6.37 Occurrence, Toxicity, and Biodegradation of Selected Emerging Priority Pollutants in Municipal Sewage Sludge

K Stamatelatou, Democritus University of Thrace, Greece
C Pakou, University of Patras, Patras, Greece
G Lyberatos, University of Patras, Patras, Greece and Institute of Chemical Engineering and High Temperature Chemical Processes, Patras, Greece

Glossary

anaerobic digestion It is a biological treatment method for stabilizing organic wastes (such as sewage sludge). It involves the concerted action of several groups of microorganisms that grow in the absence of oxygen and degrade the organic matter into a series of intermediate simpler compounds and, finally, to biogas (mixture of methane and carbon dioxide).

composting It is an aerobic, thermophilic biological process applied to stabilize and sanitize solid wastes. The waste combined with admixtures (added to secure the necessary humidity, air space, and nutrient balance) turns into a stable organic mixture suitable to be used as soil conditioner and/or fertilizer.

estrogen disruptor It characterizes any exogenous compound that interferes with the function of estrogens (female sex hormones) and has an adverse effect on the productivity of the organisms.

sewage sludge It is a mixture of solid materials in a slurry form, coming from sewage during the sewage-treatment process. It mainly consists of the solids contained in the raw sewage wastewater and the microorganisms grown in the aeration tank. Once sludge is separated from wastewater, it should undergo stabilization.

xenobiotic It is a chemical compound foreign to any living organism. The term comes from the Greek words 'xenos' (foreigner) and 'bios' (life). It includes compounds that are not produced by the body of humans and animals (such as drugs and their metabolites), as well as pollutants that have been synthesized and cannot be found in nature.

6.37.1 Introduction

The intensified urbanism and industrialization in the last decades have resulted in an enormous increase of waste (solid wastes, sewage, and gaseous emissions) production worldwide. Apart from the quantity of the wastes, their qualitative characteristics have also been affected by the disposal of toxic substances introduced in the wastes through consumable products or industrial activities. Waste treatment aims not only at reducing the hazardous effects but also at valorizing useful material and/or energy that can be recovered from the wastes through processing, according to the concept of sustainable development.

EU directive 91/271/EC and the collateral provisions oblige the member states to attend the problem of sewage treatment. Enforcement of the directive has led to the construction and operation of many sewage-treatment plants producing an appreciable quantity of sludge. Sewage sludge is a slurry residue coming from wastewater treatment. It consists of the suspended solids separated from the wastewater during the primary treatment and the excess biomass produced during the secondary and tertiary biological wastewater- treatment processes. It has been estimated that in 2005, 13 member states of the EU produced 8.330 million tons of sludge (dry weight). The breakdown in each country is depicted in **Figure 1** [1].

Sewage sludge contains organic compounds (carbohydrates, proteins, and lipids) as well as nutrients (nitrogen, phosphorus, potassium, calcium, sulfur, and magnesium) (**Table 1**). Because of the organic content and nutrient value, sludge can, in principle, substitute chemical fertilizers and be used as a soil conditioner.

The addition of organic matter to soil ameliorates its physical properties and decreases the possibility of corrosion. Degradation of organic matter releases high agricultural value components (N, S, Mg, etc.) at a slower rate than the inorganic fertilizers, rendering
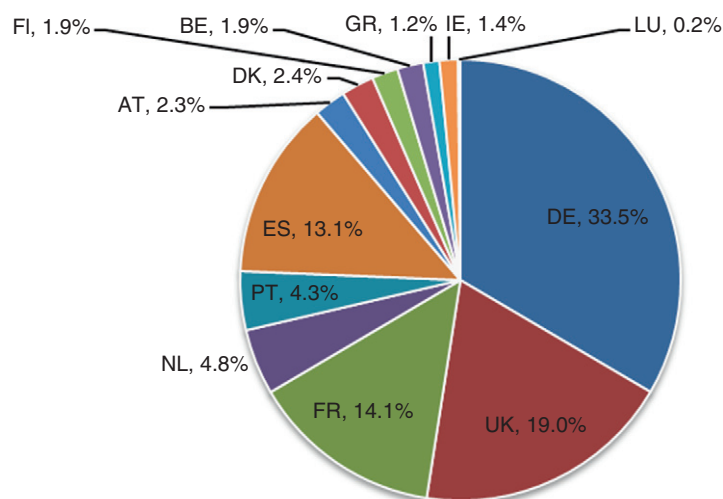
Figure 1   Production of sewage sludge in 13 European countries during 2005 [European Topic Centre on Resource and Waste Management (ETC-RWM), Facts and figures, URL: http://scp.eionet.europa.eu/facts/wastebase/quantities/index_html/]. DE, Germany; UK, United Kingdom; FR, France; NL, Netherlands; PT, Portugal; ES, Spain; DK, Denmark; FI, Finland; BE, Belgium; GR, Greece; IE, Ireland; LU, Luxembourg.

Table 1   Typical characteristics of various sludge types [2]

Sludge type	A	B_1	B_2	C	D
Dry solids (DS) (kg m^{-3})	12	9	7	10	30
Volatile solids (VS) (% DS)	65	67	77	72	50
pH	6	7	7	6.5	7
C (%VS)	51.5	52.5	53	51	49
H (%VS)	7	6	6.7	7.4	7.7
O (%VS)	35.5	33	33	33	35
N (%VS)	4.5	7.5	6.3	7.1	6.2
C/N	11.4	7.0	8.7	7.2	7.9
P (%DS)	2	2	2	2	2
Cl (%DS)	0.8	0.8	0.8	0.8	0.8
K (%DS)	0.3	0.3	0.3	0.3	0.3
Al (%DS)	0.2	0.2	0.2	0.2	0.2
Ca (%DS)	10	10	10	10	10
Fe (%DS)	2	2	2	2	2
Mg (%DS)	0.6	0.6	0.6	0.6	0.6
Lipids (%DS)	18	8	10	14	10
Proteins (%DS)	24	36	34	30	18
Calorific value (kWh t^{-1} DS)	4200	4100	4800	4600	3000

A, primary sludge with physical/chemical treatment or high pollution load (>0.5 kg BOD$_5$ kg^{-1} d^{-1}); B$_1$, biological sludge (low load, 0.07 kg BOD$_5$ kg^{-1} d^{-1} <load<0.2 kg BOD$_5$ kg^{-1} d^{-1}); B$_2$, biological sludge from clarified water (low and middle load, 0.07 kg BOD$_5$ kg^{-1} d^{-1} <load<0.5 kg BOD$_5$ kg^{-1} d^{-1}); C, mixed sludge (mix of A and B$_2$ types); D, digested sludge.

them available to the crops for a longer period. Organic matter is also a source of energy to the indigenous microorganisms of the soil. Nitrogen is an important nutrient. Nitrogen in sludge is present in organic compounds but plants utilize nitrogen in its inorganic form. Therefore, the availability of nitrogen is crucial and varies between 4% and 60% depending on the sludge type. Phosphorus is also significant because its concentration in the natural resources is very limited. The availability of phosphorus in sludge varies around 40% depending on the sludge type.

Sludge also contains contaminants such as heavy metals, pathogens, and xenobiotic compounds. The concentration of heavy metals in the sludge varies as they originate from various sources of variable nature such as sewage, rain runoffs, and industrial wastes, with the industrial component being the most determinant. The accumulation of heavy metals in the environment may affect soil properties, microorganisms, stock farming, and human health. However, the deficiency of some soil types in metals (e.g., copper) may be overcome through the addition of sludge containing such constituents [3].

Sludge is also burdened with pathogens, the number and types of which, vary and depend on the size and health of the human population, the sewage network, and the industrial activity in the area of sewage production. The variation is greater in smaller sewage networks.

Extensive studies have been performed concerning the environmental risk assessment of heavy metals and pathogens in sewage sludge. Regulations with maximum limits of metals and pathogens have been established. This is not the case for xenobiotics, however.

Table 2   Maximum limit values of xenobiotics in sludge in mg kg^{-1} dry weight of sludge (to be used in agriculture)

Xenobiotic	LAS	DEHP	NPE	PAHs
Suggested values to be incorporated in 86/278EU directive	2600	100	50	6
Austria				6
Denmark	1300	50	10	3
France				1.5–5
Sweden			100	3

Although the EU directive 86/278/EC does not determine limits in xenobiotics for using sludge for agricultural purposes, some European countries have imposed limit values for certain xenobiotics (Table 2) such as linear alkylbenzene sulfonates (LAS), nonylphenol ethoxylates (NPEOs), phthalates (e.g., di-2-ethyl-hexyl phthalate, DEHP) and polycyclic aromatic hydrocarbons (PAHs).

Xenobiotics are usually recalcitrant to degradation and tend to accumulate in the environment. Anaerobic digestion, applied to stabilize the sewage sludge, has minor, if any, effect on the removal of the xenobiotics. Moreover, their concentration (expressed in kg per kg of sludge) may be increased as a result of the sludge mass reduction. On the other hand, xenobiotics have been found to be removed during composting, an aerobic biological method that is also used for sludge sanitation/stabilization [4]. The present article focuses on some dangerous xenobiotics present in sludge (phthalic acid esters (PAEs), PAHs, and surface-active agents). Complementary information addressing the occurrence and properties of pharmaceutical and personal care products (PPCPs) as well as the biodegradation processes aimed at reducing the micropollutant burden on water and wastewater are to be found in Chapter 6.38 by Forrez et al (this volume).

6.37.2   Phthalic Acid Esters (Phthalates), PAEs

Phthalates are widely used as plasticizers. Plasticizers are small organic molecules added in polymers in proportions of 1–50% to decrease the temperature glass transition making polymers softer and flexible. In Western Europe, 1 million tons of phthalates are produced annually, 900 000 of which are used as additives in plastics from polyvinyl chloride (PVC). Products made of PVC are widely used daily including plastic transparent bags, plastic toys, medical appliances, construction, and insulation materials. Apart from their utilization as plasticizers, phthalates are also used in dye solvents, glues, cosmetics, detergents, and so forth. Table 3 summarizes the most important PAEs, their main physicochemical properties, and their common applications [5]. The solubility of these compounds in water is difficult to be determined due to their tendency to form emulsions.

PAEs are not chemically bound on polymers. As a result, they can easily escape and spread to the environment during the production and the utilization of products that contain them. Moreover, due to their low vapor tension, PAEs are easily evaporated and diffuse into the atmosphere; they are trapped in aerosols and, through rainfall, end up in receiving water bodies and soil. As a result, the PAEs have been detected in samples taken from sewage, air, surface water, soil, and aquatic organisms [6]. The concentrations of PAEs have been found to vary from 0.3 to 77 ng m^{-3} in atmospheric air samples, from 0.3 to 98 μg l^{-1} in surface water samples, from 0.2 to 8.4 mg kg^{-1} dry weight in soil samples, and from 28 to 154 mg kg^{-1} dry weight in sludge samples. In a recent study, the fate of six PAEs in various stages of a sewage-treatment plant was studied (Figure 2), and it was found that the DEHP was the most dominant phthalic ester and its removal was assessed to be 78.1%.

DEHP is considered to be the most important among the PAEs due to its large production, wide utilization, and intense presence in the environment. Therefore, the present article focuses on DEHP with respect to its fate in the environment, biodegradability, and toxicity.

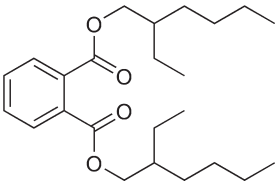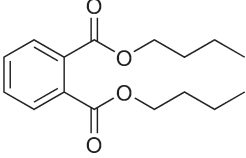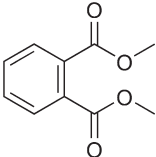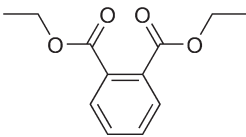### 6.37.2.1   Di-(2-Ethyl-Hexyl)Phthalate

DEHP is produced from phthalate anhydride reacting with 2-ethylhexanol. The annual production of DEHP sums up to 4 million tons, 95% of which is being used in the manufacturing of PVC products.

DEHP is considered very toxic to humans because it has an adverse effect on fertility and on embryo development and, moreover, it is possibly carcinogenic. Tests on animals (in vivo) as well as laboratory tests (in vitro) have shown that DEHP and its metabolites have an impact on vital organs such as the heart, kidney, and the reproductive system. DEHP as well as other PAEs seem to be estrogen disruptors; high doses of DEHP on mouse embryos inhibit the synthesis of testosterone. Further to its effect on humans, DEHP has been found to be toxic to other organisms such as plants, marine organisms, and anaerobic microorganisms.

DEHP has been detected in higher concentration values than all the other phthalates in raw or treated sewage. Due to its low solubility in water and high octanol–water distribution coefficient, DEHP tends to get absorbed on the particulate organic matter of wastewater and ends up in sludge. Typical concentrations of DEHP in various sludge types are listed in Table 4 based on measurements performed in sludge samples taken from four sewage-treatment plants in Seville.

The high value of DEHP in the anaerobically digested sludge can be attributed to its low biodegradation under anaerobic conditions. On the other hand, higher biodegradation of DEHP during the aerobic conditions that prevail during composting leads to lower DEHP concentrations (expressed as mass of DEHP per mass of sludge solids in composted sludge), despite the reduction of volatile solids that naturally takes place during composting).

Table 3   Typical PAEs, their main characteristics and applications

Full name	Abbreviation	Chemical structure	Physicochemical properties	Applications
Di-(2-ethyl-hexyl) phthalate	DEHP		MW: 390.5 Log K_{ow}: 7.94 Solubility in water: 0.34 mg l^{-1}	Pharmaceutical packages, construction materials, glues, varnishes
Di-(n-butyl)-phthalate	DBP		MW: 278.4 Log K_{ow}: 4.45 Solubility in water: 11.2 mg l^{-1}	Solvent, aroma fixative, plasticizer of nitrocellulose and poly acetate vinyl ester
Di-methyl-phthalate	DMP		MW: 194.2 Log K_{ow}: 1.61 Solubility in water : 4200 mg l^{-1}	Solvent, plasticizer of cellulose derivatives, insect repellant
Di-ethyl-phthalate	DEP		MW: 222.2 Log K_{ow}: 2.38 Solubility in water : 1100 mg l^{-1}	Solvent, plasticizer of cellulose derivatives, cosmetics
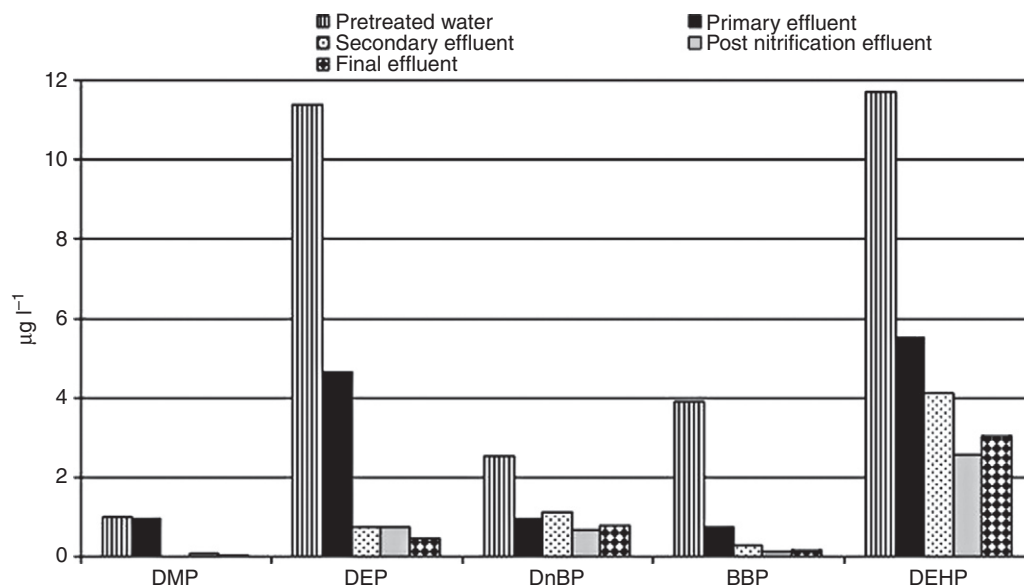
Figure 2   Average values of six PAEs in various stages of a sewage-treatment plant [6].

Biodegradation is the main mechanism of degradation of PAEs in the environment (the rates of hydrolysis and photolysis are very low). Several bacteria (such as actinomycetes) are able to degrade PAEs under aerobic and anaerobic conditions. PAEs with long alkyl chain (such as DEHP) are mineralized at a slower rate. However, as a temperature increase favors DEHP biodegradation under aerobic conditions, sludge composting, as a thermophilic aerobic biological process, results in high DEHP removal efficiencies

Table 4 Concentration of DEHP in primary, secondary, dehydrated anaerobically digested, and composted sludge in samples taken from four sewage-treatment plants in Seville [7]

Sample	Range (mg kg^{-1} dw)	Average (mg kg^{-1} dw)	Relative standard deviation (%)
Primary sludge	12–103	53	53
Secondary sludge	34–92	65	32
Dehydrated anaerobically digested sludge	13–345	159	70
Composted sludge	24–124	75	41

Table 5 DEHP removal during sludge composting

Composting system	Sludge type	DEHP (mg kg^{-1} dw)	Removal	References
Closed vessel (10 l)	Raw	3–6	91% in 25 days	[8]
Closed vessel (220 l)	Raw, dehydrated	0.057	58% in 85 days	[9]
Closed vessel (220 l)	Anaerobically digested, dehydrated	0.077	34% in 85 days	[9]
Rotary drum (5 m^3)	Anaerobically digested, dehydrated	0.077	32% in 28 days	[9]
Windrows	Activated sludge and grass	28.67	94% in 135 days	[10]
Windrows	Anaerobically digested, dehydrated	36.37	60% in 143 days	[11]
Closed vessel (110 l)	Primary and secondary, dehydrated	296	85% in 18 days	[12]

(Table 5). However, biodegradation of DEHP is active during the subsequent steps too (such as the maturation step) rendering the whole process duration an important factor for the DEHP removal.

6.37.3 Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs are an important class of organic contaminants originating from natural (forest fires, volcano eruption, and disintegration of organic matter) or anthropogenic sources (controlled burning of fuels for the production of energy, industrial processes such as petrol distillation, coke production, and gaseous emissions from vehicles). They are hydrocarbons with two or more fused aromatic rings in linear or branched position. They are formed from the incomplete incineration or pyrolysis of mineral fuels and other organic materials at high temperatures (500–900 °C).

The Environmental Protection Agency (EPA) of USA has characterized 16 PAHs (benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene, indeno(1,2,3-cd)pyrene, acenaphthene, acenaphthylene, anthracene, benzo(ghi)perylene, fluoranthene, fluorene, naphthalene, phenanthrene, and pyrene) as high priority contaminants, while 7 more (benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene, and indeno(1,2,3-cd)pyrene) are considered potentially carcinogenic. Some PAHs are suspected to cause cancer of the skin, lung, and breast. It has also been shown that they do not only cause cancer through mutations in DNA but also propagate it by affecting the growth rate of cancer cells. Apart from the carcinogenic effects, PAHs cause irritation on eyes and skin as well as endocrine disruption. After entering the human organism, they are distributed in the various tissues, particularly the adipose tissues. Their impact on health depends on various factors such as the duration and manner of exposure of the organism to PAHs as well as the age and the sex of the person.

PAHs, due to the presence of the fused aromatic rings in their structure and their low water solubility, are recalcitrant to degradation and tend to accumulate in the environment. Table 6 refers to the main physicochemical properties of some extensively studied PAHs. It is obvious that PAHs of high molecular weight are less soluble in water and have low vapor tension, while melting and boiling points are increased substantially.

PAHs are abundant in the environment and have been detected in samples of atmospheric air, soil, sediments, sewage wastewater and sludge, surface water and aquatic organisms, plants, and food as well. The main route of contamination is through the atmosphere. The concentration of PAHs in the atmosphere is at levels of nanograms per cubic meter with a wide spatial and time range. For example, the operation of internal Combustion incinerators in the winter results in higher concentration of PAHs in the atmosphere. The sum of 15 PAHs was found to vary between 395 and 1842 µg kg^{-1} of soil, 404 and 883 µg kg^{-1} of river sediments. High variation of PAHs is common in marine samples too; the sum of 24 PAHs was found to be 2.22 mg l^{-1} in the Cretan Sea and 1056 mg l^{-1} in the Corinthian Gulf [13]. Wastewater and sludge also contain significant quantities of PAHs as described in the following paragraph.

Sewage-treatment plants receive PAHs from various sources such as car emissions, industries, incineration ovens, and heater burners. Hydrocarbons are transferred through the atmosphere by settlement or precipitation. Due to the hydrophobicity of PAHs, they tend to absorb on the organic particulate matter of sludge and end up in this matrix. Various studies focus on the fate of PAHs in sewage-collection systems and sewage-treatment plants. For example, the results of a

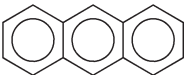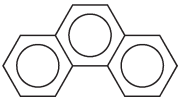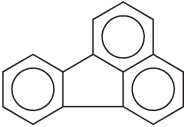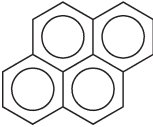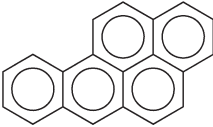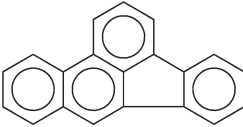**Table 6**   Chemical structure and physicochemical properties of PAHs

PAH	Molecular formula	Chemical structure	No of rings	MW (g mol^{-1})	Melting point (°C)	Boiling point (°C)	Vapor tension (Pa in 25°C)	Solubility in H_2O (mg l^{-1})	Log K_{ow}
Napthalane	$C_{10}H_8$		2	128	80.2	218	11	3.0	3.36
Anthacene	$C_{14}H_{10}$		3	178	216.4	342	1.0E-3	0.015	4.46
Phenantherene	$C_{14}H_{10}$		3	178	100.5	340	2.0E-2	1–2	4.46
Fluoranthene	$C_{10}H_8$		4	202	108.8	375	1.2E-3	0.25	5.33
Pyrene	$C_{16}H_{10}$		4	202	150.4	393	6.0E-4	0.12–0.18	5.32
Benzo[a] pyrene	$C_{20}H_{12}$		5	252	178.7	493	4.0E-7		6.32
Benzo[b] fluoranthene	$C_{20}H_{12}$		5	252	168.3	481	6.7E-5		6.04

Table 7   Mean values of concentration of the sum of 16 PAHs in samples taken from various points of the sewage collection system of Paris

PAHs	Heavy traffic streets	Ring roads	Highways	Subways
Naphthalane	0.73	3.42	1.7	-
Anthacene	0.36	0.39	0.36	0.47
Phenanthrene	2.40	3.32	3.12	4.86
Fluoranthene	3.63	4.94	4.32	5.96
Pyrene	5.37	7.19	6.13	8.64
Benzo[a]pyrene	1.16	0.93	0.83	1.09
Benzo[b]fluoranthene	1.85	1.75	1.54	2.09
Sum of 16 PAHs	21.7	28.2	22.3	30.9

research on the fate of PHAs in 26 different reservoirs of the sewage-collection system in the city of Paris, which receive runoffs and street washing water, show that higher levels are observed in areas with underground tunnels, while lower concentrations are observed in open highway areas[14] (Table 7).

A sewage-treatment plant in Paris receives wastewater coming from this sewage-collection system together with wastewaters from various industries. The raw wastewater in the inlet of the plant contained 25 000 µg l$^{-1.}$ PAHs, out of which 40% accounted for phenanthrene, 21% naphthalene, 15.5% fluoranthene, and pyrene in lower, but notable, proportion. It was estimated that the PAH removal was 98%, either through biodegradation or sorption on the solids. Specifically, 26.7 kg yr^{-1} enter the sewage-treatment plant and 0.53 kg yr^{-1} escape through the outlet. On the other hand, the quantity of PAHs that remain in the sludge is high.

Another research focusing on the PAH in sludge in two wastewater-treatment plants (municipal and industrial wastewater-treatment plants) in Spain shows that the total concentration of 16 PAHs in sludge is approximately 5 mg kg^{-1} dry weight (Table 8).

PAHs can be removed through volatilization, photolysis, chemical breakdown, and disintegration by microorganisms with the latter being the main mechanism of their degradation in the environment. PAHs can be mineralized or converted to simpler compounds through biodegradation. The rate of biodegradation in natural systems (soil, sediments, water, etc.) depends on factors such as the pH, the temperature, the oxygen concentration, the microbial population and its extent of acclimation, and the chemical structure of the PAH. A great variety of bacteria, fungi, and algae, able to degrade PAHs, have been isolated from sediments and soils contaminated with PAHs

In aerobic conditions, biodegradation is initiated with the introduction of oxygen atoms in the aromatic ring catalyzed by the enzyme dioxygenase. PAHs with two or three rings are relatively easily biodegraded by aerobic microorganisms, while in the case of high-molecular-weight (and consequently higher number of aromatic rings) PAHs, the biodegradation extent and rate are lower. Moreover, mixed microbial cultures are more efficient in the mineralization of PAHs than pure cultures. In the case of a mixture of bacteria and algae, the removal of PAHs was up to 85% [15].

In the case of anaerobic digestion, the mechanism of biodegradation has not been clarified. PAHs with two to three rings are anaerobically biodegradable, but it is not clear whether or not biodegradation of PAHs with more rings is possible. Generally, there is a lack of literature data concerning this topic, although there are studies of novel biodegradation mechanisms such as the role of sulfur-reducing bacteria on the bioconversion of PAHs. For more details on this topic see Chapter 6.10 by Madsen (this volume).

The higher efficiency of microorganisms to degrade PAHs under aerobic rather than anaerobic conditions implies that among the various methods of sludge treatment, composting results in high biodegradation removal of PAHs, because it is an aerobic thermophilic process (Table 9). However, a significant part of the removal during sludge composting is attributed to volatilization, assisted by the high-temperature levels developed during the process. A recent study showed that the removal of PAHs contained in sludge in high quantities (70.91 mg of 9 PAHs kg^{-1} dry weight and 95.05 mg of 16 PAHs kg^{-1} dry weight) exceeded 79% during a composting period of 50 days [16]. It was assessed that 50% of the reduction took place during the thermophilic phase of the composting, because the temperature favors mobility of the contaminants and their solubility in water, rendering them more available to microorganisms.

The aeration system during composting is also an important factor as far as removal of PAHs is concerned. Forced aeration is more effective than reversing a static pile of composting mixture. Mixing sludge with green wastes has been found to lead to remarkable levels of PAH removal reaching even 100% [17]. The maturation stage of composting has also been found to favor PAHs removal.

Table 8   Concentration of PAHs (µg kg^{-1} dry weight) in samples of sludge from sewage treatment plants

PAHs	Sewage secondary sludge	Industrial wastewater primary sludge
Naphthalane	198	93
Anthracene	234	61
Phenanthrene	2030	357
Fluoranthene	629	56
Pyrene	702	187
Benzo[a]pyrene	35	32
Benzo[b]fluoranthene	52	45
Sum of 16 PAHs	5520	1460

Table 9   PAHs removal during sludge composting

Composting system	Sludge type	Sum of 16 PAHs (mg kg^{-1} dw)	Removal	References
Closed vessel (100 l)	Anaerobically digested, dehydrated	10.39	87.5% in 353 days	[18]
Windrows	Secondary, dehydrated	28.6	70% in 56 days	[19]
Continuously aerated static pile	Secondary, dehydrated	28.6	85% in 56 days	[19]
Intermittently aerated static pile	Secondary, dehydrated	28.6	94% in 56 days	[19]
Windrows	Activated sludge and green wastes	0.48	68-100% in 90 days	[17]
Closed vessel (800 l)	Raw sludge and rape seed residues	95.05	79% in 50 days	[16]

The indigenous microbial population of the composting mixture contributes to PAH removal. PAH biodegradation is limited by the absorption in the sludge solids resulting in their low bioavailability. Bioavailability is further limited by the irreversible binding of the hydrocarbons with a large number of rings to humic acids. As a result, composting results in the biodegradation of PAHs (due to the intense microbial activity) and the limitation of their bioavailability (due to the humification). In this sense, compost made from sludge or other organic wastes containing PAHs is a stabilized and safe to utilize product, because PAHs have been either biodegraded or remain absorbed strongly in the compost with negligible mobility.

6.37.4   Surface-Active Agents (Surfactants)

Surface-active compounds are organic chemicals that reduce the surface tension of a liquid increasing its wetting capability. They are mainly amphiphilic compounds containing a hydrophilic and a hydrophobic group in their molecule. The presence of both groups in the molecule gives surface-active compounds a fundamental physical property that permits them to form micelles in solution. The formation of micelle is responsible for the cleaning and dissolving properties of the surface-active compounds. The concentration of surface-active compounds above which the formation of micelles starts is called critical micelle concentration. Figure 3 depicts a micelles where the hydrophobic group (tail) is orientated toward the micelle interior, while the hydrophilic group (head) is orientated toward the exterior due to the favorable interactions with water.

The surface-active compounds are categorized based on the charge of the hydrophilic group into anionic, cationic, and nonionic. They are used in many industrial applications such as the manufacturing of cosmetics, detergents, personal care and household use products, dyes, textiles, polymers, and agrochemicals.

The substitution of natural soap detergents with synthetic surfactants initiated a period of environmental pollution. The usage of synthetic surfactants increased by three orders of magnitude, while the use of natural surfactants decreased by more than 50% between 1940 and 1970. Until 1960, propylene tetramer benzene (PTB) was the main surfactant. In this period, the first foaming problems appeared in sewage-treatment plants and rivers. PTB was recalcitrant to biodegradation due to its branched chain. The prohibition of this surfactant led to the usage of more biodegradable surfactants with linear alkyl chain. Today, the most widely used surfactants are the LAS. LAS account for more than 40% of all surfactants. Another common class of surfactants is alkyl phenol ethoxylates (APEs).

6.37.4.1   Linear Alkylbenzene Sulfonates (LAS)

The LAS belong to the general class of anionic surfactants. They appeared in the surfactant market in 1964 for the first time, in order to substitute for the difficult to biodegrade surfactants. LAS are a mixture of isomers and homologs, each of which contains an aromatic ring sulfonated on the para-position and an alkyl chain. A complete description of these compounds can be found in the website of HERA (Human & Environmental Risk Assessment on Ingredients of European household cleaning products) [2]; Table 10 lists their main physicochemical properties.

LAS toxicity depends on the length of the alkyl chain and the position of the aromatic ring in it. LAS with longer alkyl chain are more toxic. Moreover, LASs become more toxic as the aromatic ring is positioned further to the edge of the chain. The toxic effect of LAS on microorganisms may be caused by the reduction of the surface tension on the cells. The reduction of the polarity of the cellular membrane (due to the adsorption of surfactants on it) results in its malfunction; the nutrients and oxygen cannot enter the cell and the toxic intracellular products cannot be removed from the cell. Both cases cause cellular decay.

LAS at low concentrations ($0.02–1.0 \, \text{mg} \, \text{l}^{-1}$) in the aquatic environment have adverse effects on living organisms (fish and mollusks). Similarly, LAS at $40–60 \, \text{mg} \, \text{kg}^{-1}$ dry weight of soil may cause problems in the reproduction and growth of invertebrates and other organisms of the soil ecosystem.
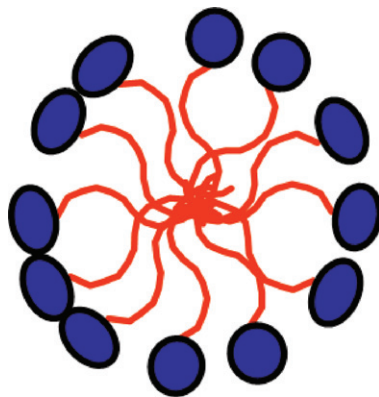

Figure 3 Depiction of a micelle. The hydrophobic group (tail) is orientated toward the micelle interior, while the hydrophilic group (head) is orientated toward the exterior.

Table 10   Physicochemical properties of LAS

*Molecular weight (average C11.6)**	*342.2 g·mol^{-1}*

Molecular structure	$CH_3(CH_2)_n\text{-}CH\text{-}(CH_2)_n\text{-}CH_3$
	SO_2Na

Density	1.6 kg· l^{-1}
Vapor tension	3–17E-13 Pa at 25°C
Solubility in water	250 g· l^{-1}
Log K_{ow}	3.32
CMC	0.65 g· l^{-1}
Boiling point	637 °C
Melting point	277 °C

*Average C11.6: average number of carbon atoms contained in one mole of LAS for typical LAS mixtures.

Most of the surfactants used in households and industry end up in sewage-treatment plants. A large portion of LAS is removed from the aqueous phase of the wastewater in the first stages of the sewage-treatment process, due to either adsorption on the sludge or sedimentation in the presence of calcium or magnesium. The LAS homologs with the longest alkyl chain have a higher tendency to adsorb on the solids, and become less dissolved when interacting with calcium.

In conventional sewage-treatment plants, LAS removal takes place at high percentages (95–99%). Table 11 gives typical values of LAS concentration in sewage-treatment plants in various countries.

LAS tend to accumulate in the sludge and this depends on the sludge type and the processes taking place in the treatment procedure. Primary sludge usually retains 10–20% of LAS contained in the raw wastewater. This percentage may be increased to 30–35% if the water hardness is high.

Generally, the determining factor for the fate of LAS in sewage sludge is the aerobic conditions prevailing during sludge treatment. As these anionic compounds are easily biodegradable in the presence of air, the aerobic treatment of sludge leads to reduction of LAS to a large extent. This is why LAS concentration is higher in anaerobically treated sludge than the aerobically stabilized sludge (Table 12).

Table 11   LAS concentration in the inlet and outlet as well as the removal percentage in sewage treatment plants in various countries

Country or region	Inflow (mg l^{-1})	Effluent (mg l^{-1})	Removal (%)	References
Holland	3.4–8.9	0.019–0.07	98–99.6	[20]
	1–15	0.039	99.1	[21]
Spain	5.71	0.39	> 97	[22]
India	5.57	0.67	88	[23]
USA	4.6	0.068	98.5	[24]
Europe	3–21	0.008–0.27	99	[2]

Table 12   The concentration of LASs in different sludge types

Country	Sludge type	LAS concentration (mg kg^{-1} dw)	References
Switzerland	Anaerobically digested	2900–11900	[25]
Germany	Anaerobically digested	1600–11800	[26]
Germany	Anaerobically digested	1330–9930	[20]
Germany	Aerobically digested	182–432	[20]
Spain	Aerobically digested	500	[27]
Spain	Anaerobically digested	12100–17800	[28]
England	Anaerobically digested	9300–18800	[29]

Table 13   LAS biodegradation during sewage sludge composting

Composting system	Sludge type	LAS (mg kg^{-1} dw)	Removal	References
Composting tunnel	Anaerobically digested plus sawdust	300	96.6% in 40 days	[28]
Composting tunnel	Anaerobically digested plus sawdust	450	97.4% in 40 days	[28]
Closed vessel (10 l)	Raw plus straw	150	99% in 25 days	[3]

Biodegradation is a very significant process for LAS removal from sewage and sewage sludge. Microorganisms can utilize LAS for nutrients and energy or co-metabolize LAS through the initial catabolic reactions. The factors affecting LAS biodegradation are the chemical structure of the molecule and the prevailing aerobic or anaerobic conditions. Under aerobic conditions, LAS are mineralized to carbon dioxide, water, and sulfate ions. Mixed populations of microorganisms are more effective in converting a variety of alkyl subunits contained in LAS, because they are a mixture of organic compounds. In this sense, composting involving a mixed population of aerobic microorganisms (interacting with relationships of commensalism and synergism) favors LAS biodegradation (Table 13). On the contrary, under anaerobic conditions, LAS biodegradation is hardly feasible.

6.37.4.2   Alkyl phenol ethoxylates (APEs)

APEs are a significant group of nonionic surfactants. They are used in the manufacturing of cleaning products. They are also utilized as dispersing agents in the paper pulp industry, emulsifiers in dye manufacture, means for dissolution and flotation, constituents of agro insecticides and herbicides, and in many other industrial applications. The majority of APEs is used as aqueous solution and is commonly disposed into treatment plants of municipal and industrial wastewaters.

The production of APEs amounted to 500 000 tons in 1997, 80% of which were NPEOs and 20% were octylphenol (OP) ethoxylates. Biodegradation of these APEs results in the formation of nonylphenol (NP) and OP, which are more recalcitrant and toxic compounds. As their metabolic products have been found to be more toxic than the parent compounds, the APE applications have been limited since 1984.

APEs were suspected to mimic estrogens already in 1938. Moreover, NP was found to be responsible for the propagation of breast cancer cells. NPEO and NP can mimic natural hormones. For example, NP mimics 17b-estradiol due to their common chemical structures. This hormone influences the growth and maintenance of the female characteristics of organisms. It also interacts with endocrine and skeleton systems.

The physicochemical properties of APEs (Table 14) determine their fate and that of their metabolites in the environment. The solubility of APE depends on the number of the polar groups attached to the hydrophilic group of the molecule. APEs with less than five ethoxylate groups are characterized as practically insoluble in water. Moreover, the solubility of OPEOs (12.6–24.5 mg l^{-1}) is significantly higher than NPEOs (5.43–7.65 mg l^{-1}), implying the effect of the length of the hydrophobic chain on the solubility of the compound. The logarithm of the octanol–water distribution coefficient (log K_{ow}) varies between 3.90 and 4.48 for the APEs resulting in the strong sorption of these compounds in to the organic matter of sewage sludge.

Much research has focused on the fate of NPEOs in a sewage-treatment plant. The main metabolites of the biotransformation of NPEOs are NP and NPEOs with one or two ethoxylic groups (NPEO1 and NPEO2 respectively). Typical concentration values of NPEOs and NP in sludge in various sewage-treatment plants in Europe are reported in Table 15. NP concentration varies between 0.675 and 601 mg kg^{-1} dry weight of sludge, while NPEO concentration varies between 2.1 and 135 mg kg^{-1} dry weight. Moreover, the distribution of the nonylphenolic compounds in digested sludge is 95% for the NP and 5% for the sum of NPEO1 and NPEO2,

Table 14   Chemical structure and physicochemical properties of NPEOs and NP
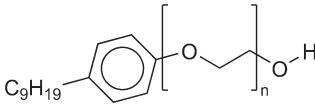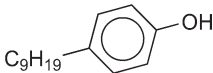
APE		Molecular weight (g mol^{-1})	Solubility in water (mg l^{-1})	Log K_{ow}
Nonylphenol ethoxylate, NPEOn		n = 1: 264	3.02	4.17
		n = 2: 308	3.38	4.21
		n = 3: 352	5.88	4.20
		n = 4: 396	7.65	4.30
Nonylphenol, NP		220	5.43	4.48

Table 15   Typical concentration values of NP and NPEO in sludge

Country	Sludge type	NP (mg kg^{-1} dw)	NPEO (mg kg^{-1} dw)	References
Spain	Dehydrated	172–601	21–135	[30]
Portugal	Dehydrated	234	2.1	[30]
Germany	Dehydrated	25.5	21	[30]
Holland	Industrial	6.8	40.16	[31]
Denmark	Raw	0.675	23.72	[32]
Switzerland	Raw	190	490	[33]
	Stabilized	1500	165	[33]

Table 16   Biodegradation of NPEOs during sludge composting

Composting system	Composting mixture	NPEO load (mg kg^{-1} dw)	Removal (%)	References
Windrows	Dehydrated sludge and green wastes	(NPEO mixture)14000	91.5 in 14 weeks	[34]
Isothermal closed reactor (10 l)	Sludge, straw and green wastes	(sum of NP, NPEO1 and NPEO2)	>50% in 28–90 days	[35]
Closed reactor (60 l)	Anaerobically digested sludge and sawdust	(4-NP)	53–81% in 14 days and 92% in 42 days	[36]

partly because of the hydrophobic nature of NP (compared to NPEOs) and partly because of the NP being the major metabolite of NPEO biodegradation.

Biodegradation is the main mechanism of APE degradation in the environment and starts with the reduction of the length of the poly ethoxylic chain leaving the phenolic ring untouched. The main products during biodegradation are APEs with one or two ethoxylic units as well as alkylphenols (primary biodegradation). APEs in the wastewater can be removed up to 99% in a sewage-treatment plant, corresponding mostly to primary degradation. Under anaerobic conditions, the biodegradation of APEs and their metabolites seems to be limited. In the absence of oxygen, the initial ω-oxidation, which is needed to shorten the alkyl chain cannot be performed. On the other hand, under aerobic conditions, APE mineralization is possible by mixed microbial consortia. Sludge stabilization through composting results in high removal percentages of NPEOs due to the rich microbial consortium growing during the composting process (Table 16). In experiments where the temperature peak reached 65 °C, the NP degradation decreased [35]. This implies that either NP biodegradation is performed by microorganisms that cannot grow at high temperatures or the toxicity of NP increases with temperature. The maturation phase, however, taking place at lower temperatures and for prolonged time intervals, favors NP removal.

6.37.5   Conclusions

Certain classes of xenobiotics contained in widely consumable products (such as surfactants in detergents and APEs in packaging materials) or resulting from daily activities (such as PAHs in vehicle gas emissions) end up in municipal sewage and, subsequently, in municipal sewage sludge. Sludge stabilization is realized through anaerobic digestion and/or composting, and major concerns arise concerning the suitability of the stabilization product for disposal. Degradation of LAS, NPEOs, DEHP, and PAHs is negligible or impossible under anaerobic conditions. As a result, the concentration of xenobiotics, expressed in mass per mass of sludge dry matter, is increased in digested sludge (compared to their concentration in the raw sludge) since there is an appreciable solid reduction during anaerobic digestion. On the other hand, degradation of the aforementioned xenobiotics is extended under aerobic conditions. Therefore, composting of sludge leads to a significant degree of xenobiotic removal in addition to sludge stabilization and hygination. The high temperatures prevailing during the initial phase of composting may either increase or decrease the degradation rate, probably due to an increase of the compound toxicity on the microorganisms. In any case, the maturation phase seems to favor the overall xenobiotic removal through biodegradation and/or enmeshment of the compounds firmly in the solid matrix, rendering the composting process the most suitable biological method for xenobiotic elimination from sludge.

References

[1] Hoffmann G, Gehring M, Bilitewski B, et al. (2008) Sewage sludge treatment in Europe: Current situation and trends. Second Conference on Small and Decentralized Water and Wastewater Treatment Units, May 2–4. Skiathos island, Greece.

[2] HERA (2009) Human and Environmental Risk Assessment on ingredients of European household cleaning products, Version 4.0, URL: http://www.heraproject.com/RiskAssessmant.cmf.

[3] Singh RP and Agrawal M (2008) Potential benefits and risks of land application of sewage sludge. *Waste Management* 28: 347–358.

[4] Pakou C, Kornaros M, Stamatelatou K, and Lyberatos G (2009) On the fate of LAS, NPEOs and DEHP in municipal sewage sludge during composting. *Bioresource Technology* 100(4): 1634–1642.

[5] Stapples CA, Peterson DR, Parkerton TF, and Adams WJ (1997) The environmental fate of phthalate esters: A literature review. *Chemosphere* 35: 667–749.

[6] Dargnat C, Teil MJ, Chevreuil M, and Blanchard M (2009) Phthalate removal through wastewater treatment plant. Case study of Marne Aval station (France). *The Science of the Total Environment* 407: 1235–1244.

[7] Aparicio I, Santos JL, and Alonso E (2009) Limitation of the concentration of organic pollutants in sewage sludge for agricultural purposes: A case study in South Spain. *Waste Management* 29(5): 1747–1753.

[8] Moeller J and Reeh U (2003) Degradation of DEHP, PAHs and LAS in source separated MSW and sewage sludge during composting. *Compost Science and Utilization* 11: 370–378.

[9] Marttinen SK, Hänninen K, and Rintala JA (2004) Removal of DEHP in composting and aeration of sewage sludge. *Chemosphere* 54: 265–272.

[10] Amir S, Hafidi M, Merlina G, *et al.* (2005) Fate of phthalic acid esters during composting of both lagooning and activated sludges. *Process Biochemistry* 40: 2183–2190.

[11] Gibson RW, Wang MJ, Padgett E, *et al.* (2007) Impact of drying and composting procedures on the concentrations of 4-nonylphenols, di-(2-ethylhexyl) phthalate and polychlorinated biphenyls in anaerobically digested sewage sludge. *Chemosphere* 68: 1352–1358.

[12] Cheng HF, Kumar M, and Lin JG (2008) Degradation kinetics of di-(2-ethylhexyl) phthalate (DEHP) and organic matter of sewage sludge during composting. *Journal of Hazardous Materials* 154: 55–62.

[13] Tsapakis M, Stephanou EG, and Karalassi I (2003) Evaluation of atmospheric transport as a nonpoint source of polycyclic aromatic hydrocarbons in marine sediments of the Eastern Mediterranean. *Marine Chemistry* 80: 283–298.

[14] Blanchard M, Teil MJ, Ollivon D, *et al.* (2004) Polycyclic aromatic hydrocarbons and polychlorobiphenyls in wastewaters and sewage sludges from the Paris area (France). *Environmental Research* 95: 184–197.

[15] Lei AP, Hu ZL, Wong YS, and Tam NFY (2007) Removal of fluoranthene and pyrene by different microalgal species. *Bioresource Technology* 98: 273–280.

[16] Hua L, Wu W, Liu Y, *et al.* (2008) Effect of polycyclic aromatic hydrocarbons removal in sewage sludge. *Water, Air and Soil Pollution* 193: 259–267.

[17] Hafidi M, Amir S, Jouraiphy A, *et al.* (2008) Fate of polycyclic aromatic hydrocarbons during composting of activated sewage sludge with green waste. *Bioresource Technology* 99: 8819–8823.

[18] Oleszczuk P (2006) Influence of different bulking agents on the disappearance of polycyclic aromatic hydrocarbons (PAHs) during sludge composting. *Water, Air and Soil Pollution* 175: 15–32.

[19] Cai QY, Mo CH, Wu QT, *et al.* (2007) Bioremediation of polycyclic aromatic hydrocarbons (PAHs)-contaminated sewage sludge by different composting processes. *Journal of Hazardous Materials* 142: 535–542.

[20] Matthijs E and de Henau H (1987) Determination of LAS. Determination of linear alkylbenzenesulfonates in aqueous samples, sediments, sludges and soils using HPLC. *Tenside Surfactants Detergents* 24: 193–199.

[21] Venhuis SH and Mehrrar M (2004) Health effects, environmental impacts and photochemical degradation of selected surfactants in water. *International Journal of Photoenergy* 6: 115–125.

[22] Moreno A, Ferrer J, Ruiz Bevia F, *et al.* (1994) LAS monitoring in lagoon treatment plant. *Water Research* 28: 2183–2189.

[23] Mungray AK and Kumar P (2009) Fate of linear alkylbenzene sulfonates in the environment: A review. *International Biodeterioration and Biodegradation* 63: 981–987.

[24] di Corcia A, Samperi R, Belloni A, *et al.* (1994) LAS pilot study at the "Roma-Nord" sewage treatment plant and in the Tiber River. *La rivista italliana delle sostanze grasse* LXXI: 467–475.

[25] Mc Evoy J and Giger W (1986) Determination of linear alkylbenzene sulfonates in sewage sludge by high-resolution gas chromatography mass spectrometry. *Environmental Science and Technology* 20: 376–383.

[26] de Henau H, Matthijs E, and Hopping WD (1986) Linear alkylbenzene sulfonates LAS in sewage sludges, soils, sediments: Analytical determination and environmental safety considerations. *International Journal of Environmental Analytical Chemistry* 26: 279–293.

[27] Berna JL, Ferre J, Moreno A, *et al.* (1989) The fate of LAS in the environment. *Tenside Surfactant Detergent* 26: 101–107.

[28] Prats D, Ruiz F, Vazquez N, *et al.* (1997) Removal of anionic and nonionic surfactants in a wastewater treatment plant with anaerobic digestion: A comparative study. *Water Research* 3: 1925–1930.

[29] Holt MS and Bernstein SL (1992) Linear alkylbenzene in sewage sludges and sludge amended soils. *Water Research* 26: 613–624.

[30] Petrovic M and Barcelo D (2000) Determination of anionic and nonionic surfactants, their degradation products and endocrine-disrupting compounds in sewage sludge by liquid chromatography/mass spectrometry. *Analytical Chemistry* 72: 4560–4567.

[31] de Voogt P, de Beer K, and van der Wielen F (1997) Determination of alkylphenol ethoxylates in industrial and environmental samples. *Trends in Analytical Chemistry* 16: 584–595.

[32] Vikelsoe J, Thomsen M, Carlsen L, and Johansen E (2002) NERI Technical report No 402. National Environmental Research Institute Denmark, http://technical-reports.dmu.dk.

[33] Brunner PH, Capri S, Marcomini A, and Giger W (1988) Occurrence and behaviour of linear alkylbenzenesulfonates, nonylphenol, nonylphenol mono- and nonylphenol diethoxylates in sewage and sewage sludge treatment. *Water Research* 22: 1465–1472.

[34] Jones FW and Westmoreland DJ (1998) Degradation of nonylphenol ethoxylates during the composting of sludges from wool scour effluents. *Environmental Science and Technology* 32: 2623–2627.

[35] Moeller J and Reeh U (2003) Degradation of nonylphenol ethoxylates (NPE) in sewage sludge and source separated municipal solid waste under bench-scale composting conditions. *Bulletin of Environmental Contamination and Toxicology* 70: 248–254.

[36] Das KC and Xia K (2008) Transformation of 4-nonylphenol isomers during biosolids composting. *Chemosphere* 70: 761–768.

Relevant Websites

http://www.dehp-facts.com – DEHP Information Center.
http://ecpi.org – European Council for Plasticizers and Intermediates (ECPI).
http://waste.eionet.eu.int – European Topic Centre on Resource and Waste Management (ETC-RWM).