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Phase distribution and removal of pharmaceuticals and personal care products during anaerobic sludge digestion

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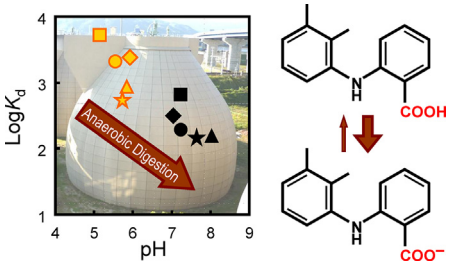
HIGHLIGHTS

- The fate of 48 PPCPs during anaerobic sludge digestion was investigated in STPs.
- We measured concentrations of PPCPs in both the liquid and solid phases of sludge.
- Several antimicrobial compounds remained in digested sludge at mg/kg-dry level.
- The distribution of selected PPCPs between the two phases changed during digestion.
- Triclosan and triclocarban were moderately degraded, while carbamazepine was not.

GRAPHICAL ABSTRACT



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ABSTRACT

The fate and removal of 48 pharmaceuticals and personal care products (PPCPs) during anaerobic digestion of sewage sludge were investigated in four full-scale sewage treatment plants (STPs). We measured concentrations in both the liquid and solid phases of the sludge to compare the distribution ratios (K_d) between phases before and after digestion. The results showed changes in K_d values of PPCPs with carboxyl or amino functional groups, probably due to a shift of dissociation equilibrium with the increase in pH. Sulfamethoxazole and trimethoprim were almost completely degraded (>90%); triclosan, triclocarban, and ofloxacin were moderately degraded (around 30–50%); but carbamazepine was not eliminated. To our knowledge, this is the first report that shows (i) the occurrence and removal of several tens of PPCPs by anaerobic sludge digestion in full-scale municipal STPs and (ii) the change of distribution between the liquid and solid phases during digestion.

1. Introduction

Recycling and reuse of materials have become increasingly important. Treated sludge generated in sewage treatment plants (STPs) can be viewed as a resource [1], providing water, biomass, and renewable energy and materials. Roughly half of the treated sludge generated in STPs is applied (as biosolids) to land in the USA, the EU, and Canada [2], but only about 14% in Japan [3]. Some countries in the EU (e.g., Portugal, UK, Ireland, and Spain) apply agricultural use for more than 60% of sludge disposed [4]. In Spain, the proportion is projected to increase from 65% (in 2006) to 85% by 2015 [5]. However, it is necessary to consider residual contaminants when treated sewage sludge is released into the environment [6], as organic contaminants have been found in both treated sludge and effluent [7–9].

Pharmaceuticals and personal care products (PPCPs) are emerging as contaminants of waters, and their presence, environmental fate, and effect on aquatic organisms have been studied [10].

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Discharge from STPs is a main source of pollutants in receiving waters [11]. Reports of the occurrence of PPCPs and their removal in sewage treatment processes have improved our knowledge of their concentrations and the efficiency of their removal [12,13]. Some PPCPs are removed from water by adsorption onto sludge [14–16]. However, there is little information on their concentrations, fate, and removal of PPCPs in sludge treatment processes, although the fate of endocrine-active compounds has been partially revealed [2].

It is important to understand the fate of newly recognized contaminants during sludge treatment for risk assessment. Residues of multiple PPCPs were found in biosolids in the USA [17]. Land application of reclaimed water and biosolids might lead to contamination of soil and groundwater; recently, PPCPs were found in recycled organic manure produced from sewage sludge [18]. The uptake of PPCPs by plants and their toxic effects when supplied in reclaimed wastewater and biosolids have been reported [19]. In addition to their effects on the environment, their effects on biological treatment processes should be taken into account; for example, antibiotics could harm the microbial community in sewage treatment systems, especially methanogens, which are vital to anaerobic sludge digestion [20].

Anaerobic digestion, one of the major methods of sludge stabilization, reduces the load of organic chemicals and pathogens, and is used to treat approximately 30% of thickened sludge (on a dry-solids content basis) in Japan [3]. It is now attracting attention for energy and resource recovery, and will gain in importance in the future. Several research papers have been published on the occurrence, fate and effects of emerging contaminants during sludge anaerobic digestion [21]. Until now, however, there has been very limited information on those of PPCPs. Regarding the occurrence, several PPCPs were found in anaerobically digested sludge at concentrations ranging from μg/kg-dry to mg/kg-dry [22–25]. However, the concentrations of PPCPs in both the liquid and solid phases of sludge were rarely considered, which led to limited information on distribution characteristics between phases (e.g., distribution ratio (K_d)) [26]. K_d value enable easy prediction of the concentration in digested sludge and the residual extent in solid of treated sludge (e.g., dewatered or dried sludge). Carballa et al. [27] studied the behavior and removal of 13 PPCPs during anaerobic digestion of sludge in lab-scale digesters under different conditions of temperature and solids retention time (SRT). They reported removal efficiencies of targeted PPCPs and observed no influence of temperature and SRT on their removal. The removal efficiencies for norfloxacin and ciprofloxacin were reported by Golet et al. [15] (10% and 11%) and Lindberg et al. [25] (14% and 43%) at one STP in Switzerland and Sweden, respectively. Samaras et al. [28] collected sludge before and after digestion at one STP in Greece and demonstrated that ibuprofen and naproxen were significantly reduced (>80%), while triclosan was slightly removed (around 20%). Thus, the impact of anaerobic sludge digestion on the fate and removal of PPCPs is known for a limited number of compounds.

The objective of this study was to reveal the removal and fate of a number of PPCPs during anaerobic sludge digestion in full-scale STPs. For this reason, we took sewage sludge at the inlet and outlet of anaerobic digestion tank from 4 STPs in Japan and measured the concentrations of 48 PPCPs in both the liquid and solid phases of the sludge, to provide removal efficiencies during anaerobic digestion and K_d values in digested sludge for a wide range of PPCPs.

2. Materials and methods

2.1. PPCPs

We considered 48 PPCPs (Table S1) on the basis of their level and frequency of detection in Japan [29]. All analytical standards and isotopically labeled compounds used as surrogate standards were of high purity (mostly >98%). The variety of chemical structures and therapeutic categories of compounds was wider than reported elsewhere [27]. All standard solutions were prepared in methanol and stored at −30 °C.

2.2. Sample collection and sewage treatment plants

Sampling campaigns were conducted at 4 STPs in the winter of 2010. The STPs are located in the Kansai region (i.e., Kyoto and Osaka prefectures) of Japan, and treat 160,000 to 610,000 m^3/day of municipal sewage from 160,000 to 770,000 people. Sewage water treatment includes primary clarification, biological treatment, secondary clarification, and disinfection by chlorine. The biological treatment consists of a conventional activated sludge process. Primary and waste activated sludges are thickened mainly by gravity sedimentation and then anaerobically digested in mesophilic or thermophilic conditions (Table 1). At STP-A, 2 treatment trains (i.e., processes A-1 and A-2) run in parallel from thickening to digestion of sludge.

Sludge (500 mL or 1 L) was collected as a grab sample at the inlet (thickened sludge) and outlet (digested sludge) of the digestion tank at each STP (Fig. S1). At STP-B, thickened primary sludge and waste activated sludge were separately put into the digestion tank, so each was collected and analyzed separately. The theoretical concentration of PPCPs in the thickened sludge at STP-B was estimated from the concentrations in the primary and waste activated sludges with consideration of the flow of each. At the other STPs, a mixture of thickened primary and waste activated sludges was collected, except in process A-2, where only thickened waste activated sludge was put into the digestion tank. At the outlet of the digestion tank at STP-A, the supernatant liquor was additionally collected, because sludge is separated into digested sludge and the supernatant liquor in the second digester tank at this STP. The number of samples taken from each STP was 6, 4, 2, and 2 samples from STP A, B, C, and D, respectively.

Table 1
Operational conditions of the targeted anaerobic digesters and characteristics of sludge.

STP	Process	Origin of sludge[a]	Flow (m^3/day)	SRT (day)	Temp. (°C)	Biogas (m^3/day)	VSS reduction (%)	Thickened sludge			Digested sludge		
								TSS (g/L)	VSS (%)	pH	TSS (g/L)	VSS (%)	pH
A	A-1	P, W	190	30	30	4700	63	21	88	5.9	11	73	7.0
	A-2	W	180	30	32	4000	60	28	78	5.1	11	59	7.2
B		P, W	750	19	36	11,000	58	34	87	5.5	16	74	7.2
C		P, W	440	25	51	9500	64	46	82	5.8	17	62	8.0
D		P, W	760	20	55	16,000	58	50	81	5.7	21	64	7.6

[a] P: primary sludge; W waste activated sludge; SRT: solids retention time; TSS: total suspended solids; VSS: volatile suspended solids.