for sewer leakage

To demonstrate the effects of wastewater exfiltration on urban groundwater, monitoring wells in the city of Rastatt, which serves as the case study in this paper, were tested for a wide range of wastewater-specific marker species. The challenge in using marker species is unambiguously and exclusively linking them to a wastewater source, or locating and quantifying all other sources (e.g., fertiliser input, industrial spillages and contaminated sites, landfills, septic tanks, subsurface construction works). The low concentrations of marker species, between μg/l and ng/l, require significant analytical effort. In addition to containing illegally discharged hazardous substances, such as chlorinated hydrocarbons, wastewater from leaky sewers also includes a constant and highly diverse mixture of legally used chemicals, containing many substances for which no adequate toxicological information is available. These so-called “emerging pollutants” include pharmaceutical residues, endocrine disruptors and personal care products (PCPs). Since 1995, considerable research efforts have been devoted to detecting these emerging pollutants in surface waters and wastewater (Hirsch et al., 2000a, 1999; Richardson and Ternes, 2005; Stuart et al., 2012; Ternes et al., 2002b).

Personal care products (PCPs), such as liquid bathing additives, soaps, skin-care products, shampoos and dental care products, are produced and used in large amounts worldwide. In the early 1990s, the annual production volume for Germany alone exceeded 550,000 metric tonnes (Ternes et al., 2002a). Considerable persistence and bioaccumulation potential was shown for a number of PCPs, including musk fragrances, disinfectants, antiseptics, some repellents and sunscreen agents (Ternes et al., 2002a). Pharmaceutical residues have already been detected in the drinking water in Berlin, Germany (Heberer, 2002; Heberer and Stan, 1996; Stan et al., 1994; Stan and Linkerhägner, 1992). Clofibric acid, which is used as a blood lipid regulator, was found in 64 tap water samples in Berlin with concentrations between 10 and 165 ng/l (Heberer, 2002; Stan et al., 1994) and detected in deeper groundwater below the outskirts of Berlin as a result of sewage farm operation (Scheytt et al., 2000). Iodinated organic compounds already constitute an important fraction of urban wastewater (Jekel and Wischnack, 2000), especially downstream from hospitals (Larsen et al., 2000).

Caffeine was used as an anthropogenic marker for wastewater contamination of surface waters in Switzerland (Buerge et al., 2003). The concentrations measured in Lake Zürichsee correlated with precipitation data. Combined sewer overflows are believed to be the cause of this correlation.

Boron has also been used in previous studies as a wastewater trace substance (Gäbler and Bahr, 1999; Härig and Mull, 1992), and a substantial amount of literature on boron concentrations in the aquatic environment is available. Notably, the Rastatt case study assessed boron transport using a numerical groundwater model (Wolf et al., 2006). Other proposed marker species (Barret et al., 1999; Ellis and Revitt, 2002), including chlorination by-products (THM), faecal steroids (coprostanol), synthetic estrogens, detergents, chlorinated solvents and stable isotopes (^{15}N), have not been screened for in Rastatt but may be incorporated in future analytical programmes.

More recently, primidone and carbamazepine were used to distinguish groundwater from different wastewater input sources and different groundwater ages in cases where other indicators failed to distinguish the different water types (Scheytt, 2008). A broad screening exercise for pharmaceutics and hormones in the aquatic environment was conducted between 2000 and 2002 in Baden-Württemberg by the environmental agency (LfU, 2002), parallel to the measurements of this thesis in Rastatt. In total, 180 samples were taken from 105 different groundwater observation wells and analysed for 74 different substances. The most prominent findings are for sotalol, phenazone, propyphenazone, carbamazepine, diclofenac and dehydrato-erythromycin, as summarised in (LfU, 2002; Sacher et al., 2001).

In surface waters, correlations between potassium, carbamazepine and other pharmaceuticals were observed and interpreted as the result of wastewater discharge being the common entrance pathway for these substances (Nödler et al., 2011).

1.4. Iodinated X-ray contrast media

Iodinated X-ray contrast media (ICM), such as iopromide (IPM), are frequently applied in clinical diagnoses to image soft tissues (Seitz et al., 2006). The annual worldwide ICM consumption in X-ray diagnostics is approximately 3000 tones. Because of their recalcitrance, ICM concentrations are barely affected by wastewater treatment plants and are consequently discharged into receiving waters (Putschew et al., 2001). For example, effluent concentrations of up to 21 μg/l IPM have been found in rivers and lakes (Ternes and Hirsch, 2000). Some of the ICMs can be transformed into a number of transformation products (TPs), which have also been detected in aquatic environments (Kormos et al., 2010). Although ICMs are believed to be harmless, any subtle effects of mixtures of ICM and their metabolites or other micropollutants are unknown and may pose ecological or human health dangers (Pomati et al., 2006). Given their very low biodegradability, they may also accumulate in the environment.

ICMs have excellent potential for use as wastewater markers because they have no background environmental concentration; no natural sources are known. Their typical concentrations in wastewater are 100–1000 times above the detection limit. These compounds are very stable and behave conservatively (iodated X-ray contrast media are designed to pass through the human body without interaction). The iodinated aromatic ring is extremely stable under conditions encountered in aquatic environments (Kormos et al., 2010).