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An artificial sweetener and pharmaceutical compounds as co-tracers of urban wastewater in groundwater

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HIGHLIGHTS

- A sweetener and pharmaceutical compounds were useful as co-tracers of wastewater in groundwater.
- Similar co-tracer distributions indicated a single wastewater plume.
- Different co-tracer distributions and concentration ratios indicated two or more domestic septic plumes.

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ABSTRACT

Groundwater in urban areas can be affected by numerous wastewater sources. Distinguishing these sources can facilitate better management of urban water resources and wastewater, and protection of urban aquatic environments. A single wastewater tracer, even if ideal (i.e. low background levels, non-reactive, low detection limits, etc.), would be unable to accomplish this task. Here, we investigated the potential advantages of using a suite of anthropogenic chemicals as co-tracers to distinguish wastewater sources that contribute to groundwater contamination at two urban sites. We considered both relatively ubiquitous and non-ubiquitous tracers in wastewater. At the Jasper (Alberta, Canada) site, concentrations of an artificial sweetener, two pharmaceutical compounds, and a degradate of nicotine in groundwater were strongly correlated as co-tracers. This evidence, along with the similar spatial distributions of these co-tracers could be used to delineate and distinguish a single municipal wastewater plume. At the Barrie (Ontario, Canada) site, there was moderate to strong correlation of the wastewater co-tracers, but local differences in their distributions and in the ratios of their concentrations could be used to infer that mixtures of two or more domestic septic plumes were present in the groundwater at this site. This study demonstrates the benefit of applying a suite of tracers to urban groundwater affected by wastewater contamination. This approach should be applicable at other urban sites.

1. Introduction

The fate of wastewater in the urban environment is an emerging area of research that addresses the increasing emphasis being placed on sustainable management of urban ecosystems (e.g., Buerge et al., 2009; Scheurer et al., 2009; Gasser et al., 2010; Rieckermann et al., 2010; Oppenheimer et al., 2011; Wolf et al., 2012). This area of research has prompted a search for chemical tracers or indicators of wastewater. In part this has involved the search for an “ideal” chemical tracer that could be used to determine quantitatively to what extent the wastewater has mixed with ambient groundwater, and to determine where plumes of wastewater-impacted groundwater have migrated.

The characteristics or requirements of an “ideal” (“conservative”, “good”) wastewater tracer or indicator in receiving waters have been outlined by previous researchers (e.g., Gasser et al., 2010; Dickenson et al., 2011; Oppenheimer et al., 2011; Scheurer et al., 2011). An ideal tracer would be present in wastewater at concentrations that are well above the analytical detection limit and that do not vary significantly over time. Furthermore, this ideal tracer must be conservative, meaning that, with respect to groundwater, it would travel in the dissolved phase at the average groundwater velocity, with no losses by chemical or biological attenuation processes. The ideal tracer would also be absent or at orders of magnitude lower levels in groundwater that is unaffected by wastewater; thus the tracer would typically be an anthropogenic compound. It should also be found in most wastewater sources; Dickenson et al. (2011) used a detection frequency of at least 80% in wastewater effluents to identify potential indicator compounds. Finally, there must be a suitable method to analyze the tracer, which is affordable, with a low limit of quantitation, minimal matrix interference, and good accuracy and precision.

Numerous tracers for wastewater have been proposed to date. Chloride and nutrients have been used as tracers for wastewater plumes in the past. But both can have natural and other anthropogenic sources,

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such as landfills, road salt, or fertilizers, limiting their applicability. Pharmaceuticals have been proposed as being very specific to wastewater. Given their selective uses, their presence can be sporadic in wastewater (e.g., from septic systems: Seiler et al., 1999). They have also been found in landfill leachate (Buszka et al., 2009). Some of the other anthropogenic chemicals that have been proposed as wastewater tracers are subject to moderate to strong biological attenuation in the environment (e.g., caffeine and cotinine, a degradate of nicotine; Seiler et al., 1999; Bradley et al., 2007). Many of the pharmaceuticals and other chemicals are known to sorb to solid materials (commonly organic matter) in the subsurface; for example, Williams et al. (2006) observed significant sorption of carbamazepine to soil. Artificial sweeteners have recently been applied as wastewater tracers, with acesulfame showing much promise as a conservative tracer for wastewater in groundwater (Buerge et al., 2009; Van Stempvoort et al., 2011a). However, there may be issues with landfill sources (Van Stempvoort et al., 2011b) and urban background levels, i.e. groundwater affected by food and beverage spills and infiltration of city water supplies sourced from rivers receiving treated wastewater. The use of multiple wastewater tracers is a tool that can be employed to increase the confidence of identifying wastewater. For example, Seiler et al. (1999) concluded that the co-occurrence of nitrate, caffeine and pharmaceuticals is an "unambiguous" indication of domestic wastewater contamination, "except under unusual circumstances."

Urban hydrologic environments have a myriad of potential wastewater sources that can impact groundwater. These include intentional releases from water treatment plants, such as soil aquifer treatment, in which partially treated wastewater is infiltrated through soil to groundwater for further "purification" in the subsurface (e.g., Idelovitch and Michail, 1984; Drewes et al., 2006; Scheurer et al., 2009). Wastewater is also released to the subsurface from domestic septic systems (e.g. Ingallinella et al., 2002; Katz et al., 2011). But there is also unintended and largely unknown leakage from sewers (e.g., Rieckermann et al., 2010; Wolf et al., 2012) and holding reservoirs. Surface water bodies that receive wastewater may also be sources where they recharge the groundwater (Buerge et al., 2009). Given this complexity, simple detection of a wastewater impact may not be sufficient. Indeed, it will often be desirable to learn whether more than one wastewater source was involved in contamination of groundwater within a given area, while also confirming specific wastewater sources.

Here we propose that the use of a wide spectrum of wastewater tracers, including both those considered nearly-ideal (e.g. acesulfame) and others less-than-ideal (e.g., a plume-specific pharmaceutical compound), could serve to distinguish single from multiple wastewater sources in groundwater. A key aspect is incorporating both ubiquitous and non-ubiquitous tracers, because non-ubiquitous tracers may help identify specific wastewater sources, for example if unique tracers are present in wastewater derived from individual household septic systems.

1.1. Objectives and approach of this study

The main objective of this study was to field-test the idea that an array of common co-tracers of wastewater could distinguish between groundwater affected by single and multiple wastewater sources. We selected an array of anthropogenic chemicals, predominantly artificial sweeteners and pharmaceuticals, as candidate co-tracers of wastewater. We also analyzed chloride, which is a chemically conservative anion often detected at elevated concentrations in wastewater plumes.

Two urban sites were selected where shallow groundwater impacted by wastewater was discharging to streams. One site is adjacent to a municipal waste lagoon, while the other is in a residential area serviced through individual septic systems. At both sites shallow groundwater samples were collected at close intervals (about 5–20 m) along a single stream reach. Given their close spacing, and the inferred cross-plume orientation of the stream-reach transects (Table 2; Section 2.2), we suggest that any samples collected from the same plume would contain residual wastewater tracers of very similar age and composition. Conveniently, this should limit the temporal effects on tracer concentrations, from source composition or attenuation processes along the flow path, which are unknown.

1.2. Theory

In order to differentiate the impacts by different wastewater sources on groundwater at each site, correlation analysis and the spatial distributions of the co-tracers were considered. For two or more samples from the same plume, we expect all nearly-ideal co-tracers to be strongly correlated. For example in the case of two tracers (Tr1, Tr2), we expect the ratio of their concentrations (C_{Tr1}/C_{Tr2}) to remain the same during dilution by mixing with groundwater that lies outside of the plumes (Fig. 1), as through mechanical dispersion. Adding more tracers gives greater confidence in identifying a plume. For example, with three tracers we expect strong correlation between all three, and nearly-constant ratios of their concentrations: C_{Tr1}/C_{Tr2}, C_{Tr1}/C_{Tr3} and C_{Tr2}/C_{Tr3}.

When sampling two or more plumes, ubiquitous co-tracers could have different concentration ratios (Fig. 1), thus weakening their correlation. Non-ubiquitous co-tracers potentially allow an even better differentiation of plumes, by either their presence or absence (Fig. 1). Pharmaceuticals may be especially useful in this regard for individual household septic plumes given some of their highly-specific (thus non-ubiquitous) usage for various medical conditions. However, if any of the co-tracers are measured at concentrations close to their detection limit, then non-detections could yield false negatives in dilute samples. Non-ubiquitous co-tracers may even be useful when they are only detected in a few samples when correlation analysis cannot be practically applied.

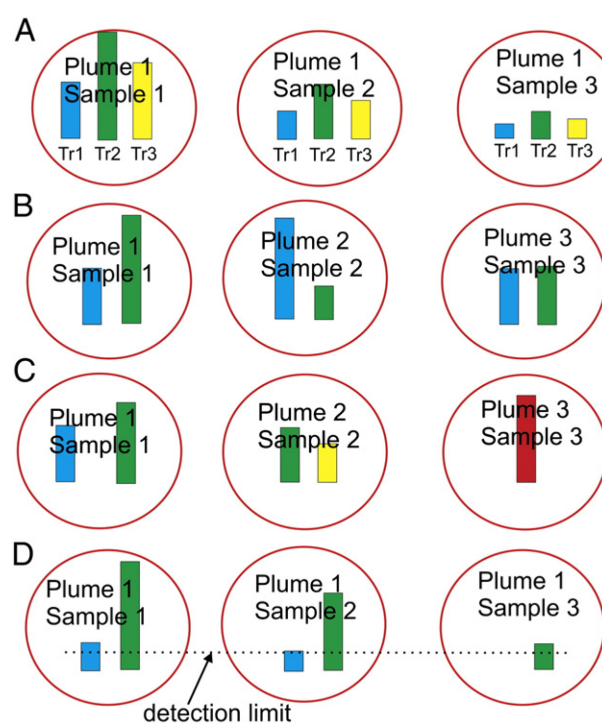

Fig. 1. Illustration of four hypothetical scenarios of the use of multiple tracers. (A) For two or more samples from same wastewater plume, we expect nearly-ideal tracers to be strongly correlated, and ratio of their concentrations (e.g., C_{Tr1}/C_{Tr2}) to be unaffected by dilution. (B) When sampling two or more plumes, ubiquitous tracers could have different concentration ratios, and thus be weakly correlated. (C) Non-ubiquitous tracers potentially allow better differentiation of plumes, by presence/absence of various tracers (D). Tracers measured close to their detection limits could yield false negatives or false positives.