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Anionic surfactants in treated sewage and sludges: Risk assessment to aquatic and terrestrial environments

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Abstract

Compared to low concentrations of anionic surfactants (AS) in activated sludge process effluents (ASP) (<0.2 mg/L), upflow anaerobic sludge blanket-polishing pond (UASB-PP) effluents were found to contain very high concentrations of AS (>3.5 mg/L). AS (or linear alkylbenzen sulfonate, LAS) removals >99% have been found for ASP while in case of UASB-PP it was found to be $\leqslant$30%. AS concentrations averaged 7347 and 1452 mg/kg dry wt. in wet UASB and dried sludges, respectively. Treated sewage from UASB based sewage treatment plants (STPs) when discharged to aquatic ecosystems are likely to generate substantial risk. Post-treatment using 1–1.6 d detention, anaerobic, non-algal polishing ponds was found ineffective. Need of utilizing an aerobic method of post-treatment of UASB effluent in place of an anaerobic one has been emphasized. Natural drying of UASB sludges on sludge drying beds (SDBs) under aerobic conditions results in reduction of adsorbed AS by around 80%. Application of UASB sludges on SDBs was found simple, economical and effective. While disposal of treated UASB effluent may cause risk to aquatic ecosystems, use of dried UASB sludges is not likely to cause risk to terrestrial ecosystems.

Keywords: Anionic surfactants; Up-flow anaerobic sludge blanket (UASB) process; Activated sludge process; Aquatic risk; Terrestrial risk

1. Introduction

Anionic surfactants (AS) in sewage are found as a result of the use of consumer products like detergents, cleaning and dish washing agents, personal care products, etc. The largest group of AS is linear alkylbenzene sulfonate (LAS). Range of LAS concentration in sewage of 3–21 mg/L has been reported (Holt and Bernstein, 1992). Physical and biological methods of sewage treatment remove AS and prevent them from reaching the natural environments. The removal efficiency of surfactants depends on the method of treatment. Some widely used methods of sewage treatment are: (a) aerobic methods like activated sludge process (ASP), and oxidation pond (OP), and (b) anaerobic method like upflow anaerobic sludge blanket (UASB) process.

The removal of LAS in ASP based sewage treatment plants (STPs) includes sorption to the sludge particles and biodegradation with a total removal of 95–99% (Feijtel et al., 1995; Field et al., 1995; Prats et al., 1997; Matthijs et al., 1999; Holt et al., 2003; SIDS, 2005). Total LAS removal has also been found very high (>97%) in a lagoon treatment by Moreno et al. (1994). Most of the LAS removed through biodegradation (>83%) was truly mineralized due to high residence time (30 days) in ponds. Under aerobic conditions, total mineralization of LAS proceeds through degradation of the alkyl group by means of ω-oxidation, β-oxidation, desulfonation, and finally degradation of the phenyl ring (Haggensen et al., 2002).

Anaerobic biodegradation of AS has historically been believed not to occur. However, indications of some removal/primary biodegradation of LAS under anaerobic

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conditions have been reported in few recent publications (Denger and Cook, 1999; Angelidaki et al., 2000; Almendariz et al., 2001; Haggensen et al., 2002; Mogensen and Ahring, 2002; Sanz et al., 2003). The limited information indicates that (a) LAS can be used as a source of sulfur by anaerobic bacteria under sulfur limited conditions (Denger and Cook, 1999), (b) benzenesulfonic acid and benzaldehyde may be produced as metabolites under thermophilic range (Mogensen and Ahring, 2002), (c) LAS can be degraded using NO_3^- as the electron acceptor in the acidogenic step of a 2 stage UASB reactor (Almendariz et al., 2001), (d) degradation may occur if innoculum from aerobic environments is used (Angelidaki et al., 2000), (e) increased removal of LAS is possible if bioavailable fraction of LAS is increased (Haggensen et al., 2002), and (f) surfactant can be partially used as a carbon and energy source by anaerobic bacteria in the presence and absence of additional source of carbon (Sanz et al., 2003). It could be concluded that although the anaerobic biodegradation of LAS is difficult without the presence of molecular oxygen but under certain conditions they are biodegraded. A large difference in AS concentration is also found in aerobically and anaerobically digested sewage sludges (McAvoy et al., 1993). In general, sludges exposed to aerobic condition contain far less LAS than primary and anaerobically digested sludges. It is suggested that LAS is enriched in anaerobic treatment plants due to adsorption and does not really undergo biodegradation.

Surfactants show a pronounced ecotoxicological effect on aquatic and terrestrial organisms. Venhuis and Mehrvar (2004) has reported that 0.02–1.0 mg/L LAS in aquatic environment can damage fish gills, cause excess mucus secretion, decrease respiration in the common goby, and damage swimming patterns in blue mussel larva. It is also reported that 40–60 mg LAS/kg dry wt. of sludge is toxic to the reproduction and growth of soil invertebrates and earthworms. AS once applied in a terrestrial ecosystem reduce rapidly due to aerobic microbial activity. Half life has been found to range from 7 to 40 days (Jensen, 1999, 2001; HERA, 2004; Ying, 2006). The risk of utilizing LAS enriched sludges to land also depends on frequency of sludge application in addition to concentration of LAS in the dried sludge. Information on their occurrence and fate at different steps of their journey, i.e. in sewers, wastewater treatment plants, sewage sludges, and ultimately in receiving surface waters or terrestrial environments is of utmost importance to assess the predicted environmental concentration (PEC) and consequently the environmental risk it may pose.

Anaerobic sewage treatment technology has been successfully used in India as over 25 UASB based STPs with total installed capacity of more than a million m^3/d are currently working. However, in spite of the full-scale application of UASB since over 15 years, fate of AS in UASB based STPs is not known. Limited information available is based on research carried out in laboratories and reported results are varying in nature as the experiments and scenarios investigated by the authors were different (Denger and Cook, 1999; Angelidaki et al., 2000; Mogensen and Ahring, 2002; Sanz et al., 2003). Literature on the removal in oxidation ponds is also very limited (Moreno et al., 1994). Risk generated by UASB effluents and sludges to both aquatic and terrestrial environments is not assessed. This paper presents results of an extensive risk assessment study carried out over a period of 21 months using European Union Technical Guidance Document (EU-TGD). More number of UASB based STPs were selected for this study as removal of AS has not been evaluated in full-scale UASB based STPs.

2. Methods

Eight UASB, OP, and ASP based STPs located in Haridwar (29°58′N, 78°13′E), Saharanpur (29°58′N, 77°23′E), Muzaffarnagar (29°28′N, 77°44′E), Ghaziabad (28°40′N, 77°28′E), and Noida (28°20′N, 77°30′E) were selected for the study. Their installed capacities ranged from 9 to 70 ML/d. Haridwar and Muzaffarnagar are situated along river Ganga and Kali, respectively while Saharanpur, Noida, and Ghaziabad are situated along river Hindon in a stretch of around 250 km.

2.1. UASB based STPs

Five UASB polishing pond (UASB-PP) based systems were studied. Same treatment-sequence is followed at all the five selected UASB based STPs (Saharanpur: 38 ML/d; Ghaziabad: 56 and 70 ML/d; and Noida: 27 and 34 ML/d). Study was carried over a period of 21 months (August 2004 to April 2006) covering different seasons. The combined UASB-PP systems were designed to handle 200 mg/L of influent biochemical oxygen demand (BOD; 5 day, 20 °C), and 400 mg/L of influent suspended solids (SS) for meeting the required Indian standards of 30 mg/L of BOD and 50 mg/L of SS in the final effluent. Sewage after preliminary treatment (removal of screenings and grit) is uniformly distributed at the bottom of UASB reactors (HRT = 9.4–10.3 h). The UASB effluents are discharged to 1–1.6 day detention, non-algal, anaerobic PPs for tertiary treatment. UASB sludge is applied on sludge drying beds (SDBs). Treated sewage is discharged into river Hindon and dried-stabilized sludge is utilized as a resource for nutrients recycling and soil improvement on grasslands, agricultural fields, and plantations. Following four wastewater and sludge samples were collected monthly from every STP (i) raw sewage, (ii) treated effluent, (iii) UASBR sludge and (iv) dried sludge.

2.2. Oxidation ponds based STPs

Two OP based STPs of installed capacities of 32.5 and 9 ML/d located at Muzaffarnagar and Noida, respectively were selected for the study. Both the STPs have same sequence of units, i.e. screen chambers-grit channels-primary OPs and secondary OPs. Raw and treated sewage samples were collected over a period of ten months (April 2005 to January 2006). Treated sewage is used for irrigation by nearby farmers.

2.3. Activated sludge process based STP

One conventional ASP based STP of 18 ML/d capacity situated at Haridwar was selected for the study. Sequence of the treatment is: screens-grit chambers-primary settling tanks (PST)-aeration basins-and secondary settling tanks (SST). Sludge from PST and SST is processed through sludge thickners-anaerobic sludge digesters and sludge drying beds. Samples of raw and treated sewage along with dried sludge were collected only between February 2005 and March 2005.

2.4. Analysis

At all the STPs considered in the present work, sewage reaches after multistage pumping. It is primarily because of flat topography of the cities and presence of number of water channels. At every stage, sewage is detained for a short time and gets mixed up in the sewage sump. It is finally collected at the main pumping station (MPS) just ahead of each STP. From MPS, it is pumped round the clock more or less at a uniform rate. It flows through the STPs by gravity. Prior to August 2004, the 2-hourly samples were composited at the plants (based on 2-hourly average flow) to prepare a 24-h flow-weighted composite sample. Composite samples were analyzed along with 2-hourly grab samples. This exercise was repeated twice at each STP. Results are not reported in this paper. Distinct diurnal variations in characteristics were not observed. It was presumably due to a general leveling effect during collection system (due to multistage pumping), and treatment (due to long retention times in reactors). Based on this, it was decided to collect only grab samples during the present study. Grab samples of wet UASB reactor and dried SDB sludges were also collected in polyethylene containers. At STPs different number of UASB reactors and SDBs are installed (UASB reactors 3–4 and SDBs 10–24) while number of PPs installed is fixed at two irrespective of plant capacity. Samples were collected from combined streams and not from individual reactors. Sewage and sludge samples were collected around tenth of every month. All samples were collected, preserved, and transported as per methods listed in Standard Methods (APHA, 1998, 2005).

AS were measured in samples of sewage as methylene blue active substances (MBAS) as prescribed in Standard Methods (APHA, 1998, 2005). LAS (Hach, USA) was taken as a reference. LAS usually contribute 70–90% of MBAS (Painter and Zabel, 1989). AS in sludge samples were extracted by soxhlet extraction technique using methanol (Marcomini and Giger, 1987) and than analyzed using MBAS method. All AS concentrations are reported in this paper as "mg/L for sewage and mg/kg dry wt. for sludge samples (calculated as LAS, mol. wt., 318)". A spectrophotometer (DR 4000, Hach, USA,) was used for colorimetric measurements.

3. Results and discussion

3.1. UASB-PP based STPs

Wide variations in influent characteristics were noticed. Over the period of study, total AS ranged from 2.19 to 9.82 mg/L. Bar diagrams of average values of MBAS in raw sewage and in final effluent for each of the STP is given in Fig. 1 along with respective error-bars. Plant wise, average concentrations of AS ranged from 3.60 to 4.91 mg/L resulting in average removals of only 8 (56 ML/d STP, Ghaziabad) to 30% (70 ML/d STP, Ghaziabad). On the contrary, average BOD removals ranged from 78% to 84%. In a UASB-PP system aerobic conditions do not develop at any stage. The polishing ponds that receive effluent from UASB reactors are different than conventional waste stabilization (or oxidation) ponds that treat raw sewage. PPs were designed for a significantly shorted hydraulic retention time (HRT) of 1–1.6 days compared to oxidation ponds (20–30 days). Algal growth is not expected at HRT $<$ multiplication rate of algal cells at 20 °C, i.e. 2–2.5 days. PPs could be defined as non-algal, anaerobic, and having short HRT of 1–1.6 days. Use of such PPs for post-treatment of UASB effluents is a widely accepted practice especially in India. It can be attributed mainly to low initial cost and their easy design, operation, and maintenance. Accordingly, effluents were found to be devoid of oxygen at all the STPs throughout the study period. This was perhaps the main factor which contributed towards limited reduction of 8–30% of AS. AS is strongly sorbed to sludge due to its hydrophobic character. Prats et al. (1997) have also suggested that a large amount of the load of AS into sewage treatment plant is associated with suspended material. It is subsequently withdrawn from UASB reactor as sludge is removed. Part of it is also removed in PP as biosolids escaping from UASB reactor settle. It is presumed that aerobic post-treatment of UASB reactor effluent can substantially reduce AS concentration rather than an anaerobic option like PP. Many aerobic post-treatments have been tried including ASP, trickling filter (TF), aerated lagoon (AL), and down-flow hanging sponge (DHS) etc. However, MBAS has been measured as a parameter only by Gasi et al. (1991) while using ozonation as post-treatment of UASB effluent. The effluent from UASB reactor contained 4.63–5.30 mg/L of AS. Application of ozone for 30 and 50 min resulted in effluent AS concentrations of 1.52 and 0.53 mg/L, respectively. Ozone oxidized AS effectively.

Average concentrations of AS in wet UASB and finally dried SDB sludges along with error-bars for five treatment works over a period of 21 months are shown in Fig. 2. UASB wet sludges contained considerable amount of AS concentration. It varied from 4480 to 9233 mg/kg dry wt.

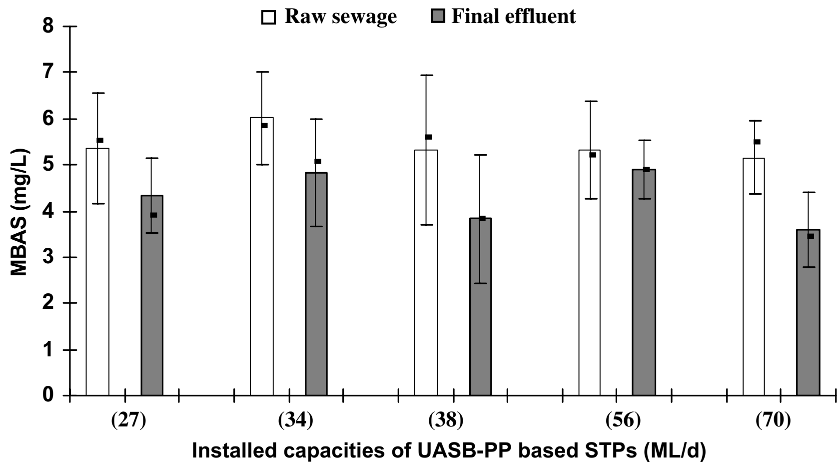


Fig. 1. UASB based STPs: average MBAS in raw sewage (I bar for each STP), and in final effluent (II bar for each STP).

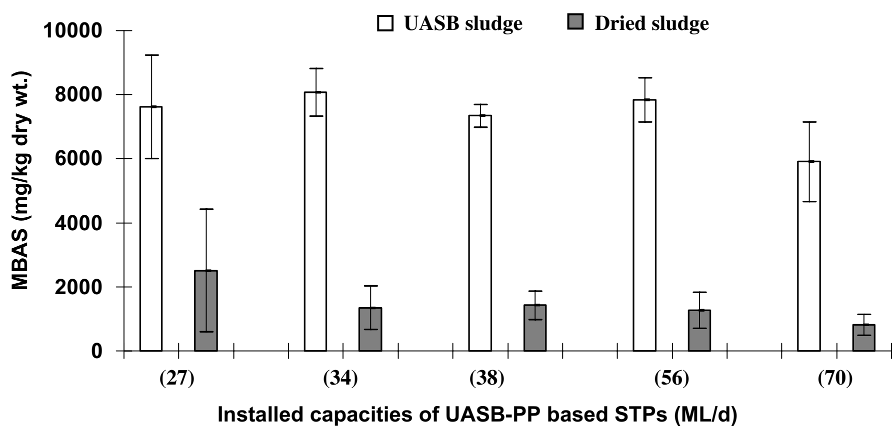


Fig. 2. Average MBAS in UASB reactor waste sludges (I bar for each STP), and finally dried-stabilized sludges (II bar for each STP).

Average values ranged from 5982 mg/kg dry wt. (70 ml/d STP, Ghaziabad) to 7997 mg/kg dry wt. (34 ML/d STP, Noida). Variations of AS over 21 months period were minimum at 38 ML/d STP at Saharanpur (standard deviation = 355 mg/kg dry wt.) and maximum at 27 ML/d STP at Noida (standard deviation = 1616 mg/kg dry wt.). When data of all the plants were analyzed together, AS averaged 7347 mg/kg dry wt. Municipal sludges in India have not been analyzed for AS concentrations earlier. The AS concentrations in dried-stabilized sludges were also found to range widely from 336 to 5880 mg/kg dry wt. with an overall average of 1452 mg/kg dry wt. for the five STPs. Wide variations were mainly due to wider fluctuations at 27 ml/d STP at Noida. Relatively lower concentrations were observed at 70 ml/d STP at Gaziabad. Drying on SDB on an average resulted in an overall AS reduction of around 80% (7347–1452 mg/kg dry wt.). Among the STPs, maximum reduction of around 85% was observed at 70 ML/d STP at Gaziabad and minimum of around 66% at 27 ML/d STP at Noida. Application of anaerobic wet UASB sludge on SDBs not only resulted in drying and volume reduction but also in considerable elimination of AS. Sludge from reactors is spread on SDBs in a thin layer of about 10–20 cm on a periodic basis. On SDBs, with time, reduction in moisture content along with the development, widening, and deepening of cracks takes place. This allows air to reach even at deepest layers of sludge. Tilling/milling operation further help in distribution of oxygen. Under such conditions aerobic biodegradation of AS occurs. Reduction of AS followed first-order kinetics. AS degradation rate constant (k_{AS}) and half life of AS were found to be 0.034 d^{-1} and 20 days, respectively.

3.2. OP based STPs

Average composition of raw sewage received at two OP based STPs during the period of 10 months of the study was almost similar to the raw sewage composition at UASB based STPs. Anionic surfactants measured as MBAS varied from 3.53 to 7.59 mg/L (average 5.89 mg/L). Removal of AS at two STPs varied widely. The average concentrations of AS in treated sewage were found 3.31 and 0.67 mg/L resulting in average removals of around 47% and around 88% at 9 and 32.5 ML/d STPs, respectively. At 32.5 ML/d STP at Muzaffarnagar, DO in treated effluent was found to range from 3.5 to 29.3 mg/L and pH from 8.3 to 9.8. Frequently, DO exceeded saturation concentration. Contrary to this at 9 ML/d STP, DO concentration of 1.9 mg/L was detected only once and pH was observed only between 7.5 and 7.9. DeLeenheer (2004) suggested that minimum DO of 0.2 mg/L is required for aerobic degradation of AS. Because of good algal growth final effluent of Muzaffarnagar plant always appeared green while that from STP at Noida appeared blackish. The high level of algal photosynthetic activity not only raises the pH of the ponds at Muzaffarnagar but also increases its DO content. Removals in OPs are multi-factorial, dependent on a synergistic interaction between pH, DO, humic substances, light, etc. The multi-parametric synergistic interactions as expected in OPs do not seem to occur in OP system at Noida resulting in unacceptable levels of AS removal. Although both STPs were initially designed as oxidation ponds adopting same design criteria, the one at Noida was not being properly operated and did not qualify to be designated as OP mainly due to absence of algae.

3.3. ASP based STP

Final effluent contained on an average 0.13 mg/L AS with a removal of around 94%. Removal of AS was found to be much higher compared to that found in UASB-PP systems.

3.4. Removal efficiencies of AS in different treatment systems: a comparison

Average AS concentration in the treated effluents and percentage removals for different STPs are summarized in Table 1 (columns 4–5). Concentrations of LAS (or AS) in treated sewage from previous studies and present work are compiled in Fig. 3. Low effluent LAS (or AS) concentrations (<0.2 mg/L) in case of ASP are quite clear. Compared to this UASB-PP effluents contain very high concentrations of AS (>3.5 mg/L). LAS (or AS) removals >99% have been reported by several researchers for ASP while in case of UASB it was found to be ⩽30%.

Following sequences of sewage-sludge treatment are generally used:

(a) Aerobic sewage treatment (ASP) – aerobic sludge digestion.
(b) Aerobic sewage treatment (ASP) – anaerobic sludge digestion.
(c) Aerobic sewage treatment (ASP) – anaerobic sludge digestion – aerobic sludge drying and stabilization.
(d) Anaerobic sewage treatment (UASB) – aerobic sludge drying and stabilization.

Information about concentrations of LAS (or AS) in different types of sludges is summarized in Fig. 4. A large difference in AS concentration is found in aerobically and anaerobically processed sewage sludges irrespective of nature of sewage treatment (i.e. aerobic or anaerobic). Aerobically digested sludges have been found to contain very low concentrations ranging from 100 to 500 mg/kg dry wt. while anaerobically digested sludges have been reported to contain substantially higher concentrations ranging from 4660 to 30,200 mg/kg dry wt. Average concentration of LAS in aerobically digested sludges has been estimated only 150 (±120) mg/kg dry wt. compared to average of 10,500 (±5200) mg/kg dry wt. for anaerobically digested sewage sludges (McAvoy et al., 1993). Third sequence, i.e. anaerobic sludge digestion followed by natural drying of sludge on SDB for a period ranging from few weeks to few months (depending on climatic conditions) has been found to yield 150–5200 mg/kg dry wt. In case of UASB, sludges are directly applied on SDBs (Sequence 4) without any pretreatment (thickening, digestion, etc.). Production of sludge is also considerably less in case of UASB compared to ASP. This results in a simple least expensive but effective method of UASB sludge management. Average treated dried sludge concentrations ranged from 810 to 2510 mg/kg dry wt.

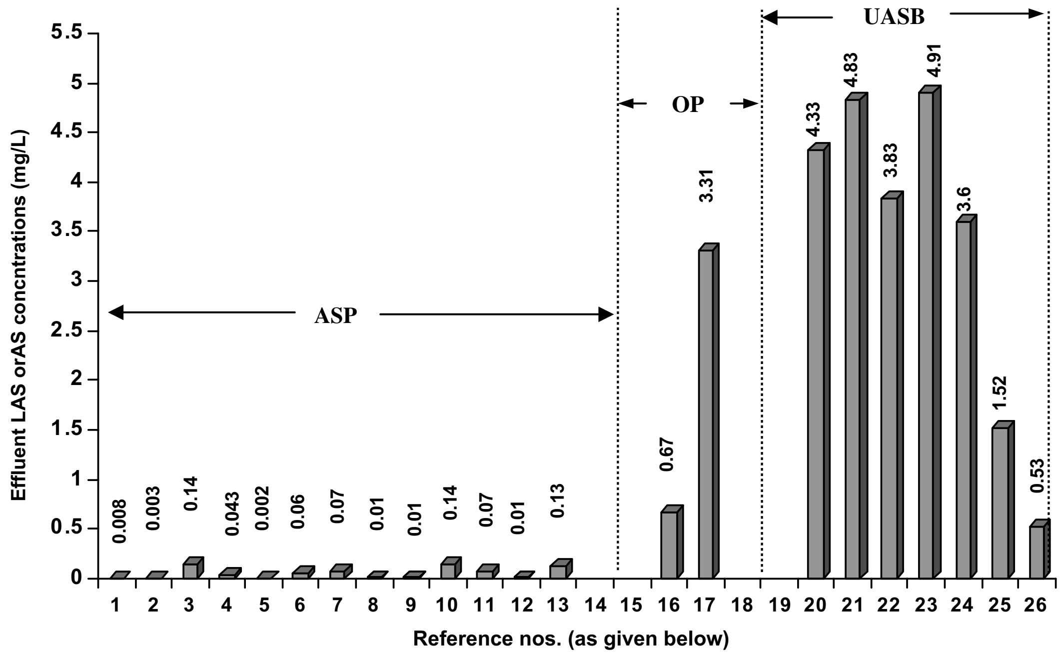
3.5. Risk assessment: aquatic environment

The risk assessment to aquatic environment due to the presence of AS in treated sewage was evaluated according to the procedure laid down in European Union Technical Guidance Document (EU-TGD, 1996, 2002a). Risk is assessed depending on (a) predicted environmental

Table 1
UASB, OP and ASP based STPs: effluent concentrations and estimated PEC, and RQ values (aquatic ecosystem)

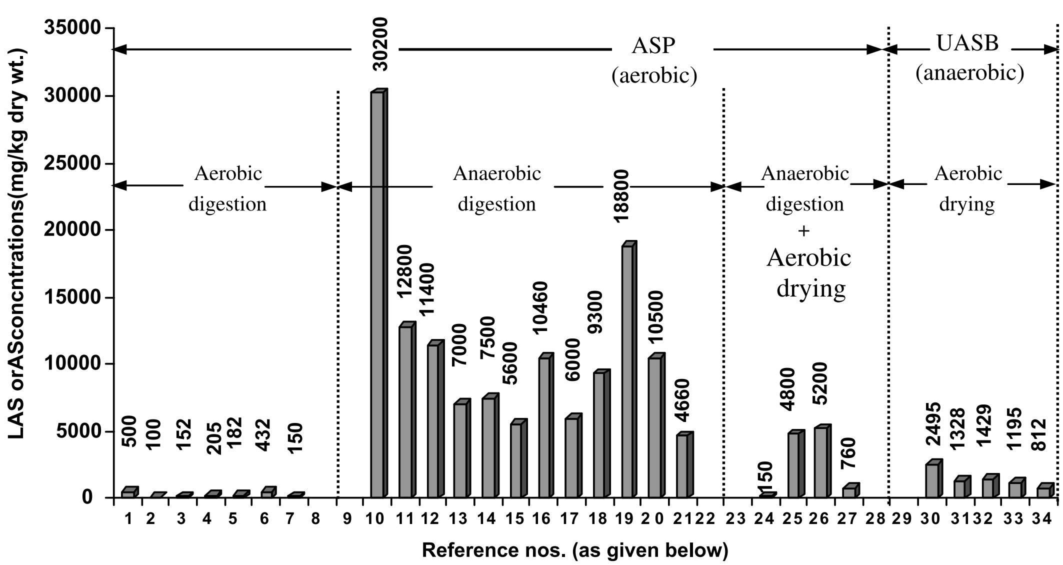
STP	Capacity (ML/d)	Average AS conc. (mg/L)		Average % removal		PEC_{water} (mg/L)	RQ[a]	RQ[b]
		Influent	Effluent	AS	BOD			
UASB	27	5.35	4.33	19	81	0.433	16.0	1.60
UASB	34	6.01	4.83	20	78	0.483	17.9	1.79
UASB	38	5.36	3.83	29	84	0.383	14.2	1.42
UASB	56	5.32	4.91	8	82	0.491	18.2	1.82
UASB	70	5.16	3.60	30	81	0.360	13.3	1.33
OP	9	6.22	3.31	47	76	0.331	12.3	1.23
OP	32.5	5.57	0.67	88	80	0.067	2.48	0.25
ASP	18	2.05	0.13	94	92	0.013	0.48	0.05

[a] $PNEC_{water}$ = 0.027 mg/L (Petersen et al., 2003).
[b] $PNEC_{water}$ = 0.27 mg/L (HERA, 2004).



1	Feijtel et al. 1995	7-12	Feijtel et al. 1995	22	Present study, 38 ML/d
2	Field et al. 1995	13	Present study, 18 ML/d	23	Present study, 56 ML/d
3	Prats et al. 1997	16	Present study, 32.5 L/d	24	Present study, 70 ML/d
4	Matthijs et al. 1999	17	Present study, 9 ML/d	25-26	Gasi et al. 1991
5	Holt et al. 2003	20	Present study, 27 ML/d		
6	SIDS 2005	21	Present study, 34 ML/d		

Fig. 3. ASP, OP and UASB based STPs: concentration of LAS or AS in treated effluent.



1- 6	SIDS 2005	24	Painter and Zabel 1989	31	Present study, 34 ML/d
7	DeWolf et al. 1998	25	Berna et al. 1989	32	Present study, 38 ML/d
10 - 17	SIDS 2005	26	Prats et al. 1997	33	Present study, 56 ML/d
18-20	Jensen et al. 1999	27	Present study, 18 ML/d	34	Present study, 70 ML/d
21	SIDS 2005	30	Present study, 27 ML/d		

Fig. 4. ASP and UASB based STPs: concentration of LAS or AS in different types of sewage sludges (SIDS, 2005; Painter and Zabel, 1989; Berna et al., 1989; Prats et al., 1997).

concentration (PEC) of AS, and (b) predicted no effect concentration (PNEC), i.e. the concentration below which unacceptable effects on organisms are not likely to occur. Risk assessment is based on the risk quotient (RQ) which can be calculated by using

$$RQ = PEC/PNEC \quad (1)$$

$RQ > 1$ indicates a risk of adverse effect to the environment.

3.5.1. PEC_{Water}

The measured average concentrations of anionic surfactants in final effluents from different STPs are summarized in Table 1 (column 4). EU-TGD has suggested a dilution factor of 10 (TGD default dilution coefficient) which was used to calculate predicted environmental concentration in receiving water (PEC_{water}, Table 1, column 7).

3.5.2. $PNEC_{Water}$

No observed effect concentrations (NOEC) of LAS worked out by Petersen et al. (2003) based on long-term laboratory screening tests for aquatic plants/organisms at three trophic levels (algae, crustaceans, and fish) are 18, 0.27, and 0.90 mg/L, respectively. SIDS (2005) has also mentioned several references in which NOEC of 0.27 mg/L has been utilized for assessment of risk to aquatic environment. Values reported are for LAS while in the present work AS were determined. However, since LAS predominate among AS, NOEC values reported for LAS were used to calculate PNEC. An assessment factor of 10 has been suggested (EU-TGD, 2002) for the estimation of PNEC for LAS. An assessment factor of 10 is normally applied when long-term toxicity NOECs are available for at least three species across three trophic levels. This yields lowest value of predicted no effect concentration in receiving water ($PNEC_{water}$) of 0.027 mg/L. However, HERA (2004) has stated value of $PNEC_{water}$ as 0.27 mg/L derived based on species-sensitivity-distribution (SSD) along with mesocosm approach.

Calculated values of RQ for different STPs for both the approaches are also given in Table 1 (columns 8 and 9). Values of RQ (using first approach, i.e. $PNEC_{water} = 0.027$ mg/L) were also calculated taking LAS or AS concentrations in treated effluents as reported by several research workers (Fig. 3). These values of RQ are arranged in Fig. 5. Values of RQ ranged from 13.3 to 18.2, and 1.33–1.82 for UASB-PP based STPs using the two values of $PNEC_{water}$ of 0.027 and 0.27 mg/L respectively. For all the five UASB-PP based STPs, RQ values were found to be greater than desired value of <1. Even ozonation of UASB effluent as tried by Gasi et al. (1991) did not reduce RQ to <1. Treated effluents from UASB based STPs when discharged to aquatic ecosystems are likely to generate substantial risk even at higher PNEC of 0.27 mg/L as suggested by HERA (2004). There is a need to provide effective aerobic post-treatment to UASB effluents. The RQ values calculated for the two OP based STPs (12.26 and 2.48) showed wide variation. The concentration of AS in treated effluents from OP based STPs may also generate risk to the aquatic environment. The RQ values in case of ASP reported by various research workers and also found in the present work were <1. Compared to UASB and OP based STPs, RQ for ASP is quite low.

It could be concluded that present method of post-treatment of UASB effluent is not effective as far as removal of AS is concerned. Use of any of the aerobic methods, e.g. ASP, DHS, AL, TF, OP, etc., may yield better removal of AS. Recently, at some of the STPs in India, aerated lagoons have been installed for post-treatment in place of PPs. At one of the STPs (Karnal, India of treatment capacity of 40 ML/d) a 1 ML/d DHS post-treatment experimental unit is being operated since last 4 years. However, since AS is not a monitoring parameter in India, no data regarding concentrations of AS or LAS in influent and effluent is available for ALs or DHS system.

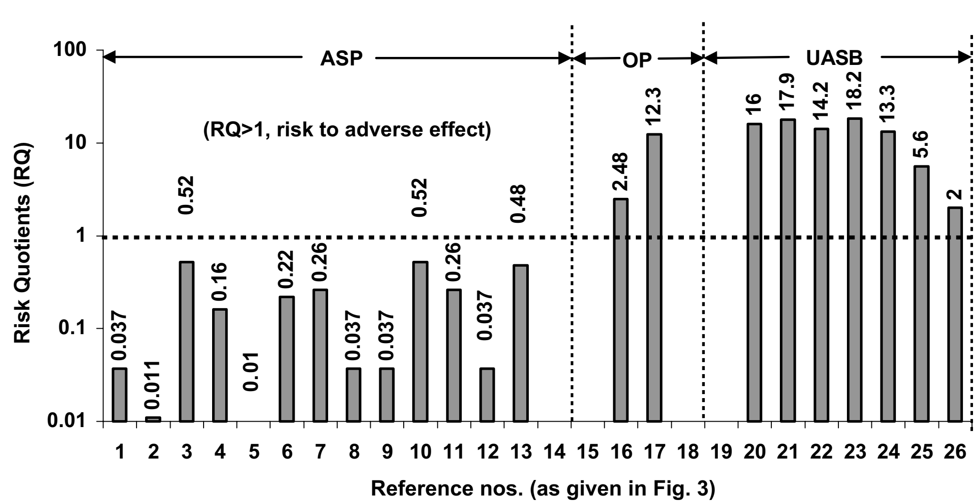


Fig. 5. Values of risk quotients to aquatic environment due to discharge of ASP, OP, and UASB effluents.

3.6. Risk assessment: terrestrial environment

The PEC is used for characterization of risk to: (a) terrestrial organisms: direct exposure and (b) to humans via crops and/or cattle product: indirect exposure. A value of PNEC of 4.6 mg/kg dry wt. has been as suggested by Jensen et al. (2001) and HERA (2004) with an idea to protect all terrestrial microbial processes and functions.

The starting concentration at time $t = 0$ in soil ($C_{\text{o soil}}$) due to one sludge application in the year can be calculated using Eq. (2) as suggested by EU-TGD (1996)

$$C_{\text{o soil}} = C_{\text{sludge}}\text{APPL}_{\text{sludge}}/\text{DEPTH}_{\text{soil}}\text{RHO}_{\text{soil}} \tag{2}$$

where C_{sludge} is the average concentration of AS in dry sewage sludge (mg/kg dry wt.) (Table 2, column 2), $\text{APPL}_{\text{sludge}}$ is the dry sludge application rate (kg/m^2 yr). Soil and agricultural soil: 0.5 kg/m^2 yr (EU-TGD, 1996). Grassland: 0.1 kg/m^2 yr (EU-TGD, 1996). $\text{DEPTH}_{\text{soil}}$ is the mixing depth of soil (m). Soil and agricultural soil: 0.20 m (EU-TGD, 1996) Grassland: 0.10 m (EU-TGD, 1996), RHO_{soil} is the bulk density of wet soil (1500 kg/m^3).

The concentration of AS is high just after sludge application (in the beginning of the growing season), and much lower at the end of the year due to removal processes. Therefore, the concentration of AS in soil needs to be averaged over a certain time period. Different averaging times are considered (EU-TGD, 1996) for different end uses of sewage sludge. For the soil based ecosystems a period of 30 days after application of sludge is suggested. In order to determine biomagnification effects and indirect exposure to man, extended period of 180 days has been recommended.

The average concentration of AS over a certain period of time can be calculated considering the first-order biodegradation rate in the top soil. Summation of all concentrations over a certain period (30 or 180 days) and dividing by the corresponding days gives the average daily concentration. This is achieved by integrating the equation given in the EU-TGD (1996), which simplifies to the following expression (Eq. (3)) if one neglects the contribution of aerial deposition

$$\text{PEC}_{\text{local}} \text{ or } C_{\text{avg. soil}} = C_{\text{o soil}}(1 - e^{-kt})/kt \tag{3}$$

where k is the first-order rate constant in top soil (d^{-1}), t is the averaging time (d).

AS monitoring studies in sludge amended soil (Holt and Bernstein, 1992) have indicated a biodegradation rate corresponding to a half-life of 10 days, namely $k = \ln 2/t_{0.5} = 0.0693\ \text{d}^{-1}$. Taking $k = 0.0693\ \text{d}^{-1}$, values of $C_{\text{avg. soil}}$ (PEC local) were calculated for the three different end uses for five STPs (Table 2, columns 3, 5, and 7).

Taking values of PEC and PNEC, RQ were calculated for different applications and STPs (Table 2, columns 4, 6, and 8). Values of RQ were also calculated using LAS or AS concentrations reported by several investigators for different types of sludges (Fig. 4). These are compiled in Fig. 6. RQ values were found <1 except when sludge is anaerobically digested. It could be concluded that (a) aerobic digestion or (b) natural drying on SDBs of aerobic and anaerobic sludges result in biodegradation of AS in sludges to such a level that there subsequent application on land for any end use is not likely to pose any risk.

To generalize the risk characterization of AS, initial values of PECs (at the time of application of sludge) were estimated assuming a uniform ploughing depth of 15 cm and assuming that sludge is evenly distributed in the field and is homogeneously mixed in the upper layer. The risk was calculated for a series of different scenarios, reflecting different loads of AS and different degradation rates in soil. Six application rates of sludge in the range of 0.1–1.0 kg/m^2 yr were included in the calculations. Three AS concentrations i.e. the minimum, maximum, and average (336, 1474, and 5888 mg/kg dry wt.) as found in the present study on UASB based STPs were considered.

Values of initial risk quotient ($\text{RQ}_{\text{init.}}$) were calculated for different scenarios according to Eq. (4), taking time $t = 0$, i.e. at the time of application. Calculated values are presented in Table 3.

$$\text{PEC} = C_{\text{o soil}}e^{-kt} \tag{4}$$

$C_{\text{o soil}}$, were calculated using Eq. (2). It was found that values of RQ_{init} were lower than 1 for all scenarios studied for minimum AS concentrations of 336 mg/kg dry wt. At average concentration of 1474 mg/kg dry wt., values of $\text{RQ}_{\text{init.}}$ were found to increase >1, only in case of sludge application rates >0.8 kg/m^2 yr. In case of AS concentration of

Table 2
Estimated PEC and RQ values for three different applications of dried sludges

STP: capacity (ML/d)	Dried-stabilized sludge: average AS concentration (mg/kg dry wt.)	Soil		Agriculture soil		Grassland	
		PEC local (mg/kg dry wt.)	RQ	PEC local (mg/kg dry wt.)	RQ	PEC local (mg/kg dry wt.)	RQ
ASP:18	760	0.53	0.12	0.10	0.02	0.04	0.01
UASB: 27	2510	1.76	0.38	0.33	0.07	0.13	0.03
UASB: 34	1351	0.95	0.21	0.18	0.04	0.07	0.02
UASB: 38	1429	1.00	0.22	0.19	0.04	0.08	0.02
UASB: 56	1271	0.85	0.19	0.17	0.04	0.06	0.01
UASB: 70	810	0.57	0.12	0.11	0.02	0.04	0.01

PNEC = 4.6 mg/ kg dry wt. (Jensen et al., 2001; HERA, 2004).

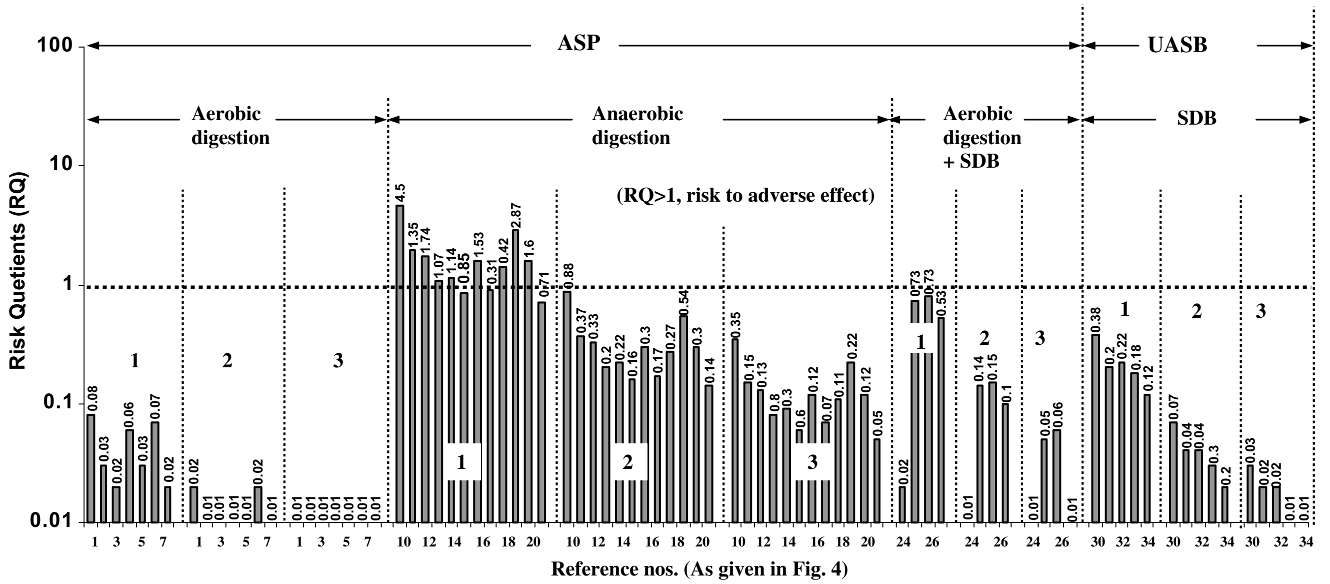


Fig. 6. Values of risk quotients for three terrestrial environments (1 = soil; 2 = agricultural soil; and 3 = grassland soil) due to application of different types of ASP and UASB sludges for most practical scenario (1. soil: average time = 30 d, half life = 10 d, $APPL_{sludge} = 0.5$ kg/m^2 yr, $DEPTH_{soil} = 0.20$ m; 2. agricultural soil: averaging time = 180 d, half life = 10 d, $APPL_{sludge} = 0.5$ kg/m^2 yr, $DEPTH_{soil} = 0.20$ m; 3. grassland: averaging time = 180 d, half life = 10 d, $APPL_{sludge} = 0.1$ kg/m^2 yr, $DEPTH_{soil} = 0.10$ m).

Table 3
Calculated RQ_{init} and time needed to eliminate risk for different scenarios

Sludge rate	Application (kg/m^2 yr)	0.1		0.2		0.4		0.6		0.8		1.0	
LAS-conc. (mg/kg dry wt.)	Half life (days)	RQ_{init}	Days	RQ_{init}	Days	RQ_{init}	Days	RQ_{init}	Days	RQ_{init}	Days	RQ_{init}	Days
336	7	0.03	–	0.06	–	0.13	–	0.19	–	0.26	–	0.32	–
	10	0.03	–	0.06	–	0.13	–	0.19	–	0.26	–	0.32	–
	25	0.03	–	0.06	–	0.13	–	0.19	–	0.26	–	0.32	–
	40	0.03	–	0.06	–	0.13	–	0.19	–	0.26	–	0.32	–
1474	7	0.14	–	0.28	–	0.57	–	0.85	–	1.14	1	1.42	4
	10	0.14	–	0.28	–	0.57	–	0.85	–	1.14	2	1.42	5
	25	0.14	–	0.28	–	0.57	–	0.85	–	1.14	5	1.42	13
	40	0.14	–	0.28	–	0.57	–	0.85	–	1.14	8	1.42	20
5888	7	0.56	–	1.14	1	2.28	8	3.41	12	4.55	15	5.69	18
	10	0.56	–	1.14	2	2.28	12	3.41	18	4.55	22	5.69	25
	25	0.56	–	1.14	5	2.28	*30*	3.41	*44*	4.55	*55*	5.69	*63*
	40	0.56	–	1.14	7	2.28	*47*	3.41	*71*	4.55	*88*	5.69	*100*

5888 mg/kg dry wt., $RQ_{init.}$ exceeded >1 for sludge application rate >0.2 kg/m^2 yr. The theoretical times which are necessary to reach a level of AS with a negligible risk ($RQ \leqslant 1$) were also estimated assuming a simple first-order degradation with half lives of 7–40 days in soil (Eq. (4)). On the basis of scenarios presented in Table 3, it could be concluded that at higher concentrations and with increasing application loads, a potential risk to the soil ecosystem can't be ruled out. However, due to degradation of AS, the impact will disappear with in a month or two. It is only likely to persist for up to 100 days under extreme sludge loading condition of 1.0 kg/m^2 yr at maximum observed AS concentration in sludge of 5888 mg/kg dry wt. and half life of 40 days.

In practice, loading rates >0.5 kg/m^2 yr are considered rare. It appears average concentration of AS in sludge from UASB based STPs, i.e. 1474 mg/kg dry wt. is not likely to cause any risk to terrestrial ecosystem. This happens to be very close to Danish cut-off value of LAS in sludges, i.e. 1300 mg/kg dry wt. It is, therefore, concluded that the cut-off values of LAS in Danish sludge of 1300 mg/kg dry wt. can be used for sludge from UASB reactors too. If values are found to increase than cut-off value, rate of sludge application may be reduced as a short-term measure. Long term measure may include better management of SDB to create aerobic environment through out the depth of the sludge. This could be achieved by frequent tilling/milling of sludges on SDBs during drying.

4. Conclusions

1. In a UASB-PP system, removal of anionic surfactants were found from 8% to 30%. Removal of AS were found much less compared to ASP based STPs.
2. UASB-PP effluents were found to have very high concentrations of AS (>3.5 mg/L) compared to low concentrations of AS in ASP (<0.2 mg/L) effluents.
3. AS concentrations averaged 7347 and 1452 mg/kg dry wt. in wet UASB and dried-stabilized sludges from sludge drying beds, respectively.
4. Post-treatment using 1–1.6 d detention, anaerobic, non-algal polishing ponds was found ineffective in reducing risk generated by UASB effluents to aquatic ecosystems. Need of utilizing an aerobic method of post-treatment of UASB in place of anaerobic one has been emphasized.
5. Natural drying of UASB sludges on sludge drying beds (SDBs) under aerobic conditions results in reduction of adsorbed AS by around 80%. Use of dried UASB sludges is not likely to cause risk to terrestrial ecosystems.

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References

Almendariz, F.J., Meraz, M., Soberon, G., Monroy, O., 2001. Degradation of linear alkylbenzene sulphonate (LAS) in an acidogenic reactor bioaugmented with a *Pseudomonas aeruginosa* (M113) strain. Water Science and Technology 44 (4), 183–188.

Angelidaki, I., Mogensen, A.S., Ahring, B.K., 2000. Degradation of organic contaminants found in organic waste. Biodegradation 11, 377–383.

APHA, 1998, 2005. Standard methods for the examination of water and wastewater, 20th and 21st ed. American Public Health Association, Washington, DC.

Berna, J.L., Ferrer, J., Moreno, A., Prats, D., Ruiz, B.F., 1989. The fate of LAS in the environment. Tenside Surfactant detergent 26, 101–107.

DeLeenheer, A., 2004. Dynamics integrated modeling of basic water quality and fate and effect of organic contaminants in rivers. Ph.D. thesis, Faculteit Landbouwkundige en toegepaste biologische Wetenschappen.

Denger, K., Cook, A.M., 1999. Note: Linear alkylbenzene sulphonate (LAS) bioavailable to anaerobic bacteria as a source of sulphur. Journal of Applied Microbiology 86, 165–168.

EU-TGD, 1996. Technical Guidance Document in support of the Commission directive 93/67/EEC on risk assessment for new notified substances and the Commission regulation (EC) 1488/94 on risk assessment for existing chemicals.

EU-TGD, 2002. Technical Guidance Document in support of the Commission directive 93/67/EEC on risk assessment for new notified substances and the Commission regulation (EC) 1488/94 on risk assessment for existing substances. (Revision of the 1996 version, Office for official publications of the European Communities. Brussels).

Feijtel, T.C.J., Matthijs, E., Rottiers, A., Rijs, G.B.J., Kiewiet, A., de Nijs, A., 1995. AIS/CESIO environmental surfactant monitoring programme. Part 1: LAS monitoring study in "de Meer" sewage treatment plant and receiving river, "Leidsche Rijn". Chemosphere 30 (6), 1053–1066.

Field, J.A., Field, M.A., Poiger, T., Siegrist, H., Giger, W., 1995. Fate of secondary alkane sulfonate surfactants during municipal wastewater treatment. Water Research 29, 1301–1307.

Gasi, T.M.T., Amaral, L.A.V., Pacheco, C.E.M., Filho, A.G., Garcia, A.D., Vieira, S.M.M., Francisco, R., Orth, P.D., Scoparo, M., Dias, M.S.R.D., Magri, M.L., 1991. Ozone application for the improvement of UASB reactor effluent. 1: Physical–chemical and biological appraisal. Ozone Science and Engineering 13 (2), 179–193.

Haggensen, F., Mogensen, A.S., Angelidaki, I., Ahring, B.K., 2002. Anaerobic treatment of sludge: focusing on reduction of LAS concentration in sludge. Water Science and Technology 46, 159–165.

HERA, 2004. HERA-LAS human and environmental risk assessment: linear alkylbenzene sulphonates, LAS. CAS No. 68411-30-3, Version 2.0, June 2004. <http://www.heraproject.com/RiskAssessment.cfm>.

Holt, M.S., Bernstein, S.L., 1992. Linear alkylbenzenes in sewage sludges and sludge amended soils. Water Research 26, 613–624.

Holt, M.S., Fox, K.K., Daniel, M., Buckland, H., 2003. LAS and boron monitoring in four catchments in the UK contribution to GREAT-ER. The Science of the Total Environment 314–316, 271–288.

Jensen, J., 1999. Fate and effects of linear alkylbenzene sulphonates (LAS) in the terrestrial environment – a review. Science and Total Environment 226, 93–111.

Jensen, J., Lokke, H., Holmstrup, M., Krogh, P.H., Elsgaard, L., 2001. Effect and risk assessment of linear alkylbenzene sulphonates (LAS) in agricultural soils. V. Risk assessment of LAS in sludge amended soils. Environmental Toxicology and Chemistry 20 (8), 1690–1697.

Marcomini, A., Giger, W., 1987. Simultaneous determination of LAS, alkylphenol polyethoxylates, and nonylphenol by high performance liquid chromatography. Analytical Chemistry 59, 1709–1715.

Matthijs, E., Holt, M.S., Kiewiet, A., Rijs, G.B.J., 1999. Environmental monitoring for linear alkylbenzene sulfonate, alcohol ethoxylate, alcohol ethoxy sulfate, alcohol sulfate, and soap. Environmental and Toxicological Chemistry 18, 2634–2644.

McAvoy, D.C., Eckhoff, W.S., Rapaport, R.A., 1993. Fate of linear alkylbenzene sulfonate in the environment. Environmental and Toxicological Chemistry 12, 977–987.

Mogensen, A.S., Ahring, B.K., 2002. Formation of metabolites during biodegradation of linear alkylbenzene sulfonate in an up-flow anaerobic sludge bed reactor under thermophilic conditions. Biotechnology and Bioengineering 77, 483–488.

Moreno, A., Ferrer, J., Bevia, F.R., Prats, .D., 1994. LAS monitoring in a lagoon treatment plant. Water Research 28 (10), 2183–2189.

Painter, H.A., Zabel, T., 1989. The behaviour of LAS in sewage treatment. Tenside Surfactants Detergents 26, 108–115.

Petersen, G., Rasmussen, D., Maenpaa, K., Kallqvist, T., Madsen, T., Kukkonen, J.V.K., 2003. Transport and fate of surfactants in the aquatic environment. <http://www.nordtest.org/register/techn/tlibrary/tec524.pdf>.

Prats, D., Ruiz, F., Vazquez, B., Rodriguez-Pastor, M., 1997. Removal of anionic and nonionic surfactants in a wastewater treatment plant with anaerobic digestion: a comparative study. Water Research 31 (8), 1925–1930.

Sanz, J.L., Culubret, E., deferrer, J., Moreno, A., Berna, J.L., 2003. Anaerobic biodegradation of linear alkylbenzene sulfonate (LAS) in upflow anaerobic sludge blanket (UASB) reactors. Biodegradation 14, 57–64.

SIDS, 2005. Sponsor country: USA, Dossier on LAS (draft).

Venhuis, S.H., Mehrvar, M., 2004. Health effects, environmental impacts, and photochemical degradation of selected surfactants in water. International Journal of Photoenergy 6, 115–125.

Ying, G.G., 2006. Fate, behavior and effects of surfactants and their degradation products in the environment. Environmental International 32 (3), 417–431.