Variation in removal efficiency of micropollutants in on-site sewage facilities studied using target and non-target analysis

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Abstract
On-site sewage treatment facilities are designed to reduce emissions of nutrients to surface waters whereas their capacity to remove organic micropollutants is much less studied. In this project the removal capacity of micropollutants was studied in a selection of facilities representing various techniques. In- and outgoing water was sampled using grab samples in a first campaign followed by time proportional sampling over 24 hours in a second campaign. Samples were analysed using both target and non-target approaches aiming at identifying unique signatures and unravelling the pattern of emitted micropollutants. Removal efficiency varied for certain chemicals from traditional treatment techniques versus soil beds and e.g. several pesticides, pharmaceuticals, perfluoroalkyl substances, and organophosphorus substances were detected in outgoing water.

Keywords
on-site sewage treatment facility, micropollutants, pharmaceuticals, soil bed, package treatment

INTRODUCTION
In Sweden, approximately 700 000 private households are not connected to public sewage treatment plants (STPs). Conventional centralised STPs are not feasible for sanitation of sparsely populated areas, and therefore more cost-effective small-scale treatment facilities are used. Most of these consist of sludge separation with subsequent treatment with soil or infiltration beds, while a small percentage of on-site sewage treatment facilities (OSSFs) are based on package treatment facilities. The treated wastewater is thereafter drained to groundwater or surface water. Up to date, there are few studies that have focused on micropollutants emitted from OSSFs [1,2] and on the assessment of the current treatment techniques applied. In this study, we screened wastewaters from OSSFs for a large number of chemicals and compared the emissions from OSSFs with large and medium scale STPs. Identified micropollutants from OSSFs were prioritized based on their concentration levels, removal efficiency in OSSFs, and in silico based data on their toxicity, persistency and bioaccumulation potential.

MATERIAL AND METHODS
Influent and effluent wastewaters were taken from several soil beds and package treatment facilities in the vicinity of Stockholm and Umeå, Sweden. In addition, influent and effluent wastewaters from three large scale and three medium scale conventional wastewater treatment plants in Sweden were monitored. Sampling was organized in two campaign where the first sampling, completed during autumn 2013, included grab samples from 12 different OSSFs and a second sampling campaign, completed autumn 2015, included five large soil beds which were monitored over 24 hours. Sewage water was analysed after clean-up using both LC-MS and GC-MS based techniques.
RESULTS AND DISCUSSION
Applying the non-target GC-MS based approach a set of 652 compounds were identified after blank reduction which was further filtrated down to a set of 352 tentatively identified compounds. These compounds were scored using a protocol including calculated estimates of persistency, bioaccumulation potential, and risk to aquatic organisms plus whether they were listed as industrial chemicals of high or low production volumes. Among the identified compounds were pharmaceuticals like aspirin, caffeine, carbamazepine, ethosuximide and mirtazapine; organophosphates like tris(1,3-dichloroisopropyl)phosphate and tri(2-chloroethyl) phosphate; rubber and plastic additives like 2-(methylthio)benzothiazole and n-butyl benzenesulfonamide; personal care product ingredients such as α-tocopheryl acetate and the UV stabilizers octyl salicylate, oxybenzone and octocrylene; linear alkyl benzenes like 5-phenylundecane and 4-dodecanylbenezene. Surface active compounds 2,4,7,9-tetramethyl-5-decyn-4,7-diol and N,N,N',N'-tetraacetylethylenediamine, flavor and fragances like α-cumyl alcohol and galaxolide, pesticides like 2,3-dichlorobenzonitrile and diethyltoluamide. Based on their individual removal pattern these will be further studied in the second sampling campaign.

Approximately 120 candidate substances were positively detected using the exact mass compound database for the LC-MS based approach. Among these almost half of them could be finally confirmed and quantified by using analytical standards. In addition from the target analysis, 27 compounds were identified. Among the approximately 80 micropollutants, 15 per- and polyfluoroalkyl substances substances (PFAS) were detected in the wastewater samples dominated by the shorter chain PFASs in low ng/L range. The occurrence of pesticides in these samples (13 substances detected) could be explained by the infiltration of ground water into the OSSFs. This could, at least, explain the detection of 2,6-dichlorobenzamide, which is a metabolite of the pesticide dichlobenil and highly ubiquitous in ground water in Sweden. A large number of pharmaceuticals were detected and some compounds were found at high µg/L levels (such as the analgesics and anti-inflammatory acetaminophen, ibuprofen and diclofenac, caffeine, the antihypertensives losartan and valsartan, the diuretic furosemide and the anticonvulsant drug lamotrigine). The overall removal of PFASs and pesticides in OSSFs was similar to the ones observed in large and medium scale STPs. However, for pharmaceuticals, a higher reduction efficiency could be seen in soil bed systems that could potentially be explained by a longer retention time and variation in microbiota.

CONCLUSIONS
A wide range of micropollutants were identified in waste water from OSSFs. A varied pattern of removal efficiencies among the target chemicals were identified in soil beds, package treatment facilities and conventional STPs. A prioritization protocol was developed using fate and effect parameters and removal efficiencies to reach a set of case study chemicals that are studied in detail in large soil beds and STPs in a second sampling campaign.

REFERENCES

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