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Short Communication

Pilot survey of methamphetamine in sewers using a Polar Organic Chemical Integrative Sampler

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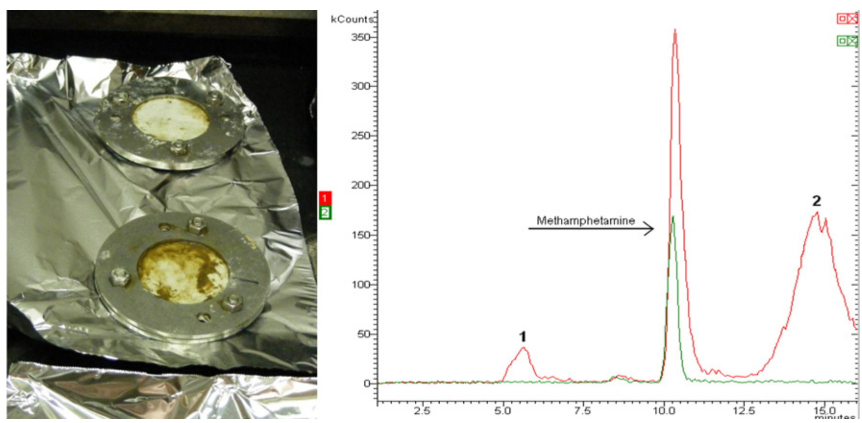
HIGHLIGHTS

- Polar Organic Chemical Integrative Samplers (POCIS) were deployed into sewer lines.
- Proof-of-concept was established for using POCIS devices in the sewage system.
- POCIS sorbent extracts were analyzed via HPLC–MS/MS.
- Methamphetamine was detected within the sewage collection system.
- The data encourage research for future use as a forensic tool in law enforcement.

GRAPHICAL ABSTRACT



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ABSTRACT

A pilot study for the qualitative detection of methamphetamine at sites within a sewage collection system adjacent to locations suspected to harbor illegal drug activities was investigated and preliminary findings are reported. Sewage samples were collected over a time interval of four weeks using a Polar Organic Chemical Integrative Sampler (POCIS) deployed directly into the sewer line. The POCIS sorbent was extracted and analyzed via high-performance liquid chromatography tandem mass spectrometry (HPLC–MS/MS). Methamphetamine was found in sewage from one of three sampling sites at a concentration greater than the HPLC–MS/MS method detection limit (MDL) of 3 ng/mL. The goal of this research was to establish proof-of-concept of the feasibility for sampling and analysis using POCIS devices in the sewage collection system. The data encourage further testing and research. The ability to pinpoint the presence of methamphetamine in the sewer may in the future be used as a forensic tool in law enforcement.

1. Introduction

Methamphetamine — also known as "meth," "speed," and "crank," — is a highly addictive, powerful nervous system stimulant. Because methamphetamine is so addictive, it is illegal to manufacture or use methamphetamine, except by prescription, under U.S. Federal Law. In the United States, the Drug Enforcement Administration (DEA) classified methamphetamine as a Schedule II substance, available only by prescription but

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rarely prescribed (DEA Fact Sheet: Methamphetamine, 2013). Methamphetamine is illegally sold in pill, capsule, powder, and chunk form. In its pure form, the hydrochloride salt of methamphetamine is yellow to colorless, although the street drug may be colored due to impurities. The drug can be created cheaply and easily in clandestine, "clan," labs and can be smoked, snorted, inhaled, or injected. Because methamphetamine is so cheap and easy to produce, clandestine labs have proliferated and have been found in all states of the United States. In 1993, DEA officials estimated that 218 labs existed; in 2004 almost 15,000 labs were seized (109th Congress Report, House of Representatives, 2013). In Tennessee, USA, law enforcement agencies across the state have encountered approximately 7600 clandestine methamphetamine labs from 1998 to present (Cleanup of Methamphetamine Contaminated Properties, 2013).

Illicit drugs, such as methamphetamine, can enter source waters through wastewater treatment plant effluents (i.e., human excretion), and via manufacturing in clandestine laboratories (USEPA, 2008). Pharmaceutical and personal care products (PPCPs) in the environment are not regulated in the United States but enter the urban water cycle and have the potential to negatively affect water quality. Upon contamination of a water source, methamphetamine produced in a clandestine laboratory cannot be distinguished from methamphetamine consumed and excreted by humans.

Based on published reviews from both the United States and Europe (Vazquez-Roig et al., 2013; Zuccato and Castiglioni, 2009, 2011; Kasprzyk-Hordern, 2011; van Nuijs et al., 2011; Castiglioni and Zuccato, 2010; Boles and Wells, 2010; Castiglioni et al., 2008), measurable concentrations of amphetamine and methamphetamine — two of a class of drugs known as amphetamine-type stimulants (ATSs) — have been found in wastewater, biosolids, surface water, and sediment. Local news reports have chronicled several instances of clandestine methamphetamine laboratories and arrests for methamphetamine possession and abuse, lending credence to the hypothesis that it would be found in wastewater. However, no previous studies have been conducted to detect the presence of methamphetamine directly from sewer pipes.

Wastewater and surface water samples for research are generally collected through traditional water sampling techniques, such as grab sampling or composite water sampling. A grab sample is collected simultaneously in its entirety and reflects a single data point in time, while a composite sample involves collecting discrete samples taken at specific intervals of time and combining them at the end of the sampling period into a single sample. The composite sample reflects an average concentration of the analyte in the water source over the sampling time period. However, grab samples, and even composite samples, only capture information at that moment or over a specified short sampling period. In addition, grab and composite sampling techniques may miss important events, such as high or low flow, precipitation, and variability in chemical loading.

As an alternative, passive sampling devices are being used to monitor hydrophilic/hydrophobic contaminants such as pesticides, PPCPs, and illicit drugs in aqueous environments, and are designed to stay in the aqueous environment for several days, weeks, or even months (Harman et al., 2012). The Polar Organic Chemical Integrative Sampler (POCIS) device combines the ability to integrate exposure over time during a range of hydrologic conditions with the ability to accumulate a detectable mass of a compound that may be present in a water sample at concentrations below the method detection level (Alvarez et al., 2005). The design of the POCIS device allows it to mimic the exposure of the respiratory system of aquatic organisms to dissolved chemicals (Alvarez et al., 2004). POCIS samplers have been employed for quantitative identification of numerous wastewater-related contaminants, including methamphetamine in surface water (Jones-Lepp et al., 2012; Bartelt-Hunt et al., 2009), sediment (Alvarez et al., 2012), and wastewater (Harman et al., 2011; Bartelt-Hunt et al., 2009; Jones-Lepp et al., 2004). POCIS sampling rates (a value needed for quantitative back-calculation of environmental concentrations) have been determined for some compounds, including methamphetamine (Bartelt-Hunt et al., 2009, 2011; Harman et al., 2011; Alvarez et al., 2007). However, even though the membrane in POCIS devices is not as subject to biofouling as other membrane types (Alvarez et al., 2004), biofouling can still occur, causing uptake kinetics and subsequently, laboratory-derived calibration data to be modified (Mills et al., 2007).

The goal of this research was to establish a proof-of-concept regarding the feasibility for sampling and analysis in the sewage collection system and to provide a qualitative assessment of the occurrence of methamphetamine using POCIS, because raw sewage near the source is not as dilute as wastewater influent, and is more likely to cause biofouling of the POCIS device. Therefore, the research reported in this paper focuses on the preliminary findings from a pilot study that used POCIS devices to monitor raw sewage for methamphetamine in the sewage collection system before the raw sewage reaches a wastewater treatment plant. The ability to pinpoint the location of methamphetamine in the sewer may at some time in the future be used as a forensic tool in law enforcement.

2. Material and methods

2.1. POCIS deployment and sampling

Sampling occurred at sites in Cookeville, TN, USA that were known hotspots for drug activity because information about methamphetamine-related arrests is published regularly in the local newspaper. POCIS devices were deployed in three different sewer lines originating from three buildings suspected to harbor illegal drug activities. For privacy purposes, the sites will be referred to as Site 1, Site 2, and Site 3. Although deployment canisters can be used to house the devices, the small size of the sewer pipes tested in this research prevented the use of canisters, such that two devices were held together with a plastic zip tie and were placed inside city-owned sewer lines at the junction between the private sewer line and the city-owned line. The samplers were deployed for a total sampling period of 27 days.

2.2. POCIS characteristics

AQUASENSE-P POCIS devices were obtained from Environmental Sampling Technologies (St. Joseph, MO) as based on a patented design (Petty et al., 2002) consisting of 200 mg of Oasis hydrophilic-lipophilic balanced (HLB) sorbent contained between two membranes made of hydrophilic polyethersulfone (PES) with a 0.1 μm pore size and a 41 cm^2 surface area. Upper and lower stainless steel support rings are used to seal the device and prevent loss of sorbent. Although two POCIS devices were used for sampling each site, the devices were extracted separately. Extraction of the POCIS devices and HPLC–MS/MS analysis for methamphetamine are described in supplementary data associated with this manuscript.

3. Results and discussion

3.1. Pilot monitoring using POCIS devices

The POCIS device configuration used in this research consisted of 200 mg of Oasis HLB sorbent sandwiched between PES membranes with a surface area of 41 cm^2 as purchased from the manufacturer. This construction meets standardized surface area to sorbent/lipid volume (SA/V) specifications described by Alvarez et al. (2007, 2012). Pharmaceutical POCIS devices are designed to be appropriate for most pharmaceuticals and contain only HLB sorbent, as opposed to the pesticide POCIS devices that contain three different sorbents and target pesticides as well as hormones and wastewater treatment chemicals. HLB sorbents are made by polymerizing divinylbenzene (lipophilic) and *N*-vinylpyrrolidine (hydrophilic) monomers. They are capable of extracting acidic, basic and neutral analytes, which may be polar or nonpolar. Methamphetamine — a weak base — is a 2° amine with a $pK_a = 10.38$. No sorbents other than HLB were tested in this research.