Probabilistic Risk Assessment for Linear Alkylbenzene Sulfonate (LAS) in Sewage Sludge used on Agricultural Soil

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Abstract

Deterministic and probabilistic risk assessments were developed for commercial LAS in agricultural soil amended with sewage sludge. The procedure done according to ILSI Europe’s Conceptual Framework [Schowanek, D., Carr, R., David, H., Douben, P., Hall, J., Kirchmann, H., Patria, L., Sequi, P., Smith, S., Webb, S.F., 2004. A risk-based methodology for deriving quality standards for organic contaminants in sewage sludge for use in agriculture—conceptual Framework. Regul. Toxicol. Pharmacol. 40 (3), 227–251], consists of three main steps. First, the most sensitive endpoint was determined. This was found to be the chronic ecotoxicity of LAS to soil invertebrates and plants. Additional endpoints, such as potential for plant uptake and transfer in the food chain, leaching to groundwater, surface erosion run-off, human health risk via drinking water, plant consumption and soil ingestion were also systematically evaluated but were all assessed to be of little toxicological significance. In the second step, a back-calculation was conducted from the Predicted No-Effect Concentration in soil (PNECsoil) to a safe level of LAS in sludge (here called ‘Sludge Quality Standard’; SQS). The deterministic approach followed the default agricultural soil exposure scenario in the EU-Technical Guidance Document (TGD). The SQS for LAS was calculated as 49 g/kg sludge Dry Matter (DM). In order to assess the potential variability as a result of varying agricultural practices and local environmental conditions, two probabilistic exposure assessment scenarios were also developed. The mean SQS was estimated at 55 and 27.5 g/kg DM for the homogeneous soil mixing and soil injection scenarios, respectively. In the final step, the resulting SQS values were evaluated for consistency and relevance versus available information from agricultural experience and field tests. No build-up, adverse impact on soil fertility, agronomic performance, or animal/human health have been reported for agricultural fields which have received sludge with high LAS levels for up to 30 years. Distribution statistics of LAS concentrations in anaerobically digested sewage sludge measured across Europe were created (mean value: 5.56 g LAS/kg sludge DM). When compared to the above mean SQS values, adequate risk characterisation ratios of 0.08–0.2 were found. The ‘ecological risk’ parameter calculated for anaerobic sludge from the probabilistic approaches was below 3%. A regulatory Limit Value for LAS of 2.60 g/kg sludge DM was originally proposed in the 3rd Draft of the Working Document on Sludge [CEC, 2000b. Working Document on Sludge. Third Draft, Brussels 27 April 2000, DG. Environment, 18 p.]. The current assessment, based on an updated dataset and a refined assessment procedure, suggests that the need for a limit value for LAS in sewage sludge cannot be substantiated on a risk basis.

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1. Introduction

ILSI Europe (the European Branch of the International Life Sciences Institute, http://europe.ilsi.org) has developed a Conceptual Framework (CF) which aims to serve as a ‘roadmap’ to perform scientifically consistent and holistic sludge risk assessments of organic chemicals (Schowanek et al., 2004). As such, the CF can be used for priority setting of chemicals for further risk assessment, and also allows to define threshold levels (here called ‘Sludge Quality Standards’) below which no significant adverse effects are expected, even from prolonged application. The proposed CF emphasizes the need for a systematic approach to risk assessment for sludge used in agriculture. The ultimate aim is to broadly protect public health and the environment, while maintaining the possibility for sludge use in agriculture.

Hence, the CF proposes a risk-based methodology to assess the need for and derive as necessary a SQS for organic contaminants in sewage sludge. A SQS is defined as the level of chemical in sludge which is fully protective of the soil that receives it, for a well defined application scenario. As such, a SQS can be interpreted in risk assessment terms as a Predicted No-Effect Concentration (PNEC). From a sludge management- or agricultural perspective, a SQS is easier to work with than a limit value defined for the receiving soil.

The example chemical chosen to illustrate the application of ILSI’s CF is the surfactant Linear Alkylbenzene Sulfonate (LAS, CAS# 68411-30-3; EINECS# 270-115-0). Commercial LAS enters agricultural soil solely via application of sewage sludge. Sufficient fate and toxicity data are available for LAS to conduct this exercise. Several risk assessments of LAS in the terrestrial environment have been published over time and have introduced subsequent refinements (Mieure et al., 1990; De Wolf and Feijtel, 1998; Jensen, 1999; Jensen et al., 2001; HERA, 2004). The present paper uses data from a recently revised terrestrial effects assessment for LAS provided by Jensen et al. (2007), combined with a new and refined probabilistic exposure assessment approach. Other relevant information that has been published over the last 5–6 years covers the investigation of LAS leaching in soils and groundwater (McAvoy et al., 2002), uptake by plants (Mortensen et al., 2001), and higher tier microbial sensitivity assessment (Brandt et al., 2003; Kristiansen et al., 2003; Vinther et al., 2003). The effect of lower temperature on LAS biodegradation was studied by Prats et al. (2006), showing the potential for efficient degradation in activated sludge down to at least 9 °C. Advances were also made with regard to the integration of probabilistic techniques in ecological risk assessment (Posthuma et al., 2002).

The chemical LAS is a low to moderately toxic (HERA, 2004), non-bioaccumulative (Tolls et al., 1997; HERA, 2004), high production volume anionic surfactant, employed in detergents and cleaning products. It was introduced in 1964 as the readily biodegradable replacement for highly branched AlkylBenzene Sulfonates (ABS) (www.lasinfo.org). It is presently used at rates of 350,000–400,000 t/y (or 2.7–3.0 g/(capita day)) in Western Europe (HERA, 2004). The commercial product, which is the subject of this paper, is a mixture of closely related isomers and homologues, each containing an aromatic ring sulfonated at the para position and attached to a linear alkyl chain. The linear alkyl chain has typically 10 to 13 carbon units, approximately in the following mole ratio C_{10}-C_{11}:C_{12}:C_{13} = 13:30:33:24, an average carbon number near 11.6, and a content of the most hydrophobic 2-phenyl isomers in the 18—29% range (HERA, 2004). Thus, commercial LAS consists of more than 20 individual components. The ratio of the various homologues and isomers, representing different alkyl chain lengths and aromatic ring positions along the linear alkyl chains, is relatively constant across the various household applications (HERA, 2004). The sorptive properties and aquatic toxicity of LAS are known to increase with increasing alkyl chain length (Garcia et al., 2002; Hatfield Venhuis and Mehrvar, 2004). Mineralization rates in river water and sediments showed overall little variation among different chain length homologues and structural isomers (Larson, 1990). The C_{13}-LAS homologue is presented in Fig. 1.

LAS is readily biodegradable and is highly removed (total removal 95–99.9%) in well functioning activated sludge wastewater treatment systems (HERA, 2004; Prats et al., 2006). The mass fraction removed via adsorption to sewage sludge in the primary settler is around 20–25%. The remainder of the removed fraction is almost entirely biodegraded in the aeration basin (Rapaport and Eckhoff, 1990). The main degradation pathway of LAS is initiated by an o-oxidation of the alkyl chain, followed by β-oxidations that result in formation of SulfoPhenylCarboxylic acids (SPC) as intermediates. The cleavage of the benzene ring ultimately yields CO₂, H₂O, and SO₄²⁻ (HERA, 2004, and references cited therein).

![LAS Chemical Structure](image-url)
LAS is, however, not degraded to any significant extent in anaerobic sludge digesters (AISE-CESIO, 1999). LAS concentrations present in sewage sludge have been reviewed (e.g., De Wolf and Feijtel, 1998; Ducray and Huyard, 2001; HERA, 2004; Jensen and Jepsen, 2005). Considerably higher concentrations were noted in anaerobically digested sludges (1000–30,000 mg/kg dry matter (DM)), versus fresh aerobic sludges (typically <1000 mg/kg DM), or than in aerobically stabilized sludges (100–500 mg/kg DM). There are several reasons for the elevated levels of LAS in anaerobically digested sludges: high usage volumes, sorption to primary sludge, precipitation as insoluble Mg/Ca-salts in the primary settler (Kd sludge = 1000–4000 l/kg depending on chain length; Rasmussen, 1999; Garcia et al., 2002), absence of anaerobic degradation, and the solids concentration effect caused by the digestion process. Biodegradation resumes however after a few days if the anaerobic sludge is stored aerobically, composted, or applied to land (Ward and Larson, 1989; Madsen et al., 1999; Prats et al., 1999; Madsen and Winther-Nielsen, 1999; Carlsen et al., 2002). LAS concentrations decrease by 75% when digested sludge is stabilized aerobically for 2–3 months prior to land application (Winther-Nielsen, 1999).

Concentrations of LAS in sludge-amended soils have been monitored (e.g., Matthijs and De Henau, 1987; Holt et al., 1989; Holt and Bernstein, 1992; Winther-Nielsen, 1999; State Agency for Environmental Protection Baden-Württemberg, 2003) and are the combined result of concentration in sludge, application rate, mixing depth, biodegradation and leaching rate, and the time of sampling. LAS concentrations in Danish sludge-amended soils were reviewed by Solbe (1999), and were below 20 mg/kg soil immediately after application. LAS in agricultural soil undergoes rapid biodegradation, reflecting the ‘ready biodegradability’ of LAS. Measured primary and ultimate biodegradation half-lives in soil during the growing season are ≤7 and 30 days, respectively (Holt et al., 1989; Figge and Schöberl, 1989; Jensen, 1999; Prats et al., 1999; HERA, 2004). Due to this rapid biodegradation, the actual Predicted Environmental Concentration in soil (PECsoil) for LAS will typically range between 0.1 and 1 mg/kg in the middle of the growth season (Solbe, 1999). For risk assessment, primary degradation rates are considered more relevant than ultimate degradation rates, since toxicity of LAS (and other surfactant types) is known to disappear quickly following alkyl chain shortening/oxidation (HERA, 2004, and references cited therein). Yet, for an assessment of accumulation potential in soil (in case of yearly sludge addition), mineralization rates are considered to be more indicative since this also covers the degradation of metabolites.

The mechanism of (eco)toxicity of LAS is non-specific polar narcosis, i.e., perturbation of cell membranes (Schwuger and Bartnik, 1980). The toxicological data show that LAS has a low acute toxicity in rats, is not a contact sensitizer, is not genotoxic in vitro or in vivo, does not induce tumours in rodents, and does not induce either reproductive toxicity, developmental or teratogenic effects (HERA, 2004). The LD₅₀ (Lethal Dose, 50%) for rats ranges from 1086 to 1980 mg/kg bodyweight (bw). The LD₅₀ for mice is 2205 mg/kg bw. The overall systemic NOAEL (No Observed Adverse Effect Level) for LAS was calculated as 68 mg/kg bw d (HERA, 2004). According to CESIO’s (www.cefic.org/cesio) recommendation, LAS is classified as ‘harmful if swallowed’ (R22) at concentrations equal or greater than 65% (mass/volume), while the substance is not classified at lower concentrations.

Whether or not to regulate concentrations of specific organic contaminants in sludge and agricultural soil has been intensively debated over the past years. A Limit Value of 2600 mg LAS/kg sludge DM was proposed in the 3rd Draft of the Working Document on Sludge on Sludge (CEC, 2000b). A lower value of 1300 mg/kg sludge DM is currently written in the Danish national legislation (Statutory Order 823, 2006). The presence of organic pollutants has led to a complex and presently unresolved discussion on the best options for sludge disposal, which in practice cannot seen in isolation from other sludge quality issues (such as heavy metals, pathogens, nutrients), cost considerations, and local sludge management tradition and infrastructure.

2. Application of ILSI’s conceptual framework to the sludge risk assessment of LAS

2.1. Background to ILSI’s conceptual framework (CF)

ILSI’s CF for risk assessment of organic contaminants applied with sewage sludge to soil (Schowanek et al., 2004) is illustrated in Fig. 2. The CF is essentially consistent in terms of transfer pathways and evaluation endpoints with similar schemes described in the EU-TGD (CEC, 1996, 2003), in the US-EPA Sewage Sludge Use and Disposal Regulations, Part 503 Standards) describing 14 exposure pathways (US-EPA, 1993), and in Ryan (1994). It is also in line with the integral management and protection objectives of the EU Water Framework Directive (CEC, 2000a) (http://europa.eu.int/comm/environment/water/water-framework/index_en.html).

2.2. Step 1: effects assessment; identification of the most sensitive toxicological endpoint

2.2.1. Toxicity to soil microflora, fauna, and crops

According to ILSI’s CF (Fig. 2), the effects assessment to soil microorganisms, fauna and plants/crops is a central step. Over the last decade there have been a series of subsequent studies and publications that focused on the risk of LAS towards terrestrial organisms, and the derivation of a representative PNECsoil (Kloeper-Sams et al., 1996; De Wolf and Feijtel, 1998; Jensen, 1999; Solbe, 1999; Jensen et al., 2001). The latter authors proposed a PNECsoil value of 4.6 mg LAS/kg soil DM. This value
has since been a reference point in several regulatory assessments (e.g., SCHER, 2005) and review papers (e.g., HERA, 2004). However, in a recent manuscript by the same group (Jensen et al., 2007) the PNEC_soil has been revisited based on various new pieces of information. These were in particular novel and more robust effects data from Krogh et al. (2007) for some species of the soil fauna (i.e., Folsomia candida, Aporrectodea caliginosa, and Enchytraeus crypticus). The reader is referred to the (Jensen et al., 2007) paper for an in depth review and interpretation of the old and new data, but a short summary is provided below.

2.2.1.1. Toxicity to soil microorganisms. Microbial parameters (10 functional or structural endpoints) were reviewed but not further used by Jensen et al. (2007) in the PNEC_soil assessment. For background, EC_{10} values for microbial processes observed in the laboratory ranged from <8–793 mg aqueous LAS/kg soil DM. Microbial iron reduction was the parameter most sensitive to LAS (extrapolated value of 5 mg/kg; Jensen et al., 2001), but this endpoint was not considered relevant for aerobic agricultural soils (Jensen et al., 2007). Another rationale was that the lowest microbial effect concentrations had been observed in the case of dosing of aqueous LAS solutions, whereas in reality LAS enters soil in a sludge matrix, where bioavailability was shown to considerably mitigate toxic effects (Elsgaard et al., 2001; Gejslsbjerg et al., 2001). For example, ammonium oxidation, an important aerobic transformation process showed a lowest EC_{10} value of 14 mg/kg for aqueous dosing, versus 68 mg/kg for LAS in a sludge matrix (Elsgaard et al., 2001). In the latter study, microbial communities also showed a strong recovery potential.

More ecologically realistic microbiological tests carried out in the field at concentrations even up to 31 g LAS/kg sludge (i.e., the highest levels conceivable in sludge), and applied in lines without mixing into the soil showed no effect on heterotrophic respiration in the sludge compartment per se. The activity and metabolic quotient (i.e., microbial activity per unit of biomass) were actually stimulated in the surrounding soil (Brandt et al., 2003). Considering the relative higher sensitivity of plants and invertebrates, the key soil processes mediated by bacteria are considered to be protected at the suggested PNEC value (35 mg/kg, see below).

2.2.1.2. Toxicity to soil fauna. According to all available data reviewed by Jensen et al. (2007), LAS does not appear to be acutely toxic to invertebrate soil fauna (LC_{50}/EC_{50} typically >500 mg/kg). Results of longer-term, chronic ecotoxicity tests with more sensitive endpoints are available today for nine soil invertebrate genera (Jensen et al., 2001, 2007; HERA, 2004). The papers and original study reports were thoroughly reviewed in order to identify any major deviations from internationally accepted guidelines. Robust summaries of key studies were subsequently produced and were made available on http://www.lasinfo.org/regulatory_affairs.html#a03. Tested organisms considered relevant for the risk assessment were:

- Oligochaetes (earthworms): Eisenia fetida, a litter dwelling species, two species (Aporrectodea spp.) that feed on fungi, soil, and plant material, and Enchytraeus sp. an enchytraeid earthworm that occurs in high densities in the upper soil layers and plays an important role in decomposition and soil formation. Furthermore, a
toxicity test with Lumbricus terrestris, a primary decomposer earthworm, is reported (Swigert, 1989). However, this test is considered a short-term test (14 days) for this relatively slow growing species, and it has therefore not been included in the HCs_{5,50} calculation. (NB: a Hazardous Concentration HC_{5,50} is the median value of the 5th percentile of the lognormal Species Sensitivity Distribution (SSD) of all available NOEC and/or EC_{10} values. This means that the NOEC and/or EC_{10} values for 95% of the species are above the HC_{5,50} value (Posthumua et al., 2002)).

- Insects: springtails (Collembolans, i.e., small wingless insects with an abdominal jumping organ: Folsomia spp., Isotoma, Hypogastrura). Collembolans feed on decaying plant material and fungi. Numerous reproduction data for the springtail species Folsomia fimetaria are available (Holmstrup and Krogh, 1996; 2001; Holmstrup et al., 2001; Jensen and Sverdrup, 2002). These data cover exposure in different soil types using different LAS salts. The geometric mean of data from seven chronic studies with Folsomia fimetaria is 107.6 mg/kg (individual data not shown here). This number was used in the present risk assessment. In a recent study Krogh et al. (2007) tested the toxicity of LAS to the springtail Folsomia candida. The data for the two related springtail species have been separated in the HC_{5,50} calculation.

- Arachnids: the herbivorous grazer Platynothrus peltifer, and the predatory mite Hypoaspis aculeifer (Jensen et al., 2001).

The lowest number from the soil fauna species sensitivity distribution is an EC_{10} of 27 mg/kg soil for Enchytraeus sp.

2.2.1.3. Toxicity to plants. Twelve laboratory (14 and 21 days) phytotoxicity tests are available today for LAS. Robust summaries were equally posted on “http://www.lasinfo.org/regulatory_affairs”. In all of these experiments, LAS was added as an aqueous solution, and thus the dataset will err on the conservative side for application via sludge. A variety of species were tested, some major crop species and some without agronomic relevance. Growth was found to be the most sensitive endpoint for all species. In a previous assessment (Jensen et al., 2001), “negligible effects” concentrations were extrapolated using EC_{50} (Effect Concentration, 50%) values and an arbitrary extrapolation factor of 10. These extrapolated values were used to calculate a HC_{5,50} for terrestrial plants. In the updated (Jensen et al., 2007) assessment, the original data were consulted in order to derive the EC_{10} values (or the NOEC (No observed Effect Concentration) when no classical dose response was observed). These extrapolations are considered more appropriate compared to a generic use of an arbitrary extrapolation factor (10), as they are based on the actual data. The lowest EC_{10} value for plants was 55 mg LAS/kg soil DM for Galinsoga parviflora.

2.2.1.4. Summary of the results. The total of terrestrial dataset considered as representative hence comprises 21 data points; 12 for plants and 9 for invertebrates. The sensitivity profile of the latter two groups of species towards LAS conformed with a lognormal distribution as shown by a Kolmogorov-Smirnov test (results not shown). LAS has a non-specific mode of action operating via general membrane disturbance, which can explain the fact that there is no major difference in sensitivity between plants and invertebrates. The datasets for plants and invertebrates have therefore been merged by Jensen et al. (2007) for use in risk assessment. The SSD calculation has resulted in a new HC_{5,50} value of 35 mg LAS/kg soil DM (Jensen et al., 2007). This 5th percentile of the SSD was taken in this assessment as the PNECsoil, and revises the previous value of 4.6 mg/kg as published in Jensen et al. (2001).

2.2.2. Indirect exposure route via soil; uptake by plants and animals

LAS is not significantly taken up and accumulated by plants. The bioavailability of LAS applied to soil via sludge is limited due to adsorption to the associated organic matter. In studies with sludge-amended soils used with various crops, limited LAS uptake by the plants was observed and no leaching of LAS was detected in soil cores (Figge and Schöberl, 1989; Figge and Bieber, 1999; Mortensen et al., 2001). Studies with radiolabelled LAS have shown minimal uptake in, or adsorption to, roots and tubers, while transport to the stem and leaves was negligible (Figge and Bieber, 1999). Limited plant translocation of LAS was also reported by Knaebel and Vestal (1992). The risk of plant uptake and subsequent LAS transfer to animals or humans has also been judged to be minimal (CEC, 2001). Models exist to calculate plant uptake to roots, stems and leaves (e.g., EUSES model) based on physico-chemical properties, but in view of the above experimental evidence modelling work would not provide additional precision. Direct foliar uptake on cropland or pastures is also irrelevant since the sludge needs to be injected or immediately worked into the soil.

There are no cases reported in the literature of contamination by LAS of crops or cattle due to the use of sludge on agricultural soils under the provisions of the current Sludge Directive (86/278/EEC). Ingestion of agricultural food products is not expected to contribute to any significant extent to the total LAS exposure of consumers (HERA, 2004). Therefore, a calculation of a Margin of Exposure (MoE) for indirect exposure of cattle, and subsequently humans, was not further pursued.

LAS is not bioaccumulative and does not transfer through the aquatic food web (Tolls, 1998). Specific HPLC analyses in the water phase and in fish body during a OECD 305E test showed that LAS reached a steady state concentration in fathead minnows (Pimephales promelas) in about 3 days. Biotransformation contributed to more than 40% of the elimination, as shown for pure 2-phenyl-C_{12} LAS (Tolls et al., 2000). The Bioconcentration factor
(BCF) in fathead minnow for the tested LAS homologues ranged from 2 to 990 l/kg, generally increasing with increasing alkyl chain length. The BCF of C\textsubscript{11.6} commercial LAS mixture was 66 l/kg, whereas the LAS fingerprint in surface water (C\textsubscript{10.8}) had a BCF of 16 l/kg (Tolls et al., 1997). Similarly, based on the low bioavailability of LAS in soil, and given the low BCFs observed for commercial mixtures of LAS in fish, LAS is not expected to bioaccumulate from soil pore water into the terrestrial food chain. However, measured BCFs or Bioaccumulation Factors (BAFs) for soil invertebrates, such as earthworms, have not been reported to our knowledge.

2.2.3. Indirect exposure route via drinking water; leaching and run-off

Rasmussen (1999) used the one-dimensional leaching model MACRO to assess the transport of sludge-applied LAS in soil. Transport was assumed to occur either in association with colloidal matter or with Dissolved Organic Carbon (DOC). None of these processes contributed significantly to the LAS mass balance in soil, and percolate concentrations were estimated to be below 25 μg/l Rasmussen (1999). The degree of leaching of LAS to depths below 1 m is expected to be <1.3% of the LAS applied with sludge according to Madsen and Winther-Nielsen (1999). The maximum calculated LAS concentration in European groundwaters was 37 μg/l (De Wolf and Feijtel, 1998; Jacks et al., 2000), i.e., well below the maximum admissible surfactant concentration in drinking water of 200 μg/l, defined as laurel sulfate in Directive 80/778/EEC (NB: the current Directive (CEC, 1998) does not specifically regulate surfactants). The limited leaching potential of LAS to groundwater (an important drinking water source in most EU countries) is corroborated by experimental data (Figge and Schöberl, 1989; Figge and Bieber, 1999; McAvoy et al., 1994, 2002; Nielsen et al., 1997). According to HERA (2004) the maximum measured concentration of LAS actually measured in a sample of groundwater was 3 μg/l. Contamination of groundwater used for drinking water production is therefore not of significant concern. This is further elaborated in the risk calculation below:

Assuming an exposure scenario where a person would consume 2 l groundwater/day (CEC, 1998), 100% oral bioavailability of LAS in humans, and 60 kg body weight, the realistic worst case daily human oral intake of LAS from drinking water can be estimated as [(3 μg/l) × (2 l)]/(60 kg bw) = 0.1 μg/(kg bw day). For direct and indirect human health effects, the Margin of Exposure (MoE) is the ratio of the NOAEL or an appropriate substitute, to the estimated or actual level of human exposure to a substance. According to HERA (2004), a systemic NOAEL for LAS of 68 mg/(kg bw day) should be used to calculate the MoE values in the different exposure scenarios. For a daily systemic dose of 0.1 μg/(kg day), the MoE for the oral route drinking water = systemic oral NOAEL/estimated systemic dose = 68,000/0.1 = 6.8 × 10\textsuperscript{5}. This scenario is conservative since it does not take into account further polishing of the groundwater before consumption, as would be normally the case.

No measured LAS surface erosion fluxes and run-off data are reported to our knowledge, but this diffuse input is likely to be a negligible source of LAS in surface waters when compared to the continuous point source input of LAS via sewage treatment plant effluents. Kannan et al. (2007) used the SWAT 2000 model to predict the diffuse-source transfer to surface water for LAS sorbed to sludge used on land. The maximum predicted dissolved phase concentrations were always below 5 μg/l.

Ample of studies report monitored LAS concentrations in rivers, with levels varying broadly from a few μg/l to several 100 μg/l as a function of local LAS usage, the incidence and performance of the treatment plants, and the local hydrological situation (for more specific information see, e.g., Holt et al., 1998; Schröder et al., 2002; HERA, 2004; Hatfield Venhuis and Mehrvar, 2004). Surface water used for drinking water preparation is normally extensively treated. In this process LAS is eliminated to a very high degree, and has never been reported to occur at any concern level in treated drinking water. Indirect exposure through drinking water represents also a comfortable MoE when the former maximum admissible surfactant concentration in drinking water of 200 μg/l is used as a benchmark (68,000 μg/(kg bw day)/6.6 μg/(kg bw day) = 10,303).

2.2.4. Direct human exposure; soil ingestion and respiration of vapours or airborne dust

ILSI’s CF covers the assessment of potential direct oral (i.e., soil pica) or respiratory exposure to humans. A series of simple and conservative calculations are provided below:

2.2.4.1. Soil pica. Scenarios for soil pica from the literature have been listed in Schowanek et al. (2004), although these can be considered as quite unusual events. In the first instance a single exposure is considered where a child (20 kg) would ingest 60 g of sludge-amended soil. Assuming the LAS concentration is equivalent to the terrestrial PNEC, 35 mg/kg, this would lead to an exposure of:

\[
\text{0.060 kg/d} \times 35 \text{ mg/kg} = 2.1 \text{ mg LAS/day,}
\]

or
\[
0.105 \text{ mg LAS/(kg bw day)}
\]

Compared with the LAS LC\textsubscript{50} (Lethal Concentration, 50%) for rats of 1086 mg/kg bw (HERA, 2004) and making abstraction of eventual extrapolation factors from rats to humans, this shows the absence of any acute intoxication risk from ingesting sludge-amended soil. The MoE in this case = 1086/0.105 = 10,342.

Secondly, for a worst case prolonged uptake of 60 g soil/day, the comparison should be made against the systemic NOAEL for LAS of 68 mg/(kg bw day). This leads to a MoE of 68/0.105 = 648.

The MoE value suggests that the risk is negligible for a child with soil pica behaviour (NB: further information on...
different soil pica scenarios can be found in the US-EPA Exposure Factors handbook; http://www.epa.gov/ncea/pdfs/efh/front.pdf).

2.2.4.2. Volatilization and respiration of vapours. LAS is known as a non-volatile compound, and in addition occurs mainly adsorbed to sludge. Therefore any significant exposure via this pathway can be considered unlikely. In ECE-TOC (2002), a simple equation is provided to estimate volatilization half-lives from chemicals in soil, based on work from Burkhard and Guth (1981), which confirms this assessment:

The volatilization half-life,

\[ T_{1/2} = \frac{1}{2} \left( \frac{KOC \times S}{VP} \right) \]

where KOC is the organic carbon-normalized soil sorption coefficient, S is the water solubility (mg/l) and VP is the vapour pressure (Pa). When applied to LAS, this leads to:

- \( Kd \) soil = 2–20 l/kg (10 average) (Painter, 1992; M caverny et al., 1994; Rasmussen, 1999).
- \( KOC \) soil = \( Kd/Foc = 10/0.02 = 500 \) l/kg (fraction soil organic carbon is assumed 2%).
- \( S = 250,000 \) mg/l (0.25 kg/l) (HERA, 2004).
- \( VP = 3 \times 10E-13 \) Pa (HERA, 2004).

Hence, \( T_{1/2} \) is estimated at approximately 6583 days (~18 years), i.e., a very low volatilization rate from soil and therefore a negligible exposure. In practice, LAS will have been degraded long before it would volatilize.

2.2.4.3. Respiration of airborne dust. Since LAS adsorbs quite strongly to sludge and soil particles (see above), this route should be explored as an occupational health scenario for farmers working in dusty and windy conditions. Only particles smaller than 10 µm, the so-called PM10 fraction, can penetrate deep into the lungs. In the case of soil these are clay and smaller silt particles, or fine dust of organic nature (e.g., soot).

Systemic exposure to dust particles and aerosols can be estimated according to (HERA, 2004) as:

\[ \text{Exp}_{\text{systemic}} = C \times Q \times T \times (n/bw) \]

where

- \( C \), respirable and bioavailable concentration of chemical in air (µg/m³).
- \( Q \), ventilation rate (0.8 m³/h).
- \( T \), duration of exposure (e.g., 8 h).
- \( n \), number of events/day (frequency) (e.g., 1/day).
- bw, Body Weight (farmer of 70 kg).

For soil with 35 mg LAS/kg DM (assuming equal distribution of LAS over a soil particle fractions) and a conservatively high PM10 level of 100 µg/m³, the concentration of LAS in air is 0.0035 µg/m³.

The systemic exposure is therefore calculated as:

\[ 0.0035 \times 0.8 \times 8 \times 1 \times 1/70 = 0.32 \text{ ng LAS/(kg bw day).} \]

This exposure—even if fully bioavailable and taken up via the lungs—has a MoE of \( 68 \times 10^6/0.32 = 221.5 \times 10^6 \), which indicates an insignificant risk.

From these different human exposure scenarios it can be concluded that direct human safety considerations will not dictate the SQS for LAS in agricultural soil. Margins of exposure increase from oral soil uptake (pica), to drinking water intake, and to respiration of soil dust particles.

2.3. Step 2: soil exposure assessment and back-calculating of sludge quality standards

The most sensitive endpoint according to ILSI’s CF for LAS dosed to land via sludge is terrestrial toxicity. The PNEC for a soil exposed to LAS was estimated to be 35 mg/kg soil DM, based on a combined SSD of the terrestrial fauna and flora.

The second step in the process consists of back-calculating a safe level of LAS in sludge (i.e., the SQS) from the PNECsoil value. The underlying principle is that at the SQS, the addition of sludge to soil according to a well defined scenario would not exceed the PNECsoil. The difficulty here lies in defining representative sludge application and soil exposure scenarios. One could opt for a standardized, deterministic, approach as defined in the EU TGD (CEC, 2003), or explore a series of scenarios that reflect the inherent variability of sludge handling, agricultural practice, and soil properties across Europe. In this paper we will compare both approaches.

2.3.1. EU TGD scenario for calculating the SQS

In the EU TGD (CEC, 2003), which is the benchmark for both European industry and regulators regarding the safe use of chemicals, a single deterministic scenario is proposed for risk assessment in different environmental compartments (including soil). The TGD scenario for exposure of sewage sludge on agricultural soil was taken as the basis for back-calculating a SQS for LAS. Model parameters for this default scenario are summarized in Table 1.

A realistic worst case assumption in the EU TGD is that the sewage sludge (either fresh aerobic sludge, or anaerobically digested) is added directly onto land following production, i.e., without an aerobic storage/stabilization period. In reality, sludge is added on cropland only in spring prior to seeding, or in autumn after the harvest. This implies that a sludge storage period can range from 0 to approximately 150 days. On grassland, however, sludge can be used at any time of the year but it must be injected below the surface.

It should also be noted that, according to the TGD, the PEC (Predicted Environmental Concentration) is calculated taking into account 30 days ‘time-weighted averaging’ during which biodegradation can occur. This means in practice that for biodegradable chemicals not the initial
PECSOIL (i.e., the highest exposure value at time zero) is used in the risk assessment, but a concentration which represents the modelled average value over the first 30 days. The logic here is that seeding or planting usually takes place a few days or weeks after sludge amendment, such that the use of the initial concentration would be rather conservative.

If no degradation time is taken into account, the SQS is based on the initial soil concentration and is calculated as (CEC, 2003):

\[
\text{SQS} = \frac{\text{PEC}_{\text{soil}} \times \text{dilution factor sludge/soil} \times 35 \text{mg/kg sludge DM} \times 600 \text{mg LAS/kg sludge DM}}{10,000 \text{mg LAS}}
\]

(where: dilution factor sludge/soil = weight of the soil DM/weight of the added sludge DM).

The formula for the 30 days ‘time-weighted averaging’ is:

\[
\text{SQS} = \frac{\text{PEC}_{\text{soil}} \times t \times k}{(1 - e^{-kt})} \times \text{dilution factor sludge/soil or,}
\]

\[
35 \times (0.069 \times 30/(1 - 0.126)) \times 600 = 49,736 \text{ mg LAS/kg sludge DM}
\]

The latter SQS is about 38 times above the Danish Limit Value of 1.3 g LAS/kg sludge DM, and 19 times above the draft EU Limit Value (2.6 g/kg). This large difference can be attributed to the combination of three factors: (1) an upward revision of the PNECsoil, (2) the use of the ‘time-weighted averaging’ concept, and (3) a slightly higher dilution factor. The 2.4-fold difference between the 21 g/kg and the 49 g/kg values illustrates the impact of the time-averaging concept. Due to rapid degradation, this factor does play a significant role for LAS.

Another way to express the outcome is as a ‘safe loading’ of LAS per surface area and per time. The above SQS values correspond to 105 kg LAS/ha year (initial concentration) and 249 kg LAS/ha year (30 days time averaging), respectively.

2.3.2. Sensitivity analysis of the SQS

Wastewater treatment infrastructure, sludge management and agricultural practice vary across Europe, and local factors will lead to spatial and temporal differences in the SQS. Some of the main elements of variability associated with sludge application on cropland are explored below. These may stem from (local) factors such as sludge application rate, chemical half-life (as varying with climate and season), soil mixing depth, soil density, etc. Another variable, but one which was not further explored in a quantitative way in this analysis, is the reduction of LAS levels during aerobic sludge storage (Knudsen et al., 2000), or through composting (Moeller and Reeh, 2003). It is assumed in the assessment that the sludge is transferred directly from the waste water treatment plant to the field. In reality, LAS degradation often occurs incidentally during storage and provides additional reassurance that SQS values derived here are conservative.

A Monte Carlo (MC) procedure was used to deal with multiple sources of variability. According to Schnoor (1996) the steps in the MC analysis include: (1) determining the function and variables that are to be analysed and the distribution of all parameters that vary in space or time, (2) sampling each of the parameter distributions using a random number generator, (3) repeating the sampling step a number of times (e.g., 1000×) until a stable statistical output is obtained, and (4) plotting and analysing the output data.

For the MC analysis Palisade’s @Risk software version 4.5 (www.palisade.com) was used, which works as a Microsoft XL spreadsheet plug-in. Table 1 provides an

<table>
<thead>
<tr>
<th>Parameter</th>
<th>TGD (PEClocal soil) parameters</th>
<th>Distribution of parameters for the sensitivity analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yearly application rate sludge</td>
<td>5000 kg DM/ha year</td>
<td>Triangular distribution (trigen)(^a) with 4000 as mode, 2500 as 5th percentile and 10,000 kg/ha as 95th percentile (truncated at 1500 and 13,000 kg/ha)</td>
</tr>
<tr>
<td>RHOsoil (bulk density)</td>
<td>1500 kg/m(^3)</td>
<td>Lognormal distribution with mean = 1350 kg/m(^3), SD 150 (truncated at 1000 and 1700 kg/m(^3))</td>
</tr>
<tr>
<td>Depth soil</td>
<td>0.2 m (0.1 for grassland) (assumes homogeneous mixing)</td>
<td>Scenario a: 0.15–0.25 m: trigen distribution with mean = 0.2 m (truncated at 0.15 and 0.25 m) Scenario b: 0.1 m (single value)</td>
</tr>
<tr>
<td>Dilution factor sludge/soil</td>
<td>600</td>
<td>Calculated as dependent variable</td>
</tr>
<tr>
<td>Averaging time to calculate initial exposure</td>
<td>30 days</td>
<td>30 days</td>
</tr>
<tr>
<td>Biodegradation half-life in soil: scenarios</td>
<td>Primary biodegradation: (T_{0.5} = 10) days ((k = 0.069/day))^b</td>
<td>Primary biodegradation: lognormal distribution of half-life with mean = 10 days and SD = 5 days</td>
</tr>
<tr>
<td></td>
<td>Mineralization: (T_{0.5} = 0) days ((k = 0.023/day))</td>
<td>Mineralization: lognormal distribution with mean = 30 days, SD = 15 days (for information, data not presently used in the simulations)</td>
</tr>
<tr>
<td>Aerobic stabilization or sludge post-treatment processes</td>
<td>Not considered</td>
<td>Not considered</td>
</tr>
</tbody>
</table>

\(^a\) Trigen: a type of triangular distribution in the @RISK software.

\(^b\) The TGD 2003 uses a half-life of 30 days as default value, which is overwritten here by a value of 10 days based on field monitoring data.
overview of the variable parameters and their assumed distribution. Some perspective on the choice of the parameter distributions is provided below.

2.3.2.1. Application rate. Across Europe, the average sludge application rate is around 4000 kg/ha (dry solids basis), although the range is large (2–12 tonne DM/ha), depending on the frequency of application and the restrictions on nutrient and heavy metal additions adopted by individual Member States within the framework of EC Directive 86/278/EEC. Application rates below 2000 kg/ha are of little agricultural benefit and are therefore seldom applied. For the MC analysis a bounded, triangular distribution was selected with mode = 4000 kg/ha, 5th percentile = 2500 kg/ha and 95th percentile = 10,000 kg/ha.

2.3.2.2. Soil bulk density (RHO). This parameter depends essentially on the composition of the soil, its structure and organic matter content. Based on empirical data in (Stöckle and Nelson, 1993; Kätterer et al., 2006) the RHO parameter was approximated by a lognormal distribution with mean = 1350 kg/m³, SD = 150, with range truncated at 1000 and 1700 kg/m³.

2.3.2.3. Incorporation depth. It is known from agricultural practice that the application of sludge to soil does not always result in sludge and soil being homogenously mixed. For this reason two different scenarios were considered:

(a) Homogeneous mixing: sewage sludge spread on top of the soil and then thoroughly ploughed and harrowed at a mixing depth of 0.15–0.25 m (the normal range for soil cultivation). For the simulation a triangular distribution was selected with a mode of 0.2 m and truncated at 0.15 and 0.25 m.

(b) Non-homogeneous mixing: the objective is to simulate the injection of sewage sludge, and situations where solid sludge will remain as discrete “pieces” in soil when incorporated through ploughing to 0.2 m depth or more. It is known from agricultural practice that very heterogeneous situations can exist, where residual sludge particles will only slowly disintegrate into the surrounding soil. A limited mixing depth (0.10 m) was assumed to cover such cases. In this scenario, parts of the soil and its organisms are not exposed to sludge. This provides a biological reservoir from which the exposed part can be (re)colonised. For the simulation a uniform depth of 0.1 m was selected.

2.3.2.4. Biodegradation half-lives. In several laboratory and field studies, soil degradation rates of LAS have been measured (Holt et al., 1989; Ward and Larson, 1989; Holt and Bernstein, 1992; Knaebel et al., 1990; Knaebel and Vestal, 1992; Jensen, 1999; Gejlsbjerg et al., 2003). In these studies either commercial LAS or a a representative homologue (e.g., C12) were used. The decay has typically been modelled by a first order process, although the kinetics over several half-lives can be more complex and multiphasic. In the case of LAS, irreversible binding or aging processes do not seem to play a major competing role during the degradation process, as shown by the total degree of mineralization obtained (see e.g., Gejlsbjerg et al., 2003). The distribution of measured biodegradation half-lives for chemicals in general in the environment is usually asymmetric and well described by a lognormal function, i.e., with a tail towards longer half-lives. This is a common choice for natural variables that are themselves composed of several (sub)variables (Vose, 1996). As an average of all available data for LAS, lognormal distributions with mean half-life of 10 and 30 days were taken for, respectively, primary degradation (i.e., loss of parent and surfactant function) and mineralization (i.e., CO₂ release).

For sewage sludge homogeneously mixed into soils (probabilistic scenario a), the outcome of the Monte Carlo simulation is a lognormal-type curve with mean, 5th and 95th percentile SQS at 55,338, 19,074, and 125,807 mg LAS/kg sludge DM, respectively. For sewage sludge injected into the soil (probabilistic scenario b) these numbers correspond to 27,652, 9937, and 61,790 mg LAS/kg sludge DM– approximately half the values for scenario a (Fig. 3).

2.3.3. Distribution of LAS in European sludges

In order to interpret the probabilistic SQS information from a sludge risk management viewpoint, the above values can be compared against the distribution of LAS levels in sludge in a particular country, or for the entire EU. A distribution of LAS in Danish sludge was prepared for the mid-nineties period by Törslöv et al. (1997), and these data were further updated by Jensen and Jepsen (2005).

Since the aim of this paper was to cover the pan-European situation rather than Denmark only, new approximative distributions were made based on reported LAS concentrations in aerobic and anaerobic sludges from all EU countries for which data could be found in science papers and public reports. The data collected cover the time period 1988–2006. The total use of LAS over this period has been relatively stable (fluctuations less than 15% based on CESIO statistics). A limitation of this approach is that the amount of available data differed considerably from country to country; most of the reported data were measured in Denmark, Spain, Italy, UK, and Germany. Separate distributions were made for aerobic and anaerobic sludges, in order to avoid potential bias introduced by the (unknown) relative incidence of treatment technologies across Europe.

The distribution of LAS in aerobic sludges was characterised by a mean of 176 and a median of 100 mg LAS/kg sludge DM. The maximum value was below 1000 mg/kg (distribution not shown). Given these low values, aerobic sludges were not considered relevant in the context of LAS sludge risk assessment.
The distribution of anaerobically digested sludges (Fig. 4—represented as cumulative probability and based on ca. 155 data points) showed a mean of 5564 and median of 4284 mg LAS/kg sludge DM. These values relate to the concentrations in anaerobic sludge as leaving the reactor. The largest value included in the dataset was 30,200 mg/kg, but this value is a clear outlier: no other data were found above 20,000 mg/kg, and most data are below 15,000 mg/kg. The distribution of LAS in anaerobic sludge was further analysed by means of Palisade’s Best Fit 4.5 software, and was best described by a Beta distribution (Fig. 4). This showed that the estimated 10th and 90th percentile are situated at 880 and 12,010 mg LAS/kg sludge DM, respectively (490 and 15,070 mg/kg for the 5th and 95th percentiles). Due to the large dataset, the presence or absence of single extreme values did not significantly affect the distribution parameters.

2.3.4. Overview of risk characterisation ratio (PEC/PNEC) for LAS in sludge

Table 2 provides an overview of the Risk Characterisation Ratio (RCR) for the deterministic and probabilistic assessment scenarios. The calculations are based on the mean values of the measured LAS distribution (PEC) and the calculated SQS distributions (PNEC). The results for the 3 different approaches indicate comfortable safety margins (i.e., RCRs well below 1). This indicates that the presence of LAS in sludge used on agricultural land, either thoroughly mixed or injected, does not represent a safety issue. The impact of inherent variability around this average situation will be further analysed in Section 2.4.3.

2.4. Step 3: validation, discussion, and conclusions

In the final, third, step of the procedure a number of reality checks were made, including an evaluation of the risk for accumulation of a chemical over time, a comparison of the effects assessment (based on laboratory data) with available field evidence, and a further sensitivity analysis of the RCR.

2.4.1. Assessment of potential accumulation over time

The TGD (CEC, 2003) provides a series of equations to calculate the concentration of a chemical after 10 years of use for a single annual application.

\[
F_{\text{acc}} = e^{-365k}
\]

(where \(F_{\text{acc}}\) = fraction accumulated after 1 year)

\[
C_{\text{sludge soil}_{x}} = C_{\text{sludge soil}_{1}} \times \left[1 + \sum_{n=1}^{\infty} F_{\text{acc}^n}\right]
\]

(where \(C_{\text{sludge soil}_{x}}\) = concentration in soil after \(x\) yearly additions of sludge)

Calculating \(F_{\text{acc}}\) for a mineralization half-life of 30 days \((k = 0.023)\) leads to less than 2% of the initial concentration left after 6 months, and less than 0.1% after 1 year. This is in line with the modelling work done by Jones and Stevens (2002). Given this low residual value, there is no further need for an assessment over longer periods. A soil mineralization half-life of 30 days was used since this value is considered more relevant than primary degradation half-life to assess potential build-up of chemicals or metabolites over longer periods.

Based on information from field studies, LAS does indeed not accumulate as a result of repeated additions at normal (yearly) intervals. After a few years without sludge addition, residual LAS drops to values below 1 mg/kg soil (Holt et al., 1989; Solbe, 1999; Carlsen et al., 2002). Since there is no risk of accumulation, a downward correction factor on the calculated SQS is not required.

2.4.2. Information from field studies: soil fertility and crop productivity

The SQS, which in the above probabilistic modelling is based on laboratory/greenhouse effects data only, should...
also be validated with field data, where available. The ‘litmus test’ of this risk assessment and associated SQS derivation is the confirmation of good and sustained agronomic performance in sludge-amended soils that have been amended with high and repetitive doses of a chemical, as well as the absence of any significant, irreversible, ecotoxicological effects in the soil ecosystem. While there are several field studies with sludge containing LAS, only few further explore the link between actual exposure and agricultural performance or soil fertility. Yet, no study in the literature has associated LAS with a reduced soil fertility or lower crop production. Moreno-Caselles et al. (2006) report that LAS (spiked directly into the soil) can influence the mineral and macronutrient content of broccoli plants. Nutritional value is an endpoint not normally dealt with in terrestrial risk assessment, but nevertheless may require further investigation.

One of the most informative field studies in the context of validation of the SQS was performed with simulated sludge injection lines of 4×4 cm, located in the 7–11 cm soil horizon of an oat field in Denmark (Brandt et al., 2003; Petersen et al., 2003). Sludge was artificially spiked with 10 and 50 g LAS kg⁻¹ sludge dry matter, resulting in 7.1 and 31.3 g LAS kg⁻¹ in injection lines placed into the soil, as measured at the start of the experiment in spring (NB: for perspective, the highest level of LAS ever recorded in anaerobic sludge is around 30 g/kg, which is similar to the highest dose applied here). The experiment included a control treatment with sludge without additionally spiked LAS. The sludge lines and the surrounding soil gradually blended over the year. This experiment closely resembles the non-homogeneous mixing scenario, for which a SQS (mean) is around 28 g/kg soil DM.

Growth of the oats was stimulated by the presence of sludge, particularly in the first months. Sludge and soil were sampled during the growing season and analysed for the soil invertebrates: microarthropods, earthworms and enchytraeids. Short-term, i.e., within the first month, colonisation of the sludge by soil invertebrates was inhibited by LAS, except for two groups of mites. Longer-term, the collembolans Folsomia fimetaria and Willemia sp. were negatively affected but had recovered in the sludge lines by the end of the season. The collembolan Mesaphorura macrochaeta and the prostigmatid and astigmatid mites were in excess of the control sludge in the two LAS treatments, and did not drop to control levels by September. Earthworms had also recovered in autumn. The sole group of organisms that had not fully recovered in the lines by the end of September were the enchytraeids (a small type of earthworm that lives in the upper layers of soil). However, the population in the soil surrounding the lines was stimulated at the highest LAS level. It is exactly the same group of enchytraeids that were negatively affected by LAS in the sludge lines of the experiment in Denmark.

Table 2: Risk characterisation for LAS in European sludges based on mean values

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Mean measured LAS level (mean, 5th and 95th percentile) (mg LAS/kg sludge)</th>
<th>Mean of SQS Distribution (mean, 5th and 95th percentile) (mg LAS/kg sludge)</th>
<th>RCR</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGD</td>
<td>5564</td>
<td>49,736</td>
<td>0.112</td>
</tr>
<tr>
<td>Probabilistic a</td>
<td>5564 (500, 15,000)</td>
<td>55,338 (19,075, 125,807)</td>
<td>0.101 (0.29–0.044)</td>
</tr>
<tr>
<td>Probabilistic b</td>
<td>5564 (500, 15,000)</td>
<td>27,652 (9937, 61,791)</td>
<td>0.201 (0.56–0.09)</td>
</tr>
</tbody>
</table>

Fig. 4. Measured and fitted cumulative frequency distribution for LAS in anaerobically digested sludges in EU Member States, covering the period 1988–2006.
raecids that was found to be the most sensitive in laboratory experiments (Jensen et al., 2007).

From the above it can be concluded that LAS, at least at the extreme (initial) level around 31 g/kg, exerts a reversible stress on the soil faunal community and stimulated oat growth. The field study executed with LAS above the mean SQS derived for sludge injection (27.6 g/kg) application did not demonstrate long-term adverse effects in the soil, and is therefore consistent with the laboratory data.

2.4.3. Discussion and interpretation of the sensitivity analysis

The TGD scenario calculations derive a SQS benchmark value of 49,736 mg LAS/kg sludge DM. This suggests that all European sewage sludge can be safely used on land, at least with regard to contaminant LAS, since the SQS is well above the maximum concentration ever observed in Europe.

The probabilistic analysis allows the variability around a deterministic outcome to be dimensioned. In a probabilistic mindset, even if the mean PEC is below the mean PNEC, there still may be some ‘ecological risk’. This is because low extremes of the PNEC distribution may concur with high extremes of the PEC distribution (van Straalen, 2002). The probabilistic scenario a (homogeneous mixing) leads to a skewed, lognormal-like distribution with a mean SQS of 55,338 mg/kg sludge DM. Mainly because of the choice of the sludge application distribution, this scenario results in a somewhat higher mean SQS value than for the TGD scenario. The lower 5th percentile of the SQS falls around 19,075 mg/kg sludge DM. The probabilistic scenario b, with a single mixing depth of 0.1 m, leads to a mean SQS of 27,652 mg/kg sludge DM. The lower 5th percentile is around 9937 mg/kg sludge DM. Only the left part of the SQS curves below 30,000 mg/kg (i.e., highest observed PEC) is relevant from a probabilistic risk assessment point of view, while the right (upper) side of the distributions has no practical meaning.

To visualize the probability of actual concentrations in sludge (PEC) exceeding the PNEC (SQS) both type of distributions were plotted on the same cumulative probability distribution graph (Fig. 5).

At the mean measured concentration of LAS there is no overlap of the curves (as is also evident from the RCRs in Table 2). There is negligible overlap between the measured LAS distribution at the 95th percentile for the SQS scenario a. In other words, regardless of the concentration in sludge, LAS can be applied without risk if homogeneously mixed over 20 cm soil depth.

For the injection scenario (b), there is a small overlap between the curves. In this case, the so called ‘ecological risk parameter’ was estimated according to van Straalen (2002) by means of an approximative numerical procedure, based on graphical interpolation of the cumulative probability curves. The PEC curve below the 80th percentile shows no significant overlap with the SQS curve for scenario b. For the PEC interval 80–90%, the mean cumulative probability of exceeding the SQS is ca. 6%. Similarly, for the 90–100% PEC interval, this value is ca. 21%. The probability of combined (independent) events is given by

\[ P(A \cap B) = P(A) \times P(B) \]

Hence the probability of exceeding the SQS from injecting anaerobic sewage sludge = \( (0.1 \times 0.06) + (0.1 \times 0.21) = 0.027 \) (2.7%). When applying a more exact probabilistic risk quotient method (non-parametric calculation procedure) based on the data in the distributions, as described in Verdonck (2003), the outcome is 2.35%.

2.4.4. Main conclusions

Deterministic and probabilistic approaches were followed to perform a risk assessment for LAS in anaerobic sewage sludge. LAS in aerobic sewage sludge was not further considered in this paper because the concentrations are much lower and irrelevant from a risk assessment perspective.

In the deterministic approach according to the EU TGD, and based on a recently revised terrestrial PNEC of 35 mg LAS/kg soil DM, the SQS is calculated as 49,736 mg LAS/kg sludge DM. When compared to a pan-European distribution of anaerobically digested sludges (mean = 5564 mg/kg DM), all measured levels are well below this criterion. Hence no risk is identified for LAS in sludge (RCR = 0.112).

Two additional probabilistic scenarios were developed, taking into account the variability associated with anaerobic sludge application on soils. For scenario a (homogeneous mixing), the mean SQS increases slightly to 55,338 mg LAS/kg sludge DM (RCR = 0.1). There was no significant overlap of the simulated SQS distribution curve with the measured LAS PEC curve in sludge. As such the ecological risk of this scenario was close to zero.

For scenario b (injection), the mean SQS was estimated at 27,652 mg LAS/kg DM (RCR = 0.20). Only once has an LAS concentration (30,200 mg/kg) above this mean SQS been recorded. There was a slight overlap between the
PEC and SQS curve; the associated ecological risk parameter was calculated as 2.35%. This is overall a very low risk, also bearing in mind that not all sludge in Europe or in a given country is anaerobically treated, and secondly, that not all anaerobic sludge is applied via injection.

The conclusion of this assessment of exposure and effects for LAS in sludge and soils, backed up by relevant field evidence, is that LAS in anaerobic sludge does not represent a significant ecological risk. From this perspective there is no scientific basis for specific regulatory limits for LAS in sludge as present in earlier EU draft legislation, nor the need to consider specific sludge management options due to the presence of LAS.

This case study can serve as an example of ILSI’s CF for a rapidly degradable, polar chemical. The authors recommend that further experience be gained with ILSI’s methodology for other categories of anthropogenic chemicals found in sludge.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, atdoi:10.1016/j.yrtph.2007.09.001.

References


