



Determination of emerging contaminants in wastewater utilizing comprehensive two-dimensional gas-chromatography coupled with time-of-flight mass spectrometry



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ABSTRACT

An analytical method for identification of emerging contaminants of concern, such as pesticides and organohalogens has been developed and utilized for true discovery-based analysis. In order to achieve the level of sensitivity and selectivity necessary for detecting compounds in complex samples, comprehensive gas chromatography coupled with time-of-flight mass spectrometry (GC × GC–TOFMS) was utilized to analyze wastewater samples obtained from the Pennsylvania State University wastewater treatment facility (WWTF). Determination of emerging contaminants through a process of combining samples which represent “normal background” and comparing this to new samples was developed. Results show the presence of halogenated benzotriazoles in wastewater samples as well as soil samples from Pennsylvania State University agricultural fields. The trace levels of chlorinated benzotriazoles observed in the monitoring wells present on the property indicate likely environmental degradation of the chlorinated benzotriazoles. Preliminary investigation of environmental fate of the substituted benzotriazoles indicates their likely degradation into phenol; an Environmental Protection Agency (USEPA) priority pollutant.

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1. Introduction

The toxicological effects of unrecognized emerging contaminants in the environment have long been a point of interest among environmental scientists [1]. One well-known example of the dangers of environmental pollutants is the “Love Canal” incident, where residents were forced from their homes due to the presence of 19,000 metric tons of chemical waste once dumped below the surface [2]. More recently, hundreds of thousands of West Virginia residents were without water for days due to the negligent storing of 4-methylcyclohexanemethanol (used as a coal cleaning agent) which caused a massive chemical spill in to the Elk River, Charleston’s main water source. The company responsible, Freedom Industries, ultimately declared bankruptcy in January 2014 [3]. After such instances, investigations into the cause and clean-up are often lead by government agencies such as the U.S. Environmental Protection Agency (USEPA), the Centers for Disease

Control and Prevention (CDC) and The Chemical Safety Board. The approach can be categorized as “reactive”, in that the source of contamination is determined after a problem is known to exist.

The importance of determining the presence of emerging contaminants is outlined as one of the top five goals of the Strategic Plan (2000) for the U.S. Environmental Protection Agency’s (USEPA) Office of Research and Development. The focus of environmental forensics has primarily been on acutely toxic/carcinogenic pesticides and industrial intermediates considered “priority” pollutants that demonstrate environmental persistence. Unfortunately, the compounds that fall under this characterization represent only a small fraction of the chemicals present in the environment [4]. Additionally, present analytical methodologies mainly focus on individual compounds, rather than the mixtures that contain the compounds. As a result, environmental scientists have a limited understanding of the complete contaminant profile in a particular event [5].

Due to the multitude of tests required to not only identify the contaminant, but also determine its source, environmental forensics has traditionally been extremely time consuming. For the approach to change from reactive to proactive, a representative matrix is needed for the identification of emerging contaminants

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in the environment. Wastewater contains compounds and their respective metabolites which are continuously introduced into the aquatic environment as complex mixtures. As a result, wastewater is a commonly used matrix for analyzing environmental samples. In the past, environmental scientists have analyzed wastewater for several contaminant classes, including illicit drugs, pharmaceuticals and personal care products (PPCPs) and endocrine disruptors [6–8]. Through these studies, the relevance of utilizing wastewater to determine contaminants in environmental samples is evident.

Discovery analysis utilizing wastewater and other complex matrices requires a separation technique capable of distinguishing the thousands of potential compounds present in a sample. When the source, transport and fate of contaminants are of concern, traditional methodologies have utilized gas-chromatography–mass spectrometry (GC–MS) as the dominant instrumentation [9–11]. GC–MS methods have been developed for the identification and quantification of “priority contaminants” in water such as polychlorinated biphenyls (PCBs), pesticides, estrogenic compounds and polycyclic aromatic hydrocarbons (PAHs) [12–15]. Despite the ability of these methods to determine the presence of specific compounds, the complexity of wastewater or soil matrices often does not allow for sufficient separation using traditional gas chromatography. When analyzing samples containing more than 150–250 relevant compounds, the separation power of traditional (single column) gas chromatography decreases and has limited peak capacity [5]. Comprehensive two-dimensional gas chromatography (GC × GC) has been demonstrated as a technique capable of enhanced separation of compounds within a complex matrix [16–19]. The two orthogonally aligned columns are comprised of two different stationary phase chemistry which allows for the increased peak capacity. In order to produce narrow bands in the second dimension column, a quad-jet cryogenic modulator (LECO, St. Joseph, MI) is utilized in order to trap and refocus analyte bands as they elute from the first dimension column. The decrease in band width is primarily responsible for the increase in sensitivity. It is due to these features that two-dimensional gas chromatography has been demonstrated as having the capability to resolve an order of magnitude more compounds from a complex matrix than traditional methods [9]. One example is the application of two-dimensional gas chromatography to the petrochemical industry, specifically the determination of oil spill sources [20]. Additionally, Focant et al. [21] and Megson et al. [22] have developed a method to improve the separation of 209 polychlorinated biphenyl congeners.

With the increased peak capacity of two-dimensional gas chromatography comes a need for a detector capable of rapidly acquiring the large packets of data generated during the separation. Additionally, the narrow second dimension peaks produced during cryogenic modulation require a mass spectrometer capable of fast scanning rates for improved compound identification in complex matrices. With the addition of automatic spectral deconvolution, co-eluting compounds can be distinguished based on mass spectral data. Coupling fast-scanning time-of-flight mass spectrometry (TOFMS) with comprehensive two-dimensional gas chromatography provides the capabilities necessary for identification of compounds within a complex matrix.

Traditionally, discovery based analysis of complex samples utilizing the technique described above requires a sophisticated and knowledgeable analyst. The large number of peaks produced necessitates the analyst be capable of rapidly determining peak identity and isolating compounds of interest. This process is time consuming as most environmental samples are complex and contain background analytes introduced via normal biological processes. In order to reduce data processing time, a “normal” background can be defined in order to subtract previously recognized compounds from subsequent samples to then identify emerging contaminants of interest. Once the “normal” background of a particular matrix

has been established, this same procedure could be applied to other samples of interest.

2. Materials and methods

2.1. Water sample preparation

The Pennsylvania State University Wastewater Treatment Facility (WWTF) (Office of the Physical Plant, State College, PA) was used as a control facility to refine analytical methodology. Over the course of a year several water samples were collected throughout the various steps in the treatment process into clean 4 L amber glass bottles. At the PSU WWTF, influent sewage is divided into two separate flow streams, with one serving the Pennsylvania State University Campus and one serving the borough of State College. Wastewater samples were also collected from the pre-treatment settling tanks as well as post-treatment water tanks. Settling tanks are used as a first treatment step to separate the solid material inherent to wastewater. The Pennsylvania State University WWTF participates in a unique open loop system in which treated water is discharged onto over 600 acres of farmland and forest area that act as a “living filter”. The living filter system was proposed in the 1960s after it was determined Pennsylvania State University chemical dumping was killing fish in Spring Creek [23]. This filter acts as an intermediate step to further treat the water before it is introduced into Spring Creek, and represents an additional “purification” step that most WWTF systems would not employ. This system works by removing treated effluent from the facility and transferring it to the farmland located off campus. The water then enters the sprinkler system and is distributed to the various areas in the field. As a result, soil samples, spray water and monitoring well water were also able to be collected into 500 mL amber glass jars for additional analysis. Soil samples were collected from several areas; two from lines actively spraying, and two from a line sprayed in the last few days. Both surface soils and soils 6 inches from the surface were collected. Additionally, water directly from sprinkler head was collected.

Samples were extracted and concentrated to a final volume of 2 mL from a nominal starting volume of 500 mL, which was removed from the homogenized 4 L collection sample, following a modified USEPA 3510c extraction technique [24]. Three recovery standards were spiked into the samples in final extract concentration of 200 pg/μL: QuEChERS internal standard mix for GC–MS analysis (cat# 33267), acid surrogate mix (cat# 31025) and revised B/N surrogate mix (cat#31024) (Restek Corp., Bellefonte, PA, USA). These standards were chosen as they contain environmentally relevant compounds such as polychlorinated biphenyls (PCBs) and cover a wide range of both acidic and basic compounds. These compounds are listed in Table 1. Each sample was serially extracted three times under acidic conditions (pH = 2) and three times under basic conditions (pH = 11) using dichloromethane as the extraction solvent (Avantor, Center Valley, PA, 18304 cat# 9264-03). If an emulsion occurred, the sample was centrifuged for 3 min at 3000 rpm (IEC Centra-8 Centrifuge, Geneva 20-Switzerland) in order to achieve necessary separation of phases. Kuderna–Danish evaporation was then used to concentrate samples to a final volume of 2 mL. Internal standards, SV internal standard mix (Restek Corp., Bellefonte, PA, USA cat# 31885), were added to each sample to result in a final concentration listed in Table 1.

2.2. Soil sample preparation

The soil samples were prepared using a modified USEPA 3550C ultrasonic extraction technique [25]. 30 g of each sample and 60 g of anhydrous sodium sulfate (nominal weights) were weighed (Metler Toledo-MS204S, Columbus, OH) and mixed together in a

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