SCREENING OF PERSISTENT ORGANIC POLLUTANTS IN SLUDGE FROM SEWAGE TREATMENT PLANTS IN SWEDEN

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Introduction

Municipal sewage treatment plants (STPs) can be considered as a main route for anthropogenic substances into the environment, thus, sewage sludge is as a relevant matrix in order to estimate the diversity and presence of the many chemicals used in today's society. Sewage sludge contains nutrients, originating from the sewage water, which should be brought back to productive soil, but unfortunately, environmental and health hazards will also accumulate in the sludge. Perfluorochemicals, antibiotics, and triclosan are examples of substances that previously have been detected in sludge.[1,2,3] The purpose of this study was to perform a screening of persistent organic pollutants (POPs), with emphasis on polar substances seldom investigated, in sewage sludge from seven Swedish STPs of different sizes. Their location and size, and type of activity connected to the STPs can be seen in Figure 1.

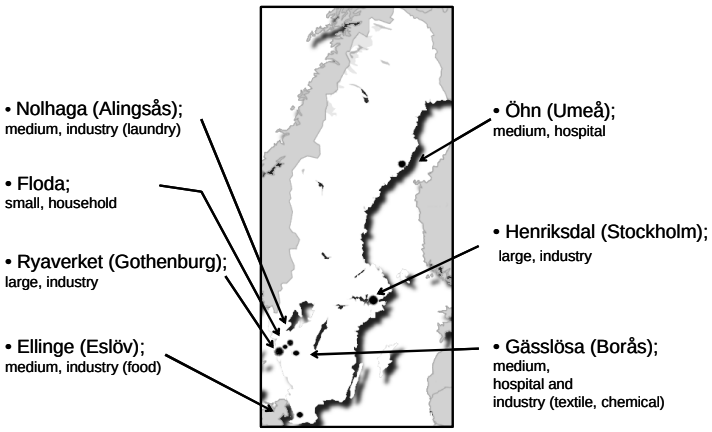


Figure 1. Location, size, and type of activity connected to the investigated Swedish sewage treatment plants.

Materials and Methods

The sewage sludge samples (digested dewatered sludge) were collected at seven different STPs in Sweden in the autumn of 2004. The following plants were investigated: Ryaverket, Gothenburg (STP 1); Nolhaga, Alingsås (STP 2); Öhn, Umeå (STP 3); Henriksdal, Stockholm (STP 4); Gässlösa, Borås (STP 5); Floda (STP 6); and Ellinge, Eslöv (STP 7). The sampling occurred during normal working conditions and after a period of normal weather conditions. Composite samples (n=3) of each STP were collected in dark bottles within one hour after the sludge dewatering and they were stored in the freezer at –18 °C until chemical analysis. The analyses were performed at various Swedish laboratories experienced in the analysis of the target substances.

Results and Discussion

The following POPs have been analyzed in the sludge; phthalates, polybrominated diphenylethers (PBDEs), fluoroquinolones (FQs), triclosan, buthylhydroxytoluene (BHT), organophosphorus (OPs), organotin compounds (OTCs), chlorophenols (CPs), perfluorochemicals (PFCs), polychlorobenzenes (PCBz), polychlorobiphenyls (WHO-PCBs), polychlorinated dibenzo-*p*-dioxins and -furans (PCDD/Fs). In order to illustrate the levels of the POPs out of a Swedish perspective, the median of the sum concentration of each group analogue obtained at each STP was used, see Figure 1. Phthalates contribute to the highest load, about five orders of magnitude higher concentration than PCDD/Fs, with the remaining POPs ranging in between.

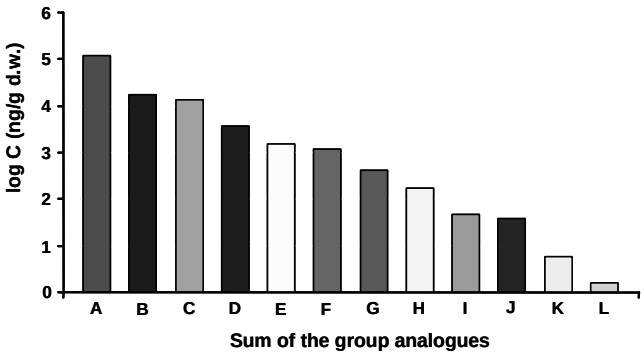


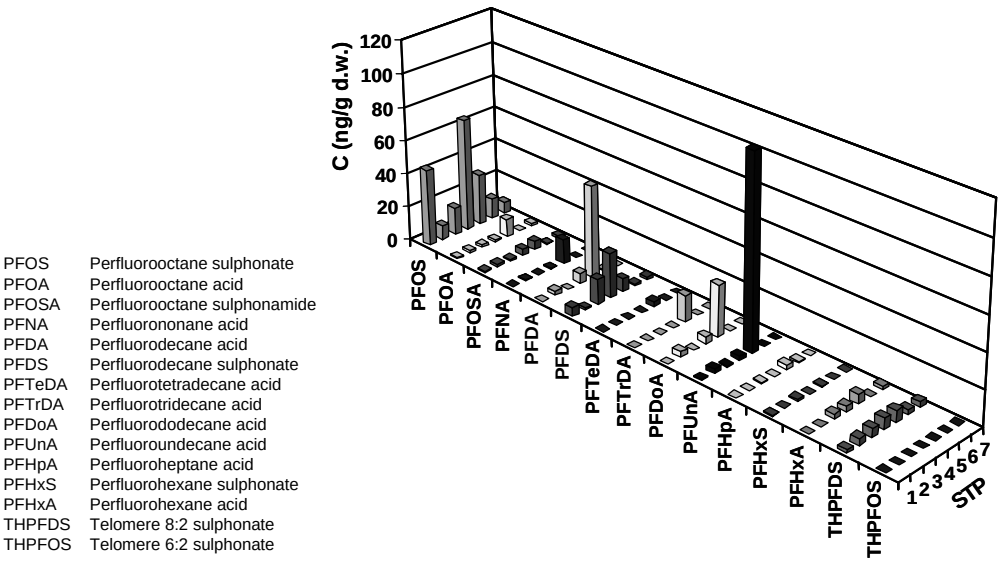
Figure 1. Median values of the sum concentrations of group analogues of persistent organic pollutants in sewage sludge from sewage treatment plants in Sweden. Abbreviations; A: sum of phthalates, B: sum of PBDEs, C: sum of FQs, D: triclosan, E: BHT, F: sum of OPs, G: sum of OTs, H: sum of CPs, I: sum of PFCs, J: sum of PCBz, K: sum of WHO-PCBs, L: sum of PCDD/Fs.

Perfluorochemicals (PFCs) are widely used in consumer and industrial applications due to their surface active properties. Therefore, PFCs are popular for use in paper, textile, and carpet products. Following PFCs; perfluorooctane sulphonate (PFOS), perfluorooctane acid (PFOA), perfluorooctane sulphonamide (PFOSA), perfluorodecane acid (PFDS), and telomere 8:2 sulphonate (THPFDS) were detectable in all STPs, with PFOS in highest concentrations (ranged from 6 to 70 ng/g dry weight (d.w.)), see Figure 2. 93 % of the perfluorochemicals occurred in one STP (STP 5) in the concentration range of 0.5 to 110 ng/g d.w. STP 5 is processing sewage water from the textile industry which, in turn, may use these substances during manufacturing which probably will contribute to the occurrence of the major part of the PFCs. Despite today's absence of PFOS utilization in the Swedish textile industry, high levels of PFOS can be measured in the sludge since PFOS is a degradation product of several PFCs.[1]

Norfloxacin, ofloxacin, and ciprofloxacin are synthetic substances belonging to the antibiotic subgroup fluoroquinolones (FQs). These substances have a huge field of applications hence they are frequently used in medicinal treatment. Norfloxacin and ciprofloxacin were detectable in relatively high concentrations (ranged from 3 to 9 mg/kg d.w.) in all STPs, see Figure 3, whereas ofloxacin was measured in lower concentrations (approximately 1.5 mg/kg d.w.) or was undetectable (limit of detection, LoD: 0.1 mg/kg d.w.). This concentration gradient of FQs correlates well with the prescribed mass in human medicine in Sweden, since these substances mainly undergo sorption to sludge during sewage water treatment.[2,4]

Organotin compounds (OTCs) have been used as anti-fouling composition (partly forbidden in Sweden from 1989 and in EU from 2003). Nowadays, the plastics industry is the dominating user of OTCs in Sweden, e.g. monobuthyltin (MBT) and dibuthyltin (DBT) as stabilizer in PVC. MBT and DBT were measured in significant higher concentrations (ranged from 106 to 233 ng Sn/g d.w. and from 115 to 263 ng Sn/g d.w., respectively) than tributhyltin (TBT, between 0.5 and 110 ng Sn/g d.w.) in all STPs, see Figure 3. The remaining OTCs: monophenyltin (MPhT); diphenyltin (DPhT); and triphenyltin (TPhT) were below LoD (0.37; 0.29; 0.43 ng Sn/g d.w., respectively).

The distribution pattern of FQs and OTCs within STPs is comparatively similar to the pattern between the STPs.



PFOS	Perfluorooctane sulphonate
PFOA	Perfluorooctane acid
PFOSA	Perfluorooctane sulphonamide
PFNA	Perfluorononane acid
PFDA	Perfluorodecane acid
PFDS	Perfluorodecane sulphonate
PFTeDA	Perfluorotetradecane acid
PFTrDA	Perfluorotridecane acid
PFDoA	Perfluorododecane acid
PFUnA	Perfluoroundecane acid
PFHpA	Perfluoroheptane acid
PFHxS	Perfluorohexane sulphonate
PFHxA	Perfluorohexane acid
THPFDS	Telomere 8:2 sulphonate
THPFOS	Telomere 6:2 sulphonate

Figure 2. Concentrations of the perfluorochemicals in sewage sludge from Swedish sewage treatment plants (STPs). Abbreviations; STP 1: Gothenburg; STP 2: Alingsås; STP 3: Umeå; STP 4: Stockholm; STP 5: Borås; STP 6: Floda; and STP 7: Eslöv.

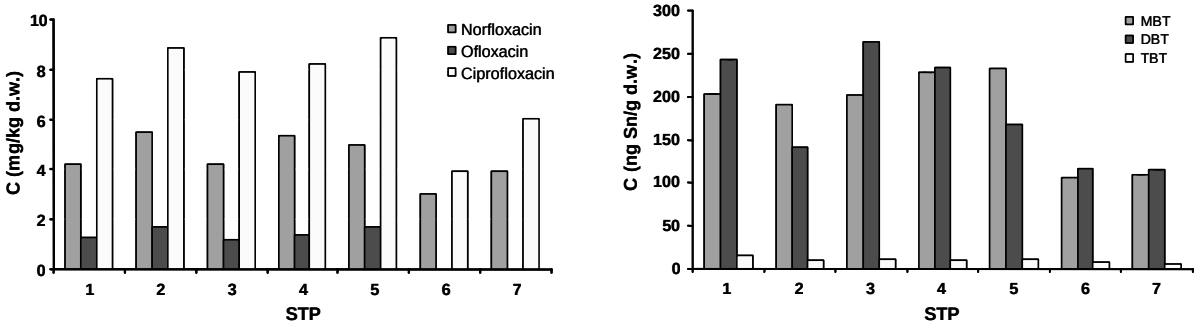


Figure 3. Concentrations of the antibiotics (left) and organotin compounds (right) in sewage sludge from Swedish sewage treatment plants (STPs). Abbreviations; MBT: monobuthyltin; DBT: dibuthyltin; TBT: tributhyltin; STP 1: Gothenburg; STP 2: Alingsås; STP 3: Umeå; STP 4: Stockholm; STP 5: Borås; STP 6: Floda; and STP 7: Eslöv.

Phthalates are commonly used as softening agent in plastics and they belong to a group of chemicals based upon phthalate acid. Buthylhydroxytoluene (BHT) has a wide field of application, where the main part is utilized as stabilizer in plastics and rubber. Di-(2-ethylhexyl) phthalate (DEHP), di-iso-decyl phthalate (DIDP), and di-iso-nonyl phthalate (DINP) were the phthalates detectable in all STPs, together with BHT (10-220 mg/kg d.w. and about 1.5 mg/kg d.w., respectively), see Table 1. DEHP is the most commonly used phthalate in Sweden (more than 50 % of the total employment) and was also detectable in highest concentrations. The other five phthalates; dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-buthyl phthalate (DBP), buthylbensyl phthalate (BBP), and di-n-octyl phthalate (DOP), were below their respective LoD.

Chlorophenols (CPs) work as a bactericide used in e.g. impregnating agent. Only a few CPs, viz. 2-monoCP; 2,6-diCP; and 2,4+2,5-diCP, were barely above LoD in the investigated STPs, see Table 1. The remaining CPs were below LoD (0.02 mg/kg d.w.): 3-monoCP; 4-monoCP; 2,3-diCP; 3,5-diCP; 3,4-diCP; 2,4,6-triCP; 2,3,5-triCP; 2,4,5-triCP; 2,3,6-triCP; 3,4,5-triCP; 2,3,4-triCP; 2,3,5,6-tetraCP; 2,3,4,6-tetraCP; 2,3,4,5-tetraCP; and pentaCP. Triclosan (2-(2,4-dichlorophenoxy)-5-chlorophenol) is a bactericide commonly occurring as additive in

e.g. toothpaste and deodorant. The sewage sludge, representing all STPs, consists of triclosan in relatively high content (approximately 4 mg/kg d.w.).

Table 1. Concentrations (mg/kg d.w.) of the phthalates, buthylhydroxytoluene, chlorophenols, and triclosan in sewage sludge from Swedish sewage treatment plants (STPs). Abbreviations; CP: Chlorophenol; STP 1: Gothenburg; STP 2: Alingsås; STP 3: Umeå; STP 4: Stockholm; STP 5: Borås; STP 6: Floda; and STP 7: Eslöv.

	STP						
Phthalates/BHT	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Di-(2-ethylhexyl) phthalate (DEHP)	95	60	220	60	41	65	34
Di-iso-decyl phthalate (DIDP)	35	21	23	30	54	10	14
Di-iso-nonyl phthalate (DINP)	60	31	78	32	24	29	21
Buthylhydroxytoluene (BHT)[1]	0.64	1.6	1.5	0.81	2.4	2.2	0.83
Chlorophenols/Triclosan							
2-monoCP	<0.020	0.028	<0.020	0.022	<0.020	0.036	<0.020
2,6-diCP	<0.020	0.028	<0.020	0.022	<0.020	0.036	<0.020
2,4+2,5-diCP	0.07	0.021	<0.020	0.042	0.062	0.064	0.034
Triclosan	8.3	2.4	5.5	4.6	3.7	3.4	1.8

[1]BHT: semi-quantitative analyzed, the results are presented in benzylbensoate-equivalents.

In conclusion, the overall distribution pattern of POPs within the investigated STPs is comparatively similar, hence it seems to be independent of location and size of the plants, as well as type of activity connected. However, one clear exception to this statement is the variation in the distribution pattern of PFCs between the studied STPs. The variation may be due to the type of activity connected to the plants, as textile industry seems to influence the levels of PFCs in the sludge.

Acknowledgements
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References

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