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Use of two artificial sweeteners, cyclamate and acesulfame, to identify and quantify wastewater contributions in a karst spring

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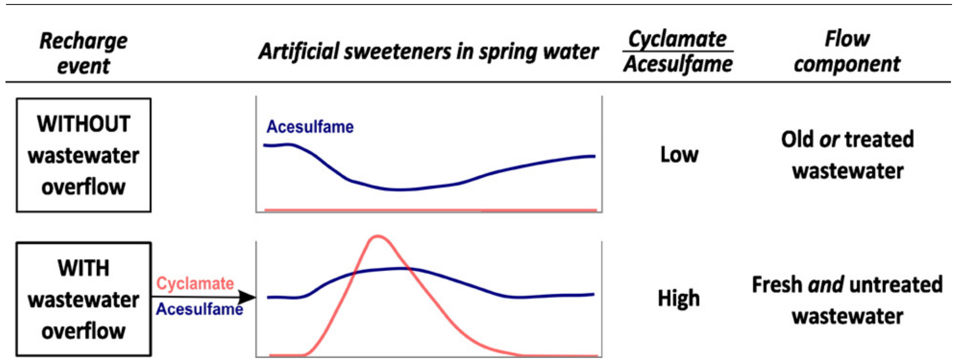
HIGHLIGHTS

- Acesulfame was detected in all karst spring water samples.
- Cyclamate was only detected in spring water after a wastewater spill.
- Fresh untreated wastewater was identified from cyclamate/acesulfame ratios.
- Cyclamate was used for quantification of fresh untreated wastewater.
- Faecal indicator bacteria showed a simultaneous breakthrough with cyclamate.

GRAPHICAL ABSTRACT



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ABSTRACT

The identification and differentiation of different sources of contamination are crucial aspects of risk assessment in water resource protection. This is especially challenging in karst environments due to their highly heterogeneous flow fields. We have investigated the use of two artificial sweeteners, cyclamate and acesulfame, as an indicator set for contamination by wastewater within the rural catchment of a karst spring. The catchment was investigated in detail to identify the sources of artificial sweeteners and quantify their impact. Spring water was analysed following two different but typical recharge events: (1) a rain-on-snow event in winter, when no wastewater overflow from the sewer system was observed, and (2) an intense rainfall event in summer triggering an overflow from a stormwater detention basin. Acesulfame, which is known to be persistent, was quantified in all spring water samples. Its concentrations decreased after the winter event with no associated wastewater spillage but increased during the summer event following a recent input of untreated wastewater. Cyclamate, which is known to be degradable, was only detected following the wastewater inflow incident. The cyclamate signal matched very well the breakthrough of faecal indicator bacteria, indicating a common origin. Knowing the input function, cyclamate was used quantitatively as a tracer in transport modelling and the impact of 'combined sewer overflow' on spring water quality was quantified. Signals from artificial sweeteners were compared to those from bulk parameters (discharge, electrical conductivity and turbidity) and also to those from the herbicides atrazine and isoproturon, which indicate 'old' and 'fresh' flow components, respectively, both originating from croplands. High concentration levels of the artificial sweeteners in untreated wastewater (cyclamate and acesulfame) and in treated wastewater (acesulfame only) make them powerful indicators, especially in rural settings where wastewater input is relatively low, and in karst systems where dilution is often high.

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1. Introduction

Karst aquifers form important drinking water resources in many parts of the world but are well-known for their vulnerability to contamination (Ford and Williams, 2007). Furthermore, many karst springs typically exhibit a rapid response to heavy rainfall or snow-melt (e.g. through increased discharge and water quality deterioration) (Pronk et al., 2006). The spatially heterogeneous and time-variable flow in karst aquifers is reflected in exceptionally broad and time-dependent spectra of water residence times within the aquifers and in spring water (Maloszewski et al., 2002; Einsiedl, 2005). Transit times from the earth surface to springs may range from hours or days (rapid 'conduit flow') to years, decades, or even longer (slow 'matrix flow') (Lauber and Goldscheider, 2014; Geyer, 2008). Flow components in spring waters that have short transit times (i.e. where there is direct transfer of water from the surface to the spring) occur predominantly during high discharge events and pose problems for raw water management like microbial contamination (Heinz et al., 2009). Rain-on-snow events in particular can cause high flood peaks and they are increasingly common in medium-elevation mountain ranges of central Europe (Freudiger et al., 2014).

Organic micropollutants are increasingly being used as indicators, not only for water quality assessment but also for a better understanding of karst systems (e.g. Reh et al., 2015). Organic micropollutants are especially suitable because, unlike most of the conventional indicators (inorganic ions, electrical conductivity), they do not have natural background concentrations and many of them have quite specific applications and are used in specific areas. These micropollutants are a vital tool for the development and validation of water safety plans ('Know Your Catchment', WHO, 2005); they are source-specific indicators and can help to assess the relative importance of different contamination sources, such as manure and domestic wastewater in rural catchments (Tran et al., 2015). The herbicides atrazine and metazachlor have, for example, been used to identify 'fresh' and 'old' flow components (with short and long transit times, respectively) originating from cropland in water from the Gallusquelle spring, in Germany (Schiperski et al., 2015b; Hillebrand et al., 2014). Hillebrand et al. (2012a) had previously used caffeine as an indicator for fresh, untreated domestic wastewater in the same spring water.

Acesulfame and cyclamate are artificial sweeteners that are widely used in food, beverages, drugs, and dental hygiene products (Lange et al., 2012). A number of studies have shown artificial sweeteners to be useful indicators for domestic wastewater in both surface water and groundwater (e.g. Buerge et al., 2009; Scheurer et al., 2009; Wolf et al., 2012; van Stempvoort et al., 2013). They are found in higher concentrations in wastewater than most other organic micropollutants (Lange et al., 2012). Cyclamate is significantly eliminated during biological wastewater treatment, leading to much lower concentrations in treated wastewater than in untreated wastewater (Buerge et al., 2009). Considerable attenuation of cyclamate in groundwater has been reported by Robertson et al. (2013), probably due to biodegradation. A multi-tracer test within the Gallusquelle catchment showed no retardation for cyclamate and gave a rough estimate of 60 days for the half-life of cyclamate (Hillebrand et al., 2015). In contrast, wastewater treatment is far less effective at removing acesulfame (Scheurer et al., 2009). Robertson et al. (2013) estimated the half-life of acesulfame in a wastewater plume within a porous aquifer to be at least 15 years. No retardation has been observed for acesulfame in porous aquifers (van Stempvoort et al., 2013) or karst aquifers (Hillebrand et al., 2015). Its high concentrations in wastewater and relatively high persistence make acesulfame a useful indicator for investigating long-term impacts of domestic wastewater.

Our objective in this research was to investigate the use of cyclamate and acesulfame in karst spring water as a raw water quality indicator set and to use the concentration ratios of these two compounds to derive additional information on the origin of wastewater and the pathways that it follows. Two different recharge events were compared, one including a significant release of wastewater and one with no such release. On the catchment scale, input functions were studied with the aim of using artificial sweeteners to quantify the impact that wastewater had on spring water quality and to improve quantitative risk assessment for karst water resources. Artificial sweetener concentrations were compared to those of other indicator compounds (caffeine, isoproturon, atrazine, desethylatrazine) and faecal indicator bacteria, and their limitations and advantages are discussed.

2. Materials and methods

2.1. Study site

Gallusquelle spring is a perennial karst spring in the low mountain range known as the Swabian Alb (south-western Germany). The average discharge is about 0.5 $m^3\ s^{-1}$ at the gauged outlet (0.12–5 $m^3\ s^{-1}$). Depending on the discharge at the outlet an additional discharge of up to 0.2 $m^3\ s^{-1}$ is estimated to pass into the confining alluvial sediments below the outlet. However, all mass balance calculations in this study are based on the surface (measured) discharge or mass flux at the spring. Recharge is predominantly diffuse passing into the slow reservoir (with long transit times). Following high intensity precipitation or snow-melt events about 5–10% of the precipitation or meltwater was detected in the spring water as direct recharge with transit times of a few days. Most of the recharge occurs in winter and spring (Sauter, 1992). The phreatic zone crosses bedded, marly and massive Upper Jurassic limestone (ox2 to ki2/3) and has an estimated thickness of 20 m (Geyer, 2008). Flow in the phreatic zone is governed by highly karstified structures, generally, following a south-eastward direction (e.g. Oehlmann et al., 2013). The mean age of the spring water has been estimated using ^{85}Kr isotopes to be 3 to 4 years (Geyer, 2008).

The spring's catchment area (Fig. 1) covers about 45 km^2 (Sauter, 1992) and is rural in character with 55% forest, 27% cropland, 15% grassland and only 3% urban areas (LGL-BW, 2015). The main sources of untreated wastewater contamination within the Gallusquelle catchment are the combined sewer system of the Bitz community (3700 people, little industry) and its stormwater detention basin (SWDB). More than 99% of the population is connected to the combined sewer system (Stat. LA BW, 2014). Heinz et al. (2006, 2009) pointed out the relation between deteriorations in spring water quality and SWDB overflow. On the north-eastern boundary of the catchment a former sinking stream (the Fehla stream) contains a high percentage of treated wastewater from a wastewater treatment plant with about 12,000 people connected. Due to heavy clogging of the stream bed it is not clear if there is a present-day connection to the Gallusquelle spring.

2.2. Sample collection

2.2.1. Wastewater and wastewater-impacted surface water

The main sewer for the community of Bitz and the Fehla stream were both sampled for organic micropollutants during a one-week sampling programme in October 2012, with 64 and 43 samples collected from each, respectively. Sampling was combined with discharge measurements (using the salt dilution method in wastewater and hydrometer measurements in the Fehla stream) for use in mass flux calculations. Fehla water was sampled once again under flood conditions on 19 December 2012, without any discharge measurement. Stormwater from the SWDB was sampled for organic micropollutants and faecal indicator bacteria within minutes of the overflow that occurred at 16:20 on 29 July, 2013 (the summer event).

2.2.2. Spring Water

The spring water was sampled for organic micropollutant analysis between 16 and 27 December 2012 following a combined rain and snow-melt event that started on 14 December (the winter event).