

OCCURRENCE AND WATER PARTITIONING OF PFOA AND PFOS IN BIOGAS PLANT END PRODUCTS AND UPTAKE BY RADISH

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Introduction

Biogas technology is a competitive process for managing biodegradable wastes and by-products and a green method for energy production. End products from biogas plants (BGP) can be used as fertilizers or soil improvers, which is of prior importance in recycling depleting nutrients, such as phosphorous. Waste water treatment plant (WWTP) sludge, organic biowaste, animal manure, industrial by-products or other organic material can be used as raw materials in BGPs. Many harmful chemicals used in households and industry may end up in these products. When BGP end products are used as fertilizers, these compounds may accumulate into the soil and they may be taken up by edible plants. We analyzed concentrations of perfluorinated octyl acid (PFOA) and perfluorinated octyl sulphonate (PFOS) in digestates from nine BGPs and liquid fractions from mechanical separation of the digestates (reject water) from seven BGPs in Finland.

PFOA and PFOS belong to a diverse group of perfluorinated alkyl compounds (PFAC) that have been used in various applications e.g. electronic parts, fire fighting foams, photo imaging, hydraulic fluids and textiles. The production and use of PFOS, its salts, and perfluorooctane sulfonyl fluoride (PFOS-F) have been severely restricted by the Stockholm Convention in 2009. However, these compounds still exist in the environment since approximately 85% of indirect emissions of PFOS into the environment are a result of losses from consumer products during use and disposal (e.g. from carpets, clothing paper, and packaging)¹.

Materials and methods

Digestate samples from nine BGPs and reject water samples from seven BGPs were collected in March and June 2011. Samples were taken from the process immediately after the biogas reactor. Reject water was separated from the digestate by means of a spin dryer or a filter belt press. Process parameters of the plants as well as raw materials and their approximate ratios are displayed in Table 1.

For plant tests, 100 g of digestate from the plants D and H was mixed per 1 liter of sandy soil (organic C 2% and clay 18%) taken from a conventional agricultural field without any known history of urban waste amendments. Also digestate from a third plant was used in the experiment, but concentrations of PFOA and PFOS from this digestate were not analyzed. We used inorganic fertilizer (NPK) as a control treatment. All treatments had four replicates. Radish (*Raphanus sativus*) was used as a test plant. Plants were grown in 5 liter pots (altogether 6.5 kg of soil-digestate mixture in each) under a glass roof during summer 2011. Pots were watered twice a week with equal amounts of water and no plant protection chemicals were used. After nine to ten weeks, test plants were harvested, roots washed free from soil and delivered to the laboratory for PFOA and PFAS analysis. Root fresh weight yield was lowest (40 g/pot) in the mineral fertilized treatment and highest in the treatment D (100 g/pot).

For PFOA and PFOS analysis, reject water samples were centrifuged and the supernatant was extracted by SPE (Oasis HLB cartridge). Digestate samples were freeze dried, ground and extracted with methanol. The plant samples were extracted and cleaned with a modified QuEChERS procedure. Mass labeled internal standards were added prior to extraction. The obtained extracts were evaporated to dryness and redissolved in methanol. The extracts were analyzed using ultra performance liquid chromatography (UPLC®) coupled with tandem mass spectrometry (MS/MS). LC effluents were water and methanol buffered with ammonium acetate. An isolator column was placed before the injector to delay signals originating from the instrument. The analytes were quantified with triple quadrupole mass spectrometer (Xevo TQ MS, Waters) using electrospray ionization (ESI) and multiple reaction monitoring. The final results were recovery corrected.

Results and Discussion

Dry matter contents of digestate and reject water samples in BGPs are described in Table 1. In most of our samples concentrations of PFOA and PFOS were higher in March than in June (Table 1). These differences can partly be explained by differences in the quality of incoming water from households and industry to the WWTPs. For instance metal plating and other industrial processes can contribute to the elevated PFAC concentrations in effluents to the WWTP², and these emissions can have large temporal fluctuation. Large variations in concentrations of PFOA and PFOS within sludges from an individual WWTP have previously been reported by Ma et al. (2010)³ and by Pan et al. (2010)⁴. PFAC-compounds have been reported to be present in snow and rain water⁵ and street runoff⁶. Thus differences in amounts and quality of storm water may alter amounts of PFAC-compounds in incoming water to the WWTPs receiving runoffs. High differences in concentrations of PFOA and especially PFOS in digestates between sampling times can probably be explained by single lots of PFAC contaminated material (also other than WWTP sludge) in the feed of the BGPs. Also transformation of precursor molecules of PFOA and PFOS to these compounds during the waste water treatment process and anaerobic digestion at the BGPs can affect the concentration of these compounds in digestate⁷. Suggested precursors are fluorotelomer alcohols, fluorotelomer acids, perfluorooctanesulfonamide (PFOSA) and poly-fluoroalkyl phosphates (PAPs).

There was a large variation in concentrations of PFOA and PFOS in the end products between different BGPs. Suominen et al (2011)⁸ reported higher concentrations of chlorinated dibenzo-*p*-dioxins and furans (PCDD/F) and of polybrominated diphenyl ethers (PBDE) in digestates from a BGP that processed only WWTP sludge than in digestate from a plant that processed pig manure. We were not able to show such a clear connection between the concentrations of PFOA and PFOS in BGP end products and origin of raw materials of the BGPs. Variation in concentration of PFAC-compounds between biosludges from BGPs can be large², and our data is too scarce to make rigorous conclusions on the occurrence of these compounds in BGP end products in Finland. Concentrations of PFOA and PFOS in digestates in this study were similar or lower than those reported in activated or digested WWTP sludge in Denmark⁹ or those summarized in different places over the world by Sun et al (2011)².

Figures 1 a and b show that 29 to 54% of the total PFOA and 8 to 22% of the total PFOS in reject waters were in the water phase. This indicates that PFOA and PFOS are relatively water soluble. Lipophilic compounds such as PCDD/Fs have low potential for plant uptake¹⁰. However, plants can take PFAC-compounds with their roots from the soil^{11,12}. Thus we wanted to assess the potential of PFOA and PFOS to accumulate in radish.

Figures 2 a and b show correlations of fresh weight concentrations of PFOA and PFOS in test soils and in radish. Our results suggest that PFOA especially, but probably also PFOS may have potential for accumulating from soil into radish. Stahl et al. (2009)¹¹ and Yoo et al. (2011)¹² reported that PFOA and PFOS can accumulate from soils into potatoes, maize, barley, wheat and perennial ryegrass. Stahl et al. (2009)¹¹ used PFOA and PFOS amended soils with concentrations of ≤ 50 mg of PFOA and PFOS. Yoo et al. (2011)¹² used soils with a known history of PFAC-containing sludge amendments with soil concentrations of 67 to 1750 $\mu\text{g kg}^{-1}$ d.w. of PFOA and 105 and 1160 $\mu\text{g kg}^{-1}$ d.w. of PFOS¹³. Our results suggest that plant accumulation of especially PFOA into radish can be detected even at very low soil concentrations (≤ 200 ng PFOA kg^{-1} f.w. soil).

Dietary intake of PFOA and PFOS dominated overall intake of PFAC-compounds in Belgium, even though dietary intake of PFOS and PFOA remained below the Tolerable Daily intake Level¹⁴. However, attention should be paid to the occurrence of PFAC-compounds in sludges and digestates in agriculture because PFAC-compounds may accumulate in soil if sludge that contains these compounds is repeatedly used as fertilizer¹³. Furthermore, as water soluble compounds PFACs may end up in ground water¹⁵.

Table 1. Dry matter contents, process parameters and concentrations of PFOA and of PFOS in digestates and reject waters from BGPs in the study. Samples were taken in March and June 2012.

Plant	Concentration in digestate ($\mu\text{g kg}^{-1}$ d.w.)			Concentration in reject water (ng l^{-1})			Hygienization or pretreatment of the material (temperature, time)	Process temperature ($^{\circ}\text{C}$)	Materials processed
	PFOA	PFOS	Dry matter content (%)	PFOA	PFOS	Dry matter content (%)			
A March A June	7.35 1.50	109 17.6	6.35 5.25	n.a. 25.6	n.a. 135	n.a. 1.1	70 $^{\circ}\text{C}$, 60 min before the biogas process	55	WWTP sludge 60% Industrial by-products 27% Municipal biowaste 13 %
B March B June	8.29 1.68	20.4 5.33	8.52 8.47	n.a. 47.2	n.a. 20.8	n.a. 0.4	No hygienization	35 to 37	WWTP sludge 99% Industrial by-products 1%
C March C June	6.17 1.16	27.6 3.77	3.69 4.14	n.a. 28.1	n.a. 37.6	n.a. 0.6	70 $^{\circ}\text{C}$, 60 min after the biogas process	37	WWTP sludge 30% Municipal biowaste 65% Industrial by-products 5%
D March D June	6.69 0.82	141 10.5	5.80 6.14	n.a. 11.2	n.a. 75.7	n.a. 0.8	70 $^{\circ}\text{C}$, 60 min after the biogas process	35 to 38	WWTP sludge 54% Pig manure 24% Industrial fat sludge 4% Industrial by-products 18%
E March E June	4.19 0.84	4.29 16.4	3.60 1.95	n.a. 18.4	n.a. 101	n.a. 0.4	70 $^{\circ}\text{C}$ by composting after the biogas process	55	WWTP sludge 91% Industrial by-products 8% Municipal biowaste 1%
F March F June	14.6 0.56	93.5 0.75	2.93 3.49	n.a. 18.0	n.a. 16.3	n.a. 1.6	70 $^{\circ}\text{C}$ by composting after the biogas process	55	Municipal biowaste 100%
G March G June	3.39 0.23	4.15 2.12	2.30 2.12	n.a. n.a.	n.a. n.a.	n.a. n.a.	70 $^{\circ}\text{C}$, 60 min after the biogas reactor	38 to 40	WWTP sludge 56% Retail shop food waste 17% Industrial by-products 27%
H June	0.56	2.38	4.11	n.a.	n.a.	n.a.	70 $^{\circ}\text{C}$, 60 min after the biogas reactor	38 to 40	Municipal biowaste 54% By products from milling 46%
I March I June	n.a. 1.35	n.a. 80.3	n.a. 9.39	186 23.1	873 812	0.65 1.2	150 to 160 $^{\circ}\text{C}$ 30 min before the biogas process	41 to 42	WWTP sludge 100%

n.a.: not analyzed

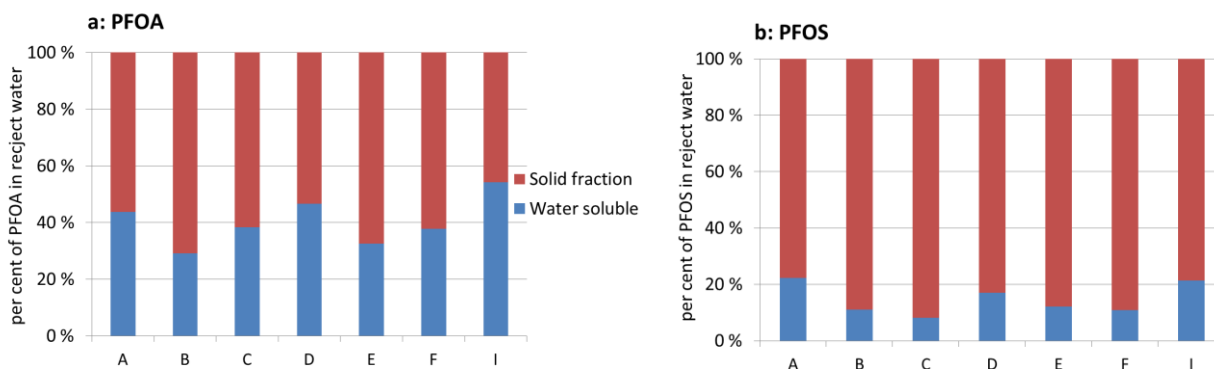


Figure 1a, b. Partitioning of PFOA (a) and of PFOS (b) into solid fraction and water phase in reject waters from seven BGPs. The plants G and H were not analyzed for reject waters.

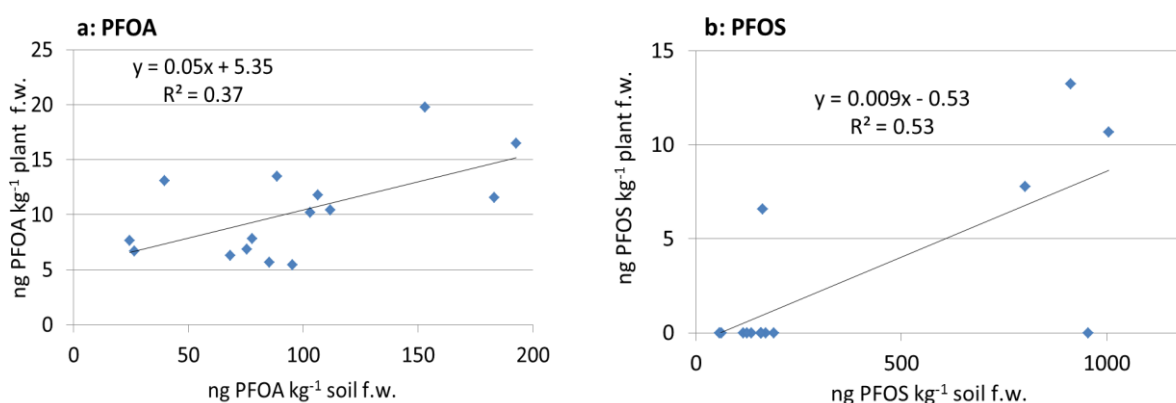


Figure 2a, b. Correlations of fresh weight concentrations of PFOA (a) and of PFOS (b) in soils and in radish.

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