the development of diseases, including allergy. DEHP in PVC materials was first suspected to promote development of asthma in children, but its adjuvant effect has only been demonstrated in an animal model (Larsen et al., 2002). Latini (2000) documented the DEHP long term toxicity and tissue deposition in animal models and the major factors influencing its action, either dose, time and age. Latini et al. (2004) documented also the fact that infants may represent a population at increased risks of exposure to DEHP. Breast milk, infant formula, baby food, inhalation of indoor air and dermal or oral exposure to indoor dust are major routes of exposure to DEHP for infants. Toys intended for mouthing (bottle nipples, teething rings, pacifiers and rattles) do not contain DEHP in Europe, Canada and United States, although it is still found in toys for older children.

#### 7.3.3 Endocrine Disrupting Properties

The two major plasticizers that are suspected to be endocrine disrupters are DEHP and DBP. These compounds are suspected to stimulate the expression of cellular oestrogen-sensitive endpoints in vitro (Moore, 2000). Most phthalates (BBP, DBP, DiBP, DEP, and DiNP) have endocrine disrupting potencies, six to seven orders of magnitude lower than  $17\beta$ -estradiol (Harris et al., 1997).

The endocrine disrupting potential of phthalate plasticizers has been reported in mammalian system (Latini et al., 2004; Koch et al., 2006). The adverse effect of PAE as DEHP on male tract development are related to alterations in gene expression of a number of enzymes and transport proteins involved in normal testosterone biosynthesis and transport in the fetal Leydig cell, and to a subsequent reduction in testosterone synthesis. Some PAEs have been shown to disrupt several genes pathways, including, cholesterol transport, steroidogenesis, intracellular lipid and cholesterol homeostasis, insulin signalling, transcriptional regulation and oxidative stress (Latini et al., 2006).

Kim et al. (2003) reported many studies on phthalates exhibiting cytotoxic and estrogenic activity in toxicity-monitoring using recombinant bioluminescent bacteria, MCF-7 cell proliferation, oestrogen receptor-binding in rat uterus, and yeasts transfected with human ER. They also mentioned studies on the development toxicity of DEHP in rats and the teratogenic effects of DEHP in mice and chicks. However, no acute toxicity of plasticizers was observed.

As reported by Hildenbrand et al. (2005), animal experiments have shown that DEHP metabolites impair infertility. The Sertoli cells of the sperm channel involved in spermogenesis, are the most affected cells. Hydrolysis and oxidation of phthalates occur in blood and the oxidative metabolites are toxics.

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### 7.4 Degradation of Toxic Intermediates

Breakdown products of organic pollutants have always been of concern. The pesticide residues are a good example. Organic pesticides tended to replace chemical pesticides because of their biodegradability, but the environmental safety is sometimes compromised by the release of toxic breakdown products (e.g. residues of organophosphate degradation). Other organic pollutants with toxic breakdown products are the non ionic surfactants, alkylphenols. They are degraded into toxic nonylphenol monoethoxylates, nonylphenols and octylphenols. They are present at high levels in environmental samples and classified as endocrine disrupting compounds by governmental authorities (La Guardia et al., 2001; Birkett and Lester, 2003). This important issue also concerns the plasticizers that have different levels of biodegradability in the environment with very few or no information on the metabolic intermediates and their respective toxicity. In fact, DEHP and other PAEs in the environment could be reservoirs of toxic metabolic intermediates (Barnabé et al., 2007; Beauchesne et al., 2007).

Numerous studies have been conducted on biodegradation of plasticizers in the environment (surface waters, soils, sediments, wastewaters, sewage sludges). These studies involved pure microbial culture, addition of microbial enzymes, microbial consortia or activated sludges. Most of these studies on fate of plasticizers have focused on the removal of the parent compounds without considering their partial breakdown products. Table 7.1 presents few studies where metabolites were identified. Phthalic acid, 2-ethylhexanol ( $C_8H_{18}O$ ) and 2-ethylhexanoic acid ( $C_8H_{16}O_2$ ) appear to have been the most frequent toxic metabolites identified during PAE biodegradation studies.

Some of the most extensive studies on the identification of metabolites after partial degradation of DEHP by common soil micro-organisms were performed by Nalli and co-workers. Their works especially demonstrated that the toxic intermediates generated by Rhodococcus rhodochrous include 2-ethylhexanol, 2ethylhexanal, and 2-ethylhexanoic acid (Nalli et al., 2002; Gartshore et al., 2003; Nalli et al., 2006a). The hydrolysis of ester bonds in DEHP, DEHA and DEHTP leads to a mono-ester and 2-ethylhexanol, which is further oxidized into 2-ethylhexanoic acid. Figure 7.1 illustrates a degradation pathway of DEHP and DEHA in the environment proposed by Nalli and co-workers.

Microbial Culture or Enzyme	Parent Compound	Metabolic Intermediates	Reference
Inocula from diluted and treated municipal solid waste	DEHP	2-ethylhexanol, 2- ethylhexanoic acid	Ejlertsoon and Svenson, 1996
<i>Mycobacterium</i> sp. and other strains <sup>1</sup>	DEHP	2-ethylhexanol, 1,2- benzenedicarboxylic acid	Nakamiya <i>et al.</i> , 2005
Pseudomonas fluorescens <sup>1</sup>	DEHP	phthalic acid, benzoic acid, phenol	Zeng et al., 2002
Fungal cutinases, yeast esterases	DEHP	1,3-isonemzofurandione, one unidentified toxic metabolites (produced by yeast esterases)	Kim et al., 2003
Arthrobacter sp., Sphingolomas paucimobilis	DMP	mono-ester, phthalic acid	Vega and Bastide (2003)
Mixed culture of Pseudomonas fluorescens, P. aureofaciens, Sphingomonas paucimobilis, Xanthomonas maltophilia	DMP	Mono-methyl phthalate, phthalic acid	Wang <i>et al.</i> , 2003
Pseudomonas fluorescens B-1	DBP	mono-butyl phthalate, phthalic acid	Xu et al., 2005
Delftia sp. <sup>1</sup>	DBP	phthalic acid, protocatechuate	Patil et al., 2006
Bacillus subtilis <sup>1</sup>	DEHP, DBP	DMP	Quan et al., 2006
Rhodococcus rhodochrous and other common soil microorganisms	DEHP, DEHA, DEHTP <sup>2</sup>	2-ethylhexanol, 2- ethylhexanol, 2-ethylhexanoic acid	Nalli <i>et al.</i> , 2002, 2006a; Gartshore <i>et al.</i> , 2003

**Table 7.1** Studies on metabolites resulting from partial biodegradation of PAEs by pure or mixed cultures or enzymes.

<sup>1</sup> New isolates.

<sup>2</sup> DEHA: di-(2-ethylhexyl) adipate. DEHTP: di-(2-ethylhexyl) terephthalate.



Figure 7.1 Degradation pathway for plasticizers, DEHP and DEHA (Horn et al., 2004; Nalli et al., 2006a).

It has been reported in controlled laboratory studies that these metabolites are more toxic to various species (mammalian models, fishes and arthropods) than the original plasticizers (Nalli et al., 2002; Horn et al., 2004; Nalli et al., 2006a). 2ethylhexanol is a well known air contaminant. 2-ethylhexanol and 2-ethylhexanal in indoor air are also suspected to be related to sick building syndrome (Nalli et al., 2006a). 2-ethylhexanol is present in breath, urine and serum of patients on haemodyalisis and from patients in intensive care unit and its origin as a metabolite of DEHP degradation, and can have antiproliferative effect. The metabolite 2ethylhexanal was not reported in most early degradation studies, most likely due to the high volatility of this compound and its tendency to partition into the gas phase. However the production of this compound and its role in the degradation pathway has recently been confirmed (Nalli et al., 2006a). Meanwhile, 2-ethylhexanoic acid is known to be recalcitrant.

The 2-ethylhexanol is not only a degradation product but is also used in the production of plasticizers for PVC resins, and both the alcohol and acid are used as

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intermediates in the manufacture of inks, paper, rubber, resins, surfactants and lubricants (Staples, 2001). Most environmental releases are presumed to occur during degradation of DEHP in water, soil and sediment (Horn et al., 2004; Barnabé et al., 2007) while they may enter environment during their manufacture, handling or use (Staples, 2001). In air, water, soil and sediment, they are subject to volatilization, adsorption to suspended solids and sediment, biodegradation and photo-degradation, but they have low persistence as noted by Staples (2001).

Field studies also confirmed that DEHP and DEHA and two of its metabolites, 2-ethylhexanol and 2-ethylhexanoic acid were present in surface waters, river sediment, freshly fallen snow, and even in tap water (Horn et al., 2004). Hence, there are reasons to believe that the toxic metabolites are widespread as their parent compounds. DEHA is a less commonly used plasticizer, which is a good additive for polymer flexibility at low temperature (Nalli et al., 2006b). DEHA tends to replace DEHP in some products such as food-grade PVC films (Goulas et al., 2007), floorings and wall coverings (Wypych, 2004) due to its higher biodegradability and less toxicity, but its environmental safety is questionable while considering the toxic intermediates formed during degradation.

In summary, the presence of toxic intermediates of DEHP and other PAEs during degradation with their parent compounds acting as reservoirs justify the importance of considering PAE plasticizers as emerging pollutants. The fate of the plasticizer parent compounds and their toxic metabolites is thus discussed in the next section.

### 7.5 Fate in the Environment

The understanding of the potential environmental pathways of plasticizers can result in appropriate management of their production and uses, and ensure health and environmental safety. This section will summarize the fate of plasticizers in different environmental compartments: water, soil and sediments, air and organisms. The microbes responsible for degradation of PAEs in the environment will also be discussed.

Briefly, plasticizers enter the environment not only through losses during their manufacture, distribution and through waste disposal, but also by leaching out of the finished product. Hence, the chief routes of environmental releases are: direct transfer (e.g. building materials), urban runoff, industrial air emission/atmospheric deposition, sewage/water distribution pipework deterioration, solid waste disposal (e.g. release of landfill leachate), industrial effluents and sewage treatment plant activities (discharge of effluent, elimination of residues through incineration, land filling and land application). The estimated releases of the three plasticizers found in the toxic release inventory (TRI) maintained by the U.S. Environmental Protection Agency (TRI, 2005) are presented in Table 7.2.

				(	. ).
Plasticizers	Air	Land	Water	Underground Injection	Off-site Waste Transfer
DBP	14,486	47,027	98	89,000	258,678
DEHP	237,093	39,840	429	0	3,820,366
DMP	229,716	1	875	2,294	424,735

Table 7.2. Estimated releases (in pounds) of three PAEs in 2005 (from TRI).

Their fate is governed by abiotic and biotic degradation, adsorption to organic matter and volatilization in aquatic and terrestrial systems. The PAEs are degraded in both aerobic and anaerobic environment, but sorption to particles decrease the degradation rate. More precisely, the PAEs undergo the following transformation into the environment:

*Abiotic hydrolysis*: PAEs are susceptible to hydrolysis, however at slow rates, and it is thought to be negligible in sewage, soils, sediments and surface waters. The products of hydrolysis are an acid and an alcohol. PAE can undergo two hydrolytic steps, initially forming the mono-ester and one free alcohol moiety and a second hydrolytic step creating phthalic acid and a second alcohol. PAEs are hydrolyzed at negligible rates at neutral pH. Acid hydrolysis of PAE is possible, but it is estimated at four orders of magnitude slower than the alkaline hydrolysis rate constants (Ziogou et al., 1989; Staples et al., 1997; Roslev et al., 1998).

*Photolysis*: Photolysis occurs through UV absorption. The mechanism may be either through direct absorption of UV radiation by the chemicals in air or by absorption of UV radiation by natural substances such as water with the formation of activated species such as singlet oxygen or hydroxy radicals that react with PAE. Photolysis appears to be much more important in the atmospheric fate of PAE than water (Staples et al., 1997).

*Biotic degradation*: Biodegradation is the main process affecting the environmental fate of PAE. Numerous studies indicate that PAE are degraded by a wide range of bacteria and actinomycetes fungi under both aerobic and anaerobic conditions.

Staples and co-workers in 1997 published an extensive review on the environmental fate of PAE. The authors described important parameters for investigating and understanding the fate and behavior of plasticizers in environment. These parameters are:

*Water solubility*: This property influences the biodegradation and bioaccumulation potential of PAE, as well as aquatic toxicity. Water solubility is also a determining factor in controlling the environmental distribution of PAE. Losses from wastewater treatment facilities, landfills and sludge-amended soils are partially a function of aqueous solubility.

*Octanol/water coefficient* ( $K_{OW}$ ): The equilibrium distribution of an organic chemical between water and octanol is an important physical constant for predicting the tendency of PAEs to partition to water, animal lipids, sediment, and soil organic matter. Relationships exist between Kow and soil sorption, water solubility, bioconcentration, and toxicity.

*Vapor pressure (VP):* It plays an important role in the fate of PAE released to the atmosphere. The ratio of the vapor pressure to the molar water solubility estimates the Henry's Law constant, which is the measure of the equilibrium distribution coefficient.

*Hydrophobicity:* Sorption of PAE to soil, sediment, or suspended solids is partially governed by the relative hydrophobicity of the compound. Hydrophobic chemicals adsorb principally to the organic matter associated with the solid.

The most commonly studied plasticizers in environment are PAEs, either DEP, DnBP, DMP, DEHP and DnOP, which are also the most commonly found in the environment (Quan et al., 2006). BBP is also part of some environmental investigations. The values of the parameters governing their environmental fate are presented in Table 7.3.

PAE	Log K <sub>OW</sub>	Aqueous Solubility (mg/ L)	Vapor Pressure (mm Hg, 25°C)	Hydrophobicity
DMP	1.61	4200	2.0E-3	+
DEP	2.38	1100	1.0E-3	+
DnBP	4.45	11.2	2.7E-5	++
BBP	4.59	2.7	5.0E-6	++
DEHP	7.50	0.003	1.0E-7	+++
DnOP	8.06	0.0005	1.0E-7	+++

**Table 7.3** Estimated values for the parameters related to environmental fate for the most abundant plasticizers in environment (Staples et al., 1997).

## 7.5.1 Air

Plasticizers as PAEs are relatively non volatile as their vapour pressures are very low (see Table 7.3). However, they are still detected in air samples in concentrations ranging from 0.2 to  $2453 \text{ ng/m}^3$ , as reported in Table 7.4.

PAE	Concentration (ng/m <sup>3</sup> )	Sample	Reference
DnBP	0.2-192	Urban air	Weschler, 1984; HSDB, 2001
	1.3-5.0	Rural/Remote	HSDB, 2001
	2453	Apartment	Wensing et al., 2005
DEHP	20-55	Office buildings	Weschler, 1984
	3.6-132	Urban	HSDB, 2001
	0.77-3.6	Rural/Remote	HSDB, 2001
	390	Apartment	Wensing et al., 2005
DMP	0.60-1.74	Office buildings	Weschler, 1984

Table 7.4. Concentrations of three PAE in various air samples.

These concentrations in air are especially attributed to building materials. Major concern has been oriented towards PAE in indoor air because they have been recognized as major indoor pollutants (Bornehag et al., 2005). Potential sources of PAE in indoor air are wall coverings, wall paints, floor coverings and electronic devices (Wensing et al., 2005), which may contain PVC. Wensing et al. (2005) reported many studies on PAE in indoor air and household dust. An apartment indoor air may contain respectively up to 390 ng DEHP m-3 and 2453 ng DBP m-3 (Table 4) while surface dust in children's room may contain about 770 mg DEHP kg-1 and 150 mg DBP kg-1. Fortunately, the analysis of Wensing et al. (2005) of indoor air showed that these values do not result in oral or dermal intake in the range of the Acceptable Daily Intake recommended as stated above.

Wensing et al. (2005) also reported studies on measurement of plastic additives such as flame retardants in vehicle indoor air, but the studies did not assess the PAE levels. Considering that PAEs are a constituent of some vehicle materials and many people pass a major time of their day in their vehicle, it is convenient to investigate the PAE present in vehicle indoor air, especially the so-called "new car odor".

When released to the atmosphere, most plasticizers will be adsorbed on airborne particulate matter, which is subjected to rain out and gravitational settling. The adsorption of phthalate by dust particles may be responsible for the widespread distribution of the chemicals in an office building (Weschler, 1984). Vapor-phase plasticizers may be subject to degradation by photochemically produced hydroxyl radicals (HO°) which can be formed by photolysis of water vapor (Lyman, 1990a).

Atmospheric fate processes including photooxidation, washout, and vaporaerosol partitioning has been reviewed by Staples et al. (1997). The authors mentioned that photodegradation via free radical attack is expected to be the dominant degradation pathway in the atmosphere with predicted half-lives of ca. 1 day for most of the investigated PAEs. DEHP may degrade in the atmosphere at relatively significant rates when compared with other plasticizers. DMP may be one of the most persistent PAE in the atmosphere with a half-life as long as about 50 days. These predicted half-lives also suggest that photo-oxidation by hydroxyl radicals could be the major mechanism to transform plasticizers released into the atmosphere (Wypch, 2004). The specific pathway for release of plasticizers into the atmosphere is described in the next sub-sections via volatilization from water and from soil and sediments.

Nalli et al. (2006a) observed a link between the partial biodegradation of plasticizers by microorganisms and presence of some volatile organic compounds in poor indoor air quality. Their observation was especially pointing towards 2-ethylhexanol resulting from the biodegradation of DEHP commonly found in building materials and household dust. The authors concluded that its presence was not as a result of abiotic degradation (hydrolysis of ester bonds promoted by pH of the concrete surface in contact with DEHP; photochemical degradation). Bjork *et al.* (2003) discussed the possibility that the pH of concrete surface can hydrolyze ester bonds of the compounds in contact with it. However, it is not a major pathway of degradation as alkaline hydrolysis of DEHP would have a half-life of 100 years (Nalli *et al.*, 2006a).

### 7.5.2 Water Compartments

Plasticizers have been detected in different water compartments notably, surface waters (streams, rivers, estuaries and marine), rain and snow, groundwater, drinking and tap water, wastewaters and process aqueous streams of sewage treatment plants. Sources of plasticizers in water compartments are enumerated in the beginning of this section. Research demonstrated the widespread occurrence of PAEs in the aquatic environment and higher amount in surface water immediately downstream from sewage treatment plant (Olivier et al., 2005). Table 7.5 presents concentrations of PAE frequently detected at high levels in various water compartments.

As previously mentioned, the fate of plasticizers in aquatic environment is governed by abiotic degradation, biodegradation, volatilization and adsorption reactions. This fate is influenced by the plasticizer solubility that affects the extent of leaching out of plastic products, the movement and fate of dissolved plasticizers in aqueous systems. This further determines the potential of removal of vapour-phase plasticizers from the atmosphere through precipitation (Wypych, 2004). The fate is also influenced by the alkyl chain length: when length increases, the adsorption and bioconcentration potentials increase while the dissolution, evaporation and biodegradation potentials decrease (Birkett and Lester, 2003; Olivier et al, 2005). Plasticizer solubility also influences its toxicity towards aquatic organisms. DEHP generally exhibits very low toxicity due to low water solubility while the lower molecular weight PAE, either DMP, DEP, DBP, DIBP and BBP, can be toxic to aquatic organisms at high concentration.

PAE	Concentration (µg/L)	Location	Reference
DnBP	0.2-42 μg l <sup>-1</sup>	Surface water, mostly rivers	Fromme <i>et al.</i> , 2002; Brossa <i>et al.</i> , 2003; Wypych, 2004
	$0.003-0.5 \ \mu g \ l^{-1}$	Precipitation	Wypych, 2004
	0.45-2.38 μg l <sup>-1</sup>	Groundwater	Wypych, 2004
DEHP	0.06-180 μg l <sup>-1</sup>	Surface water, mostly rivers	Fromme <i>et al.</i> , 2002; Brossa <i>et al.</i> , 2003; Wypych, 2004; Horn et al., 2004
	$0.002\text{-}0.43~\mu g~l^{\text{-}1}$	Precipitation	Wypych, 2004
	1.4-8 μg l <sup>-1</sup>	Groundwater	HSDB, 2001
	$130 \ \mu g \ l^{-1}$	Melted snow	Horn et al., 2004
DMP	$0.002\text{-}0.7 \ \mu g \ l^{-1}$	Rivers	Wypych, 2004

 Table 7.5 Concentrations of three PAE in various environmental water samples.

 PAE
 Concentration
 Location
 Reference

The solubility of plasticizers in water at  $25^{\circ}$ C ranges from about 0.1 mg/l to 4 000 mg/l (see Table 7.3). Once dissolved in water, plasticizers can volatilize into the atmosphere or into soil gases. However, this process is relatively slow as they mostly have a low potential for volatilization from water as expressed by Henry's Law constants lower than  $10^{-4}$  atm-m<sup>3</sup>/mole. Estimates of half-life of volatilization of plasticizers from water are considered insignificant for DEHP and DMP. It is estimated to be 114 days for DnBP in a lake scenario and 14 days in a river scenario (Wypych, 2004). Other authors estimated half-lives of plasticizers in surface water between one to 56 days and between one day and one year in groundwater (Wypych, 2004). DBP and DMP are particularly considered as biodegradable, in aerobic surface water. More precisely, the estimated half-lives are 1 to 14 days for DnBP and 1 to 7 days for DMP (Howard et al., 1991). In comparison, DEHP biodegradation half-life is estimated between 5 and 23 days.

DEHP partitions into the solid phase (suspended solids or whole sediment) and biota which decreases their presence in the water column (Birkett and Lester, 2003). In fact, adsorption can be a significant mechanism in controlling environmental fate of most of the plasticizers. It is a physicochemical process by which dissolved plasticizers may be removed from water and concentrated at the solid-liquid interfaces. Moreover, plasticizer organic carbon-water partition coefficients ( $K_{OC}$ ) are usually greater that 1000 l/kg, indicating a moderate affinity for sediments and soil. This coefficient measures the affinity of a compound to partition to organic matter which in turn will control the mobility of the solutes in water. The extent of adsorption of plasticizers is inversely proportional to their

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