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Detecting sulfamethoxazole and carbamazepine in groundwater: Is ELISA a reliable screening tool?[☆]

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ABSTRACT

In recent years, numerous studies have reported the prevalence of organic micropollutants in natural waters. There is an increasing interest in assessing the occurrence and transport of these contaminants in groundwater because a large number of people in the United States rely on groundwater for their drinking water. However, commonly used mass-spectrometry-based analytical methods are expensive and time-consuming. The enzyme-linked immunosorbent assay (ELISA) method offers an inexpensive analytical alternative that provides semi-quantitative results in a relatively quick timeframe. We investigated the use of ELISA for two commonly detected micropollutants, sulfamethoxazole (SMX) and carbamazepine (CBZ), in groundwater collected as part of two different studies, one in Minnesota and the other in Iowa. The ELISA results were compared with two mass-spectrometry-based methods: (1) direct aqueous injection-high performance liquid chromatography/tandem mass spectrometry (HPLC) and (2) online solid-phase extraction with liquid chromatography/electrospray ionization-mass spectrometry (SPE LC). Differences in SMX and CBZ observations between ELISA and both HPLC and SPE LC were analyzed using the Paired Prentice-Wilcoxon test. Estimates of bias and limits of agreement between paired observations also were calculated. The SMX determinations by ELISA yielded results that were 30 and 14% greater than HPLC and SPE LC, respectively. The CBZ determinations by ELISA yielded results that were 25 and 9% greater than HPLC and SPE LC, respectively. The ELISA determinations were in presence-absence agreement with HPLC for 83% of samples for SMX and CBZ; and with SPE LC for 76 and 80% of samples for SMX and CBZ, respectively. Results indicate that ELISA for SMX and CBZ is a reliable and cost effective screening-tool alternative to more commonly used mass spectrometry-based analytical methods.

1. Introduction

Micropollutants, including pharmaceuticals, are synthetic and naturally occurring chemicals that are currently unregulated by Federal, State, or Tribal agencies. Many micropollutants have been detected in groundwater nationwide (Barnes et al., 2008). Micropollutants commonly enter the aquatic environment through discharge of wastewater effluent (Kolpin et al., 2002), combined sewer outfalls (Raghav et al., 2013), or septic system effluent (Conn et al., 2006). Although these sources may not discharge directly to groundwater, the potential for micropollutants to reach groundwater resources may exist depending on geology, hydrology, or other factors. There is an increasing interest in assessing the occurrence and transport of micropollutants in groundwater because groundwater provides ~57 percent of the drinking water in the United States (Maupin et al., 2014).

Although treating wastewater discharge is critical to public health, it can be a major pathway of micropollutants such as sulfamethoxazole (SMX) and carbamazepine (CBZ) to the environment (Kolpin et al., 2002; Loos et al., 2013; Miége et al., 2009). Wastewater can be discharged directly to surface waters, as is common practice for wastewater treatment plants (WWTP), or can infiltrate to groundwater through land application of wastewater. Recent estimates indicate that there are ~15,000 WWTPs nationwide servicing approximately 76% of the nation's population (ASCE, 2017). Although WWTPs typically discharge to surface waters, the potential may exist for infiltration of surface water to groundwater.

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Another common wastewater treatment practice is large capacity septic systems, which are used by small communities. More than one in five homes are served by small or large septic systems which treat more than four billion gallons of sewage a day (USEPA, 2012). Although both treatment practices are generally efficient at removing traditional pollutants such as nutrients, several studies have shown that wastewater-derived micropollutants can persist through advanced wastewater treatment (Cordy et al., 2004; Carrera et al., 2008; Phillips et al., 2015). Furthermore, some micropollutants transform to more problematic chemicals in the environment and many have chemical properties that make them resistant to natural biodegradation (Raghav et al., 2013) raising concerns for human and wildlife exposure.

Analytical methods for micropollutant determinations in the environment have been advancing as research has grown more prevalent. These methods include high performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS, herein referred to as HPLC) and solid-phase extraction with liquid chromatography/electrospray ionization-mass spectrometry (SPE LC/ESI-MS, herein referred to as SPE LC) and were developed to obtain the precision and sensitivity required to quantify pharmaceuticals present in water samples at trace concentrations. The evolution of these analytical methods involves different materials and methods used for extraction to minimize matrix effects during the analysis (Fatta et al., 2007). The advantage to using mass-spectrometry-based analytical methods is that these methods can analyze many compounds at once. In the last few decades, enzyme-linked immunosorbent assay (ELISA) methods have become available as an alternative to mass-spectrometry-based methods for determining the presence of target micropollutants or a group of immunologically similar compounds in the environment. The ELISA method provides an inexpensive, semi-quantitative alternative to mass-spectrometry-based methods, with the potential benefit of detection of immunologically similar chemicals, including degradants and metabolites (Bradley et al., 2014; Close and Rosen, 2001).

Despite this newer, more efficient technology, few studies have used ELISA methods to screen environmental samples for the presence of micropollutants. The cost savings and time efficiency of ELISA methods, make ELISA a potentially valuable method for screening environmental samples for the presence of micropollutants. Comparisons between ELISA and other, more conventional methods have been conducted for atrazine (Close and Rosen, 2001), organic pollutants such as polycyclic aromatic hydrocarbons (Castillo et al., 1998), and glyphosate (Byer et al., 2008). Bradley et al. (2014, 2016a) used ELISA for determinations of SMX and CBZ, which are good indicators of anthropogenic influences because of their persistence through conventional treatment processes and thus are often detected in the environment (Clara et al., 2004; Hendricks and Pool, 2012). Despite these handful of studies comparing ELISA results to mass-spectrometry-based analytical methods, in-depth comparisons between methods have not been reported. Although the previously published analyses indicate good association between ELISA and other methods, the conclusions are based on correlation but not agreement between the two methods (Bradley et al., 2014, 2016a; Byer et al., 2008; Castillo et al., 1998; Close and Rosen, 2001). Both correlation and agreement focus on the association between two variables, but agreement also considers the degree of concordance between two variables (Altman and Bland, 1983).

In this study, we evaluate the use of ELISA for determining the presence of SMX and CBZ in groundwater. Results from two studies in which SMX and CBZ concentrations were concurrently determined by ELISA and other commonly used analytical methods (HPLC and SPE LC) were compared. The objective of this analysis was to determine the agreement of measurement between ELISA and the mass-spectrometry-based analytical methods, as well as, assess the potential of ELISA as a reliable, efficient, and cost-effective screening tool for determining the presence of SMX and CBZ in groundwater samples.

2. Materials and methods

2.1. Site description

Data used for this analysis were compiled from two studies. The first focused on identifying the presence of micropollutants in shallow groundwater near wastewater land application sites. The second focused on pharmaceutical fate in a wastewater-facility-impacted stream reach (Bradley et al., 2014, 2016a).

Nine shallow groundwater monitoring wells located northwest of Minneapolis, Minnesota (Fig. 1) were sampled for the presence of a broad suite of micropollutants, including SMX and CBZ. The nine monitoring wells are located near facilities that use land application practices for treating wastewater or irrigation. Each well is located in a surficial sand-and-gravel aquifer setting where the water table is shallow and vulnerable to contamination. Average water levels ranged from 0.6 to 12.5 m below land surface.

A total of 20 shallow groundwater sites along a stream reach near a WWTP outfall near Ankeny, Iowa (Fig. 1) were sampled for a broad suite of micropollutants. Details are provided in Bradley et al. (2014). Briefly, a network of piezometers was installed along a 100 m reach of the stream upstream and downstream from the WWTP outfall. Piezometers were installed to depths of 2.25–2.50 m below land surface.

2.2. Sample collection

Shallow groundwater monitoring wells were sampled in September 2014, May 2015, and August 2015 using a submersible groundwater pump (Grundfos, Downers Grove, Illinois); two (W1 and W2) were sampled only in May and August, 2015. Prior to sample collection, at least three well volumes were pumped from the well and physical water-quality characteristics (temperature, dissolved oxygen, pH, and specific conductance) were allowed to stabilize, consistent with standard USGS sampling protocols (U.S. Geological Survey, variously dated). Physical water-quality characteristics were measured with a Yellow Springs Instrument (YSI, Yellow Springs, Ohio) 6820 water-quality multiprobe meter by pumping groundwater through a flow-through chamber. Samples were collected for analysis of SMX and CBZ by ELISA, HPLC, and SPE LC. During sample collection, all samples were filtered using a 0.7 μm glass-fiber filter and after collection, all samples were immediately put on ice, kept at a temperature of <4 °C, and shipped to the analyzing laboratory within 24 h. Piezometer samples were collected similar to methods described above; samples were collected using a peristaltic pump after purging the piezometer for 10 min (Bradley et al., 2014). Piezometers were sampled a total of seven times between October 2012 and October 2014.

2.3. Laboratory analyses

The following laboratory analysis and laboratory quality assurance/quality control sections detail methods used for data collected during the Minnesota study. Except for the online solid-phase extraction with liquid chromatography/electrospray ionization-mass spectrometry method, which was not used in the Iowa study, methods are similar between the two studies. Details regarding analysis and quality assurance/quality control for the Iowa study can be found in Bradley et al. (2014, 2016a, 2016b).