Suominen, K. & Marttinen. S. 2013. Organic pollutants in biogas plant digestates –Environmental burden and risk to food safety. Proceedings of the 33th International Symposium on Halogenated Persistent Organic Pollutants. Daegu, Korea.

ORGANIC POLLUTANTS IN BIOGAS PLANT DIGESTATES - ENVIRONMENTAL BURDEN AND RISK TO FOOD SAFETY

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Introduction

Biogas technology is a sustainable method for managing biodegradable material and for energy production. Sludge from waste water treatment plant (WWTP), sorted municipal biowaste, industrial by-products or animal manure can be used as raw material in biogas plants (BGP). Biogas plant digestates can be used in agriculture as fertilizers or soil improvers. If the raw material for a biogas plant contains organic pollutants, they may end up in the digestate, and finally in agricultural soil. Some of the organic pollutants may have the potential to accumulate in the food chain.

We measured concentrations of polychlorinated dibenzo-*p*-dioxins and furans (PCDD/F), polychlorinated biphenyls (PCB), polybrominated diphenyl ethers (PBDE), polyaromatic hydrocarbons (PAH), bis(2-ethylhexyl) phthalate (DEHP), perfluorinated alkyl substances (PFAS), linear alkylbenzene sulfonates (LAS), nonylphenols and nonylphenol ethoxylates (NP+NPEO), hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA) in digestates from eight biogas plants. Burden of these pollutants into soil after a single addition of digestate was estimated.

Materials and methods

Sampling

Digestates were sampled from eight large biogas plants in Finland, two of them containing two lines with different feeding material. Altogether ten lines were sampled in April, May, September and December 2010, March and June 2011 and in October 2012. Samples were collected as single samples through the reactor discharge valve to the sampling vessels. The matter in the piping was allowed to flow out before the samples were taken. Dry matter contents of the digestates ranged from 0.66 to 9.3%.

Analyses

PCDD/Fs were extracted by ASE-technology using toluene as solvent, cleaned by several column technologies and quantified with GC/HRMS. PCDD/F-analyses were based on standards mod. EPA 1613, mod EPA 8280 and EN 1948-2. The modified method SFS-ISO-17993:2004 was used with PCBs, and the method for PAH-analyses was based on standard ISO 18287. PAHs and PCBs were extracted with toluene and cleaned with florisil. In the PCB-analysis, the solvent was changed to hexane and the sample was treated with sulphuric acid. PAHs and PCBs were quantified by GC/MS-technology. PBDEs were extracted by ASE using dichloromethane as the solvent, cleaned with a silica-aluminum column and quantified by LP-GC/MS/MS. For TBBPA- and HBCD-analysis, internal standards were added and samples were extracted with toluene using an ASE-apparatus. For TBBPA, modif. EPA 1614 was used with derivatization by silylation. TBBPA was analysed using GC/HRMS-technology and HBCD using GC/MS-technology. PFAS were extracted according to methods described by de Voogt et al. (2006)[1] with an extra cleaning step with hexane and analysed with LC-MS/MS. NP+NPEOs were analysed after silylation using GC/MS-technology. LAS C10-C14 was analysed by HPLC/MS-apparatus according to Horizontal Standard N 06, draft 2009, mod. DEHP was extracted by hexane and analysed by GC/MS according to Horizontal Standard N 14, draft 2009, mod.

Results and discussion:

Concentrations of the studied compounds in digestates are displayed in Table 1. Concentrations of PCB_7 (LOQ = 50 µg kg^{-1} dry weight (d.w)) and of HBCD (LOQ = 1000 µg kg^{-1} d.w.) were below limit of quantification (LOQ) in all studied digestates. Some individual high concentrations of pollutants were detected in part of our samples. Concentrations of PCDD/Fs in our samples were between <LOQ and 4.5 ng TEQ kg^{-1} d.w., except in three samples, where concentrations of PCDD/Fs were between 16 and 22 ng TEQ kg^{-1}d.w. Sum concentrations of PBDEs in our samples ranged from 6.4 to 2800 µg PBDE kg^{-1} d.w., but in one sample the concentration was

11,300 µg PBDE kg d.w. Sum concentrations of PAHs in our samples ranged from 0.1 to 2.9 mg PAH kg d.w. with one sample with higher concentration of 21 mg PAH kg^{-1}. Sum concentrations of NP+NPEO were between <LOQ and 20 mg NP+NPEO kg^{-1}, except in two samples from one plant, where concentrations were 52 and 54 mg NP+NPEO kg^{-1} d.w.

The major PBDE-compound was BDE-209 and the major PCDD/F-compound was octachlorodibenzo-*p*-dioxin. Congener profiles of the PCDD/Fs in our samples were similar to the average deposition profile of PCDD/Fs in Finland between 1997 and 2004 with OCDD as the most abundant congener[2]. The major PFAS-compound was perfluorooctane sulphonate (PFOS) and the major PAH-compound was naphthalene.

We calculated the burden of the studied organic pollutants in agricultural soil after a single addition of digestate based on measured pollutant concentrations (Table 2). We assumed that 15 tons of digestate is used per hectare. In practice, the amount used is somewhat different with each digestate and in each field depending on the nutrient and hazardous metal concentration of the digestate and field as well as the plant cultivated. For most of the compounds, a median burden of the pollutants after a single addition of digestate was of the same order of magnitude as air deposition of the same compound or compound group in Finland or other Nordic countries. However, the burden for PBDEs was about 1000 times higher than the PBDE air deposition in Finland. Also the load of NP+NPEO was slightly higher than the deposition reported in Denmark. Large variation in measured concentration of pollutants in digestates meant that the soil burdens of the pollutants also showed large variation.

Use of sludge may increase the concentration of recalcitrant pollutants in agricultural soil. In Germany, compost and sewage sludge applications increased the concentration of PCDD/F in agricultural soil from 1962 until the beginning of the 1980s[3]. After that, the concentration of PCDD/F in agricultural soil has leveled off, probably due to decreased amounts of PCDD/F in sludges, composts and deposition. PFAS[4]- and PBDE-compounds[5] are recalcitrant and these compounds have accumulated in soil, where sludge containing these compounds has been repeatedly used in agriculture. Wild et al. (1990)[6] reported that PAH-compounds have accumulated in soil when heavily PAH-contaminated sludge has been used in agriculture. However, sum concentration of PAH in Wild's study was 20 to 40 times higher than in our study. LAS-[7], NP+NPEO-compounds[8] and DEHP[9] are relatively degradable and they are unlikely to accumulate in soil.

PCBs and PCDD/Fs have a minimal potential to accumulate from soil into plants. Farmed animals can be exposed to PCDD/Fs when grazing on pastureland that has received sludge that contains PCDD/Fs[10]. However, application of sludge to arable land had only a minor effect on human exposure to PCDD/Fs[10]. PCBs in sewage sludge treated soil in Norway unlikely cause significant residues in soil or food products[11]. Khan and Cao (2012)[12] showed that PAH(6)-compounds accumulated from soil in plants, but the sum concentrations of PAHs in soil in their study were 1000 times higher than the calculated sum concentration of PAH(16) after one single amendment of digestate in this study. PAH have low accumulation potential into animals by grazing[13]. DEHP may have potential to accumulate from soil into some plants, but use of sludge likely has a minor importance on occurrence of DEHP in plants[14]. Addition of sewage sludge to pasture is unlikely to cause a large increase in tissue concentration of NP+NPEO or DEHP in pasture animals[15]. PFASs[16] and PBDEs[17] may have potential to accumulate in plants, and especially PBDEs also in food of animal origin[18]. More research is needed on the intake of PFASs by farm animals. In their present level in Belgian food, PFAS-compounds are below the tolerable daily intake (TDI)[19]. For BDE-47, -153 and -209 current dietary exposure to PBDEs in the EU does not raise a health concern[20]. For BDE-99, there is a potential health concern with respect to current dietary intake[20]. BDE-209 was more than 74% of the total concentration of PBDEs in our samples, while the proportion of BDE-99 in our samples was less than 6%.

Based on this study, agricultural use of digestates is unlikely to cause risk to food safety from compound groups other than PBDEs and PFASs. With PBDEs and PFASs, the impact of the use of biological fertilizers on food safety or on human health has not so far been comprehensively assessed.

Acknowledgements:
We thank Sami Huhtala, Helena Pyykkönen and Noora Perkola from the Finnish Environmental Institute for skillful PBDE- and PFAS-analysis and Matti Verta and his colleagues for valuable discussions. We thank the biogas plants and Finnish Water Utilities Association (FIWA) for their cooperation. This study was financially supported by the Finnish Ministry of Agriculture and Forestry.

Table 1. Concentrations of the studied organic pollutants in digestates from ten biogas lines.

Compound group	n	range	mean	median	unit per d.w.
PCDD/F	21	<LOQ–22	3.9	1.5	ng TEQ kg^{-1}
PCB_7	11	< 50	< 50	< 50	µg kg^{-1}
PBDE	16	6.4–11000	1800	1000	µg kg^{-1}
TBBPA	7	0.7–62	25	8.0	µg kg^{-1}
HBCD	7	<1000	<1000	<1000	µg kg^{-1}
PFAS	19	1.0–170	42	19	µg kg^{-1}
PAH(16)	20	0.1–21	2.1	0,7	mg kg^{-1}
NP+NPEO	20	<LOQ–54	11	7.5	mg kg^{-1}
LAS	20	<100–2000	980	1100	mg kg^{-1}
DEHP	20	1–110	230	9.5	mg kg^{-1}

Table 2. Soil burdens of organic pollutants when biogas plant digestates are used in agriculture. Amount of digestate used in agriculture 15 tons ha^{-1}.

Compound group	n	Range	Mean	Median	Atmospheric deposition per year	Unit
PCDD/F	20	<LOQ–17	3.0	1.3	Finland 0.3–1.9[21]	µg TEQ ha^{-1}
PCB	11	<LOQ	<LOQ	<LOQ	Finland 10–150[21]	ng TEQ ha^{-1}
PBDE	16	22–6900	1400	1100	Finland/Sweden 1,1–2,6[21]	mg ha^{-1}
TBBPA	7	0.3–73	20	5.5	n.d.	mg ha^{-1}
HBCD	7	<LOQ	<LOQ	<LOQ	Sweden 0,1–48[22]	mg kg^{-1}
PFAS	19	0.3–150	44	19	Finland/Sweden 78 – 130[23]	mg ha^{-1}
PAH	20	36–18000	1800	630	Finland/Sweden 77–1000[24]	mg ha^{-1}
NP+NPEO	20	<LOQ–49	11	5.0	Denmark 0,1–1,1[25]	g ha^{-1}
LAS	20	<LOQ–2100	820	850	n.d.	g ha^{-1}
DEHP	20	0.4–150	24	6.2	Denmark 1,6–10[25]	g ha^{-1}

n.d. no data available.

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