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Natural attenuation of pharmaceuticals and an illicit drug in a laboratory column experiment

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HIGHLIGHTS

- Methamphetamine, caffeine, and acetaminophen are attenuated in the columns.
- Biodegradation is influenced by the geologic material.
- The sand had little to no biodegradation.
- The undisturbed sediments showed biodegradation.
- Methamphetamine biodegraded less in the presence of the other pharmaceuticals.

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ABSTRACT

Trace amounts of pharmaceutical compounds have been detected in waters across the United States. Many compounds are released as the result of human ingestion and subsequent excretion of over-the-counter and prescription medications, and illicit drugs. This research utilized columns (30 × 30 cm) of sand and undisturbed fine-grained sediments to simulate injection of wastewater containing pharmaceuticals and an illicit drug, such as would be found in a septic system, leaky sewer, or landfill. The columns were placed in a temperature-controlled laboratory and each was injected with natural groundwater containing known concentrations of caffeine, methamphetamine, and acetaminophen. Natural attenuation of each chemical was observed in all columns. The highest amount removed (approximately 90%) occurred in the undisturbed column injected with methamphetamine, compared with little reduction in the sand column. When the suite of drugs was injected, loss of methamphetamine was less than when methamphetamine was injected alone. The subsurface sediments exhibit the ability to remove a substantial amount of the injected pharmaceuticals and illicit drug; however, complete removal was not achieved. There was little attenuation of injected pharmaceuticals in the sand column which demonstrates a concern for water quality in the environment if pharmaceuticals were to contaminate a sandy aquifer. Understanding the transport of pharmaceuticals in the subsurface environment is an important component of protecting drinking water supplies from contamination.

1. Introduction

Every day millions of Americans consume a vast array of pharmaceuticals, from common over-the-counter medications to prescription and illicit drugs. Much of the consumed medication is absorbed and metabolized by the body, but a percentage passes through unchanged and is excreted into wastewater (Ternes and Joss, 2006). This wastewater eventually finds its way back into the hydrologic system. A study in 2002 by the United States Geological Survey (USGS) conducted a large scale sampling of 139 streams across 30 states and detected 82 of the 95 targeted compounds including antibiotics, steroids, and endocrine disrupting compounds (EDCs; Kolpin et al., 2002). Though groundwater is generally considered to be less vulnerable than surface water, detectable levels of pharmaceuticals have also been found in groundwater (Drewes et al., 2003; Godfrey et al., 2007; Langford et al., 2011). Likely sources for pharmaceuticals in groundwater include septic tank effluent, leaking landfills, direct injection of treated wastewater, and leaking sewer lines (NGWA, 2008).

Illicit drugs are also finding their way into the environment in increasing concentrations. The abuse and manufacture of methamphetamine is on the rise in the United States, especially in rural areas (USDOJ, 2000). In the State of Illinois between 1994 and

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2003, the number of clandestine methamphetamine manufacture labs rose from 24 to 971 per year with 75% of all labs located rurally (TASC, 2005). Approximately one-fourth of homes in the United States utilize septic systems for wastewater discharge (USEPA, 2005) with the vast majority located in rural areas where traditional methamphetamine production methods are greatest, thus allowing for methamphetamine and other pharmaceuticals to enter the subsurface via numerous leachate fields. Previous studies have focused on methamphetamine detection in wastewater treatment systems (Jones-Lepp et al., 2004; Castiglioni et al., 2006) and in environmental surface applications (Caldicott et al., 2005), but no studies have been done on methamphetamine fate in the subsurface environment. Protection of groundwater resources across the nation is vital to help ensure access to an adequate supply of drinking water. In Illinois where the subsurface columns used within that study were extracted, approximately one-third of all households, businesses, industry, and farms depend on groundwater to supply their needs (NGWA, 2013). Nearly 45% of the state's drinking water wells draw their supply from glacial deposits, many of which are at shallow depth and have little protection from contamination (ISGS, 2009). Nationwide, fresh groundwater was withdrawn at a rate of 83.3 billion gallons per day in the year 2000 (USGS, 2005).

Caffeine is one of the most studied pharmaceuticals in the environment. It has been detected in streams across the nation (Kolpin et al., 2002; Guo and Krasner, 2009). Previous research utilizing microcosms have been done to determine the photodegradation of caffeine (Lam et al., 2004), a stream bed sediment and stream water microcosm study has shown that caffeine can have greater than 95% degradation within 32 d (Bradley et al., 2007), and a microcosm study quantified biodegradation of caffeine in liquid municipal biosolids within agricultural soils from the surface where it was most persistent in silt loam soil, followed by sandy loam and loam soils (Topp et al., 2005). Drewes et al. (2003) sampled groundwater wells downgradient of recharge basins with source waters from wastewater treatment plants. While caffeine was detected in treated effluent, it could not be detected in any of the well samples. Godfrey et al. (2007) also sampled groundwater as well as septic system effluent from a small high school. Caffeine was detected in the high school septic system effluent, but was not found to be in the sand and gravel aquifer located beneath a two-meter sand vadose zone under the leach field. However, Godfrey et al. (2007) did detect caffeine in a second sand, gravel, and cobble unconfined aquifer that is overlain by septic systems and a city sewer system. This demonstrated that caffeine can be transported through groundwater systems and into groundwater aquifers.

Acetaminophen has been detected in surface waters across the United States (Kolpin et al., 2002) and has been included in aqueous microcosm studies such as one testing the photodegradation (Lam et al., 2004). A field study of pharmaceuticals in septic systems did detect acetaminophen in the septic tank effluent of a small high school, but not in the underlying sand and gravel aquifer after the effluent had percolated through a sand vadose zone about two meters in thickness (Godfrey et al., 2007). However, research is still needed on the natural attenuation of acetaminophen in other subsurface environments.

Many other chemicals from agricultural fertilizers to industrial solvents have been studied for their persistence in the environment, with recent research beginning to include pharmaceutical compounds. While pharmaceuticals and illicit drugs have been detected in subsurface water sources, few studies have examined the natural attenuation of these substances after release into the subsurface from septic systems, leaking sewer pipes, and leaky landfills. This study utilized a controlled laboratory setting to focus on natural attenuation of caffeine, methamphetamine, and acetaminophen. These controlled experiments simulate the natural subsurface environmental setting while decreasing possible anomalies that could have occurred from natural variability. Both illicit (methamphetamine) and commonly used drugs (caffeine and acetaminophen) were chosen, as all are likely to be found in the same effluent system. Large scale (30 cm × 30 cm), undisturbed fine-grained sediment columns were extracted from the subsurface and sand columns were constructed to: (1) determine if natural attenuation of methamphetamine in the porous media can occur; (2) determine if the presence of multiple pharmaceuticals (caffeine, methamphetamine, and acetaminophen) influences the amount of natural attenuation of methamphetamine; and (3) determine whether the porous medium (sand vs. undisturbed sediments) affects natural attenuation of the pharmaceuticals and methamphetamine.

2. Materials and methods

2.1. Field site and column construction

This study utilized the design and procedures employed by a previous investigation of BTEX (benzene, toluene, ethylbenzene, and xylenes) contaminants in undisturbed sediment columns (Lenczewski et al., 2007). The soil used in the columns was collected from a depth of 0.9 – 1.3 m at Eco Park on the northwestern corner of the Northern Illinois University, DeKalb campus. These sediments were extracted from the weakly developed modern soil located immediately above the Tiskilwa Till Member of the Wedron Formation (ISGS, 1971). Sediments near this depth are those that would receive discharge from subsurface septic system leach fields in the area, thus allowing simulation of a leach field containing pharmaceuticals.

A total of three undisturbed columns of soil were extracted from the DeKalb area subsurface to a final size of 30 cm in diameter by 30 cm in length (Fig. 1). Column material was determined by hand texturing to be silty clay with very few small gravels on the USDA soil classification scheme. Matrix colors were determined using a Munsell Soil Color Book and were determined to be 5Y 6/2, 5Y 4/1, 2.5Y 3/1, and 10YR 2/1, with redox features of 10YR 6/8. There were numerous small fractures as well as relict and modern animal burrows. The columns exhibited little to no lateral heterogeneity. The site sediments were characterized as having a porosity of 0.28, a bulk density of 1.7 g cm^{-3}, and a f_{oc} of 0.01 which was the same as previous experiments using the same soil (Leal-Bautista and Lenczewski, 2004). Undisturbed fine-grained sediments at the site were also modeled using VisualMODFLOW Pro

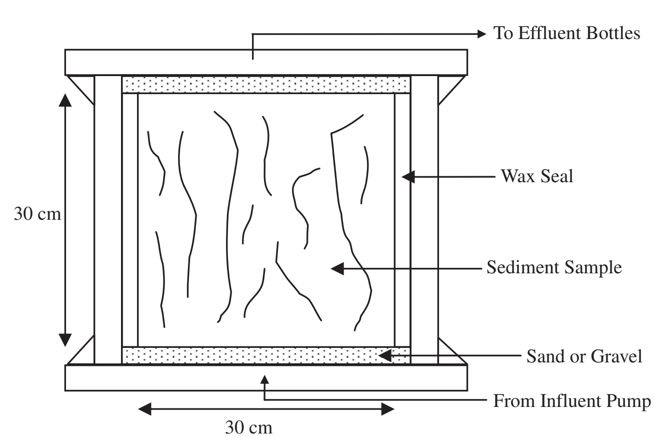

Fig. 1. Cross section through column showing construction details. (Modified from Lenczewski et al., 2007.)