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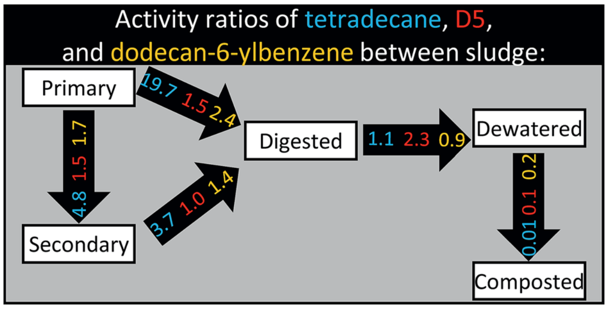
PAPER

Thermodynamic assessment of (semi-)volatile hydrophobic organic chemicals in WWTP sludge – combining solid phase microextraction with non-target GC/MS

Karina Knudsmark Sjøholm,* Matias Flyckt-Nielsen, Thomas D. Bucheli and Philipp Mayer

Equilibrium HS-SPME non-target GC/MS assessment of chemical potential of semivolatile HOCs across treatment processes revealed an increase from inlet to digested sludge, and effectiveness of co-composting as an end treatment for reduction of the exposure level of semivolatile HOCs.



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Thermodynamic assessment of (semi-)volatile hydrophobic organic chemicals in WWTP sludge – combining solid phase microextraction with non-target GC/MS†

Karina Knudsmark Sjøholm, *[ab] Matias Flyckt-Nielsen,[a] Thomas D. Bucheli[c] and Philipp Mayer[a]

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Applying WWTP sludge on arable soil has clear benefits from a resource recycling point of view but can potentially also lead to contamination of soil, agricultural products and the environment. The sludge contains a complex mixture of particularly hydrophobic organic chemicals (HOCs) that sorb to the organic matter. Equilibrium sampling was recently applied to the measurement of chemical activities of polycyclic aromatic hydrocarbons (PAHs) in secondary and digested sludge, and clear activity increases due to the anaerobic digestion treatment were observed. In the present study we extend this work to a large number of (semi-)volatile HOCs by combining automated headspace solid phase microextraction with non-targeted gas chromatography mass spectrometry. Chemical activity ratios were determined between sludge from the different stages of a WWTP and after co-composting with garden waste and sorbent amendment with activated carbon (AC) and biochar (BC). Generally, chemical activities increased from primary, to secondary, to digested sludge and the level in the dewatered sludge was not significantly different from the level in the digested sludge. The cyclic siloxane D5 behaved differently as the level was similar until the dewatering step, where it increased 4-fold. The results confirmed the earlier observation that anaerobic digestion increased chemical activity, now for a broader range of chemicals, and showed that co-composting was effective in reducing chemical activities of most of the tested (semi-)volatile organic chemicals. Of the studied compounds, activities of decamethylcyclopentasiloxane (D5) and a musk fragrance were reduced the least by co-composting.

Environmental significance statement

WWTP sludge is recycled as soil fertilizer, but it contains a mixture of (semi-)volatile hydrophobic organic contaminants (HOCs) that are potentially problematic for the environment. Differences and changes in chemical potential were measured using fully automated equilibrium headspace solid phase microextraction non-target GC/MS. The methodology was applied to sludge from all stages of a WWTP, including two different end treatments. Chemical activity ratios revealed increases in chemical potential from inlet to digested sludge, for the HOC mixture as a whole and for several individual compounds. Finally, aerobic co-composting was shown to markedly reduce the chemical potential of most measured HOCs and can thus be used as an additional end treatment for minimizing environmental risks of HOCs in sludge.

1. Introduction

The fate of the thousands of organic chemicals used in households and industries that daily end up in municipal wastewater treatment plants (WWTPs) is mostly unknown.[1] While the effluents of WWTPs are continuously investigated and known to be a source of organic micropollutants detectable in the aquatic environment,[2] the solid end-product of the treatment process, the sewage sludge or biosolid, is less well understood as a source of contaminants.[3,4] In addition the contaminants associated with the sludge will have different environmental pathways as they are introduced to soil as opposed to surface water exposed to micropollutants emitted *via* the WWTP effluent. Due to a desire for a circular economy in the society and the high value of WWTP sludge as nitrogen and phosphate fertilizer, the preferred recycling option of sludge produced in WWTPs in many European countries is application on arable

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soils.[5] However, the sludge can accumulate chemicals and transfer them when applied to the environment. Especially the hydrophobic organic chemicals (HOCs) that preferentially sorb to the organic matter in the sludge are of concern, as their availability for both aerobic and anaerobic transformation processes is limited when sequestered into the microstructures in the sludge.[6,7] There is a need for a better understanding of the behaviour and fate of HOCs during sewage treatment processes.[8] This will also aid in risk assessment of application of digested sludge on arable soils.

Digested sludge is in many cases used directly as soil fertilizer, whereas different options exist when the regulatory thresholds of heavy metals, and in some countries a few organic substances, for land application are not met. In contrast to this, some countries, *e.g.* Switzerland, have completely forbidden the use of WWTP sludge as soil fertilizer following the precautionary principle. The non-recycling options are incineration which is expensive and landfill which still has potential for environmental contamination if leaching occurs. Co-composting with other biogenic waste is one option to obtain a product that is more suitable for recycling and agricultural applications. Co-composting involves bio-oxidation of the organic matter into more stable and less degradable material and can potentially also reduce the contaminant level in the sludge.[9,10] Co-composting of WWTP sludge is in some cases practiced in Europe.[11] A relatively new approach for producing sludge suitable for land application is stabilizing HOCs in sludge with amendment of strong sorbing materials such as activated carbon (AC) or the cheaper product biochar (BC).[12] Sorbent amendment to reduce the bioavailability and exposure risk of HOCs has for some years been used to remediate contaminated sediment,[13] and a significant reduction of pore water polycyclic aromatic hydrocarbon (PAH) concentration in sewage sludge has been reported as a result of AC and BC amendment, with AC being the most effective.[12,14]

The chemical activity of a HOC is proportional to its freely dissolved concentration (C_{free}) and it quantifies the energetic level of a HOC relative to its reference state and thus expresses its chemical potential.[15] The chemical activity of a substance is equal in all phases of an equilibrated system, and differences in chemical activity (*i.e.*, differences in chemical potential) drive spontaneous processes such as diffusion and partitioning.[16] The fate and exposure of a HOC in sludge is closely linked to its chemical activity, which thus becomes a crucial bioavailability parameter.[16] Additionally, calculated or measured chemical activities also facilitate comparisons across matrices with different sorbent properties and capacities.[17] This asks for chemical activity measurements of HOCs in sludge from the different stages of the WWTP plant as well as in sludge that has been treated by co-composting and sorbent amendment.

Chemical activity can be determined with equilibrium sampling devices that utilize the partitioning of freely dissolved molecules between a matrix and a polymer reference phase.[18] The partitioning of molecules between the matrix and the polymer is driven by differences in chemical activity[19] until reaching a thermodynamic equilibrium (*i.e.*, the same chemical activity in the polymer and the sample). Solid phase microextraction (SPME) with a polydimethylsiloxane (PDMS) coated fibre is such a partitioning based method that can be applied in equilibrium mode for measuring chemical activity.[19] Solid phase microextraction has the great advantage of minimal sample preparation, since the PDMS coated fibre is used for (i) efficient enrichment of analytes, (ii) exclusion of the matrix and (iii) the direct introduction *via* thermal desorption of the analytes onto the gas chromatograph. In addition, SPME can be fully automated, having the advantages of both high throughput and high reproducibility. Headspace (HS)-SPME gas chromatography mass spectrometry (GC/MS) was recently applied to determine optimal composting times for various treatments of pig manure.[20] In that study, SPME was operated in kinetic mode and the GC-MS analysis was non-target *i.e.*, using all the peaks in chromatograms acquired from mass spectrometry in scan mode.[20] The present study goes one step further by combining equilibrium HS-SPME with non-targeted GC-MS analysis, which allows determination of chemical activity ratios from peak height ratios between two samples. We expected this methodology to be a powerful tool in investigating differences and changes in the chemical potential of (semi-) volatile HOCs in sludge.

Hence, the aims of this study were as follows: (1) To compare the chemical potential of (semi-)volatile HOCs in sludge stages across a WWTP by applying fully automated HS-SPME GC with non-target mass spectrometry. (2) To apply the developed method to the measurement of the reduction in chemical potential (*i.e.* exposure level) of (semi-)volatile HOCs obtained by using co-composting and sorbent amendment, respectively, as an end treatment of digested sludge.

2. Materials and methods

2.1 Sludge samples

Sludge samples from primary settling, secondary settling after aerobic biological treatment, anaerobic digestion (20–25 days), dewatering, and co-composting were collected as 20 L grab samples in October 2017 at a Danish WWTP receiving both industrial and domestic wastewater (250.000 person equivalents). The co-composting involved mixing of the digested and dewatered sludge (50%) with hay (3–5%) and garden waste (45–47%) followed by weekly turning over of the 200–250 m long, 2.5 m high and 5.5 m wide windrows for a period of three months followed by three months of maturing. Sludge samples were collected and stored in buckets protected from light. During transportation the temperature of the samples did not exceed 20 °C, and they reached the laboratory within 2 h where they were stabilized with sodium azide (0.02% w/w) and stored at 4 °C. The dry weight percentage of all sludge samples was determined after drying overnight at 105 °C. After drying, loss on ignition (LOI) at 550 °C overnight was used to determine the organic matter (OM) content of the different sludge stages.

2.2 Sorbent amendment

The digested sludge was treated with AC (carbon powder, activated, Norit GSX, steam activated, acid washed; Alfa Aesar

GmbH & Co KG, Karlsruhe, Germany) and BC (Biochar from Miscanthus, surface area = 362 m^2 g^{-1}). For further details, please refer to ref. 21. Both AC and BC were amended to a concentration of 5% weight per dry weight. All treated samples were prepared in duplicate. The digested sludge was mixed with the adsorbents in 60 mL jars. The AC was added directly to the sludge while the BC was first ground with a ceramic pestle and mortar and afterwards passed through a 2.0 mm sieve to obtain a more homogeneous powder. After addition of the adsorbents, the jars were put on rollers at 60 rpm for 7 days, at a constant temperature of 20 °C before HS-SPME-GC/MS analysis. The digested sludge was prepared in four replicates without sorbent amendment to serve as reference samples.

2.3 Chemical analysis

For all analyses, 6 mL sludge sample was poured into 20 mL amber HS vials (Mikrolab Aarhus, Denmark) and sealed with magnetic screw caps with an 18 mm thread PTFE/silicone septum (Sigma-Aldrich, Copenhagen, Denmark). Negligible depletion conditions were ensured as the organic carbon content was at least 1800 times higher than the PDMS mass on the fibre. The HS-SPME-GC/MS analysis was performed with a CTC PAL RSI 85 auto sampler (CTC Analytics AG, Zwingen, Switzerland) mounted on an Agilent 5977A MSD GC coupled to a 7890B MS (Agilent Technologies, CA, USA). The SPME fibre used was 7 μm (bonded) PDMS with needle size 23 (Supelco, Bellafonte, PA, USA). The SPME fibre was conditioned according to the manufacturer's instructions prior to use. The optimal SPME sampling time was determined after a kinetic study where sampling was performed at 5, 10, 20, 30 and 60 min at a sampling temperature of 35 °C. Consequently, the fully automated SPME sampling was conducted at 35 °C for 60 min at an agitation speed of 250 rpm. The fibre was desorbed for 10 min in the split/splitless inlet at 315 °C. The long desorption time at high temperature was chosen to ensure that the whole HOC mixture was desorbed and injected, as well as the fibre was cleaned before next sampling. The injection inlet was operated in splitless mode with a septum purge flow of 3 mL min^{-1} for 10 min. Thereafter, the purge flow to the split vent was 100 mL min^{-1} for 10 min and then the gas saver was activated. Post-desorption conditioning time for the fibre was 1 min. The GC/MS system was operated in electron ionization (EI) mode at 70 eV. An Agilent 122-5562UI DB-5ms 60 m × 250 μm × 25 μm column was used. The carrier gas was helium at a flow rate of 1.2 mL min^{-1}. The initial column temperature was set to 50 °C for 10 min. The temperature was then increased at a rate of 10 °C min^{-1} to 150 °C which was held for 20 min before increasing to 250 °C at a rate of 1.5 °C min^{-1} and finally the temperature was increased to 310 °C at a rate of 30 °C min^{-1}. The final temperature was held for 1 min. The total GC cycle time was 110 min. The MSD transfer line temperature was set to 250 °C. The MS source temperature was 230 °C. The samples were analysed by full scan MS from 50 to 500 amu, and with a gain factor of 3. Headspace vials with 5 mL of Milli-Q water and empty vials were included in each run as blanks. Furthermore, duplicate samples of 5‰ diesel oil in triglyceride oil (MCT-Öl, MANSKE GmbH, Schwäbisch Hall, Germany) served as a reference mixture which was used to account for differences in instrument sensitivity, and retention time drift, and to confirm identification of *n*-alkanes in the sludge. The reference mixture was analysed as all the other samples. For confirmation of identification 0.01‰ decamethylpentasiloxane (D5) (purity 97%, Sigma-Aldrich A/S, Copenhagen, Denmark), tetradecane (≥99% purity, Sigma-Aldrich Chemie GmbH, Munich, Germany) and undecane (≥99% purity, Fluka AG, Switzerland) in miglyol (Caesar & Loretz GmbH, Hilden, Germany) were analysed with the same method as that of the sludge samples.

2.4 Data processing

The full scan data files obtained using ChemStation (Agilent Technologies) were exported to MassHunter Qualitative analysis vers. B-07.00 (Agilent Technologies) for further data treatment. The Agile 2 integrator was used and compounds were found by deconvolution using the algorithm for molecular features. The subtracted background spectrum was set to be the spectrum at the peak start. The compound filter was set to absolute area ≥ 5000 counts, and relative area ≥ 1% of the largest peak. The height filter was set to relative height ≥ 2.00% of the largest peak. In practice this was absolute peak height ≥ 5000. Peak height ≥ 5000 was considered the "quantification level" whereas a peak height < 5000 but distinguishable from the baseline was assigned a value of 1000 and marked with the symbol '*' in the graphs. The abundance value of the height of the base peak *m*/*z* for each molecular feature found was used in further data treatment. Only peak heights from the same sequence were compared, and activity ratios were calculated from data from the same sequence. The "total peak area" is the sum of areas extracted by MassHunter in the deconvolution. Peaks with retention time less than 15 min and more than 60 min were excluded from this analysis as peaks appearing before 15 min were considered background noise, and a very limited number of peaks appeared after 60 min (180 °C). Tentative compound identification was performed using the spectral library NIST vers. 2.2. Manual check of *m*/*z* ratios, base peak heights and compound ID was performed using Enhanced MSD ChemStation vers. D.03.00.611. Final data treatment and modelling were performed using GraphPad Prism vers. 7.03.

3. Results and discussion

3.1 Equilibrium times of HS-SPME

For evaluation of equilibrium in the sludge–air–PDMS fibre system, 16 molecular features (retention time and base peak ion; listed in Table ESI1 in the ESI†) were selected across the entire chromatogram with the only selection criterion being that they should cover the retention time range from 15–60 min. Examples of compounds with short, medium and long retention times are shown in Fig. 1 (the remaining are shown in Fig. ESI1 in the ESI†).

A simple first order equation was fitted to the measurements and the obtained plateau was compared to the measured response for a 60 minute sampling time (Fig. ESI2 in the ESI†).

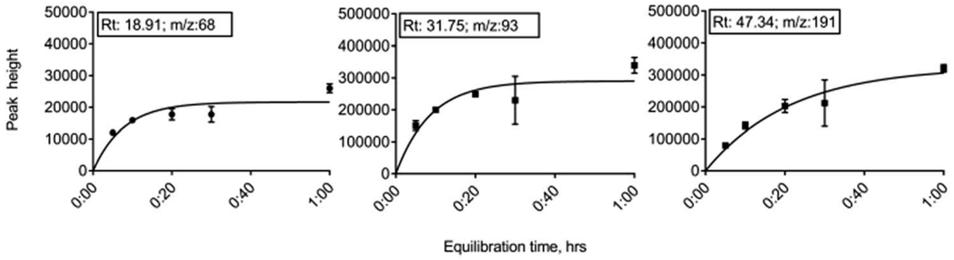

Fig. 1 Base peak height of molecular features with short, medium and long retention times against headspace sampling time.

For fourteen of the selected molecular features, measurements after 60 minutes of sampling were very similar to or within a factor of two from the plateau. The sum of areas under all molecular features with 15–60 min retention time did also reach equilibrium (Fig. ESI1 in ESI†) within 60 min. It was concluded that the developed SPME method reached (near) equilibrium within 60 min over the full range of molecular features detected and hence it is capable of measuring the chemical potential of (semi-)volatile HOCs in sludge.

3.2 Chemical potential of (semi-)volatile HOCs in sludge across a WWTP treatment chain

To compare the chemical potential of (semi-)volatile HOCs in sludge stages across a WWTP, the developed fully automated equilibrium HS-SPME-GC/MS method was applied on the five sludge stages without any sample preparation, other than the initial stabilization with azide. The sum of all peak areas (Fig. 2A) and the total number of peaks (Fig. 2B) detected in the deconvolution were then used for initial assessment of differences and changes in the chemical potential of HOCs in the different sludge stages.

The total area and the number of peaks increased from primary to secondary to digested sludge. As the total peak number also increased, it was not only the chemical activity of the compounds present that was increasing, but also more compounds were appearing, either degradation products or compounds "released" during digestion of the matrix. The levels were similar in the digested and in the dewatered sludge whereas the levels decreased dramatically in the composted stage. The observations on the composted stage will be further discussed in Section 3.3. Recently, we reported similar observations of the increase from secondary to digested sludge using a different kind of equilibrium sampler to measure chemical potential of PAHs in secondary and digested sludge.[22] In that study, as well as in the present, the sorptive capacity in the form of OM was reduced in the digested compared to the secondary sludge (67 to 57% on dry weight basis) (Table 1). As the OM reduces during digestion the chemical potential of HOCs in the aqueous phase of the sludge increases because the sorption capacity is reduced, a phenomenon called solvent depletion.[23] It is well-established within wastewater science that a drawback of the digestion treatment is the increase in the concentration of non-degradable hydrophobic chemicals associated with the sludge.[24] The novelty of the present study is an analytical approach that can actually measure this increase in terms of chemical potential.

Both a reduction in OM and a change in the quality of the OM present will change the chemical potential of the chemicals in the aqueous phase. The primary and secondary sludge had similar OM contents (Table 1), but the quality of the two types of OM may differ substantially, which might explain the increase in chemical potential from primary to secondary sludge. For example, composition analysis of various lipids in the primary sludge revealed plant and animal origins, while the lipids from the activated sludge were mainly of microbial origin.[25] The level and number of peaks did not differ significantly between the digested and the dewatered sludge, which is reasonable as the only process between the two is removal of water by application of a dewatering agent.

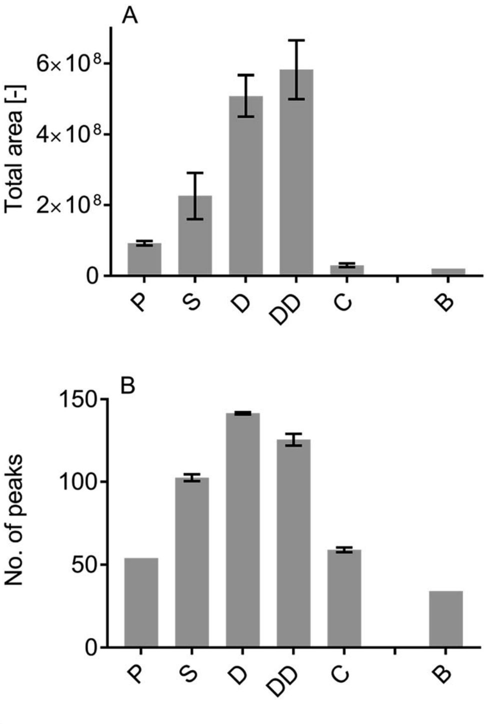

Fig. 2 (A) Sum of peak areas of molecular features with 15 to 60 min retention time in each measured sludge stage. (B) Total number of molecular features extracted and eluting in the 15 to 60 min retention time window in each measured sludge stage. P: primary; S: secondary; D: digested; DD: digested and dewatered and C: composted sludge; B: blank.

Table 1 Dry weight (DW) and organic matter (OM) content in the five different sludge stages

Sludge stage	Dry weight[a] (% of total weight)	OM[b] (% of dry weight)
Primary	2.24	67.5
Secondary	8.31	66.5
Digested	4.66	56.5
Dewatered	25.0	57.1
Composted	48.5	33.0

[a] Measured as weight loss after drying overnight at 105 °C. [b] Measured using loss on ignition at 550 °C overnight.

To evaluate the differences in chemical potential at the single substance level between sludge stages, activity ratios (ARs) were calculated relative to the level in the primary sludge (Fig. 3). Four substances representing the general observations were selected (Fig. 3A–D). The base peak heights for all the selected substances are presented in Fig. ESI4 and ESI5 in the ESI.† The four substances, limonene used as a fragrance in cleaning and personal care products, *p*-cresol from wood preservation and a metabolite from hydrocarbon degradation, D5 (confirmation of identification given in Table ESI2 and Fig. ESI3 in the ESI†) from personal care products and industrial applications, and a widely used industrial solvent alkylated benzene, are commonly reported in total extractions of sewage sludge.[3,26] The ARs of limonene followed the observation on total area; the chemical activity increased from primary to secondary and to digested and dewatered sludge. The included alkylated benzene followed the same pattern. The AR of D5 in both the secondary and digested sample was at the same level as in the primary sludge, *i.e.* around one, whereas in the dewatered sludge it increased to four. This observation raises the suspicion that the dewatering agent used by the WWTP contained D5. For WWTPs using the produced biogas as an energy source, D5 and other similar siloxanes cause problems,[27] which is why there is not only an environmental but also technical interest in understanding the behaviour of D5 within WWTP processes. *p*-Cresol, as the only studied substance, has a higher AR in the secondary than in both the digested and the dewatered sludge, pointing in the direction of some degradation of this small molecule during the WWTP process.

In addition, ARs of *n*-alkanes are included in Fig. 3E. The levels of alkanes in the primary sludge were relatively low, and they increased to secondary, and from secondary to digested sludge. Previous studies also report findings of *n*-alkanes in the final sludge and the origin might be spills of petroleum oils.[26,28,29] As the alkanes are readily biodegradable and expected to degrade before the wastewater reaches the WWTP, the increase can also be due to alkane formation within the treatment plant. This is consistent with the literature as the end-product of fatty acid biosynthesis, acyl-ACP, can be converted into acyl-aldehyde which, in the presence of aldehyde decarbonylase, can be converted into alkanes.[30]

It has previously been reported that the unsaponifiable organic matter of the sludge matrix contains C9–C16 *n*-alkanes,[31] which is why research into WWTP sludge as a potential biofuel is relevant.[32] All the observed alkanes in the present study (C11–C17) had increasing ARs relative to the primary sludge until the dewatered sludge stage.

3.3 Co-composting as an end treatment to reduce the chemical potential of (semi-)volatile HOCs

As described in the previous section the general observation for the (semi-)volatile HOCs was that their chemical potentials increased during the WWTP process. To reduce the potential harmful effects that (semi-)volatile and other chemicals might have on the environment an additional end treatment is beneficial before applying the sludge on arable soil. Co-composting is one way to do this. Application of the developed equilibrium HS-SPME-GC/MS method on co-composted sludge from the same WWTP as the rest of the samples revealed that the chemical potential was reduced significantly and beyond simple dilution effects from additional feedstock. The reduction was observed both on the single substance level (Fig. ESI4 and ESI5 in the ESI†) and on the level of the HOC mixture as a whole (Fig. 2). By co-composting, the reduction in chemical potential of the mixture as a whole was 95% (±0%), and the total number of peaks was reduced by 53% (±2%). The reduction in the co-composted sludge was observed compared to both the dewatered and the primary sludge. This means that, for the compounds studied here, the full treatment chain including co-composting is effective in reducing the chemical potential of contaminants.

(Semi-)volatile HOCs were removed in the co-composting stage either by volatilization, degradation or sorption to the added mixing material, or a combination of these processes. In Fig. 4 the activity ratios of 13 different substances in the co-composted sludge to the dewatered sludge are shown. Physical–chemical properties of the 13 substances are listed in Table ESI3 in the ESI.† The level of removal was substance dependent. The alkanes were almost completely removed by the co-composting, which is reasonable as they are highly volatile and biodegradable. Humulene is also volatile and in addition the chemical activity reduction observed in the co-composted sludge can be due to sorption to the biowaste that the sludge was mixed with. Although the activity of D5 was reduced, D5 was not completely removed in the co-composting despite the high volatility of the compound. The sludge does already have a large sorption capacity which might buffer the fraction of D5 available for sorption on the biowaste added in the co-composting. This "buffer-capacity" may also be the reason why the very volatile D5 was not completely removed by volatilisation. Versalide, a fragrance in detergents and personal care products, is less volatile and the least reduced of the studied compounds. As for D5, the loads of versalide and similar hydrophobic musk fragrances in wastewater and thereby in sludge are high.[3,33] From an environmental perspective the incomplete reduction is of concern as musk fragrances have potential estrogenic and anti-estrogenic effects[34] while D5 and other cyclic siloxanes have potential adverse effects on aquatic and soil living organisms.[33]

Amendment with AC and BC was also tested as an end treatment to reduce the chemical potential of (semi-)volatile

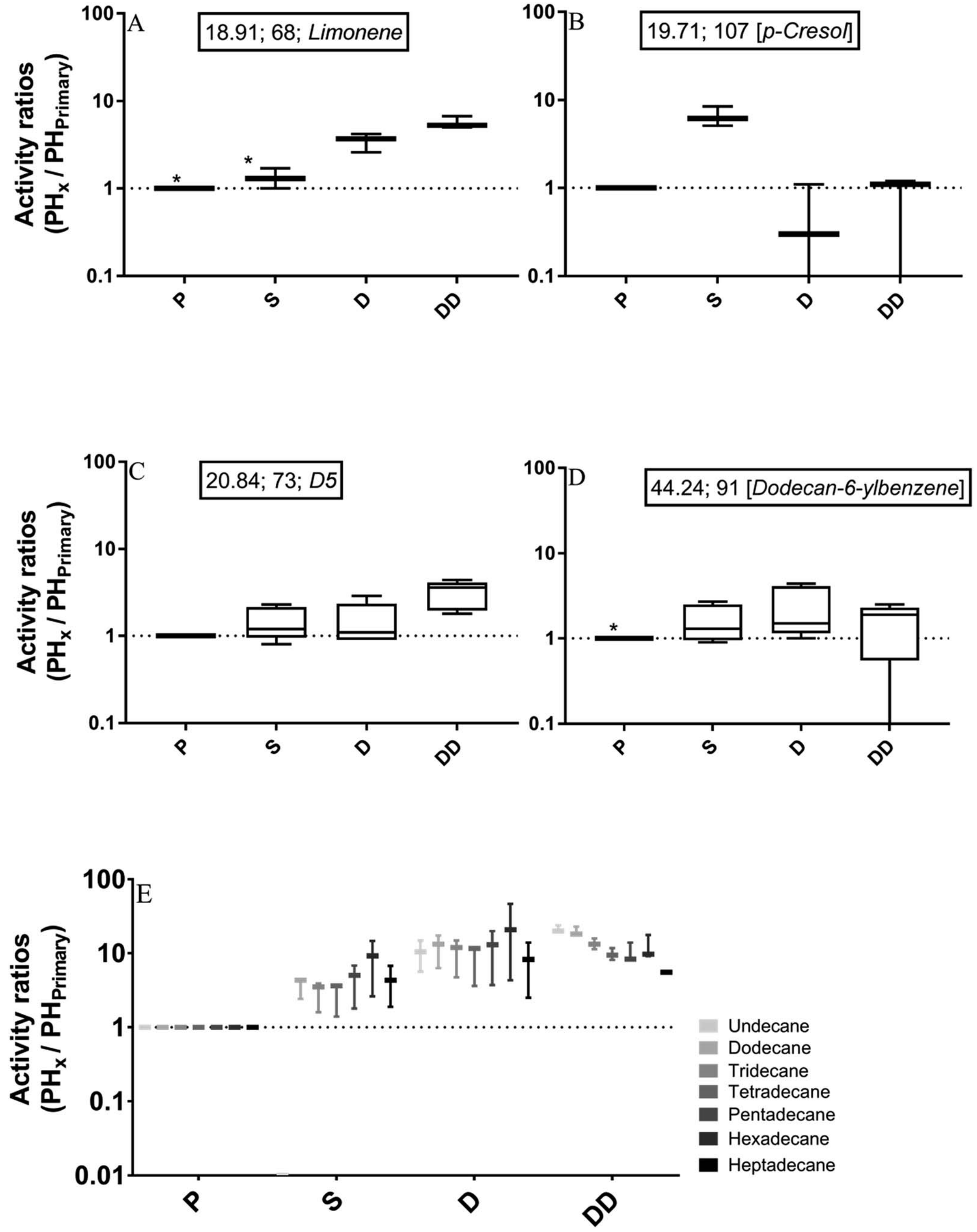

Fig. 3 Activity ratios expressed as peak height in *x* sludge stage divided by peak height in primary sludge. The box plots are mean, min and max, and standard deviation for (A) limonene, (B) *p*-cresol, (C) D5, (D) dodecan-6-ylbenzene and (E) detected *n*-alkanes. Values below the data processing limit were manually checked and marked with the symbol '*' if present in the chromatogram and data manually extracted in ChemStation. $n = 5$ for D5 and dodecan-6-ylbenzene, and $n = 3$ for limonene, *p*-cresol and alkanes. ID of molecular features: retention time; *m*/*z* of base peak ion [tentative ID from NIST]. P: primary; S: secondary; D: digested; DD: digested and dewatered sludge.

HOCs. The non-activated Miscanthus BC used in this study did not have a significant reduction effect on the chemical activity, and hence C_{free}, of (semi-)volatile HOC in sludge (Fig. ESI6 in the ESI†). Activated carbon did have a reduction effect, though, both on the total (semi-)volatile HOC level (Fig. ESI6 in the ESI†) and on single substances' level. However the variability between the batches of AC treated sludge was too high as some batches showed significant reductions while others did not. Therefore data on the single substance level is not included. The reduction in chemical potential of the mixture as a whole was 38%, and the total number of peaks was reduced by 15% after amendment with 5% AC in the batch where reduction was observed. Adsorption on AC is stronger if π–π dispersion interactions between the aromatic structures on the sorbent surface and the adsorbate are a possibility.[35] For the (semi-)volatile compounds studied here, this was the case only with dodecan-6-ylbenzene, an alkylated aromatic compound which was reduced to some degree (data not shown).

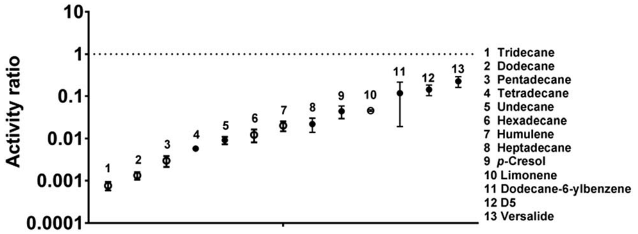

Fig. 4 Chemical activity ratios of semi-volatile HOCs in composted sludge relative to dewatered sludge sorted by value. $n = 3$, open symbols are ARs where the peak height in the composted stage in at least 1 of the 3 samples was <detection limit, but distinguishable from the baseline and assigned a value of 1000.

4. Conclusions

A fully automated equilibrium HS-SPME-GC/MS method was successfully developed and applied on four sludge stages from all steps in a WWTP and the subsequent co-composting end-treatment. With the method, it was possible to determine changes in the chemical potential of (semi-)volatile molecular features in the sludge, as well as changes in the whole mixture of (semi-)volatile HOCs within the sludge. Generally, chemical activity increased from primary, to secondary, to digested sludge and the level in the dewatered sludge was not significantly different from the level in the digested sludge. The cyclic siloxane D5 behaved differently as the level was similar until the dewatering step, where the level increased 4-fold. For all single substances studied and for the mixture as a whole the co-composting end-treatment was generally effective in reducing the chemical potential of (semi-)volatile HOCs again. However, the incomplete reduction of cyclic siloxanes such as D5 and a musk fragrance requires further investigations. With the purpose of optimising the overall reduction in chemical potential of potentially harmful compounds investigations of the mechanisms that increase chemical potential especially during the anaerobic digestion process are needed.

Conflicts of interest

The authors state that there are no conflicts to declare.

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