Organic Contaminants in Sewage Sludge for Agricultural Use

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Population density in the EU

yellow: <50
red: >500 inhabitants per km²
(BBR 2000)
Expected Sludge Use

Sludge Destination in 2005 [1000 t dm/a]

Legend

1.400

TOTAL

REUSE

Data from Magoarou (2000)
Method

- a literature search run was done in January 2001 by means of the “The Scientific & Technical Information Network” (STN International)
- more than 30 EU experts and members of ISO TC 190 and CEN TC 308 were contacted
- the Internet was searched
- references were taken directly from the literature
Material

From more than
- 2,000 papers in the field
- 800 papers were preselected and
- 150 papers were finally selected for use
Standards for sewage sludge in EU (03.2001)

<table>
<thead>
<tr>
<th></th>
<th>AOX (mg/kg)</th>
<th>DEHP (mg/kg)</th>
<th>LAS (mg/kg)</th>
<th>NP/NPE (mg/kg)</th>
<th>PAH (mg/kg)</th>
<th>PCB (mg/kg)</th>
<th>PCDD/F (ng TEq/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EU 2000 (3rd draft)</td>
<td>500</td>
<td>100</td>
<td>2600</td>
<td>50</td>
<td>6&lt;sup&gt;1&lt;/sup&gt;</td>
<td>0.8&lt;sup&gt;2&lt;/sup&gt;</td>
<td>100</td>
</tr>
<tr>
<td>Denmark</td>
<td>-</td>
<td>50</td>
<td>1.300</td>
<td>10</td>
<td>3&lt;sup&gt;1&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sweden</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>50</td>
<td>3&lt;sup&gt;3&lt;/sup&gt;</td>
<td>0.4&lt;sup&gt;4&lt;/sup&gt;</td>
<td>-</td>
</tr>
<tr>
<td>Lower Austria</td>
<td>500</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.2&lt;sup&gt;5&lt;/sup&gt;</td>
<td>100</td>
</tr>
<tr>
<td>Germany</td>
<td>500</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.2&lt;sup&gt;5&lt;/sup&gt;</td>
<td>100</td>
</tr>
<tr>
<td>French</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.5 - 4/ comp</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
# German Threshold Values for Organic Contaminants in Soils

<table>
<thead>
<tr>
<th>compound</th>
<th>unit</th>
<th>Pathway soil-plant</th>
<th>Pathway soil-man playgrounds</th>
<th>Pathway soil-man parks</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldrine</td>
<td>mg/kg soil</td>
<td>-</td>
<td>2</td>
<td>10</td>
<td>BMU (1999)</td>
</tr>
<tr>
<td>BaP</td>
<td>mg/kg soil</td>
<td>1</td>
<td>2</td>
<td>10</td>
<td>BMU (1999)</td>
</tr>
<tr>
<td>DDT</td>
<td>mg/kg soil</td>
<td>-</td>
<td>40</td>
<td>200</td>
<td>BMU (1999)</td>
</tr>
<tr>
<td>HCB</td>
<td>mg/kg soil</td>
<td>-</td>
<td>4</td>
<td>20</td>
<td>BMU (1999)</td>
</tr>
<tr>
<td>HCH-mix.</td>
<td>mg/kg soil</td>
<td>-</td>
<td>5</td>
<td>25</td>
<td>BMU (1999)</td>
</tr>
<tr>
<td>PCP</td>
<td>mg/kg soil</td>
<td>-</td>
<td>50</td>
<td>250</td>
<td>BMU (1999)</td>
</tr>
<tr>
<td>PCB 6</td>
<td>mg/kg soil</td>
<td>-</td>
<td>0,4</td>
<td>2</td>
<td>BMU (1999)</td>
</tr>
<tr>
<td>PCDD/F</td>
<td>ng I-Teq/kg</td>
<td>40</td>
<td>100</td>
<td>1,000</td>
<td>UM (1996)</td>
</tr>
</tbody>
</table>
General Statements

… among fertilizers sewage sludge is generally the product carrying the highest load of organic contaminants (Kj ÖLHOLT 1997).

… the limit values for AOX, PCB and PCDD/F are intended as precautional and are not justified solely by toxicological implications (SAUERBECK & LESCHBER 1992).

… persistent compounds such as PCBs, PCDD/Fs and PAHs are generally not transferred from soil to crops, meat and milk although the possible evaporation of PCBs and foliar uptake needs more attention … little is known about the uptake of phthalates and nonylphenole (RUDLING et al. 1997).

… to prevent elevated levels in digested sewage sludge, substances from laundry- and dish-washing detergents or surface cleaners must be aerobically and anaerobically degradable (Giger et al. 1997).
AOX Selected Statements

adsorbable organic halogenated compounds

... AOX is not a measure for toxicity

... paper pulp industry, manufacture of PVC and waste incineration are important sources of AOX formation

... some organic halogens may be transformed in the soil to more toxic compounds such as vinyl chloride, which is a known human carcinogen (Salkinoja-Salonen et al., 1995; AURAS 2001).

... concentrations in 90% of German sludge samples were below the German limit values and concentrations have been decreasing in recent years (UMK-AG 2000).
AOX occurrence in sludge

Data: UMK-AG 2000
NPE selected statements
Nonylphenole (+ Ethoxylates)

... NPEs are used as surface active agents in cleaning products, cosmetics and hygienic products, and in emulsifications of paints and pesticides and are slowly being phased-out of the market

... there has been a significant reduction of nonylphenole (+ ethoxylates) in Norwegian sewage sludges between 1989 and 1997 (PAULSRUD et al. 2000)

... of the UK samples three exceeded the proposed EU limits (JONES & NORTHCOTT 2000).

... in Germany NPE is a relevant contaminant in waste water; amounts have decreased since the eighties, because industries voluntarily reduced the amounts used in cleaners (UMK-AG 2000).
NPE occurrence in sludge

LAS selected statements

Linear alkylbenzene sulphonates

… the rapid biodegradation of LAS after application has to be taken into account

… the detergents LAS and nonylphenole, have no effect on earthworms and collembola at presently allowed doses of sludge (KROGH et al. 1996)

… LAS content of Norwegian sewage sludges is in general far below the Danish standard (Törslöv et al. 1997), because most Norwegian households use eco-labeled detergents (Paulsrud et al. 2000).

… in Germany the amounts of LAS used are approximately constant (UMK-AG 2000).

… the majority of the UK samples exceed the LAS proposed EU limits (Jones & Northcott 2000)
LAS occurrence in sludge

Contents (mg/kg dm)

Törslöv et al., 1997, Paulsrud et al. 2000
DEHP selected statements

Di-2-(ethyl-hexyl)-phthalate

... a significant reduction of phthalates (DEHP) was found in Norwegian sewage sludges (Paulsrud et al. 2000)

... in Germany, the use of DEHP is decreasing slowly, because DEHP is replaced by more highly substituted phthalates and other plasticizers (UMK-AG 2000).
DEHP occurrence in sludge

Contents (mg/kg dm)

- Norway (1)
- Norway (2)
- Sweden (3)
- Denmark (4)
- Denmark (4)

EU 2000 3rd draft

- median
- minimum value
- maximum value

PAH selected statements
Polycyclic Aromatic Hydrocarbons

... benzo(a)pyrene concentrations in root (carrots), tuberous or leavy vegetables can surpass the critical value of 1 µg/kg BaP fm when soil concentrations are above 1 mg/kg BaP (see DELSCHEN et al. 1996, ROMMEL et al. 1998).

... therefore in Germany a threshold value for BaP in soil was set (1 mg/kg, BMU 1999)

... shifting from coal to oil for heating and improvements in heating technology ... resulted in a steady decrease of PAH concentrations in sewage sludges (UMK-AG 2000)

... Norway: The PAH content was well below the Swedish and Danish standards (PAULSRUD et al. 2000)

... UK: all samples were above EU limit, even those from WWTPs with purely rural, domestic wastewater (JONES & NORTHCOTT 2000)

... the EU proposals include limit values for the sum of 9 PAHs, but it is not clear what criteria have been used to select these compounds.
PAH occurrence in sludge

Contents (mg/kg dm)

there are very few fresh or ongoing primary emissions of PCBs into the environment (JONES & NORTHCOTT 2000).

in Germany concentrations have been nearly constant during the last decade (UMK-AG 2000).

the high stability of heavily chlorinated PCBs in the sludge, calls for a more precautious use of sewage on surface soils in public areas (AMUNDSEN et al. 1997).

UK: all below proposed EU limit (JONES & NORTHCOTT 2000)

Germany: all samples below German limit (BMU 1999a)

Ireland: all samples below German limit (MCGRATH et al. 2000)

Norway: all samples far below German and Swedish Standards (PAULSRUD et al. 2000)
PCB occurrence in sludge

Contents (µg/kg)

- Norway (1)
- Sweden 1993 (2)
- Sweden 1999 (3)

PCDD/F selected statements

Polychlorinated dibenzo-p-dioxins and -furans

... 20 to 40% of the PCDD/F entering German WWTPs comes from imported cotton textiles that were treated with PCP (HORSTMANN & MCLACHLAN 1994).

... the banning of PCP use in Germany and restrictions on the allowable concentrations in consumer products brought about a significant reduction in PCDD/F levels in sewage sludges (UMK - AG 2000).

... atmospheric deposition provides a direct source of PCDD/Fs to foliage, transfer of PCDD/Fs from soils and translocation to the shoots are negligible, except in Cucurbitacea (HÜLSTER 1994).

... most of PCDD/F stays in the peel of roots (JONES & SEWART 1995).

... PCDD/F transfer into livestock via soil ingestion or uptake of sludge adhering to feed are believed to be the major exposure route for humans (>99%), while intake from water and air are negligible (WILD et al. 1994).

... Norway: all samples below German Standard (PAULSRUD et al. 2000)

... Germany: average sewage sludges are below limit of "Klärschlammverordnung" (BMU 1999a)

... monitoring of sewage sludges for PCDD/Fs should be reduced (UMK-AG 2000)
PCDD/F occurrence in sludge

Contents (ng TEq/kg dm)

PCDD/F

EU 2000 3rd draft

median

minimum value

maximum value

Data: AEA Technology 1999
PBB/PBDE statements

Polybrominated Biphenyls (PBB) and Diphenyl Ether (PBDE)

... the ubiquitous presence of polybrominated biphenyls (PBB) and polybrominated diphenyl ether (PBDE) flame retardants in the environment has begun to attract international attention (RENNER 2000).

... Sweden has requested a freeze on the use of PBB and PBDE with EU authorities, because of an increase of concentrations found in breast milk and fish (HELLSTRÖM 2000)
ED’s statements

Endocrine disruptors

... more than a hundred chemicals are suspected to have hormone-like effects in organisms, most are likely to be found in sewage sludge (SMITH 2000).

... SMITH (2000) states that natural estrogens are readily biodegraded by the activated sludge process,

... PÄRT (2000) reports that little is known about the extent to which natural hormones (estrogens) and pharmaceutical residues are accumulated in sewage sludge and what happens with these compounds when the sludge is used on soils.
PCA statements

Chlorinated paraffins

... because of their widespread and unrestricted use PCAs are now present in a range of environmental compartments (TOMY et al. 1998).

... PCAs do not occur naturally and are of concern because of their toxic properties and capacity to bioaccumulate (BMU 1999a).

... total concentrations in UK sewage sludges of the short-chained and medium-chained PCAs ranged between 7-200 mg/kg and 37-9700 mg/kg, respectively, nonetheless, some of the sludge samples contain very high levels of these substances (JONES & NORTHCOTT 2000).

... at present a satisfactory evaluation of the environmental effects of chlorinated paraffins seems not possible (BMU 1999a).
TBTO statements

Organotins

... municipal wastewater and sewage sludge are contaminated with organotins.

... tributyltin compounds are among the most hazardous organic pollutants known for aquatic systems. (FENT et al. 1995).

... according to UMK-AG (2000) knowledge about pathways of organotin compounds in the environment and its presence and fate in sewage sludges is not yet satisfying.
VOC statements
Volatile organic chemicals

... sludge application to agricultural land is unlikely to increase the VOC concentration of the soil to levels which may cause concern for human health and the environment (WILSON et al. 1994).

... volatilization and loss of VOC occur rapidly from soils, yet VOC may present a hazard to agriculture when spread on soils with high content of organic carbon (WEBBER & GOODIN 1992).
### Summary: Classification of substances

<table>
<thead>
<tr>
<th>Substance</th>
<th>Mammalian/human toxicity (acute)</th>
<th>Ecotoxicity</th>
<th>Water solubility</th>
<th>Persistence</th>
<th>Concentration levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>AOX (summative parameter)</td>
<td>-</td>
<td>aquatic: high; terrestrial: medium; bioaccumulation: high</td>
<td>high; enhances mobility of other pollutants</td>
<td>medium</td>
<td>high, indicator</td>
</tr>
<tr>
<td>LAS</td>
<td>medium</td>
<td>aquatic: medium; terrestrial: medium; bioaccumulation: high</td>
<td>low</td>
<td>medium</td>
<td>high</td>
</tr>
<tr>
<td>DEHP (low)</td>
<td>aquatic: medium to high; terrestrial: low; bioaccumulation: high</td>
<td>high</td>
<td>low</td>
<td>medium</td>
<td>high</td>
</tr>
<tr>
<td>Nonylphenole (medium)</td>
<td>aquatic: high; terrestrial: medium; bioaccumulation: high</td>
<td>high</td>
<td>medium</td>
<td>medium</td>
<td>high</td>
</tr>
<tr>
<td>B[a]P single substance (PAH)</td>
<td>carcinogenic; mutagenic; teratogenic</td>
<td>high; bioaccumulation: high</td>
<td>low</td>
<td>high</td>
<td>high</td>
</tr>
<tr>
<td>PCBs, single substances/summative parameter</td>
<td>medium; tumour promoting, immunotoxic</td>
<td>aquatic: high; terrestrial: high; bioaccumulation: high</td>
<td>low</td>
<td>high</td>
<td>low and continuing to decline</td>
</tr>
<tr>
<td>PCDD/ Fs, single substance/summative parameter</td>
<td>high; carcinogenic</td>
<td>aquatic: high; terrestrial: high; bioaccumulation: high</td>
<td>low</td>
<td>high</td>
<td>low</td>
</tr>
<tr>
<td>TBT Tributyltin oxide</td>
<td>high</td>
<td>aquatic: high; bioaccumulation: high; endocrine effect</td>
<td>medium</td>
<td>high</td>
<td>high</td>
</tr>
</tbody>
</table>
Selected Suggestions

(1) A Harmonized EU Priority List based on key substances and toxicity equivalence factors should be developed.

(2) Soil - Water - Air Integrated Research should be initiated on the relative importance of contamination sources (e.g. air-soil versus sludge-soil pathway).

(3) To facilitate updating of the EU guideline on sewage sludge a EU-data bank should be build up.

(4) Information on the fate of contaminants in soils is incomplete. Therefore intensive permanent soil observation (> 50 years) should be established EU-wide as a prerequisite for final evaluation of persistence.

(5) Tolerable total yearly input rates have to be established including all contamination pathways. These rates could later be used for a EU-soil-protection Directive.

(6) In respect to the pathway soil - plant, the introduction of a limit value for soil concentrations of BaP into the EU-Initiative is recommended.