Journal of Environmental Management 153 (2015) 1–10

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Pharmaceutical residues in sewage sludge: Effect of sanitization and anaerobic digestion

Jonas Malmborg [a, *], Jörgen Magnér [b]

[a] Tekniska verken i Linköping AB (publ.), Department of Biogas R&D, P.O. Box 1500, SE-58115 Linköping, Sweden
[b] IVL Swedish Environmental Research Institute Ltd, P.O. Box 21060, SE-10031 Stockholm, Sweden

ARTICLE INFO

Article history:
Received 30 October 2014
Received in revised form
20 January 2015
Accepted 26 January 2015
Available online 31 January 2015

Keywords:
Sewage sludge
Anaerobic digestion
Sanitization
Pharmaceuticals
Micropollutants

ABSTRACT

The fate of pharmaceutical residues in treatment of WWTP sludge was evaluated during mesophilic anaerobic digestion (AD) and six sanitization technologies (pasteurization, thermal hydrolysis, advanced oxidation processes using Fenton's reaction, ammonia treatment, thermophilic dry digestion, and thermophilic anaerobic digestion). Sludge spiked with a selection of 13 substances was used and in total 23 substances were detected. A correlation between substance lipophilicity and sludge partitioning was found after sample centrifugation, with e.g., SSRI drugs (90–99%) and estrogens (96–98%) mainly found in the solid phase. A correlation between lipophilicity and persistence of pharmaceutical residues during AD was also detected, indicating that hydrophobic substances are less available to degrading microorganisms. Overall, AD was found to be the most effective technology in reducing a wide spectrum of organic substances (in average ca 30% reduction). Similar effects were obtained for both AD treatments, suggesting that temperature (mesophilic or thermophilic) is less important for micropollutant reduction. Advanced oxidation processes using Fenton's reaction also affected several compounds, including substances showing general stability over the range of treatments such as carbamazepine, propranolol, and sertraline. Pasteurization, ammonia treatment, and thermophilic dry digestion exhibited relatively modest reductions. Interestingly, only thermal hydrolysis efficiently removed the ecotoxicologically potent estrogenic compounds from the sludge.

1. Introduction

Pharmaceutical residues pass naturally through the human body and are excreted either as the parent compound or as metabolites into sewage. Many pharmaceutical residues pass through wastewater treatment plants (WWTP) virtually unaffected. When present in the environment above a certain concentration, these compounds can have adverse effects on wildlife. Much attention has been given to their effects on aquatic life (Brodin et al., 2013; Kvarnryd et al., 2011; Metcalfe et al., 2001; Schwaiger et al., 2004; Triebskorn et al., 2007). However, fractions of the residues are sorbed on suspended solids in the wastewater and are therefore found in sludge. The partitioning between water and solids is rapid and is usually at equilibrium before reaching the WWTP (Falås, 2012). In the treatment plant, the solids are commonly separated through sludge sedimentation in primary and secondary clarifiers. There have been several studies on the occurrence of pharmaceutical residues in sewage sludge. Steroid hormones, primarily estrogens, are frequently examined due to their potent effect on the endocrine system. Among the endocrine disruptors, estrone (E1), 17β-estradiol (E2), 17α-ethinylestradiol (EE2), and estriol (E3) have been found to exert the majority of the estrogenic activity in wastewater (Nelson et al., 2007; Salste et al., 2007). In sludge, two studies reported E1, E2, and EE2 at levels between 1 and 50 μg/kg total solids (TS) in different sludge types (Andersen et al., 2003; Ternes et al., 2002). Paterakis et al. (2012) found residues of E2 and EE2 in the same concentration range (3–18 μg/kg TS), but reported a higher range (32–158 μg/kg TS) for E1 in primary and mixed sludge. Other studies have reported higher concentrations,

Abbreviations: AD, anaerobic digestion; AOP, advanced oxidation process; DMSO, dimethyl sulfoxide; E1, estrone; E2, 17β-estradiol; EE2, 17α-ethinylestradiol; HRT, hydraulic retention time; LOQ, limit of quantification; MAD, mesophilic anaerobic digestion; Na_2-EDTA, sodium ethylene diamine tetraacetic acid; NSAID, non-steroidal antiinflammatory drug; OLR, organic loading rate; SSRI, selective serotonin reuptake inhibitor; TAD, thermophilic anaerobic digestion; TH, thermal hydrolysis; TS/VS, total solids/total volatiles; VFA, volatile fatty acids; WWTP, wastewater treatment plant.

* Corresponding author.
E-mail address: malmborgjonas@gmail.com (J. Malmborg).

http://dx.doi.org/10.1016/j.jenvman.2015.01.041
0301-4797/

314–887 μg E1/kg TS in primary sludge and 67–160 μg EE2/kg TS in digested, dewatered sludge (Martín et al., 2015; SEPA, 2008).

Pharmaceuticals targeting the central nervous system can be of a lipophilic nature and therefore bind to solids. Consequently, the selective serotonin reuptake inhibitors (SSRIs) citalopram, fluoxetine, and sertraline have been reported to partition primarily to sludge (Bergersen et al., 2012; Hörsing et al., 2011; Lajeunesse, 2013). Reported levels in digested, dewatered sludge are 460–760 μg/kg TS for citalopram, 39–160 μg/kg TS for fluoxetine, and 380–770 μg/kg TS for sertraline (Fick et al., 2011; Wahlberg et al., 2010). High concentrations in different sludges have also been found for some antibiotics that are electrostatically attracted by the negatively charged sludge particles, e.g., ciprofloxacin (353–3730 μg/kg TS), norfloxacin (300–4328 μg/kg TS), and tetracycline (2430–2700 μg/kg TS) (Kümmerer, 2009; Lindberg et al., 2007; Martín et al., 2015; Wahlberg et al., 2010). Other frequently detected pharmaceuticals in sludge are the anticonvulsant carbamazepine, the antifungal ketoconazole, and the β-blockers metoprolol and propranolol (Fick et al., 2011; Helmfrid and Eriksson, 2010; Jelic et al., 2011; Samaras et al., 2014; Wahlberg et al., 2010; Woldegiorgis et al., 2007). Drugs with a lower tendency for sorption can also be found in sludge due to high mass load in the WWTP, e.g., the stimulant caffeine and the NSAIDs diclofenac and ibuprofen (Carballa et al., 2007; Jelic et al., 2011; Martín et al., 2015; Wahlberg et al., 2010). Thus, a number of pharmaceuticals are repeatedly found in sewage sludge in the concentration range of μg-mg/kg TS.

After sedimentation at the WWTP, the sludge undergoes stabilization, usually by anaerobic digestion (AD) (Appels et al., 2008; Kelessidis and Stasinakis, 2012; Samaras et al., 2014). AD is a biological treatment where the organic matter is microbiologically degraded and biogas (methane and carbon dioxide) is formed. Pharmaceutical residues are affected by AD to different extents and many are still present in detectable amounts in the digested and dewatered sludge (Fick et al., 2011; Lindberg et al., 2007; Wahlberg et al., 2010). The stabilized sludge is used on agricultural land in many countries. Roughly 50% of the treated sludge produced in the EU is applied to land (Kelessidis and Stasinakis, 2012; Martín et al., 2015). In Sweden, 25% is used for agricultural purposes and 50% is used for landfilling or construction work (SEPA, 2013). European Council Directive 86/278/EEC, on the protection of soil, regulates sewage sludge use in agriculture in the EU. In several EU countries, the Directive is complemented by national legislation on soil protection. Such legislation does not include regulation of pharmaceutical residues, but there is increasing societal awareness and debate on the fate of pharmaceutical residues during sludge management. The potential for contaminants to leach from agricultural land treated with biosolids has been demonstrated (Citulski and Farahbakhsh, 2010; McNamara et al., 2009). Another controversy in using sludge on land is the potential for pathogen, virus or parasite infections to be transferred to the environment. This potential is accentuated by few treatment steps to minimize nutrient losses during sludge recycling. Therefore, the Swedish Environmental Protection Agency has issued a proposal on requiring a sanitization step for sewage sludge before it is released into the environment (SEPA, 2013). The main sanitization method used in Sweden today, open storage for 6 months, is not approved by the proposal. Therefore, WWTPs would have to invest in new treatment technologies to meet the proposed regulatory demands, which are likely to come into force on January 1, 2019. The sanitization technologies approved in the proposal include a number of chemical and thermal treatments (SEPA, 2013). All of these reduce the infection risk but not necessarily the risk of pharmaceutical pollution. Therefore the aim of the present study was to inform future choice of sewage sludge sanitization technology by investigating the effect of different treatments on pharmaceutical residues. Pasteurization, thermal hydrolysis (TH), advanced oxidation processes using Fenton's reaction (AOP), ammonia treatment, thermophilic dry digestion, and thermophilic anaerobic digestion (TAD) were included in the study. Furthermore, mesophilic anaerobic digestion (MAD) was included, although it is not approved as a sanitization method by SEPA (2013). To minimize the risk of obtaining inconclusive results due to insufficient concentrations of pharmaceuticals in municipal sludge, sewage sludge was spiked with a selection of pharmaceuticals.

2. Materials and methods

2.1. Selection of pharmaceuticals

A total of 14 pharmaceuticals were selected based on their wastewater mass load, sludge affinity, and ecotoxicology. Trimethoprim, previously reported to be unstable during AD, was also included, as a positive control (Kjerstadius et al., 2012; Narumiya et al., 2013). Ciprofloxacin, citalopram, diclofenac, E2, EE2, fluoxetine, ibuprofen, and sertraline were purchased from VWR (Radnor, USA). Carbamazepine, metoprolol, oxazepam, propranolol, tetracycline, trimethoprim, and the internal standards carbamazepine-$^{13}C^{15}N$ and ibuprofen-D_3 were supplied by Sigma–Aldrich (St. Louis, USA). Other chemicals were obtained from commercial sources.

2.2. Addition of pharmaceuticals to sludge and digestate

Mixed sludge, i.e., primary and secondary excess sludge (approx. ratio 80:20) entering and digestate exiting a full-scale anaerobic digester were both collected at a single occasion from the Nykvarn WWTP in Linköping, Sweden. This plant treats wastewater corresponding to 180 000 person equivalents. Three samples were taken from each matrix for analysis of pharmaceutical background levels.

Oxazepam was delivered as a methanol solution. The other substances were weighed (approx. 30 mg for citalopram and sertraline and 38 mg for the others) on an analytical balance and dissolved in 1.5 mL dimethyl sulfoxide (DMSO). Ciprofloxacin could not be dissolved in DMSO, methanol, or water at neutral pH and was consequently not spiked to sludge or digestate. The solution of tetracycline turned yellowish upon dissolution, indicating immediate degradation, but was still added to the sludge and digestate.

2.2.1. Stock solution A

A 0.5 mL portion of the 12 DMSO solutions was each diluted to 10 mL using methanol. The diluted solutions and 6 mL 1 mg/mL oxazepam in methanol were then transferred to a volumetric flask and methanol was added to a final volume of 250 mL. The final concentrations were 24 mg/L for oxazepam, ca 40 mg/L for citalopram and sertraline and ca 50 mg/L for the remaining 10 substances.

2.2.2. Stock solution B

A 0.5 mL portion of each of the 12 DMSO solutions and 6 mL 1 mg/mL oxazepam in methanol were transferred to a mutual volumetric flask. Methanol was added to reach a final volume of 50 mL. However, precipitation was observed in the volumetric flask and another 5 mL DMSO were apportioned to the solution until it appeared clear. The final concentrations were 109 mg/L for oxazepam, ca 180 mg/L for citalopram and sertraline and ca 230 mg/L for the remaining 10 substances.

2.2.3. Addition of stock solution A to fresh mixed sludge

Three plastic beakers, each containing 3 kg mixed sludge, were