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# Review of Environmental Fate and Effects of di(2-ethylhexyl)phthalate

Ministry of Environment and Energy, Denmark
**Danish Environmental Protection Agency**

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# Review of Environmental Fate and Effects of di(2-ethylhexyl)phthalate

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# Content

# 1. Introduction

The present review of the environmental fate and effects of di-(2-ethylhexyl) phthalate (DEHP, CAS No. 117-81-7) has been prepared for the Danish Environmental Protection Agency. In connection with ongoing discussions of the use of PVC, the environmental impact of DEHP, which is used as plasticizer in PVC, has been discussed with the industrial organizations. The Danish EPA has therefore requested VKI Water Quality Institute and DTI Danish Technological Institute to prepare a thorough review of the environmental fate and effects of DEHP.

# 2. Physico-chemical properties

DEHP is a colourless to yellow, oily liquid with a melting point of about -50°C and a boiling point at 370°C at 760 mm Hg (TSD 1991). The density is 0.98 g/ml at 20°C and the vapour pressure is about $3.4 \times 10^{-7}$ mm Hg at 23°C (TSD 1991).

Despite the large amount of information on DEHP, there is a considerable uncertainty on biological important physico-chemical properties such as the water solubility and the n-octanol-water partition coefficient (log $K_{ow}$). Thus, these two parametres are evaluated in detail in section 2.1 and 2.2.

## 2.1. Water solubility

Several aqueous solubility data are referred in the literature. In an OECD ring test conducted in 1979, the water solubility of DEHP was determined to be 47 µg/l (OECD 1979). Quite different solubility data were determined by Howard *et al.* (1985) and Gibbons & Alexander (1989) who present solubilities of 340 and 330 µg/l, respectively. DeFoe *et al.* (1990) solubility of 270 µg/l by using a centrifugation method.

In ECETOC (1985) a number of solubility values are listed. There seems to be two groups of water solubility determinations, one around 45 µg/l and another around 340 µg/l.

*Estimated water solubility*

There are also several very different predicted water solubility data of DEHP based on log $K_{ow}$. Based on log $K_{ow}$ measurements for DEHP in the 7-8 range (Howard *et al.* 1986; De Bruijn *et al.* 1989; Brooke *et al.* 1990), the water solubility of DEHP is expected to be about 1 µg/l. Using different models, Klein (1988) predicted water solubilities of 0.001-0.04 µg/l and 0.18-2.8 µg/l based on log $K_{ow}$ values of 9.3 and 7.7, respectively.

*"Apparent" and "true" water solubility*

Both the different measured values of water solibility and the much lower estimated values based on theoretical assumptions indicate a high uncertainty in the determination of the "true" water solubility of DEHP. Theoretically, the water solubility wil decrease with increasing alkyl chain length, but measusred solubility values for phthalate esters wiht alkyl chain lenghts of 6 carbon atoms or more are in the range of 0.09-1.2 mg/l and they do not decrease with increasing alkyl chain length (Howard *et al.* 1985). The main reason for this lack of consistence with theroy is assumed to be the formation of microdroplets as a result of the density close to one of the hydrophobic liquid substance. The standard phase separation techniques used for determination of water solubility cannot separate the microdroplets from the water phase and thus, the "apparent" water solubilities measured by this technique will overestimate teh "true" water solubility.

*Solubility enchancement*

Furthermore, the water solubility of DEHP will depend on several factors such as temperature, water quality characteristics (e.g. fresh versus marine water), mixing techniques used to introduce the chemical into the solutions etc. In addition, the presence of dissolved organic matter (DOM) may increase the "true" solubility of DEHP significantly. Gibbons &

Alexander (1989) showed that bacteria were capable of producing solubility enhancing products (solubilizers, probably proteins) that increased the solubility of DEHP up to more than 5 times.

*Realistic water solubility*

Based on the above discussion, the most realistic water solubility of DEHP at environmental conditions is assumed to be about 0.05 mg/l. This value takes into account the naturally occuring water solubility enchaning factors and also the formation of microproplets or other "dissolved" fractions at natural conditions.

## 2.2. Octanol-water partition coefficient

*Literature data*

As for solubility, there are several different values in literature for the log n-octanol-water partition coefficient (log $K_{ow}$). In WHO (1991), log $K_{ow}$ is stated to be 3-5. Wild & Jones (1992) give a value of 4.5 and Batelle (in ECETOC 1985) a value of 4.88. De Bruijn *et al.* (1988) found values between 7.1-7.5 with a slow stirring method and 7.7-7.8 with a HPLC method. Klein (1988) found values from 7.7 to 9.3 with different HPLC techniques.

*Recommended value*

Sudmark *et al.* (1994) recommended a log $K_{ow}$ of 7.5 based on a critical review of the literature and since this value is in agreement with the experimental results found by De Bruijn *et al.* (1988) this value seems to be reliable.

## 2.3. Summary and conclusions

Physico-chemical properties of DEHP have been the subject of extensive literature reviews. However, despite the large body of information on DEHP, there is considerable uncertainty in some of the physico-chemical properties of this compound as a result of experimental difficulties associated with the measurements. For example, the n-octanol-water partition coefficient of DEHP is reported to range over six orders of magnitudes with log $K_{ow}$ from 3-9.3. Furthermore, there are several very different aqueous solubility data in the literature. The different values for solubility, and its dependence on the presence of ions and colloids leads to the conclusion that solubility determinations are highly influenced by the test conditions such as temperature, mixing techniques used to introduce the chemical into the test solutions, water quality characteristics etc.

In the environment formation of microdrophlets is not expected to occur. However, since the equilibrium of DEHP will be in favour of particles, most of the DEHP is expected to be adsorbed to particles in the water. Furthermore, the presence of DOM may further increase the water solubility of DEHP in nature. This may lead to higher apparent solubility values of DEHP than found in laboratory tests.

Based on a critical review of the available literature, the approximate physico-chemical properties on DEHP are summarized in Table 1.
***Table 1:** Physico-chemical properties of diethylhexylphthalate (DEHP)*

| | |
|---|---|
| **CAS-No.** | 117-81-7 |
| **Empirical formula** | $C_{24}H_{38}O_4$ |
| **Molecular weight (g/mol)** | 390.6 |
| **Density (g/ml)** | 0.98 |
| **Water solubility (mg/l at 20°C)*** | around 0.05 |
| **Vapour pressure (mm Hg, at 23°C)** | $3.4 \cdot 10^{-7}$ |
| **Henry's law constant atm · m/mol**** | $3.0 \cdot 10^{-7}$ |
| **log $K_{ow}$** | around 7.5 |

*) Colloidal dispersions with DEHP may occur. This leads to higher apparent solubility values. However, the water solubility calculated from log $K_{ow}$ may be even lower.

**) Henrys law constant describes the extent of partition between a solution and the air above according to Henrys law.

# 3. Environmental concentrations and fate

## 3.1. Concentrations in the environment

*Contamination of samples*

The quality of chemicals analysis of phthalates in environmental samples has been under debate in the recent years. One of the main problems is the common use of plastic equipment in laboratories often containing plasticizers as *e.g.* DEHP. Consequently, the samples to be analyzed may be contaminated both during sampling, storage, processing and analysis if a proper methodology has not been implemented. Thus, many of the results reported - especially in older references - may overestimate the concentrations in the samples due to contamination.

### 3.1.1. Emissions

The content of DEHP in wastewater and sewage sludge from Danish treatment plants has been measured at several occasions in recent years. An overview of the results is given in table 2. In the analysis reported by VKI (1995, 1996), considerable care was taken to avoid contamination of the samples during sampling, storage, processing and analysis. Also data from other national monitoring programmes are presented.

***Table 2:*** *DEHP in treatment plants*

| Reference | Wastewater inlet [µg/l] | Wastewater outlet [µg/l] | Removal from water [%] | Sewage sludge [mg/kg DW] | Degradation [%] |
|---|---|---|---|---|---|
| VKI (1996) | - | - | - | 3.9-170 (20 samples) | - |
| VKI (1995) | 14-49 | 0.5-28 | 43-99 | 0.9-189 | 0-70 |
| Kjølholt *et al.* (1995) | - | - | - | 17-120 | - |
| Grüttner & Jacobsen (1994) | 19-473 | 2.3-51 | 81-98 | - | - |
| Swedish data[1] | 4-167 | - | - | 25-661 (27 samples) | - |
| UK data[2] | - | 1.9 | - | - | - |
| US data[2] | 0.058-390 | - | - | - | - |

1) Cited from Kjølholt *et al.* (1995).
2) Cited from Lundberg (1994).

*Removal in WWTP*

It is a general picture that a relative high removal of DEHP from the wastewater is found during the wastewater treatment. However, due to the sorptive properties of DEHP, high concentrations are found in sewage sludge. Mass balances show that from 30% to 170% of the amount in inlet water are found in outlet water and sludge (VKI 1995). The main reason for the bad mass balances may be that the analyses of DEHP in sludge are very difficult. This may be exemplified by the analyses of the same samples at different laboratories resulting in differences of up to 2 orders of magnitude. It may be anticipated that the correct value

*Mass balances*

is somewhere in between and thus, the low concentrations measured may underestimate the real content and the high concentrations measured may overestimate the content (VKI 1995). Therefore, although the mass balances account for from 30% to 170%, it is probably more correct that about 100% of the amount in the inlet water is found in the outlet water and the sludge. Thus, although VKI (1995) reports a degradation of 0-70%, it is probably more correct to interpret the results as demonstrating only a minor biodegradation in the treatment plant (VKI 1995).

### 3.1.2. **Environmental samples**

A large number of data on concentrations of DEHP in the environment is reported by Lundberg (1994) and only a brief overview will be given here. The quality of the analyses has not been evaluated in the present report. More detailed information may be found in Lundberg (1994) and references cited therein. In general, no information on analysis methods and detection limits are available in Lundberg (1994).

*Fresh water*

In fresh water, concentrations from below the detection limit to 300 µg/l have been detected in samples from Japan, the USA, Canada, the UK, the Netherlands and Sweden. However, in most of the samples the concentrations were below 10 µg/l.

*Estuaries*

In samples from estuaries in the USA, the UK and Germany, concentrations from below the actual detection limit to 78 µg/l were determined. However, in most samples the concentration was below 1 µg/l.

*Sea water*

In samples from the Gulf of Mexico and the North Atlantic, DEHP has been found at levels of up to 0.3 µg/l, but in most of the samples the concentration was below 0.1 µg/l.

*Sediment*

In sediment samples from Sweden, Germany, the Netherlands, the UK, Canada, the USA, Japan and Antarctica, DEHP was measured in concentrations from 0.02 to 1480 mg/kg dry weight, but the levels in most samples were below 100 mg/kg.

*Soil*

In soil, concentrations from below the detection limit to 1.5 mg/kg have been measured in the Netherlands, Finland and the USA. In

*Groundwater*

groundwater, the levels of DEHP were from below the detection limits to 170 µg/l in samples from the Netherlands, the UK and the USA. In the UK the average concentration was 0.07 µg/l. In a sample from Sweden, 1800 µg/l was determined, but this value may according to Lundberg be an error due to shortcomings of the sampling technique.

*Biota*

In aquatic organisms (especially fish, crustaceans and insects), concentrations from 1 to 19000 µg/kg wet weight have been measured.

## 3.2. **Abiotic degradation**

Degradation of a substance may take place by either biological processes (biodegradation) or physico-chemical processes (hydrolysis, photolysis). Biodegradation is discussed in the next section, and the physico-chemical processes are discussed below.

*Hydrolysis*

DEHP does not hydrolyse rapidly. A half-life of 2000 years at pH 7 is reported by Howard (1989). The photolysis half-life in water is

*Photolysis*

estimated to 143 days (Howard 1989), but in practice a lower rate may be expected as only a minor part of the water body is directly exposed to sunlight. The atmospheric photodegradation of DEHP

*Photodegradation*

appears to be rapid with half-lives of less than two days (BUA 1986, Zetzsch 1991), however, detectable levels of DEHP (0.07-0.17 ppb) are found in air samples from remote marine areas (Atlantic and Pacific Oceans, Atlas & Giam 1981). Thus, in practice considerably longer degradation half-lives can be expected in the atmosphere.

## 3.3. **Biodegradation**

The most important mechanism for degradation of DEHP at environmental conditions is biodegradation and therefore, this process is discussed in details. Two types of degradation may be distinguished: complete mineralization to $CO_2$, water and salts, and transformation (primary degradation) to more or less stable metabolites. Finally, substances may be removed from environmental compartments by sorption or volatilisation. Only sorption is of relevance for DEHP.

*Extrapolation to environmental conditions*

Most data on biodegradability of DEHP (and all other substances) are obtained from laboratory tests, but as we primarily want to evaluate the degradation at environmental conditions, it is necessary to extrapolate the results. Thus, before discussing the degradation of DEHP, the differences between the conditions in laboratory tests and conditions in the environment should be discussed. Especially the following parameters are of relevance: concentration of the substance (DEHP) and other substrates, amount of suitable microorganisms, temperature, and oxygen content.

*Suitable microorganisms*

The amount of microorganisms capable of degrading a xenobiotic compound is usually low in the environment unless it has been previously exposed to the substance. With the exception of continuously exposed recipients in the vicinity of a pollution source (*e.g.* landfills and wastewater effluents), the concentrations of particular substances in the environment are often low and prevent the growth of degrading organisms (cf. Boethling & Alexander 1979). On the contrary, wastewater treatment plants may contain a microbial population which is adapted to the degradation of the most abundant chemicals in the sewage.

*Substrates*

Laboratory biodegradability tests differ markedly from the conditions in most natural environments. The chemical examined is often applied at a high concentration and as the only substrate. The substrate concentration and the duration of the tests (e.g. 28 days in ready biodegradability tests) may allow adaptation of the microbial community by growth of competent degrading microorganisms. In some laboratory tests (e.g. tests for inherent biodegradability), the inoculum may be pre-adapted to the test chemical which will normally enhance the degradation rate considerably.

*Temperature*

Laboratory tests on biodegradation are often conducted at relatively high temperatures (20-25°C, OECD 1992) which are favourable for the activity of the microorganisms. In the environment, much more variable temperatures are found and especially in the temperate regions, much lower temperatures are found during long periods of the year. At low temperatures, the activity of the microorganisms is significantly reduced, and biodegradation processes are often slow.

*Oxygen*

In laboratory tests care is taken to maintain a sufficient level of oxygen. In the environment, some compartments are always well aerated while other are dominated by anaerobic processes. In most environments there may be niches where the content of oxygen differs from the surroundings. Especially those substances with sorptive properties, such as DEHP, will tend to accumulate in environments with a low flux of oxygen (sewage sludge, sediments), and the results obtained from aerobic laboratory tests may therefore be difficult to extrapolate to environmental conditions.

### 3.3.1. **Laboratory tests**

Two major types of standardized laboratory tests on biodegradation are available: 1) ready biodegradability tests, and 2) inherent biodegradability tests.

**Ready biodegradability tests**

In tests for ready biodegradability, the inoculum of microorganisms may be derived from either activated sludge, sewage effluents, surface waters or soils. Pre-adaptation of the inoculum is not allowed. It is assumed that a chemical giving a positive result in the test will degrade rapidly in the environment (OECD 1992).

*Ready biodegradability tests*

DEHP has been tested in a number of tests for ready biodegradability. In short term tests with incubation periods of 5 days, Freitag *et al.* (1982) and Korte & Klein (1982) found a degradation of only 0-1% measured as $CO_2$. Price *et al.* (1974) tested the biodegradability of DEHP in concentrations of 3-10 mg/l in BOD bottles inoculated with 1% settled and filtered domestic wastewater. After incubation for 20 days, no biodegradability was observed. In the MITI (I) test for ready biodegradability, applying a concentration of DEHP of 100 mg/l and a concentration of inoculum of 30 mg/l, a degradation of 29% measured as BOD was found after two weeks (MITI 1992). Hüls (1994) tested the biodegradability of DEHP in a Modified Sturm Test. The medium containing DEHP in a concentration of 20.3 mg/l was inoculated with activated sludge from a treatment plant situated close to the production facilities, and the evolution of $CO_2$ was measured during 28 days at 20-22°C. After a lag phase of 4-8 days, the evolution of $CO_2$ corresponded to a mineralization of 82%. In repetitive die-away tests with additions of DEHP at weeks 3, 4 and 5 and inoculated with 10 ml/l activated sludge, 40-70% degradation measured as BOD was determined after 42 days (Blok & Booy 1984).

*Removal of DEHP*

In some tests only the removal of DEHP from the test system was determined. The removal may have been caused by either transformation (primary biodegradation) or adsorption. Tabak *et al.* (1981) studied the biodegradability of DEHP in concentrations of 5 and 10 mg/l in a static culture flask screening procedure inoculated with settled domestic wastewater. Each culture was incubated for 7 days in the dark, after which microorganisms from the culture were used as inoculum for a new culture. This procedure was repeated three times within a total degradation period of four weeks. The removal of DEHP, determined by gas chromatography, was 0%, 45%, 85% and 94% after each of the four weekly subcultures.

*Acclimated inocula*

Finally, some tests were prepared with acclimated inocula which increases the biodegrading potential of the test. The results of such tests can therefore not be used for evaluating the ready biodegradability of the substances. O'Grady *et al.* (1985) used acclimated sludge (21 days) as inoculum in a 2 days degradation test at a concentration of 3 mg DEHP/l

and found a removal of 90% of the substance. Saeger & Tucker (1976) tested the biodegradability of DEHP during 27 days at a temperature of 25°C. The inoculum was obtained from a Semi Continuous Active Sludge (SCAS) unit which was capable of degrading DEHP. A degradation of 86% measured as $CO_2$ evolution was found. Sugatt *et al.* (1984) acclimated the active sludge for 14 days before initiating the test which was run for 28 days at a temperature of 22°C. Biodegradation was measured as $CO_2$ evolution, and a mineralization of 73-92% (mean 86%) was obtained. A primary degradability of >99% was found. Price *et al.* (1974) acclimated the sewage in 45-60 days before inoculating the test system. After incubating DEHP in concentrations of 3 to 10 mg/l in 20 days, a biodegradation of 23% was determined.

**Inherent biodegradability tests**

In a SCAS test which was operated by a fill and draw procedure during 3 weeks, a 81.5% removal of DEHP in concentrations from 1 to 3 mg/l was measured in 24 hours (O'Grady *et al.* 1985). Saeger & Tucker (1976) measured 70-78% removal of DEHP in 24 hours in a SCAS test. No water soluble aromatic intermediates were detected during the test and Saeger & Tucker suggest that the intermediates are more rapidly degraded than the parent substance. Graham (1973) found 91% disappearance of DEHP in 48 hours in a SCAS test. Woock (1979) in a SCAS test with a microbial population of 2500 mg/l and a temperature of 22°C found 28-42% removal in 24 hours.

**Anaerobic degradation**

Shelton & Tiedje (1981) investigated the anaerobic degradation of DEHP at 50 mg/l in a mineral medium inoculated with digested sludge. After incubation for 56 days at 35°C, no biodegradation measured as methane production was observed. Horowitz *et al.* (1982) obtained the same result in a similar study. Shelton *et al.* (1984) found a degradation of 0-9% of DEHP added in a concentration of 20 mg/l, inoculated with digested sludge and incubated 70 days at 35°C. In a study of degradation of DEHP in a concentration of 1 mg/l, Johnson & Lulves (1975) found no biodegradation after incubation for 30 days at 22°C.

### 3.3.2. Sewage treatment plants

*WWTP simulation test*

In a test simulating a biological treatment plant, the sewage sludge was acclimated for 40 days before initiating the test (Davis *et al.* 1983). Biodegradation of DEHP in a concentration of 2 mg/l was determined during 12 days at a temperature of 23°C. An average biodegradation of 59.9% was estimated based on mass balances (measured concentrations in sedimented material, water column residuals and effluent).

*Mass balances*

Based on data from a Danish monitoring programme on DEHP in wastewater treatment plants (cf. 3.1.1 above), biodegradation of 0 to 70% was reported for treatment plants in the summer period. These values are based on mass balances, and are therefore considered maximum values and the real biodegradation is concluded to be considerably less than 70% (VKI 1995, cf. 3.1.1).

### 3.3.3. Aquatic environments

The biodegradation in the aquatic environments can be investigated in simulation tests where the environmental conditions are simulated in the laboratory. Johnson *et al.* (1984) tested the mineralization of DEHP in a concentration of 14.3 µg/l in a sediment:water (1:9) system at 22°C with

an incubation period of 28 days. The test system was operated at aerobic and anaerobic conditions, respectively, resulting in an ultimate mineralization of 13.8% and 9.9%, respectively. Subba-Rao *et al.* (1982) investigated the mineralization of DEHP in concentrations of 0.000021 to 0.2 mg/l in lake waters, and found a 35-71% mineralization in water from an eutrophic lake (incubated in 40 days, half-life 24.75 days) and no mineralization in water from an oligotrophic lake (incubated in 60 days). In a water hydrosoil microcosm, Johnson & Lulves (1975) testing DEHP in a concentration of 1 mg/l found a biodegradation of 60.4% measured as $CO_2$ evolution in 28 days.

*Primary biodegradability*

Some simulation studies only report the primary biodegradability of DEHP. Johnson *et al.* (1984) report a number of experiments on the primary biodegradability of DEHP. All experiments were performed in a sediment:water (1:9) system at 22°C with an incubation period of 28 days. The primary biodegradation of DEHP in a concentration of 18.2 µg/l was determined to be 5.9%. In various concentrations from 0.0182 mg/l to 10 mg/l, primary biodegradations from 8.47% to 19.79% were determined. At different temperatures, the primary biodegradation increased from about 1% to about 11% at increasing temperatures from 5 to 28°C. The primary biodegradation was investigated by Saeger & Tucker (1976) in a river die away test with a concentration of DEHP at 1 mg/l and a temperature of 25°C. 45% and 61% of the parent substance was not recovered after incubation in 28 and 35 days, respectively.

*Effects of substrate concentration and temperatures*

*Removal of DEHP*

Some tests report the removal of the test substance, *i.e.* either the transformation (primary biodegradability) or the sorption. In river die-away tests with marine water, Hattori *et al.* (1975) found a removal of DEHP from 31% to 88% after incubation in 14 days depending on the location of the sampling area. In similar tests with river water, they determined a removal of DEHP of 39% and 40%. In a water hydrosoil microcosm, Johnson & Lulves (1975) testing DEHP in a concentration of 1 mg/l found a 59% loss of DEHP after incubation in 30 days. Schouten *et al.* (1979) found a 50% loss of DEHP in a concentration of 0.05 mg/l after incubation in 5 days in river water.

### 3.3.4. **Terrestrial environments**

*Mineratization*

A few results from tests simulating the conditions in soil have been obtained. Fairbanks *et al.* (1985) studied the mineralization of DEHP in concentrations of 2 and 20 ppm in three different soils freshly amended with sludge. After 140 days of incubation, a degradation from 75% to 93% was found. Shankar *et al.* (1985) tested the degradation of DEHP in a concentration of 500 ppm in soils at 30°C under aerobic and anaerobic conditions, respectively. After 30 days, 92% and 36.4%, respectively, of the applied amount of DEHP could not be recovered. In columns simulating a rapid wastewater infiltration site, Hutchins *et al.* (1983) determined a reduction of the concentration from the wastewater (4.3-7.6 µg/l) to the leachate (0.011-0.16 µg/l) of 96% to >99% after acclimation. The reduction was probably a result of (primary) biodegradation as addition of the biocide mercuric chloride resulted in higher leachate concentrations. Other phthalate esters in lower concentrations (<0.5 µg/l) were not degraded which was attributed to the concentrations being to low to maintain the status and function of the degrading microorganisms (Hutchins *et al.* 1983).

*Removal*

*Primary biodegradation*

## 3.4. Bioaccumulation

### 3.4.1. Aquatic organisms

Numerous studies for the determination of bioconcentration factors (BCFs) have been performed with algae, crustaceans, fish, mussels and insects. When considering these studies it should be noted that short-term studies may not allow for an equilibrium to be established, thus underestimating the BCF (cf. Kristensen & Tyle 1991). The size of the test organism is also important, *i.e.* small organisms will have a relatively larger surface and thus, results with larger organisms may also underestimate the BCF. Below, a number of studies on bioaccumulation of DEHP is referred. Only studies where the concentrations of DEHP are measured in both the test medium and the organisms are included.

*Mesocosm studies*

In a model ecosystem, Metcalf *et al.* (1973) determined BCFs for the algae *Oedogonium* sp. (BCF: 53890), mosquito larvae (*Culex pipiens quinquefasciata*) (BCF: 107670), guppy (*Poecilia reticulata*) (BCF: 130), and clam (*Sphaerium striatinum*) (BCF: 21480) after 33 days of exposure to $C^{14}$-labelled DEHP in a concentration of 0.34 µg/l.

In a similar mesocosm study by Södergren (1982, cited from Lundberg 1994), BCFs were determined for submerged plants (*Mentha aquatica* and *Chara chara*) (BCF: 18000), sticklebacks (*Pungitus pungitus*) and minnow (*Phoximus phoximus*) (BCF: ≤ 300), and invertebrates (the amphipod *Gammarus pulex*, the snail *Planorbis corneus* and caddis flies) (BCFs: 17000-24000) after 27 days of exposure to $C^{14}$-labelled DEHP in a concentration of 1.4 mg/l. This concentration is higher than the solubility limit and consequently, the BCF values may be underestimated.

*Laboratory studies*

Sanders *et al.* (1973) determined BCFs for Aquatic sowbug (*Asellus brevicaudus*, BCF: 70-250 after 21 days of exposure), Midge larvae (*Chironomus plumosus*, BCF: 408-3100 after 7 days of exposure), Scud (*Gammarus pseudolimnaeus*, BCF: 260 after 21 days exposure), and Mayfly (*Hexagenia bilineata*, BCF: 2300 after 7 days of exposure).

In *Daphnia magna*, Brown & Thompson (1982a) determined BCFs of 189-334 (recalculated from BCFs of 140-268 based on nominal exposure concentrations) after 21 days exposure.

Barrows *et al.* (1980) found a BCF of 114 for Bluegill (*Lepomis macrochirus*) after 42 days exposure. Mehrle & Mayer (1976) exposed eggs and the hatched larvae of rainbow trout (*Oncorhynchus mykiss*) to DEHP in concentrations of 5-54 µg/l for 100 days and determined the BCF to 42-113. Fathead minnows (*Pimephales promelas*), 7.5 months old, were exposed to DEHP in concentrations of 1.9-62 µg/l for 56 days, and BCFs from 886 down to 155 with increasing DEHP concentrations were determined. In another study with *Pimephales promelas*, Mayer (1976) determined BCFs of 91-569 after exposure for 56 days.

For Blue Mussels (*Mytilus edulis*) exposed to $C^{14}$-labelled DEHP in concentrations of 4.1 and 42.1 µg/l for 28 days, Brown & Thompson (1982b) determined BCFs of 2366 and 2627, respectively.

### 3.4.2. Terrestrial organisms

Only results of a few studies on bioaccumulation of DEHP in terrestrial organisms are available. Kirchmann & Tengsved (1991) applied

*Uptake in plants*

sewage sludge to farmlands in a volume of 5 t/ha. Spring barley (*Hordeum vulgare* L.) were sown and after harvest, grains were analyzed for organic pollutants. Considering that the sludge were mixed in the upper 10 to 20 cm of the soil, BCFs of 0.14-0.27 can be calculated based on dry weight. In other studies with exposure to $C^{14}$-labelled DEHP in soil, radioactivity was found in plants, but not DEHP, and the substance is therefore expected to be metabolized in either the soil or the plants (Aranda *et al.* 1989, Schmitzer *et al.* 1988).

*Dietary studies on birds*

A few dietary studies on birds are referred by Lundberg (1994). In general, DEHP is only detected in tissues of the birds in concentrations lower than in the diet, although one study with hens reports concentrations in adipose tissue and feathers up to 100 times the concentrations in the diet after up to 230 days of dietary exposure.

## 3.5. Summary and conclusions

### 3.5.1. Concentrations in the environment

*Treatment plants*

DEHP is found both in emissions to the environment (wastewater, sewage sludge) and in environmental samples. In wastewater samples, concentrations from < 1 to 500 µg/l have been found, but during (biological) treatment the concentrations are normally reduced to < 1-50 µg/l. From 40-99% of the content of DEHP in wastewater is retained in the treatment plant. Most of the DEHP is accumulated in sewage sludge (1-660 mg/kg dry weight), and only a minor (not quantifiable) part is degraded in the treatment plants.

*Aquatic environment*

In the aquatic environment, the concentrations in fresh water are generally below 10 µg/l, in estuaries below 1 µg/l and in open oceans below 0.1 µg/l. In sediments the concentration in most samples is below 100 mg/kg dry weight. In aquatic organisms, concentrations from 1 to 19000 µg/kg wet weight have been measured.

*Terrstrial environment*

In soil, concentrations of DEHP up to 1.5 mg/kg dry weight have been measured.

The concentrations of DEHP in environmental samples clearly reflect the ubiquitous use of the substance. Even at remote areas (open oceans, sediment samples from Antarctica) the substance is found in quantifiable levels.

### 3.5.2. Biodegradation

*Aerobic biodegradation tests*

Results from a large number of investigations have been evaluated. In most tests for ready biodegradability, the mineralization (ultimate degradability) is lower than the pass level for considering the substance as readily biodegradable. However, in one test a degradation of 82% was reached. If only the removal of DEHP is determined (*e.g.* the primary biodegradability), a higher level of removal/degradation is found. The same is normally the case when acclimated activated sludge is used as inoculum. In tests for inherent biodegradability, which are more favourable for degradation, relatively high levels of degradation were observed.

*WWTP simulation test*

In a test simulating a biological treatment plant, an average biodegradation of 60% was estimated based on mass balances. However, based on mass

balances for Danish treatment plants, only a low, but not quantifiable, biodegradation is estimated.

*Simulation tests*

In studies simulating the conditions in the aquatic environment, a mineralization (ultimate degradation) from 0 to 10% was determined, although one study reports up to 70% degradation. Especially at low temperatures (5-12°C), the biodegradability was low. When only loss of DEHP (*e.g.* primary biodegradability) was measured, higher levels of removal/degradation were found.

*Anaerobic biodegradation tests*

In tests for anaerobic biodegradability, almost no degradation was found even at favourably temperatures and after relatively long incubation periods.

*Conditions on biodegradation*

It is concluded that normally acclimation of microorganisms is necessary before biodegradation of DEHP takes place. Depending on the previous exposure of the microorganisms in the environmental compartment from where the inoculum is sampled, the acclimation period in laboratory tests may be relatively brief, some times within the time period accepted in standard tests for ready biodegradability. It should be noted that many treatment plants in practice are acclimated to degrade DEHP due to the ubiquitous use and emission of the substance and this is possibly the explanation for the positive results obtained in some tests for ready biodegradability. However, even in treatment plants regularly receiving DEHP, only a low degradation of the substance is found while most of the DEHP is sorbed to particulate organic matter and thus accumulated in the sewage sludge. In comparison with the conditions in wastewater treatment plants, the degradation in the environment is considerable lower due to lack of suitable microorganisms, low concentrations of DEHP and low temperatures (cf. *e.g.* Johnson *et al.* 1984). The low biodegradability is confirmed by results of chemicals analysis of environmental samples. Finally, at anaerobic conditions lower levels of biodegradation are expected.

### 3.5.3. **Bioaccumulation**

*Aquatic organisms*

A number of studies on the bioaccumulation of DEHP in aquatic organisms has been reviewed. For different groups of organisms, the following BCF values have been determined: algae and plants: 18000-54000; crustaceans: 70-24000; fish: 40-900; insects: 400->100000; and molluscs: 2400-24000. DEHP is therefore considered very bioaccumulative in aquatic organisms.

*Terrestrial organisms*

Only very few studies are available on the bioaccumulation i terrestrial organisms. Based on these studies, DEHP is not likely to accumulate in either plants from soil or birds from dietary exposure (BCF < 1).

# 4. Effects

## 4.1. Terrestrial organisms

*Microbial activity*

No effect on soil respiration or nitrification has been observed at a concentration of 250 mg/kg in soil (Lundberg 1994).

*Earthworms*

Earthworms (*Eisenia foetida*) were exposed to DEHP via filter paper. No toxic effect could be seen even at the highest dose of 25 mg/cm$^2$ (Neunhauser *et al.* 1986, in WHO 1992).

*Plants*

Herring & Bering (1988, in TSD 1991) found no effect of DEHP on plant growth (measured as height) when growing spinach and pea plants from 14 to 16 days in soil containing 10 mg/kg. However, a 40-50% reduction in the number of germination were seen when seeds were placed in water containing 100 mg/l.

No effects were found on white mustard (*Sinapis alba*), rape seed (*Brassica rapus*) and milfoil (*Achillea millefolium*) when DEHP was sprayed in the field in amounts up to 8.75 µg/cm$^2$ (0.875 kg/ha) (Løkke & Rasmussen 1983, in TSD 1991).

A slight effect has been observed on oats (*Avena sativa*) at a concentration of 1000 mg/kg soil (Stanley & Tapp, in TSD 1991).

*Birds*

Hill *et al.* (1975, in TSD 1991) found no mortality in ring-necked pheasants or mallard ducks (10 days old) when fed with up to 5 g DEHP/kg for 5 days, followed by 3 days on a noncontaminated diet.

The $LD_{50}$ values to birds in oral exposure were 13 mg/kg (Levis & Sweet 1984, in Nikunen *et al.* 1990).

## 4.2. Aquatic organisms

*Experimental problems*

The low water solubility of phthalic acid esters causes problems when exposing aquatic organisms in toxicity tests. The formation of microdroplets, surface films and adsorption leads to difficulties in maintaining steady exposure concentrations and/or causes direct physical interference. Most aquatic toxicity studies have been using nominal concentrations of DEHP at a range from under to well above the "true" water solubility.

*Formation of microdroplets*

When test solutions are prepared in concentrations higher than the "true" water solubility of DEHP, an emulsion of microdroplets consisting of pure chemical may be formed. The formation of microdroplets or surface films may contribute to possible effects by direct physical interference. Examples of this are flotation (entrapment) or obstruction of the gas flow over the gills.

*Particles and colloids*

Small particles and colloids may increase the apparent water solubility by sorbing lipophilic substances but they may also either decrease or increase the bioavailability and thus the toxicity. For most substances, the presence of particulates and colloids probably decreases the bioavailability, but for

certain types of organisms (especially suspension feeders or detritivores) the reverse effect might be true.

When interpreting toxicity data on rarely soluble substances such as DEHP, it is very important that the above parameters are taken into account.

4.2.1. **Acute toxicity tests**

*Algae*

DEHP was tested for acute toxicity on a green algae (*Selenastrum capricornatum*) by Alexander *et al.* (CMA 1984). Since preliminary tests showed no toxicity only one concentration was used in the definitive test in which cultures of *Selenastrum* were exposed to a "saturated solution" of DEHP (0.1 mg/l). No effect was found for DEHP at 0.1 mg/l.

NO effect of DEHP on the growth of *Scenedesmus* (Algal growth inhibition test), has been found in test concentrations between 10 and > 130 mg/l in the presence of a non-toxic vehicle (Rippen 1992, Scholtz 1995a).

In only a few acute tests with freshwater animal species, enough toxicity was observed to permit the calculation of an acute $EC_{50}$ value.

*Crustaceans*

In a 48-h acute test with *Daphnia magna* a $EC_{50}$ value of 2 mg/l (nominal concentration) was found (Adams & Heidolph 1985). LeBlanc (1980) found a $EC_{50}$ value of 11 mg/l (measured concentration) with the same species in the absence of a vehicle. However, in the absence of a vehicle the toxicity to Daphnia may in part be ascribed to an indirect effect such as flotation (entrapment) or microdroplets may adhere to the surface of the animals.

An $EC_{50}$ value of more than 100 mg/l has been found from an acute toxicity study with *Daphnia magna* in the presence of a surfactant (Scholtz 1995b).

Passino (1985) tested the acute toxicity to *Daphnia pulex* and reports an $EC_{50}$ for DEHP of 0.1 mg/l.

*Fish*

DEHP showed no toxicity at the apparent solubility limit in numerous well performed acute toxicity tests with different fish species (Bluegill, Rainbow trout, Sheepshead minnow, Fathead minnow and Rainbow trout). The NOEC values determined after 96 h of exposure were in the range of 0.17->19.5 mg/l. No toxicity was seen in these acute toxicity tests with fish at the highest concentrations used and the determination of LOEC values was not possible (CMA 1983b, CMA 1983a, CMA 1984b, DeFoe *et al.* 1990). However, results of tests with fish vary with several orders of magnitude depending on the test organisms and test conditions. Thus $LC_{50}$ values have also been found between 6 and >100 mg/l (Nikunen *et al.* 1990, Scholtz 1995c). The acute fish test in which a $LC_{50}$ value of more than 100 mg/l was found, used Marlowet R 40 as vehicle and *Brachydanio rerio* as test organism. The study was well performed and in accordance with directive 92/69/EEC Part C 1.

4.2.2. **Chronic toxicity tests**

*Crustaceans*

Mayer & Sanders (1973) previously reported that DEHP affected *Daphnia magna* reproduction at a concentration of 0.003 mg/l. However, this study has been stated by the US EPA to appear to be in error because other

tests found that concentrations about 0.1 mg/l did not affect survival or reproduction (US EPA 1987).

In a chronic *Daphnia magna* reproduction study over 21 days, Brown & Thompson (1982) showed that nominal concentrations up to 100 µg/l had no effect on reproduction. However, Daphnia floated on the surface after 48 hours (25% at 0.169 mg/l and 100% at 0.304 mg/l; mean measured concentrations). They concluded that the Daphnia flotation was due to DEHP precipitation onto the Daphnids.

Adams & Heidolph (1985) reported that 1.3 mg/l DEHP significantly reduced survival and reproduction of *Daphnia magna*, whereas 0.64 mg/l did not.

Biddinger and co-workers (CMA 1983) tested the chronic toxicity of fourteen phthalate esters, including DEHP, on *Daphnia magna* in a flow-through system. Survival was the most sensitive parameter. NOEC was 0.077 mg/l and LOEC was 0.16 mg/l. The same values have also been reported by Rhodes *et al.* (1995). In these studies, no visible film was seen on the surface of the test solution. However, the test organisms were found on the surface at the LOEC.

In another 21 days chronic toxicity test with *Daphnia magna*, DEHP concentrations from 0 to 0.811 mg/l were investigated (Knowles *et al.* 1987). NOEC was 0.158 mg/l and LOEC was 0.811 mg/l based on survival and reproduction. However, survival and growth were not the most sensitive parameters. Based on the RNA/DNA ratio, NOEC was 0.072 mg/l and LOEC was 0.158 mg/l (mean measured concentrations). In this study the Daphnia were also trapped on the surface of the water. Thus, at a DEHP concentration of 0.811 mg/l, 70% of the Daphnia were floating initially. However, after 21 days this value was reduced to around 14%. After 48 hours at 0.158 mg/l about 18% were at the surface (Knowles *et al.* 1987). Whether the biochemical changes found in the present study are due to a direct action of DEHP or might be the result of stress of the Daphnia due to physical entrapment of the daphnids on the surface, is unknown.

Scholtz (1994b) investigated the chronic effects of DEHP on *Daphnia magna* survival and reproduction in a 21 days chronic toxicity test at DEHP concentrations from 0 to 14 mg/l (based on mean measured concentrations). In this test a NOEC value of 14 mg/l was found in the presence of a non-toxic vehicle (Scholtz 1994b). The test was well performed and in accordance with OECD-testguideline 202.

*Inconsistent results*

Thus, several chronic toxicity tests for daphnids have been performed with DEHP, but the results are inconsistent between different studies. In some cases chronic effects are reported while in other studies no chronic effects are observed at much higher concentrations. These inconsistencies may be attributed to physical effects e.g. surface entrapment imposed on daphnids when tested with solutions that contain undissolved DEHP.

*Physical effects*

Consequently, daphnid response may depend on the physical nature of the test solution rather than the soluble concentration of the test chemical. Experimental support for this explanation has been obtained by conducting Daphnia chronic studies at high concentrations in the presence of a non-toxic dispersant. No toxicity of DEHP on Daphnia was found in these ex-

periments at the highest concentration used. The concentrations of DEHP in these studies range from 0.1 to 14 mg/l (Brown & Williams 1994, Scholtz *et al.* 1995, Croudace *et al.* 1995). The dispersant serves to minimize the physical effects associated with the testing of concentrations that exceed the "true" water solubility. These studies have demonstrated that no chronic effects on daphnids are observed if a non-toxic dispersant is added.

*Fish*

In a 32-day early-life stage test with the fathead minnow (*Pimephales promelas*), survival was reduced with 32% at 42.4 mg DEHP/l (Horne *et al.* 1983). The mean weight of the fish in the control group was rather low at the end of the experiment, but the data indicate that the weight of the exposed fish was reduced by 16% compared to the controls.

Spehar (1986) exposed rainbow trout (*Oncorhynchus mykiss*) embryos and fry to DEHP for 90 days. The average test concentrations ranged from 0.05 - 0.5 mg/l and no significant effects were seen on embryo hatchability, larval or juvenile survival and growth.

A 168 day chronic test with Japanese medaka (*Oryzias latipes*) was conducted by DeFoe *et al.* (1990). The fry (< 1 to 3 days old) were exposed to saturated concentrations of DEHP. Survival and growth were recorded during the exposure period in the flow-through system. No significant effect on survival could be seen, but the weight of the DEHP-exposed (0.554 mg/l) fish was significantly reduced after 168 days.

Mayer *et al.* (1977) found that collagen synthesis was reduced in the vertebrae of brook trout (*Salvelinus fontinalis*) exposed to 0.0037 mg/l DEHP for 150 days, fathead minnows (*Pimephales promelas*) exposed to 0.011 mg/l for 127 days, and rainbow trout (*Oncorhynchus mykiss*) exposed to 0.014 mg/l for 90 days.

*Sediment toxicity tests*

As phthalates tend to accumulate in sediments, toxicity to organisms living in or on the sediment is essential. The effect of DEHP on the emergence of the chironomid midge, *Chironomus riparius*, was investigated. Larvae of the midge (< 24 hours post-hatch) were exposed for 28 days to sediment spiked with DEHP. Based on nominal concentrations, a NOEC value of 10000 mg DEHP/kg (dry weight) was found (Thompson *et al.* 1995).

The number of successful hatchings of frog eggs (*Rena arvalis*) decreased with increasing levels of DEHP in sediment. Approximately 50% of the eggs hatched (as compared to the controls) when exposed to sediments that contained 150 mg DEHP/kg sediment (fresh weight) (Larsson & Thuren 1987).

The US EPA together with the Chemical Manufacturers Association (CMA) and the European Council of Plasticizers and Intermediates (ECPI) are funding a study to investigate the effect of 7 phthalates on 2 species in 3 types of sediment. This study is due to be completed late in 1996.

## 4.3. Summary and conclusions

The results from ecotoxicology tests vary with several orders of magnitude. The reason for the variability should most probably be sought in

experimental difficulties arising from the low water solubility of phthalic acid esters. The formation of microdroplets, surface films and adsorption to surfaces of the test organisms leads to difficulties in maintaining steady exposure concentrations and/or causes direct physical effects.

4.3.1. **Summary of the acute toxicity studies of DEHP**

*Terrestrial organisms*

DEHP seems to have a relatively low acute toxicity to terrestrial organisms. No effect on soil respiration or nitrification has been observed at concentrations up to 250 mg/kg. No effects of DEHP have been observed on plant growth in soil containing 10 mg/kg. A slight effect has been observed on oat at a concentration of 1000 mg/kg soil. The oral $LD_{50}$ value to birds was 13 mg/kg bwd.

*Aquatic organisms*

The toxicity of DEHP to algae is relatively low (NOEC between 10 and $>130$ mg/l). In acute toxicity tests with aquatic animals, the $EC_{50}$ values for Daphnia were between 2 and 11 mg/l in the absence of a vehicle and no effect has been found at a concentration of 100 mg/l in the presence of a non-toxic vehicle. The $LC_{50}$ for fish was between 6 and $>100$ mg/l.

*No direct acute toxic effects*

The data from the acute toxicity studies suggest that DEHP does not have a direct acute toxic action to aquatic organisms. The only exception to the above generalization is the study by Passino (1985) for *Daphnia pulex* who reports an $EC_{50}$ for DEHP of 0.1 mg/l. However, based on additional toxicity tests, it seems unlikely that the high toxicity detected in this test is realistic. Thus, in general DEHP does not seem to be acute toxic to aquatic organisms at concentrations at or below the "true" water solubility of DEHP. However, adverse effects may occur at higher concentrations e.g caused by indirect effects such as flotation (entrapment) or obstruction of the gas flow over the gills. Furthermore, Daphnia as filter feeders may ingest the micelles or the micelles may adhere to the surface of the animals.

4.3.2. **Summary of the chronic toxicity studies of DEHP**

Several tests have been conducted which are useable to evaluate the chronic toxicity of DEHP.

*Crustaceans*

In chronic toxicity tests, the lowest NOEC determined for *Daphnia magna* is 0.077 mg/l (LOEC 0.16 mg/l) based on survival and 0.072 mg/l (LOEC 0.158 mg/l) based on RNA/DNA ratio (dispersant not added). However, in the presence of a non-toxic vehicle NOEC values up to 14 mg/l were found.

*Fish*

Fish seem less sensitive. However, collagen synthesis was reduced in the brook trout after exposure to DEHP (NOEC 0.0037 mg/l). Growth of fish exposed to 0.554 mg DEHP/l was significantly decreased after 168 days of exposure.

*Biochemial end-points*

In addition to the traditional endpoints, survival and reproduction, it has been shown that DEHP may have an effect on biochemical parameters such as DNA/RNA ratio and collagen synthesis in aquatic organisms.

Parameters such as hatching, survival, growth, reproduction and morphology are normally used as endpoints in evaluation of chronic toxicity data with regard to environmental effects. However, if other endpoints are available (e.g. biochemical parameters such as DNA/RNA ratio, collagen synthesis etc.) it is also important to consider these results in the overall

evaluation of the ecotoxicity of a given test substance. The evaluation of the xenoestrogenic effects of phthalate esters is an example of an important effect parameter not normally considered in the evaluation of phthalate esters with regard to environmental effects, until a few years ago.

*Potential for longterm effects*

Based on the available data from chronic tests, it is concluded that DEHP may cause longterm adverse effects in aquatic organisms (caused by direct or indirect effects).

### 4.3.3. **DEHP toxicity in the environment**

In the environment, DEHP is expected to be sorbed to particles in the water phase and the presence of DOM may furthermore increase the water solubility of DEHP. This may lead to a higher "apparent" water solubility of DEHP than predicted from the physico-chemical properties. In contrast to many laboratory experiments, microdroplets are not normally expected to contribute to toxic effects by direct physical interference to the organisms normally used in the evaluation of toxicity in the aquatic environment.

Thus, DEHP is not expected to have a direct acute toxic action to either terrestrial or aquatic organisms. Based on endpoints normally considered in the evaluation of chronic toxicity, DEHP does not seem to cause direct chronic toxic effects. However, DEHP may cause effects on biochemical parameters and thus cause longterm adverse effects in aquatic organisms.

As DEHP tends to accumulate in sediments, the evaluation of toxicity to organisms living in or on sediment is essential. Additional data concerning the lethal and sublethal effects of DEHP on sediment living organisms are therefore essential.

# 5. Environmental hazard classification

DEHP has not been considered for environmental hazard classification by the EU "Labelling Group". However, based on the above review of the environmental fate and effects of DEHP, a classification proposal may be derived.

*Parametres to be considered*

The main parameters to be considered for the environmental hazard classification are (EEC 1993):

- acute toxicity to algae, daphnia and fish
- chronic toxicity to daphnia and fish
- ready biodegradability
- bioaccumulation potential (log $P_{ow}$ or experimentally derived BCF)
- water solubility

*Acute toxicity*

No acute toxicity is observed at or below the water solubility level of DEHP (~0.05 mg/l). However, by testing emulsions of DEHP at higher concentrations, $LC_{50}$ values have been found at 2 mg/l (daphnids) and 6 mg/l (fish) and higher concentrations. No guidance for interpretation of such results for classification purposes is available, but the results should probably not be considered.

*Chronic toxicity*

No direct toxic effects after long-term (chronic) exposure have been observed at or below the water solubility level. However, indirect effects have been observed at concentrations as low as 3.7 $\mu$g/l, but how such effects should be interpreted regarding environmental hazard classification is not obvious.

*Ready biodegradability*

Generally, tests for ready biodegradability show that DEHP is not readily biodegradable. However, one test shows a high biodegradability, but whether this single result should be taken into account when classifying regarding environmental hazards is not obvious from the present practice in the EU "Labelling Group". Moreover, it should also be considered that both the results of tests simulating the environmental conditions and the results of chemicals analyses of environmental samples show that DEHP is not degraded fast in the environment.

*Bioaccumulation*

DEHP has a bioaccumulation potential demonstrated by both log $P_{ow}$ ~7.5 and the experimentally derived BCF values from 40 to >100000. Both log $P_{ow}$ and BCF are much higher than the cut-off values of 3 and 100, respectively, for considering environmental hazard classification.

*Water solubility*

The water solubility of DEHP is ~0.05 mg/l which is much lower than the cut-off value of 1 mg/l.

*Classification proposal*

Considering the criteria for environmental hazard classification (EEC 1993), it is proposed that DEHP be classified "R53: May cause long-term adverse effects in the aquatic environment". However, if the acute toxic effects observed at concentrations above the "true" solubility level is also considered, a classification of "N; R51/53: Toxic to aquatic organisms, and may cause long-term adverse effects in the aquatic environment" should be assigned.

# 6. Conclusions and recommendations

## 6.1. Conclusions

*Biodegradability*

In general, DEHP is considered not readily biodegradable. After acclimation of the microorganisms, the substance degrades relatively fast. Due to the ubiquitous use of DEHP, the microorganisms in many treatment plants are expected to be acclimated to degrade DEHP, and in some laboratory tests using microorganisms from already exposed treatment plants, the substance is found to be readily biodegradable. However, mass balances on treatment plants based on chemicals analyses demonstrate that due to the strong sorption of DEHP to particulate matter, only a minor degradation can be expected in practice. Moreover, based on tests simulating the conditions in the aquatic environment, it is concluded that the degradation in the environment is considerably lower than in treatment plants. Finally, no biodegradation is expected at anaerobic conditions.

*Bioaccumulation*

The bioaccumulation of DEHP has been investigated in numerous studies with aquatic organisms from various taxonomic groups. Bioconcentration factors from 40 to more than 100000 have been determined, and it is therefore concluded that DEHP is very bioaccumulative.

*Toxicity*

It must be concluded that no acute or chronic lethality is found at concentrations below or at the water solubility limit (0.05 mg/l). However, alterations or effects are found at biochemical level at low concentrations (NOEC = 0.0037 mg/l). Moreover, in laboratory test systems it is possible to test DEHP in concentrations considerably higher than the water solubility limit, as the substance forms stable emulsions because it is a liquid with a density close to 1 g/ml. At these conditions, acute lethal effects are found at concentrations of a few mg/l. The results can, however, not be extrapolated to environmental conditions, as such emulsions cannot be expected to form or persist in nature. Thus, in the environment no acute toxic effects are expected.

## 6.2. Recommendations

*Classification*

It is recommended that DEHP be classified "R53: May cause long-term adverse effects in the aquatic environment" because of its general low biodegradability in tests for ready biodegradability, its low biodegradability in practice in wastewater treatment plants and in the aquatic environment, its high potential for bioaccumulation, and its low water solubility.

However, as no practice has been established concerning the evaluation of toxic effects at concentrations above the water solubility limit in relation to environmental hazard classification, it is recommended that it should be discussed and decided how to interpret these data. If these toxicity data are taken into account, an environmental hazard classification with "N; R51/53: Toxic to aquatic organisms, and may cause long-term adverse effects in the aquatic environment" could be assigned.

*Further investigations*

As demonstrated in the present review, there are still some areas in the effects assessment of DEHP that deserve a further evaluation. It is there-

fore recommended that the following topics be considered for further investigations or research:

- Alterations or effects at biochemical level. What are the reasons for these changes? They might be a result of the physical effects of the substance as *e.g.* the sorption to surfaces of the test species. What are the consequences of these changes on the organism, the population, or the ecosystem?

- Oestrogenic effects. Some of the phthalates have been shown to exert oestrogenic effects. It should be further investigated and evaluated, whether this is also the case for DEHP. If so, what are then the ecological consequences?

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