Persistence of organic contaminants in Finnish sludge-amended agricultural soils

Introduction & objectives

Land application of sewage sludge produced in waste water treatment plants (WWTP) is often seen as an environmentally sound way of utilizing it. Sludge-products may contain high amounts of organic matter and nutrients necessary for plant growth. Sewage sludge may also contain organic contaminants (OCs) that may restrict its use on agricultural areas. The aim of this work was to simulate accumulation scenarios for soil accumulation of several OCs potentially present in sludge.

Materials & methods

A preliminary list of OCs was compiled from literature. The OCs considered most relevant in Finland were selected for further study. Chemical specific data was compiled from literature. Swedish concentration data was used for compounds on which Finnish data was lacking.

Data used in calculations:

- Chemical degradation half-lives (DT50)
- Predicted no effect concentrations in soil (PNEC
- Concentration in sludge, used as such, i.e. treatment of the sludge is not taken into account.

A PECool-calculator, originally developed for pesticide evaluation purposes, was used to simulate compound degradation in soil (I). For this work the simulated soil layer was changed from the uppermost 5 cm used in the official version to 20 cm. Homogenous mixing was assumed in this layer immediately after sludge application. The compound-specific application rate was estimated from reported concentrations in sludge and an annual sludge application rate of 5.6 t/ha.

Further assumptions made in calculations:

- Background concentration of 0 mg/kg soil
- Water content of a standard soil (2) was used for correcting PNEC-values expressed as wet weight basis
- A reference temperature for DT50 of 22 °C for compounds for which it was not reported

Further studies concerning the placing of biocidal products on the market.

Acknowledgements

The Finnish Ministry of the Environment and Maa- ja vesitekniikan tuki ry are acknowledged for their financial support.

References

1. Calculator for predicted environmental concentration in soils for plant protection products (PEC soil calculator) Available at: http://www.tukes.fi/pecsoilcalculator

For references on the chemical specific data, see additional material.

Conclusions

According to the simulations, most of the OCs studied here may accumulate in soils. However, few of the simulated chemicals exceeded their PNEC-values. Only triclosan accumulated to a concentration higher than its PNEC. 17β-Ethinylestradiol exceeded its PNEC immediately after application but degraded quickly. The concentrations of some compounds, such as PAHs, increased still after a 100-year simulation.

Future research

In this work chemical degradation was considered the only removal process for OCs. This may lead into overestimations of soil concentrations. In future also leaching and run-off into surface waters will be taken into account to estimate the potential risks of sludge application on waterbodies and to achieve a more accurate estimation of the soil concentrations.
WWTPs in Finland produce 150 000 dry tons of sewage sludge each year. Most of this sludge is used in landscaping while a small portion of it is used in agriculture (3 %, in 2006). While on one hand applying sewage sludge onto agricultural soils is a sustainable way of utilizing it and recycling nutrients, it is on the other hand also a potential source for soil contamination. The contaminants present in sludge may for instance accumulate into soils and harm soil ecosystems, accumulate into harvest plants or be ingested by animals or children.

While heavy metals are monitored in Finnish sewage sludge and maximum input levels are set for them in sewage products used in agriculture, no limits has been set for OCs and monitoring data on them is sparse. In Sweden, however, concentration data for a wide variety of organic contaminants in sewage sludge is available. In this work the persistence of selected OCs present in Nordic sludge samples was simulated using a PECSoil-calculator originally developed for pesticide evaluation purposes. A realistic maximum sludge application rate and concentration and degradation data was used as input in the calculator.

From a preliminary list of over 300 compounds circa 60 compounds considered most relevant in Finland were selected for further study. Only the compounds for which all necessary properties could be found were presented in this poster (see Table A1).

### Table A1. Data used in simulations

<table>
<thead>
<tr>
<th>Substance class</th>
<th>Abbreviation</th>
<th>CAS No.</th>
<th>Value</th>
<th>Value</th>
<th>Value</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFCs</td>
<td>PFOA</td>
<td>23470-99-0</td>
<td>0.0725</td>
<td>2.4</td>
<td>20,44</td>
<td>3.2</td>
</tr>
<tr>
<td>PAHs</td>
<td>B[a]A</td>
<td>49016-33-3</td>
<td>6.32</td>
<td>0.0005</td>
<td>0.0725</td>
<td>0.038</td>
</tr>
<tr>
<td>OCs</td>
<td>2,4-Dinitrotoluene</td>
<td>108-46-3</td>
<td>0.21</td>
<td>4.27</td>
<td>2.8</td>
<td>30.6</td>
</tr>
<tr>
<td>OCs</td>
<td>Benzo(a)pyrene</td>
<td>120-50-7</td>
<td>0.09</td>
<td>0.21</td>
<td>0.09</td>
<td>0.21</td>
</tr>
<tr>
<td>OCs</td>
<td>Acenaphthylene</td>
<td>120-50-7</td>
<td>0.09</td>
<td>0.21</td>
<td>0.09</td>
<td>0.21</td>
</tr>
<tr>
<td>OCs</td>
<td>Anthracene</td>
<td>120-50-7</td>
<td>0.09</td>
<td>0.21</td>
<td>0.09</td>
<td>0.21</td>
</tr>
<tr>
<td>OCs</td>
<td>Benz(a)anthracene</td>
<td>120-50-7</td>
<td>0.09</td>
<td>0.21</td>
<td>0.09</td>
<td>0.21</td>
</tr>
<tr>
<td>OCs</td>
<td>Benzo(a)pyrene</td>
<td>120-50-7</td>
<td>0.09</td>
<td>0.21</td>
<td>0.09</td>
<td>0.21</td>
</tr>
<tr>
<td>OCs</td>
<td>Benzo(b)fluoranthene</td>
<td>120-50-7</td>
<td>0.09</td>
<td>0.21</td>
<td>0.09</td>
<td>0.21</td>
</tr>
<tr>
<td>OCs</td>
<td>Benzo(k)fluoranthene</td>
<td>120-50-7</td>
<td>0.09</td>
<td>0.21</td>
<td>0.09</td>
<td>0.21</td>
</tr>
<tr>
<td>OCs</td>
<td>Chrysene</td>
<td>120-50-7</td>
<td>0.09</td>
<td>0.21</td>
<td>0.09</td>
<td>0.21</td>
</tr>
<tr>
<td>OCs</td>
<td>Dibenzo[a,h]anthracene</td>
<td>120-50-7</td>
<td>0.09</td>
<td>0.21</td>
<td>0.09</td>
<td>0.21</td>
</tr>
<tr>
<td>OCs</td>
<td>Diphenyl ether</td>
<td>120-50-7</td>
<td>0.09</td>
<td>0.21</td>
<td>0.09</td>
<td>0.21</td>
</tr>
<tr>
<td>OCs</td>
<td>Dibenz(a,h)anthracene</td>
<td>120-50-7</td>
<td>0.09</td>
<td>0.21</td>
<td>0.09</td>
<td>0.21</td>
</tr>
<tr>
<td>OCs</td>
<td>Dibenz(k)fluoranthene</td>
<td>120-50-7</td>
<td>0.09</td>
<td>0.21</td>
<td>0.09</td>
<td>0.21</td>
</tr>
<tr>
<td>OCs</td>
<td>Phenanthrene</td>
<td>120-50-7</td>
<td>0.09</td>
<td>0.21</td>
<td>0.09</td>
<td>0.21</td>
</tr>
<tr>
<td>OCs</td>
<td>Sopranol</td>
<td>120-50-7</td>
<td>0.09</td>
<td>0.21</td>
<td>0.09</td>
<td>0.21</td>
</tr>
</tbody>
</table>

### Sludge application in Finland

In Finland sewage sludge must be processed before it may be used on arable land. For sewage sludge to be accepted as a soil improvement agent it needs to be e.g. digested and fulfill criteria set for fertilizer products. Different sludge treatment methods affect OCs in different ways. In this work the concentration data was used as reported from measurements in WWTPs, i.e. OC concentrations were assumed to remain constant throughout the sludge treatment processes. This is due to the lack of data on the different treatment methods and their combinations on the concentrations of different OCs.

In Finnish sludge application rates on agricultural soils can be restricted by limits set for nutrient or metal inputs. Ultimately the maximum sludge application rate is limited by a maximum nitrogen input of 170 kg/ha yr set in the Nitrates directive (91/676/ECC). This limit and an average nitrogen content of 30.3 g/kg d.w. measured from sludge products used in agriculture 1995-2006, was used to calculate the amount of sludge applied. This resulted in an annual sludge application rate of 5.8 tons/ha/yr d.w.

### A brief description of the PECSoil-model

- Degradation is considered the only process decreasing the level of contaminants in sludge-amended soils.
- Degradation is assumed to happen according to first rate degradation kinetics.
- Soil temperature affects the degradation rate according to Arrhenius equation.
- Compound-specific concentrations are calculated for each day according to equations presented in Matsson et al. 2005.

Since the concentration of some OCs is likely to decrease also due to other processes than degradation, the PECSoil-values presented here may be overestimations. This may be the case especially for hydrophobic compounds with a low soil-water partitioning coefficient. For some compounds presented here, such as buprofen, leaching may even be a more important process in decreasing the concentrations in agriculturally relevant soil layers than chemical degradation. This will be taken into consideration in future work.
Results
According to the simulations, several of the contaminants studied here may accumulate into Finnish soils when sewage sludge is applied annually. Only a few of the contaminants degraded completely before next application. The development of compound specific risk quotients in soil for selected compounds is shown in Figure A1.

Only one contaminant (triclosan) accumulated to a concentration higher than its PNEC-level. The concentrations of some quickly degrading compounds also peaked immediately after application but did not show signs of accumulation. For instance the concentration of 17α-ethinylestradiol, an endocrine active pharmaceutical used in e.g. contraceptive pills, exceeded its PNEC-value each time sludge was applied but did not accumulate into soil.

Accumulation of OCs is strongly dependent of the half-life used in the calculations, as can be seen when comparing RQmin and RQmax presented in figure A1. For most compounds the simulated concentrations stayed well below their PNEC-levels, even when accumulation did occur.

References
EC 2002. European Union Risk Assessment Report, 4-nonylphenol (branched) and nonylphenol. EUR 20387 EN.
EC 2003a. European Union Risk Assessment Report, 1,2-benzeneedicarboxylic acid, di-C8-10-branched alkyl esters, C8-rich and di-“isonylon” phthalate (DIDP). EUR 20784 EN.
Lennart K., Andersson J., Cousins A.P., Remberger M., Brorström-Lundén E., Cato I. 2005. Results from the Swedish National Screening Programme 2004, Subreport 4: Siloxanes. IVL B1643.
Tremoen S. 2008. Screening of polyfluorinated organic compounds at four fire training facilities in Norway. SFT 2444.