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Non-target screening and prioritization of potentially persistent, bioaccumulating and toxic domestic wastewater contaminants and their removal in on-site and large-scale sewage treatment plants

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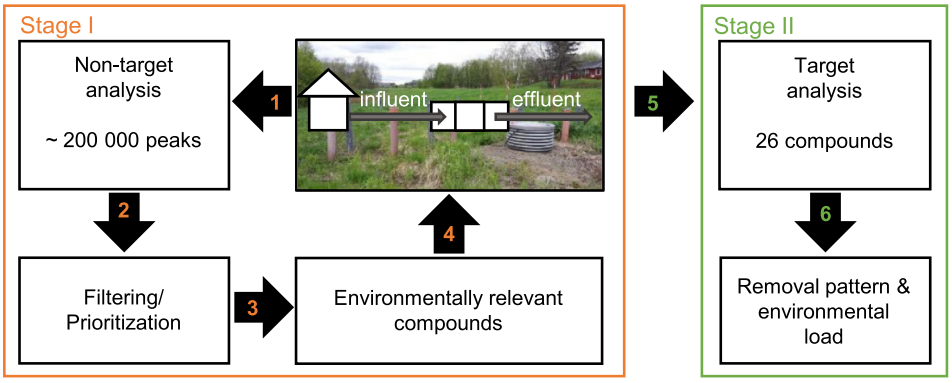
HIGHLIGHTS

- Contaminants emitted from on-site sewage treatment facilities were identified.
- A non-target screening based prioritization strategy was established.
- Top-ranked compounds were found at high levels in a follow-up study.
- TMDD and TBEP were better removed in small than in large plants.
- Hydrophilic compounds were removed less efficiently than hydrophobic compounds.

GRAPHICAL ABSTRACT



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ABSTRACT

On-site sewage treatment facilities (OSSFs), which are used to reduce nutrient emissions in rural areas, were screened for anthropogenic compounds with two-dimensional gas chromatography–mass spectrometry (GC×GC–MS). The detected compounds were prioritized based on their persistence, bioaccumulation, ecotoxicity, removal efficiency, and concentrations. This comprehensive prioritization strategy, which was used for the first time on OSSF samples, ranked galaxolide, α-tocopheryl acetate, octocrylene, 2,4,7,9-tetramethyl-5-decyn-4,7-diol, several chlorinated organophosphorus flame retardants and linear alkyl benzenes as the most relevant compounds being emitted from OSSFs. Twenty-six target analytes were then selected for further removal efficiency analysis, including compounds from the priority list along with substances from the same chemical classes, and a few reference compounds. We found significantly better removal of two polar contaminants 2,4,7,9-tetramethyl-5-decyn-4,7-diol ($p = 0.0003$) and tris(2-butoxyethyl) phosphate ($p = 0.005$) in soil beds, a common type of OSSF in Sweden, compared with conventional sewage treatment plants. We also report median removal efficiencies in OSSFs for compounds not studied in this context before, viz. α-tocopheryl acetate (96%), benzophenone (83%), 2-(methylthio)benzothiazole (64%), 2,4,7,9-tetramethyl-5-decyn-4,7-diol (33%), and a range of organophosphorus flame retardants (19% to 98%). The environmental load of the top prioritized compounds in soil bed effluents were in the thousands of nanogram per liter range,

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viz. 2,4,7,9-tetramethyl-5-decyn-4,7-diol (3000 ng L^{-1}), galaxolide (1400 ng L^{-1}), octocrylene (1200 ng L^{-1}), and α-tocopheryl acetate (660 ng L^{-1}).

1. Introduction

Wastewater is commonly treated in sewage treatment plants (STPs) to reduce the nutrient load into the environment. Whereas centralized STPs are only economically sustainable if the population is dense and large enough, smaller decentralized on-site sewage treatment facilities (OSSFs) provide a larger economic benefit for smaller communities and single households in rural areas (Corcoran et al., 2010). In the United States and Sweden, around 20% (Olshammar et al., 2015; U.S. EPA, 2008) of all households are connected to OSSFs. Sweden has 753,000 OSSFs (Olshammar et al., 2015), of which infiltration systems dominate (25%), followed by septic tanks without further treatment (22%), soil beds (SBs) (16%), grey water separation (17%), and aerobic treatment systems (ATSs) (2%) (Olshammar et al., 2015). Septic tanks consist of a container that retains wastewater and allows for sedimentation to occur. Solids and digested organic matter settle to the bottom, whereas floatable solids rise to the top and are discharged with the effluent from the tank (U.S. EPA, 2000a). These treatment systems are nowadays restricted in Sweden unless they are combined with additional treatment techniques. In soil infiltration systems, the septic tank effluent is infiltrated into the ground at the treatment site to further remove nutrients (macropollutants). SBs are similar to infiltration systems and consist of layers of soil, gravel, and sand that are surrounded by a less permeable material to prevent uncontrolled infiltration (U.S. EPA, 2000b). ATSs exist as continuous or batch-flow systems and are commonly called package treatment plants. By actively aerating the waste water, they promote biological activity and enhance degradation processes (U.S. EPA, 2000c, 2000d).

Like STPs, OSSFs are primarily designed to remove macropollutants and pathogens rather than micropollutants (Petrovic, 2003), but few studies have focused on the occurrence of organic micropollutants in OSSF effluents. Most of these studies have focused on selected target analytes, including fragrances like tonalide (AHTN) (Leal et al., 2010) and galaxolide (HHCB), the biocide triclosan (TCS) (Conn et al., 2010a, 2010b, 2006), the UV filters 2-phenyl-5-benzimidazolesulfonic acid (Leal et al., 2010) and octocrylene (OC) (Leal et al., 2010), nonylphenols (Conn et al., 2010a, 2010b; Stanford and Weinberg, 2010), bisphenol A (BPA) (Conn et al., 2010a), and steroid estrogens (Leal et al., 2010; Stanford and Weinberg, 2010). Such targeted approaches can oversee a large number of potentially relevant compounds. Non-targeted approaches can be used to generate more comprehensive information about contaminants present in a wastewater sample. We have only identified one study where non-targeted screening was used to find contaminants in grey water extracts by gas chromatography–mass spectrometry (GC–MS) (Eriksson et al., 2003). However, this study did not include any environmental relevance prioritization for the 190 tentatively identified components. In addition to concerns for emissions to surface waters, micropollutants that most likely originated from OSSFs have been detected in nearby ground water or drinking water wells, e.g. the pesticide diethyltoluamide (DEET) (Del Rosario et al., 2014), the pharmaceuticals ibuprofen (Carrara et al., 2008; Del Rosario et al., 2014) and sulfamethoxazole (Godfrey et al., 2007), the plasticizer tris(2-butoxyethyl)phosphate (TBEP) (Phillips et al., 2015), organophosphorus flame retardants (OPs) (Schaider et al., 2016), per- and polyfluoroalkyl substances, and steroid hormones (Swartz et al., 2006).

Previous studies have reported similar removal efficiencies for ATSs and STPs (Du et al., 2014; Garcia et al., 2013; Wilcox et al., 2009) and worse removal efficiencies in anaerobic septic tanks compared to aerobic systems (Conn et al., 2006; Du et al., 2014; Garcia et al., 2013; Leal et al., 2010; Wilcox et al., 2009). Removal efficiencies were mainly investigated in lab-scale (Leal et al., 2010; Teerlink et al., 2012) or field-scale experimental facilities (Conn et al., 2010b; Du et al., 2014; Garcia et al., 2013) and rarely at real household or community OSSFs (Conn et al., 2010a, 2006; Wilcox et al., 2009). Furthermore, studies examining the fate of OSSF contaminants in soil are sparse (Carrara et al., 2008; Conn et al., 2010b).

Prioritization strategies based on non-targeted data to identify environmentally relevant contaminants have previously focused on criteria such as ecotoxicity (Bastos and Haglund, 2012), exposure (Rager et al., 2016; Singer et al., 2016) or bioactivity (Rager et al., 2016). Other prioritization/ranking strategies have focused on selected groups of water contaminants, such as active pharmaceutical ingredients. These approaches prioritized based on ecotoxicity data (Sanderson et al., 2004), biodegradation, bioaccumulation and ecotoxicity data (Wennmalm and Gunnarsson, 2005), or prescription dispensation, environmental concentrations, half-lives, octanol-water partition coefficients, and ecotoxicity data (Cooper et al., 2008). Attempts have also been made to start with large inventories of industrial chemicals or pharmaceuticals and use prioritization schemes to identify potentially persistent and bioaccumulating substances (Andersson et al., 2011; Howard and Muir, 2011).

In our study we applied a two-stage strategy (Fig. 1), to increase the knowledge of micropollutants emitted from OSSFs into the environment (Stage I) and to evaluate the treatment efficiency of OSSFs (Stage II). In Stage I, we aimed to identify and prioritize environmentally relevant organic contaminants emitted from OSSFs by using a two dimensional gas chromatography–mass spectrometry (GC×GC–MS) based non-target methodology. The use of GC enabled us to identify persistent and bioaccumulating non-polar compounds, which would be difficult to detect using screening methodologies based on liquid chromatography (LC). Additionally, the use of GC×GC allowed better separation of the analytes from interferences in complex samples without extensive sample preparation. The resulting compounds were prioritized based on removal efficiencies and effluent concentrations along with environmental hazard criteria such as persistence, bioaccumulation potential, and toxicity (PBT), and environmentally relevant target analytes were selected. To widen the physicochemical property domain these target analytes were supplemented with analogues of the same classes of compounds and a few commonly used reference compounds. This facilitated the evaluation of relative removal efficiencies between different contaminants and different treatment technologies, specifically between SBs and STPs, and the quantification of environmental loads in Stage II (Fig. 1).

To the best of our knowledge, our study is the first to use a comprehensive non-targeted approach based on GC×GC–MS, combined with a

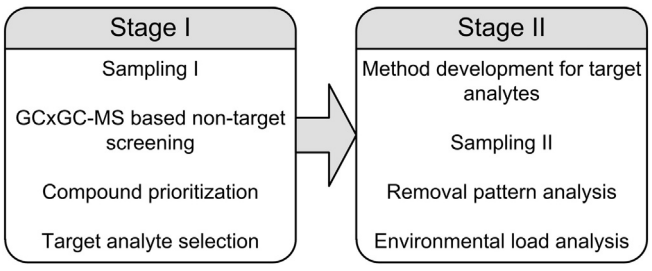

Fig. 1. Design of the study using comprehensive gas chromatography–mass spectrometry (GC×GC–MS).