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Characterizing pharmaceutical, personal care product, and hormone contamination in a karst aquifer of southwestern Illinois, USA, using water quality and stream flow parameters

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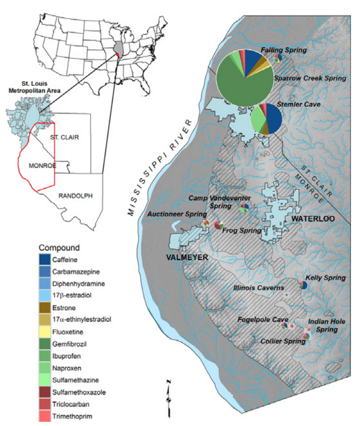
HIGHLIGHTS

- Karst aquifers are vulnerable to surficial contaminants due to their geology.
- Pharmaceutical, personal care product, and hormone levels were measured.
- 49 other water parameters, such as microbiota and ions, were measured.
- 89% of karst aquifers had pharmaceuticals and other products; 23% had hormones.
- Gemfibrozil levels were significantly related to overall PPCP contamination.

GRAPHICAL ABSTRACT



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ABSTRACT

Karst aquifers are drinking water sources for 25% of the global population. However, the unique geology of karst areas facilitates rapid transfer of surficial chemicals to groundwater, potentially contaminating drinking water. Contamination of karst aquifers by nitrate, chloride, and bacteria have been previously observed, but little knowledge is available on the presence of contaminants of emerging concern (CECs), such as pharmaceuticals. Over a 17-month period, 58 water samples were collected from 13 sites in the Salem Plateau, a karst region in southwestern Illinois, United States. Water was analyzed for 12 pharmaceutical and personal care products (PPCPs), 7 natural and synthetic hormones, and 49 typical water quality parameters (e.g., nutrients and bacteria). Hormones were detected in only 23% of samples, with concentrations of 2.2–9.1 ng/L. In contrast, PPCPs were quantified in 89% of groundwater samples. The two most commonly detected PPCPs were the antimicrobial triclocarban, in 81% of samples, and the cardiovascular drug gemfibrozil, in 57%. Analytical results were combined with data of local stream flow, weather, and land use to 1) characterize the extent of aquifer contamination by CECs, 2) cluster sites with similar PPCP contamination profiles, and 3) develop models to describe PPCP

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contamination. Median detection in karst groundwater was 3 PPCPs at a summed concentration of 4.6 ng/L. Sites clustered into 3 subsets with unique contamination models. PPCP contamination in Cluster I sites was related to stream height, manganese, boron, and heterotrophic bacteria. Cluster II sites were characterized by groundwater temperature, specific conductivity, sodium, and calcium. Cluster III sites were characterized by dissolved oxygen and barium. Across all sites, no single or small set of water quality factors was significantly predictive of PPCP contamination, although gemfibrozil concentrations were strongly related to the sum of PPCPs in karst groundwater.

1. Introduction

Worldwide, karst areas comprise 20% of land mass (White et al., 1995) and karst aquifers are a source of drinking water for 25% of the population (Ford et al., 2007a). Karst areas are characterized by relatively soluble bedrock that form solutionally-enlarged crevices, conduits, caves, sinkholes, and sinking streams (Ford et al., 2007b; Weary and Doctor, 2014). These features facilitate the transport of surface waters into underlying karst aquifers with little of the remediation that is characteristic of percolation through soils (White et al., 1995). Because of this rapid transport, karst aquifers are highly vulnerable to surficial contaminants from surface waters in their watersheds (Drew and Hötzl, 1999; Ford et al., 2007a; Kačaroğlu, 1999; United States Department of Agriculture and Natural Resources Conservation Service, 2006).

Municipal and rural wastewater treatment plant effluents, septic tank effluents, and animal manure are the main sources for a variety of contaminants in surface water. In these waters, variable amounts of particular contaminants may be present, such as nitrates in animal lagoon water (33–1370 mg/L) and septic tank effluent (0.5–78 mg/L) (Bradford et al., 2008; Robertson et al., 2016). Contaminants of emerging concern (CECs), including pharmaceuticals and personal care products (PPCPs) and hormones, are frequently detected in a variety of surface and ground waters (Erickson et al., 2014; Kolpin et al., 2002; Kuroda et al., 2012; Lee et al., 2009; Sui et al., 2015). PPCPs been measured at levels of $<$0.29–5030 ng/L in the effluent of a rural wastewater treatment plant in Illinois, USA, and at $<$0.01–1280 ng/L in the receiving river (Li et al., 2013). Septic tank effluent has contained PPCPs at 0.01–6.8 μg/L (Carrara et al., 2008) and animal lagoons have contained antibiotics at 2.5–1000 μg/L (Campagnolo et al., 2002). CECs are a particular environmental concern due to known and suspected effects on aquatic biota, even at low concentrations (Madsen et al., 2004; Peng et al., 2014; Schwaiger et al., 2004; Wollenberger et al., 2000).

Only a few works have investigated CECs in karst aquifers. The hormone 17β-estradiol was measured in a karst aquifer of Arkansas known to be impacted by poultry operations (Peterson et al., 2000) and karst springs in Missouri (Wicks et al., 2004). In a German karst catchment impacted by urban and industrial uses, 7 PPCPs were detected in about 10% of groundwater samples, with individual concentrations occasionally exceeding 100 ng/L (Reh et al., 2013). Hillebrand et al. (2012) estimated that untreated sewage accounted for 0.4% of water entering a different German karst aquifer, and proposed that caffeine could be used as a marker of recent sewage leaks. In previous studies, no other water quality markers, such as ions or nutrients, were evaluated. Also, many had limited temporal scope or only a few CECs were investigated (Hillebrand et al., 2012; Metcalfe et al., 2011; Peterson et al., 2000; Wicks et al., 2004).

In this study, karst groundwater from the Salem Plateau of southwestern Illinois was analyzed for a suite of 12 PPCPs, 7 hormones, and 49 other water quality parameters (including nutrients, ions, bacteria). PPCPs were selected for inclusion in the study based on their frequency of environmental detection, a range of commercial applications, potential wildlife impacts, and physicochemical properties (Anderson et al., 2010; Li et al., 2013; Peng et al., 2014). Data on local stream discharge, weather, and land use were also assembled. The gathered data were statistically assessed to understand the overall extent and characteristics of PPCP contamination of karst groundwater in southwestern Illinois. This research has created a vital foundation informing future management actions needed to protect drinking water sources and ecosystem integrity in this karst area.

2. Materials and methods

2.1. Study area

The Salem Plateau of southwestern Illinois forms a sinkhole plain on the western margin of the Illinois Basin. Approximately 15,000 sinkholes, numerous large springs, and the longest caves in the state are found here (Panno, 1996; Panno and Luman, 2012). The upland area is principally covered with Illinoian glacial till and residuum that are overlain by easily-eroded, wind-blown loess to a depth of about 10 m (Piskin and Bergstrom, 1975). Steep sinkholes lead into caves and other shallow karst conduits, ultimately resurging at springs which drain the karst terrain. Caves in the region are inhabited by the Indiana bat (*Myotis sodalis*) and the Illinois Cave Amphipod (*Gammarus acherondytes*) (Aley and Moss, 2001), both of which are federally-listed endangered species.

The Salem Plateau is included in the United States Department of Agriculture Major Land Resource Area 115B. Land use in this area is mixed, including agriculture (32%), forests (29%), grassland (19%), and urban areas (15%) (United States Department of Agriculture and Natural Resources Conservation Service, 2006). In areas under agriculture, it is usual for animal manure to be applied to fields. Livestock also commonly graze in watersheds of several sample locations (Table 1), but there are no large animal feeding operations in the karst region. Most residential dwellings have septic systems, which may feature leach fields, sand filters, or aeration systems. These systems are irregularly maintained (Michaud, 2005) and commonly contaminate the underlying groundwater with nutrients, sodium, chloride, pathogenic viruses, and pathogenic bacteria (Aley and Thomson, 1984; Bigari, 1994; Borchardt et al., 2003; Panno et al., 2007; Scandura and Sobsey, 1997).

Table 1
Site name, watershed basin size, and land uses for each sampling site.

Site name	Basin size (km^2)	Land uses
Auctioneer Spring	0.6^D	Forest, houses, row crops
Camp Vandeventer Spring	16.3^C	Forest, houses, row crops
Collier Spring	20.5^B	Forest, grassland, houses, livestock, row crops
Falling Spring	1.5^D	Forest, houses, row crops
Fogelpole Cave 1	3.4^D	Forest, houses, row crops
Fogelpole Cave 2	10.6^D	Forest, houses, row crops
Fogelpole Cave 3	0.2^D	Forest
Frog Spring	5.7^A	Forest, houses, livestock, row crops
Illinois Caverns	5.4^B	Forest, houses, row crops
Indian Hole Spring	18.5^B	Forest, grassland, houses, livestock, row crops
Kelly Spring	14.0^B	Forest, houses, livestock, row crops
Sparrow Creek Spring	18.5^B	Forest, houses, row crops
Stemler Cave	10.2^B	Forest, houses, livestock, row crops

A - Aley and Moss, 2009. B - Aley et al., 2000. C - Aley and Moss, 2001. D - estimated from topography and surface and sub-surface drainage patterns.