

On the Fate of Xenobiotic Compounds during Alternative Methods of Municipal Sludge Treatment

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Abstract

The stabilization of sewage sludge is of great importance for public health and for minimization of environmental impacts. Surface active pollutants (e.g. LAS, NP, NPEO, PAE, PAHs, etc.) originally contained in the wastewaters terminate in the sludge and unless they are converted during sludge treatment they may end up with sludge disposal. Land application of treated sewage sludge, the often preferred disposal method, may then lead to groundwater and/or crop contamination with these undesired xenobiotics. The aim of this work was to assess the fate of these key xenobiotics that are often found in substantial quantities in municipal sludge, in alternative sludge treatment processes. All experiments were carried out in fully automated lab-scale digesters and composting reactors. A mixture of primary and secondary sludges, taken from the Patras Sewage Treatment Plant, was formed in order to obtain representative feed material.

Anaerobic mesophilic (35°C) sludge digestion was considered first. While having no impact on the process, LAS, NP/NPEO, and PAHs were not removed. The phthalate ester DEHP was removed only partially.

Composting of either the raw municipal sludge or the anaerobically treated sludge proved to be effective in removing most xenobiotics to allowable discharge levels.

Finally, the possibility of having a brief post-aeration (1d retention time) of anaerobically treated sludges was examined with promising results. This work reports on the findings of the project BIOWASTE funded by the European Union.

1. Introduction

Sludge (usually a mixture of primary and secondary sludges) is the most significant by-product of municipal wastewater treatment. The most common management method in Europe is thickening, stabilization by anaerobic treatment and spreading on agricultural land. This yields valuable biogas, and recycles nutrients to agriculture, as well as conditioning of the soil. Composting of raw or anaerobically pretreated sludge is an additional option. Problems related to agricultural recycling of sludge include the presence of pollutants, including priority pollutants identified in the EU urban water directives. These include the linear alkylbenzene sulfonates (LAS), alkylphenol polyethoxylates (APE), phthalic acid esters (PAE), and polyaromatic hydrocarbons (PAH).

Surfactants such as linear alkylbenzene sulfonates (LAS) are anthropogenic organic contaminants, found in significant concentrations in sewage sludge. The molecule of LAS contains both a hydrophobic and a hydrophilic group and its basic structure consists of a benzene ring connected to an alkyl chain of different length (the hydrophobic end) and a sodium sulfate group (the hydrophilic end). The commercially available LAS is not a single chemical entity, but it is a mixture of

various alkyl homologues and phenyl positional isomers. Most LAS are disposed in municipal wastewaters and removed during primary and secondary sewage treatment (Marcomini and Giger, 1988; Dehenau et al., 1986; Brunner et al., 1988; Giger et al., 1987). Based on their physicochemical properties, adsorption and biodegradation are the only processes determining the fate of LAS (Marcomini and Giger, 1988; Holysh et al., 1986).

APE are common non-ionic surfactants and are still used in many applications (Talmage, 1994). During biological wastewater treatment they are partially converted to more persistent and toxic metabolites (nonylphenol; NP and nonylphenol ethoxylates; NPEO). The toxic effect of NPEO metabolites has been attributed to the ability of these compounds to mimic natural hormones (estrogens) inducing endocrine disruption of aquatic organisms (Routledge et al., 1998).

PAE are widely used industrial chemicals serving as plasticizers. It has been reported that di-ethylhexyl phthalate ester (DEHP) has xeno-estrogenic, carcinogenic and mutagenic effects (Nielsen et al 1996). DEHP has been commonly found in the sludge of municipal wastewater treatment plants and it has been reported that it is slowly biodegradable (Gavala et al., 2003).

Due to their low water solubility and high hydrophobicity, PAHs are adsorbed onto solid particles during wastewater treatment. The US EPA has identified 16 PAH compounds as priority pollutants whose levels in industrial effluents require monitoring (Heitkamp et al, 1988)

The efficient removal of these pollutants is a prerequisite for recycling excess biological sludge into the natural resource cycle. For this purpose, bioprocessing systems are necessary for the sewage sludge treatment with focus on maximal biodegradation of the organic contaminants and sludge detoxification.

The aim of this work is to investigate the biodegradation of some key organic pollutants during anaerobic digestion and composting, and the possible impact of these compounds on the particular processes. The results of this work contribute to the use of an environmentally-friendly sludge management for the sustainable recycling of sewage sludge in the agricultural soil.

Typical priority pollutants identified in the EU urban water directives

Compound	Origins	Mammalian Toxicity	Ecotoxicity	Range in sludge mg/kg d.m.	Proposed regulations mg/kg d.m.
LAS (Linear Alkylbenzene Sulfonates)	Cleaners, detergents.	medium	Aquatic: high Ter/al: medium Bioac/tion: high	11-16,100 1,600-11,800 7,000-30,200	2,600
NPEO (nonyl phenol ethoxylates)	Cleaning products, cosmetics.	medium	Aquatic: high Ter/al: medium Bioac/tion: high	24.4±17.8 23-171 55-537	50
DEHP (di ethyl hexyl phthalate)	Plastic industries, food packaging & conditioning.	Carcino-mutano-genic	Aquatic: high Ter/al: low Bioac/tion: high	24.638±0.377 25-661 3.9-170	100
Polyaromatic hydrocarbons (PAHs)	Smoke-exhaust gases, rain runoff, industries.	Carcino-mutano-teratogenic	high Bioac/tion: high	2.720-7.995 2.040-36.034	6 (sum of 11 PAHs)

2. Analytical methods

The xenobiotics were extracted from sludge in microwave assisted extraction vessels using methanol (for LAS) and 1:1 hexane:acetone mixture for the rest of the compounds. Following a brief cleanup (for moisture removal) and evaporation, the compounds were redissolved in methanol:water (1:1) for LAS, or in acetonitrile for the other xenobiotics. Analysis was by HPLC, equipped with UV-fluorescence detectors in series.

3. Anaerobic Digestion of Sludge

A mixture of primary and secondary sludge (2.5 : 1) was used for the experiments in a 3 L CSTR. The sludge characteristics were as follows:

Table 2. Sludge characteristics

Parameter	Value
TSS (g/l)	31.3
VSS (g/l)	20.4
Dissolved COD (mg/l)	1963
Total COD (mg/l)	33145
Alkalinity (mgCaCO ₃ /l)	2857
pH	6.68
NH ₃ (Kjeldahl) (mg N-NH ₃ /l)	268.8
Norg (Kjeldahl) (mg N-NH ₃ /l)	1047
Soluble carbohydrates (mg/l)	63.6

To the feed three PAHs were added: phenanthrene, fluoranthene and pyrene, as well as diethyl-hexyl phthalic ester (DEHP) at final concentrations of 0.5 mg/l for PAHs and 5 mg/l for DEHP. This was done as no significant inherent concentrations were found in the particular sludge that we had available. All digesters were initially operated at an HRT of 15d. After 84 days, the HRT of CSTR#2 was reduced to 10 d.

The generated biogas is shown on Fig.1 and Table 3. The decrease in HRT in the second reactor led to an increase in the amount of generated biogas, from 1500 ml/d to 1900 ml/d. Biogas composition in both reactors ranged between 60-70% in methane and 40-30% in CO₂.

Table 3. Biogas production rate (in ml/d)

HRT	CSTR#1	CSTR#2
15d	1433 ± 49	1461 ± 64
10d	-	1905 ± 104

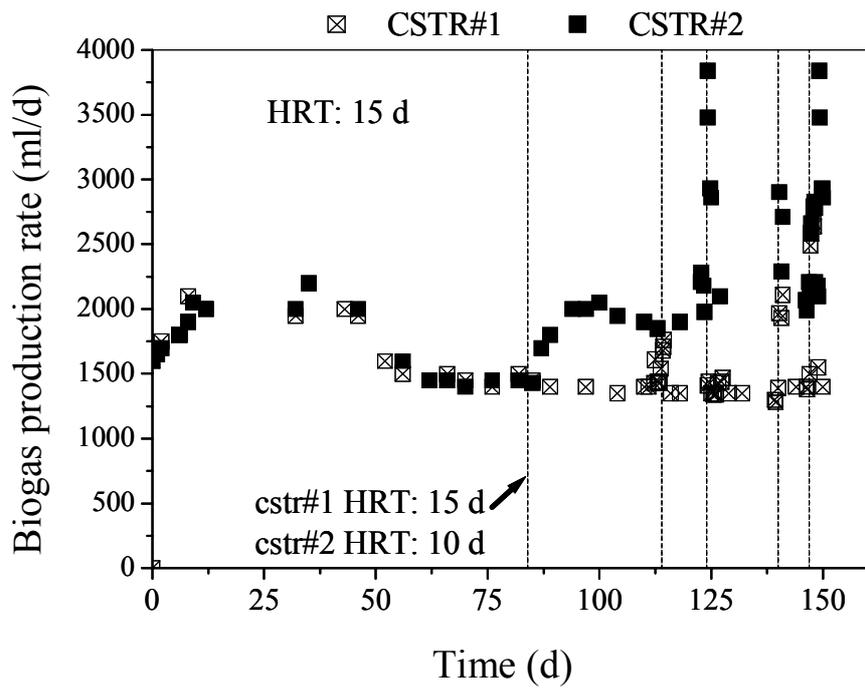


Fig.1 Biogas production rate

A 26 ± 2.4 % (CSTR#1) and 23 ± 2.7 % (CSTR#2) reduction in volatile suspended solids was observed. (Fig.2, Table 4)

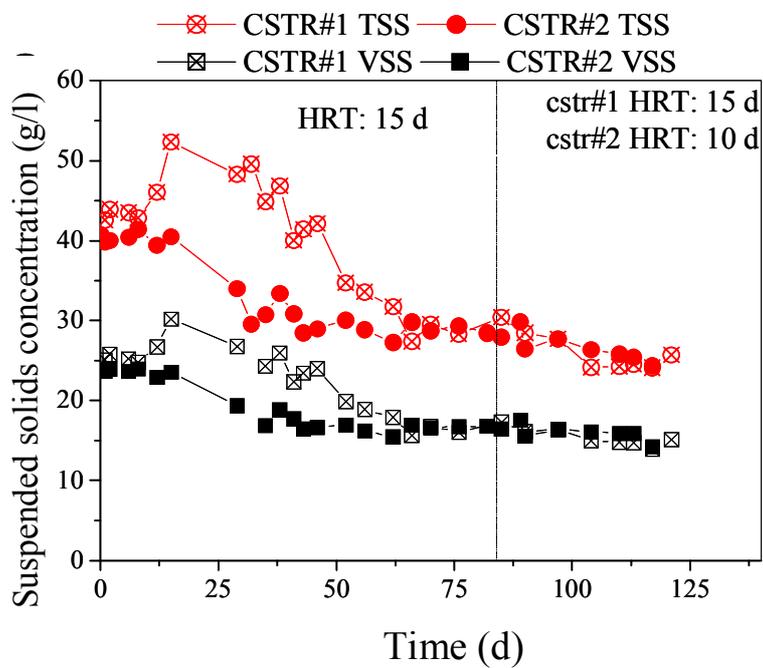


Fig.2 TSS and VSS in the anaerobic digesters

Table 4. TSS and VSS in the anaerobic digesters

HRT	TSS (g/l)	TSS (g/l)	VSS (g/l)	VSS(g/l)
	CSTR#1	CSTR#2	CSTR#1	CSTR#2
15d	25.1±1.4	-	15.1±0.8	-
10d	-	26.0±1.1	-	15.7±0.7

Dissolved COD was close to 400 mg/l, which is satisfactory. The pH ranged between 7.0-7.4 throughout the experimentation period. The evolution in these parameters is shown on Fig.3.

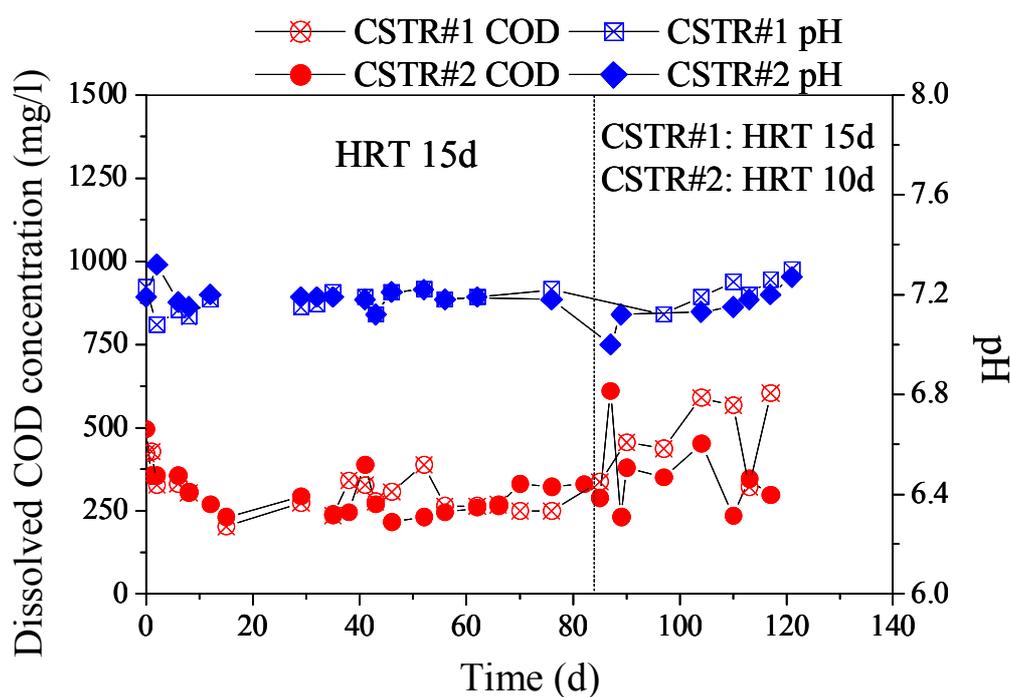


Fig.3. COD and pH in the digesters.

The fate of the xenobiotic compounds was followed (Figs.4, 5 and 6) . With the exception of DEHP (Fig.7), no biodegradation of xenobiotics was observed.

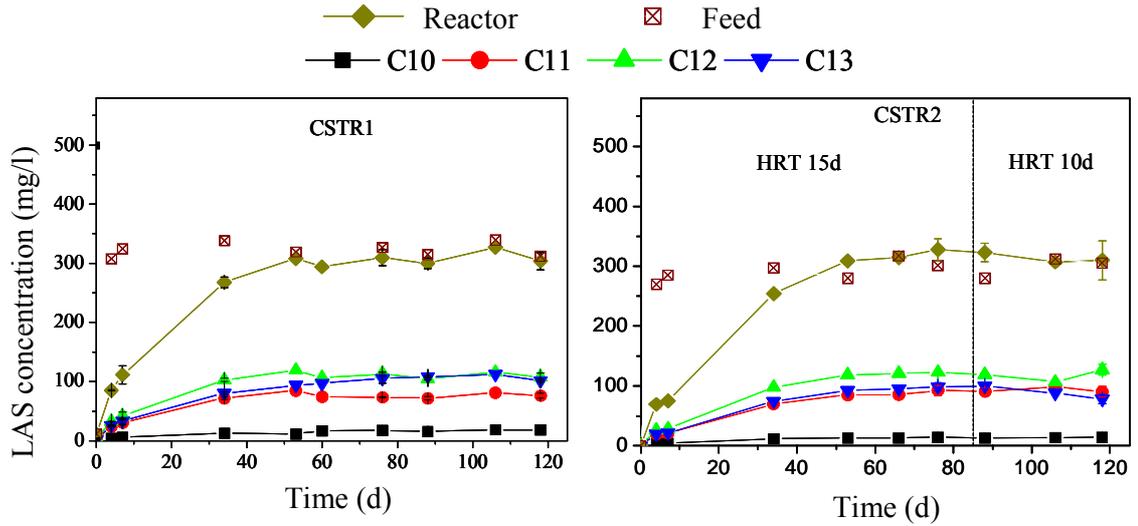


Fig.4 LAS concentrations in the two digesters

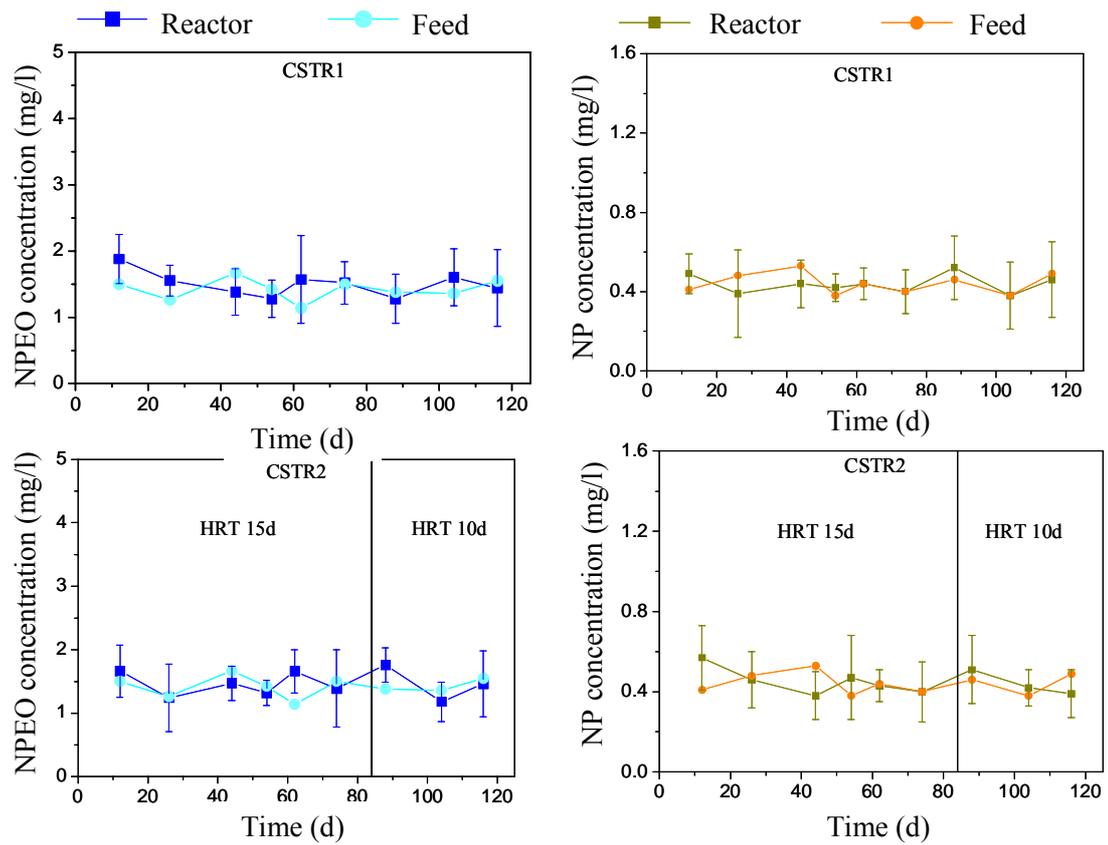


Fig.5. NPEO and NP concentrations in the two digesters.

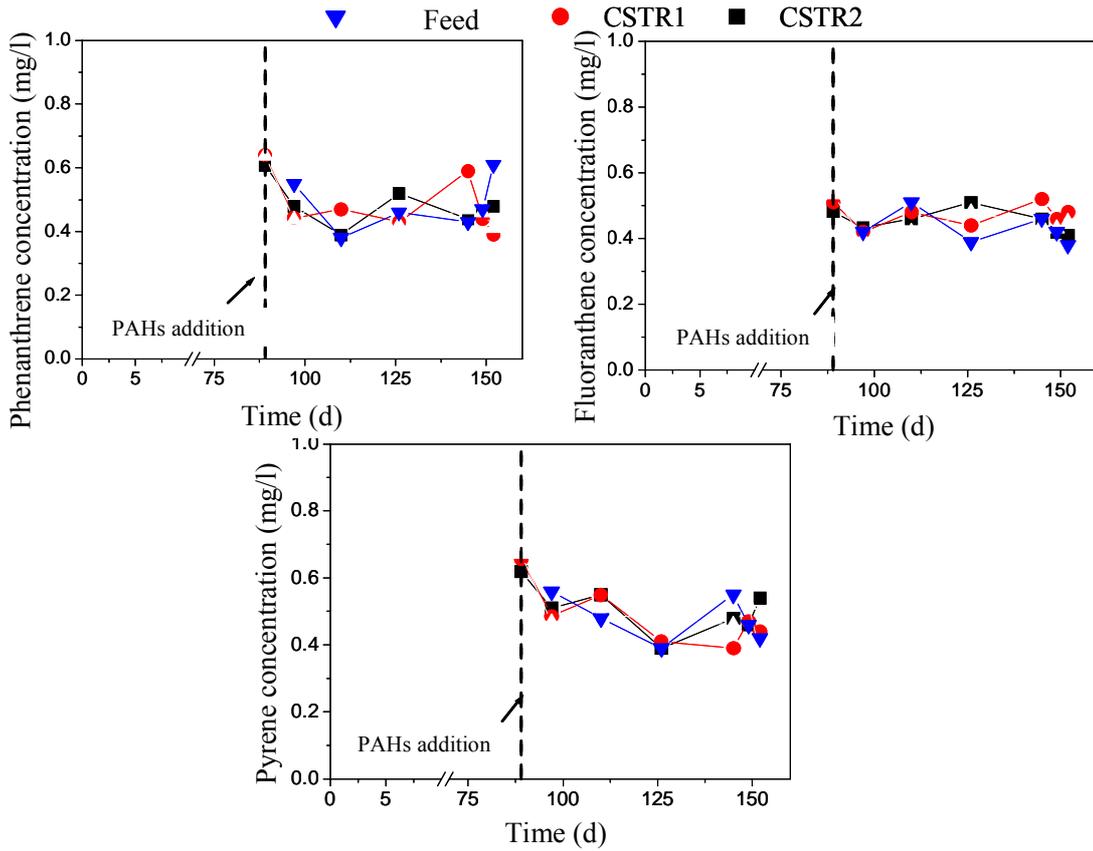


Fig.6. Concentrations of PAHs

DEHP was reduced to 4.18 ± 0.23 mg/l and 4.48 ± 0.42 mg/l in CSTR#1 and CSTR#2, respectively. This corresponds to a reduction by 31% in CSTR#1 and 26% in CSTR#2.

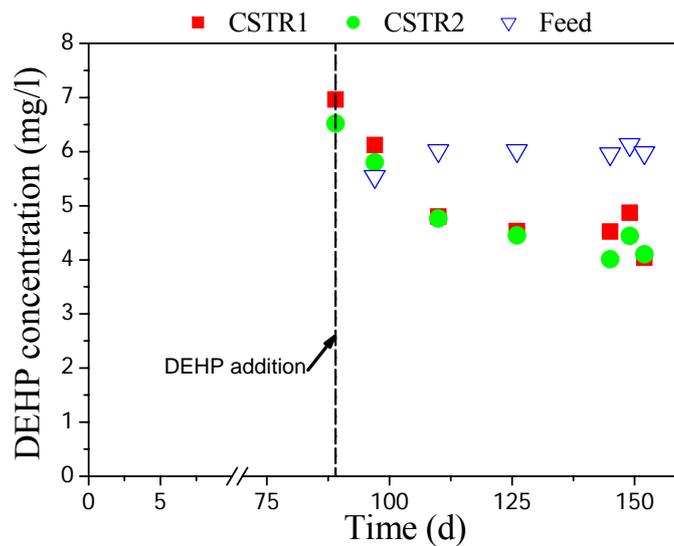


Fig.7. DEHP concentrations in the anaerobic digesters.

Table 5. Concentrations of all xenobiotics in mg/l.

	Feed.	CSTR#1	CSTR#2
LAS	323 ± 10	307 ± 11	315 ± 8
NP	0.44±0.06	0.44±0.05	0.43±0.05
NPEO	1.43±0.22	1.42±0.12	1.48±0.21
DEHP	6.02±0.07	4.18±0.23	4.48±0.42
Phenanthrene	0.47±0.09	0.46±0.05	0.46±0.08
Fluoranthene	0.43±0.05	0.45±0.04	0.48±0.03
Pyrene	0.46±0.06	0.48±0.07	0.45±0.06

From the above results, presented in Table 5, it becomes apparent that, with the exception of DEHP, for which there is a partial degradation, the other xenobiotics are not bioconverted during anaerobic digestion.

4. Sludge Composting

A schematic diagram of the aerobic lab-scale composters for bioprocessing of organic contaminants is shown on Figure 8. The composters are constructed of stainless steel and insulated with polyurethane foam and aluminum coat. They are horizontal cylinders with a volume of approximately 28 L (300 mm in diameter and 400 mm in length). The compost material is restrained on a perforated plate at the bottom of the reactor to provide an effective diffusion of the air into the mixture and allow the leachate to leave the composting bulk. The mixing of the compost material is conducted via inclined paddles which are turned by a motor connected to a mechanical turning controller. A sampling port is placed in the front side of the composter and other ports for the monitoring and control of the process have been placed on the top of the composter. The top of the composter is like a gable, as a way to collect the liquid concentrate. There are temperature and humidity sensors placed inside the composting mixture as well as on the headspace of the reactor. Air is supplied to the system via two streams: one at a minimum constant flow rate and the other one at a higher flow rate activated whenever the oxygen percent in the effluent gas stream drops lower than a preset limit. The exhaust gas is collected and analyzed with an electronic analyzer for CO₂, O₂ and N₂. A computer is used to control the operational parameters and record the data obtained from the gas analyser.

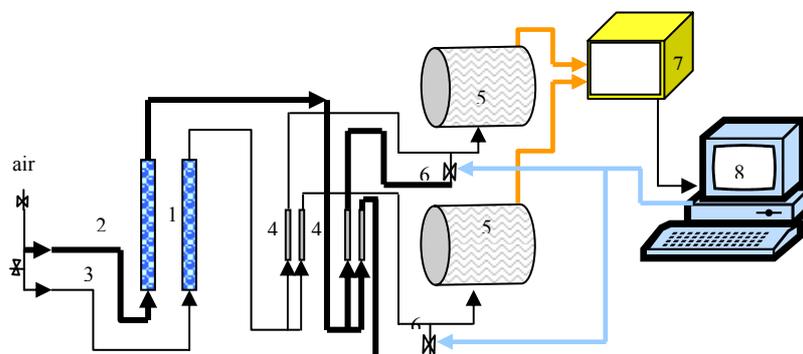


Figure 8. . Experimental configuration for composting (1. silica columns, 2. high pressure air flow, 3. low pressure air flow, 4. flow meters, 5. composters, 6. electronic valves, 7. gas analyser, 8. computer)

In two parallel composting experiments, a mixture (3.4kg) of primary and secondary sludge was used at a ratio of 2.5 to 1 as for the digestion experiments. Also, sheep manure (3.1kg) was added to the material in order to adjust the humidity of the composting material (the humidity of the sheep manure was approximately 10%). The compost product of previous experiments was used as seed inoculum, and was added in a proportion of 25% on a dry weight basis. One of the reactors contained only the inherent amounts of xenobiotics contained in the sludge mixture and the other was spiked with additional xenobiotics.

All the experiments were conducted on a batch basis. The mixture took up the $\frac{3}{4}$ of the reactor volume. The composting material was stirred twice a day at 30 rpm, for two minutes, in order to provide proper mixing and aeration to the mixture. Air was supplied to the reactor by an air pump, in order to maintain aerobic conditions. The humidity, total solid and volatile solid content as well as the pH of the composting mixture changed during the experiments (Table 6). Humidity decreased due to the temperature increase during each experiment. The volatile content of the mixture also decreased due to the biological decomposition of the organic matter. The pH of the composting mixture increased, probably because of protein decomposition and NH_3 production.

Table 6. Characterization of the composting material at the beginning and the end of each experiment ^a.

Start	Humidity (%)	55.9
	pH	7.3
	TS (% mg DM/ mg WM)	44.1±1.46
	VS (% mg VM/ mg DM)	66.5±3.03
End	Humidity (%)	43.5
	pH	8.9
	TS (% mg DM/ mg WM)	56.5±2.52
	VS (% mg VM/ mg DM)	48.9±4.40

^a The average value of three samples

The biological activity was monitored via the carbon dioxide production as shown on Figure 9. The production of carbon dioxide was maximized in the first 5 days, and then slowly decreased to very low levels indicating minimization of the biological rates. The erratic behavior of carbon dioxide in the first days was the result of the high variation of the oxygen supply rate to the composters.

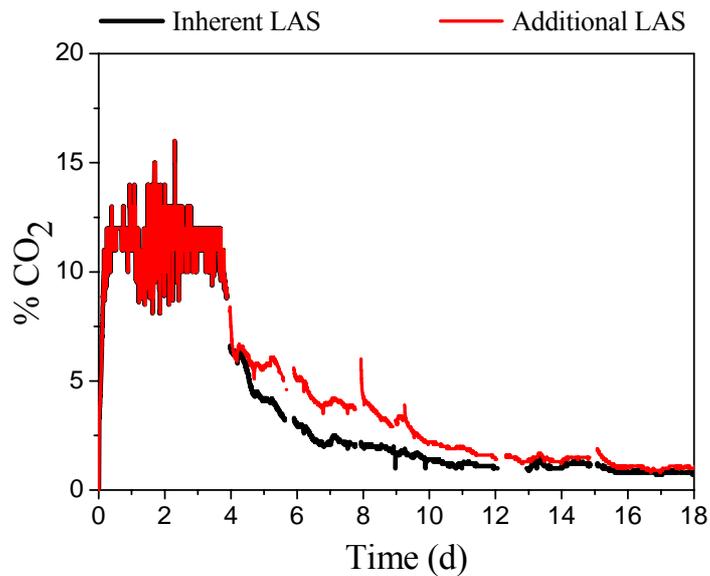


Figure 9. Percentage of CO₂ in the outlet gas flow during composting.

The biological activity also results in the acute temperature increase (Fig.10) followed by a slower decrease towards the end of the experiments. The gas compositions as well as the temperature profiles during both experiments were comparable, although, in the second reactor, the initial LAS concentration was 3-fold higher than in the case of the first reactor. This means that the presence of LAS even at the high concentration of 1,5 mg/kg T.S. (initially contained in the sludge mixture at 53,5 mg/kg T.S.) was not inhibitory to the bioprocess.

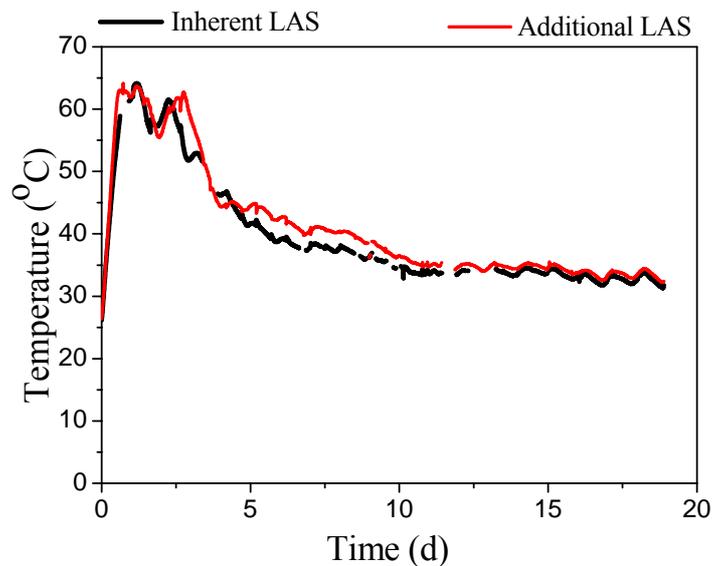


Figure10. Temperature profile of the solid mixture, during composting for the two composting reactors.

The total LAS concentration (sum of C10-C13 homologues) decreased significantly as shown on Fig. 11 in both experiments. The LAS degradation rate depended on the initial LAS concentration as shown in Figure 11. The higher the concentration, the higher was the degradation rate, although a fraction of LAS (9% to 22%) remained in the mixture unconverted at the end of the experiment. Therefore, the bioavailability of these hydrophobic compounds (LAS) is very important for assessing their ultimate fate during composting. The initial rate was higher in the first 5 days, when the temperature was also high. Actually, the duration of the maturation step could prove important in the eventual LAS removal, since at low LAS concentrations, bioavailability limitations may lead to residual LAS concentrations.

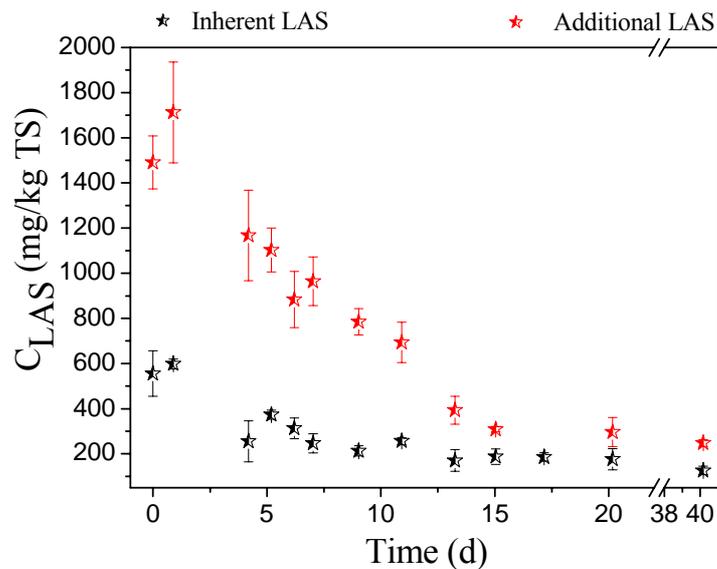


Figure 11. Total LAS concentration decrease during the composting experiments (The points represent the mean value of analysis done in three samples)

Figure 12 shows typical profiles of DEHP during composting. DEHP biodegradation by 60 % for high DEHP concentration and 98% for low DEHP concentration were observed.

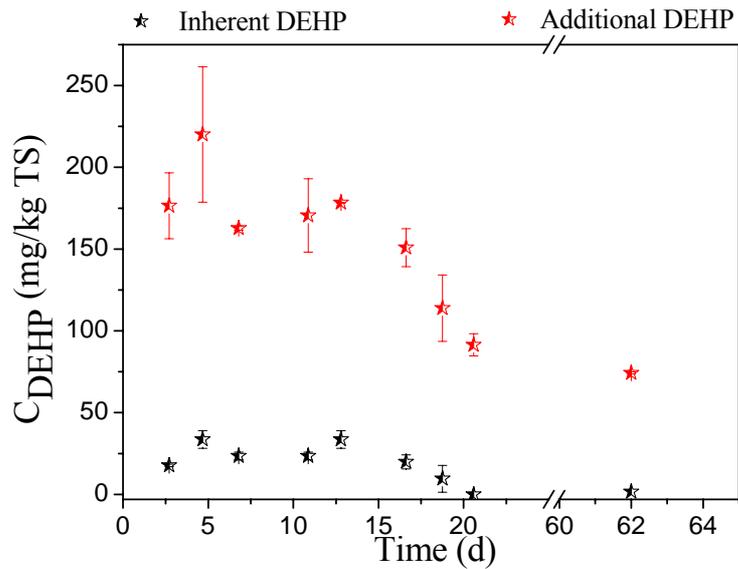


Fig.12. DEHP profiles during composting.

Figs.13 and 14 present the evolution of NPEO and NP, respectively. Extended NPEO degradation (93,5%) independent of the initial concentration is observed. Note that the concentration of NP initially increases. This is because during NPEO metabolism, NP was produced. Eventually of course the concentration of NP reaches a maximum and starts decreasing.

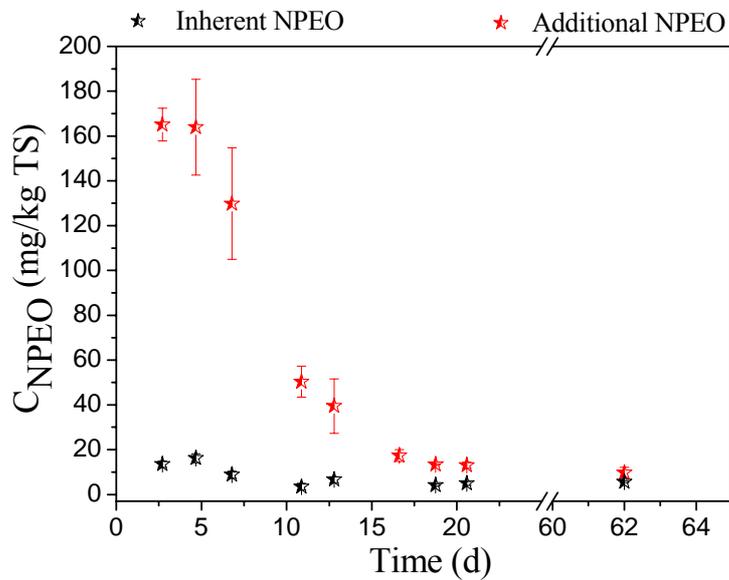


Fig.13. NPEO profile during composting.

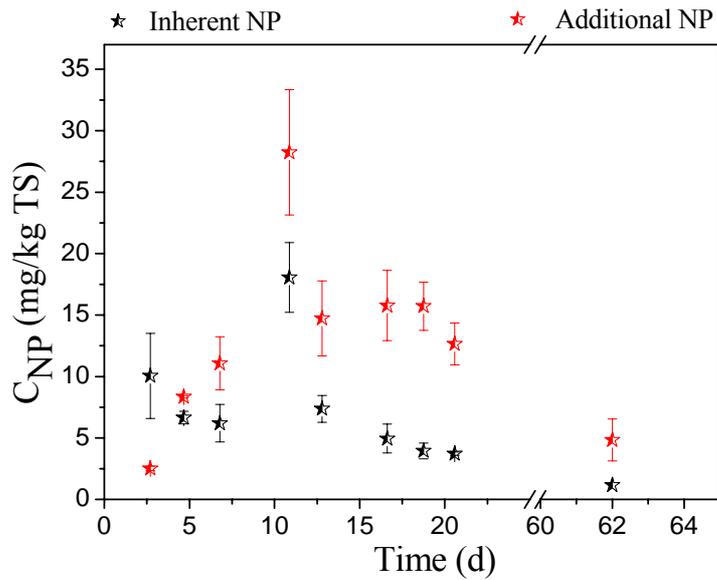


Fig.14. NP concentration during composting.

5. Short post-aeration of anaerobically digested sludge

Since under aerobic conditions, extensive biodegradation of all xenobiotics was observed, we considered having a short post-aeration step of anaerobically treated sludge. A 500 ml draw-fill reactor was fed with anaerobically treated sludge. The hydraulic retention time was initially 3d. As seen on Fig.15, at this HRT, the LAS are almost completely (90%) converted. When, however, the HRT was reduced to 1 day, LAS started coming through unconverted. The reactor recovered when the HRT was changed back to 3 d HRT and continued converting the LAS when the HRT was reduced to 2 d. On day 120, an inoculum of LAS acclimated organics was added to the reactor. The HRT was then again reduced to 1.5 d first and then to 1 d. It was then seen that complete conversion of LAS could be accomplished even at an HRT of 1 day, following this bioaugmentation. It should be mentioned that this idea was also tested with degraders of other xenobiotics, but without any success.

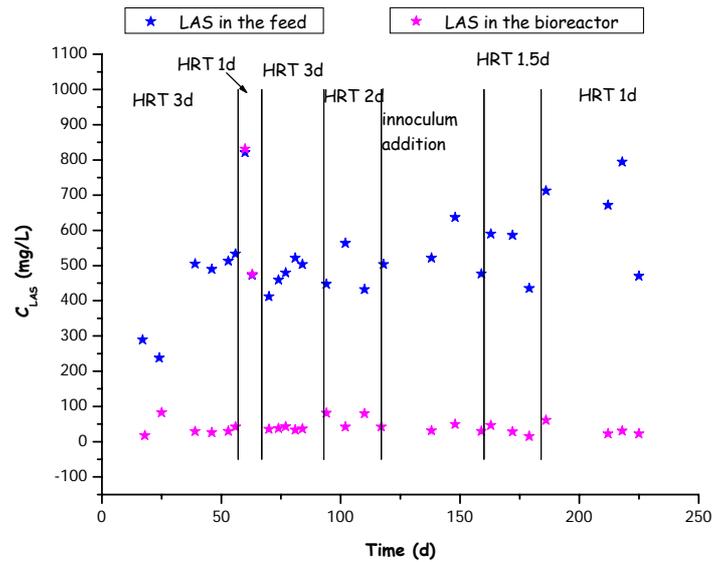


Fig.15. Profile of LAS during post-aeration of anaerobically digested sludge.

6. Conclusions

LAS, NPEO, NP and PAHs were highly persistent during anaerobic digestion of a sludge mixture, with no demonstrable removal. DEHP was partially degraded (47%).

During sludge composting the xenobiotics LAS, NPEO και DEHP are extensively degraded by 84%, 93,5% and 60%, respectively. The period of maturation leads to higher xenobiotic degradation during composting.

A short post-aeration of anaerobically digested sludge may lead to high (~90%) degradation of LAS. Bioaugmentation can help add fast degraders allowing LAS conversion even at an HRT of 1 d.

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