



## Research article

# Temporal trends of perfluoroalkyl substances in limed biosolids from a large municipal water resource recovery facility



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## ARTICLE INFO

## Article history:

Received 12 December 2014

Received in revised form

28 August 2015

Accepted 17 September 2015

Available online 27 September 2015

## Keywords:

Biosolids

Sewage sludge

Perfluorinated compounds

Perfluoroalkyl substances

Trends

Storage

## ABSTRACT

While the recycling of wastewater biosolids via land-application is a sustainable practice for nutrient recovery and soil reclamation that has become increasingly common worldwide, concerns remain that this practice may become a source of toxic, persistent organic pollutants to the environment. This study concentrates on assessing the presence and the temporal trends of 12 perfluoroalkyl substances (PFASs), pollutants of global consequence, in limed Class B biosolids from a municipal water resource recovery facility (WRRF), also known as a wastewater treatment plant. PFASs are of significant concern due to their extensive presence and persistence in environmental and biotic samples worldwide, most notably human blood samples. Class B biosolids were collected from the WRRF, prior to land-application, approximately every two to three months, from 2005 to 2013. Overall, this study found that concentrations of the 7 detectable PFAS compounds remained unchanged over the 8-year period, a result that is consistent with other temporal studies of these compounds in sewage sludges. From these analyzed compounds, the highest mean concentrations observed over the study period were 25.1 ng/g dw, 23.5 ng/g dw, and 22.5 ng/g dw for perfluorononanoic acid (PFNA), perfluorooctanoic acid (PFOA), and perfluorooctanesulfonic acid (PFOS), respectively, and these compounds were detected at concentrations 2.5–5 times higher than the remaining, detectable PFASs. Furthermore, it was observed that PFOS, while demonstrating no overall change during the study, exhibited a visible spike in concentration from late 2006 to early 2007. This study indicates that concentrations of PFASs in WRRFs have been stagnant over time, despite regulation.

This study also demonstrates that the use of glass jars with polytetrafluoroethylene-lined lids, a common storage method for environmental samples, will not influence PFOA and PFNA concentrations in archived biosolids samples.

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## 1. Introduction

Over the past decade, wastewater treatment plants (WWTP) have been re-engineering their treatment processes to focus on resource recovery, with a name change to water resource recovery facilities (WRRF). Final wastewater solids are recognized as a beneficial soil amendment (biosolids) and can help to enhance nutrient concentrations, cation exchange capacity, soil structure, porosity, water holding capacity, and hydraulic conductivity as well as decrease the bulk density of the soil (Goss et al., 2013; Wang

et al., 2008). Due to the use of biosolids for beneficial soil amendment, concerns have been raised on the current and future trends of persistent organic pollutants in biosolids.

Per- and polyfluoroalkyl substances (PFASs) are a class of anthropogenic compounds that have been utilized in various consumer and industrial products since the 1950s. The distinctive characteristics that result from the numerous C–F bonds within the perfluoroalkyl moiety of these compounds include: oleophobicity, hydrophobicity, as well as chemical and thermal stability (Buck et al., 2011; De Voegt and Sáez, 2006), making them desirable candidates for surfactants, lubricants, textile coatings, and fire retardant foams. The perfluoroalkyl moiety, in conjunction with various chemical structures and hydrophilic functional groups, has

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allowed for the formation of thousands of different PFASs. This extensive use, as well as their stability under various environmental conditions, has led to their eventual release into the environment and subsequent detection and persistence in various environmental and biotic samples worldwide, including: air (Müller et al., 2012), freshwater (Clara et al., 2009; Kovarova et al., 2011), seawater (Benskin et al., 2012), sediment (Clara et al., 2009), arctic snow (Young et al., 2007), biota (Houde et al., 2011; Kovarova et al., 2011), bird eggs (Braune and Letcher, 2013; Gebbink et al., 2011), as well as human blood, milk, and tissue samples (Barbarossa et al., 2013; D'eon and Mabury, 2011; Kannan et al., 2004; Pérez et al., 2013).

Long-chain compounds found within two PFAS subgroups, perfluoroalkyl carboxylic acid (PFCAs) and perfluoroalkane sulfonic acids (PFSAs), have drawn the attention of numerous regulatory agencies worldwide due to their persistence and ubiquitous presence in the environment (European Parliament, 2006; Stockholm Convention, 2011; USEPA, 2006, 2000). In particular, much of the concern from regulatory agencies has been focused on perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) due to their widespread past use and/or formation during manufacturing processes. In the United States (US) several manufacturers have entered a voluntary stewardship program with the US Environmental Protection Agency (USEPA) for the phase-out of PFOA and longer-chain PFCAs, as well as PFOS and PFOS-related compounds (USEPA, 2006, 2000). A directive issued by the European Union (EU) in 2006 restricted the use of PFOS (European Parliament, 2006) and in 2009 PFOS was included in Annex B of the Stockholm Convention on Persistent Organic Pollutants (POPs) (Stockholm Convention, 2011; Zushi et al., 2011). This has led numerous companies to utilize short-chain PFASs within their product formulations as substitutes for the restricted compounds (Ritter, 2010). However, as these chemicals are phased-out in developed countries, there is evidence that in developing countries, such as China, production has increased (Ritter, 2010; Xie et al., 2013; Zushi et al., 2011).

Numerous studies have shown PFCA and PFSA compounds to be present within industrial, commercial, and domestic wastewater treatment processes. These compounds have been detected in both the solid and aqueous phases throughout various treatment stages in WRRFs worldwide (Gómez-Canela et al., 2012; Guo et al., 2010; Kunacheva et al., 2011; Loganathan et al., 2007; Navarro et al., 2011; Sinclair and Kannan, 2006). Mass flow studies of PFCAs and PFSAs in WRRFs have indicated that they are not removed by traditional wastewater treatment and there is a potential for the increase in concentration of some of these compounds during the treatment process (Kunacheva et al., 2011; Sinclair and Kannan, 2006), likely a result of their formation from the biotransformation of other PFAS compounds that act as precursor compounds (Frömel and Knepper, 2010; Parsons et al., 2008; Rhoads et al., 2008; N. Wang et al., 2011). This inability of WRRFs to degrade PFCA and PFSA compounds, as well as their potential to increase in concentration during the treatment process, indicates that the WWT process can become a secondary source of these compounds into the environment. Studies have demonstrated the ability of PFASs, particularly those with a long alkyl-chain, to sorb to various types of wastewater solids (Arvaniti et al., 2014; Zhang et al., 2013; Zhou et al., 2010). In the US, wastewater sludge is often treated for human pathogens, stabilized, and then recycled via land-application (biosolids) for nutrient recovery/soil reclamation (Laternus et al., 2007; NEBRA, 2007; USEPA, 2009), drawing concern over the potential of this matrix to not only contain PFCA and PFSA compounds, but to contribute to their input into the environment. Laboratory and field studies have demonstrated the ability of some PFAS compounds to leach from biosolids into soils

while others may persist in soil surfaces (Milinovic et al., 2015; Sepulvado et al., 2011; Venkatesan and Halden, 2014). Concentrations of PFASs in soils can vary widely, depending on factors including surrounding land use as well as source (industrial versus municipal) of biosolids (if applied) and biosolids loading rates. For instance, a study on PFASs in soils in Minnesota, USA found that concentrations of PFOA and PFOS in soils ranged between less than 0.1 ng/g and above 10,000 ng/g (Xiao et al., 2015). This environmental concern is compounded by evidence of toxicological properties of these compounds (Chen et al., 2014; Ding et al., 2011; Hazelton et al., 2012; Takahashi et al., 2014).

This study focuses on the temporal trends of 12 PFCA and PFSA compounds in limed biosolids collected over an 8-year period from a large municipal WRRF in the US prior to application to agricultural fields. The results help to broaden the understanding of whether overall PFCA and PFSA concentrations are changing in the US as well as determine the change in individual compound compositions in limed biosolids over time. This, in turn, allows for the potential influence that land-applied biosolids may have as a source for PFCA and PFSA compounds in to the environment to be better understood. Finally, the study helps to show whether a commonly used laboratory storage method [jars with polytetrafluoroethylene (PTFE)-lined lids] can impact PFCA concentrations in frozen archived samples.

## 2. Materials and methods

### 2.1. Target analytes

Limed biosolids samples were analyzed for 8 PFCA and 4 PFSA compounds. The target analytes were: perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), perfluorobutanesulfonic acid (PFBS), perfluorohexanesulfonic acid (PFHxS), PFOS, and perfluorodecanesulfonic acid (PFDS). Compound structures are provided in [Table SI-1 of the Supplemental Information](#).

### 2.2. Sample collection and handling

Samples were collected from a large municipal WRRF in the Mid-Atlantic region of the US. The plant serves a region of over 2 million people and has the capacity to treat 1.4 million cubic meters ( $m^3$ ) of raw wastewater per day with an approximate daily average of 1.25 million  $m^3$  of raw wastewater per day. The WRRF consists of primary treatment, secondary treatment, nitrification-denitrification, filtration, and disinfection. Solids from primary treatment as well as the secondary and nitrification treatment processes are thickened, combined, and dewatered through centrifugation. Lime is added to this sludge mixture on a dry weight basis of approximately 15–20% to neutralize pathogenic organisms, classifying the product as Class B biosolids. General characteristics of the biosolids studied are provided in [Table SI-2 of the Supplemental Information](#) (data obtained from the WRRF's routine monitoring program). Biosolids from the WRRF are primarily land-applied to agricultural fields in the surrounding region in accordance with USEPA guidelines (Lozano et al., 2013).

Beginning in 2005, limed biosolid samples were collected approximately every two to three months as part of previous studies on POPs in biosolids (Andrade et al., 2015; Bevacqua et al., 2011). Grab biosolids samples were collected from the WRRF directly after the liming process. In the previous studies, all samples were stored in wide-mouth glass jars as this is the preferred storage method for steroid hormones, triclosan (TCS), triclocarban (TCC),

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