Technical Report

No 19

An Assessment of the Occurrence and Effects of Dialkyl ortho-PHTHALATES in the Environment

May 1985

ISSN-0773-8072-19

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Brussels, May 22, 1985

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A. SUMMARY

The widespread occurrence of a number of industrially-produced esters of o-phthalic acid (henceforward referred to as phthalates) in air, environmental waters, soils, sediments and biota has caused concern about the possibility of adverse effects on species exposed to them. In this report an evaluation of the risk of such adverse effects has been made for those phthalates on which data are available, by comparing effect- or no-effect levels with measured concentrations of the phthalates in the relevant part of the environment. Most of the available information concerns di-butyl, di-2-ethylhexyl and butyl benzyl phthalates, with much less on dimethyl and diethyl phthalates and very little on the others.

A number of general problems in obtaining and assessing information on the effects and concentration of phthalates are first described - in particular the analytical difficulties due to the ubiquitous distribution of the commoner phthalates in laboratory equipment, reagents and atmospheres. This is followed by a review of the biodegradability of phthalates which shows that there are many species of bacteria in water-treatment plants, natural waters, sediments and soils capable of degrading them. Nevertheless, phthalates are found in many natural waters and sediments. This may be attributed to the fact that most of them are lipophilic and are therefore adsorbed on sediments in a reversible adsorption/desorption process such that input to the water compartment and desorption from sediments leads to an equilibrium concentration in water. The decrease in the availability of phthalates consequent on adsorption contributes to a lowering of biodegradation rates as compared to those determined in the laboratory.

The reported environmental concentrations of phthalates in fresh and estuarine/sea waters, sediments, biota and air/rainwater are then reviewed. The analytical problems mentioned above mean that if there are errors in these concentration figures they are most likely to be on the high side. The TF concludes that :

i) concentrations in fresh and estuarine/sea waters generally cover a range up to about 10 and 0.7 µg/l, respectively, although a few much higher values have been recorded;

ii) concentrations in sediments vary widely, ranging from a few µg/kg up to 10^5 µg/kg (one higher value, 1.48 x 10^6 µg/kg dry weight, was recorded by Thuren, 1983);

iii) concentrations in biota again vary widely, between 1 and 19,000 µg/kg;

iv) concentrations in air are low, with values up to 3 ng/m³ over the sea and up to 130 ng/m³ in cities - in the latter case much of the material is adsorbed on particulate matter;

v) levels in rainwater over the sea are up to 0.2 µg/l, and "wash-out" from the atmosphere may thus be an important mechanism for the transfer of phthalates to natural waters.

Except in the case of a few sediment-core samples (for which the evidence is, however, somewhat equivocal) there are insufficient data to indicate whether environmental levels are increasing with time.

A review of the acute and chronic toxicity of various phthalates to certain micro-organisms, aquatic species and plants is then presented, including information on LC_{50}s, no-effect levels, and effect levels. From the above effect and concentration data it was concluded that :

i) there is no evidence of a risk of acute effects on environmental organisms;

ii) the maximum measured environmental levels of DEHP in freshwater are similar to those at which marginal chronic effects on freshwater fish have been observed in laboratory experiments. Thus there is a slight risk that DEHP has chronic effects on freshwater fish and this is an area where the work planned in Phase II of a CMA programme (CMA, 1981) should provide valuable information;

iii) it is highly improbable that phthalates at current levels in the atmosphere present any risk to environmental species, although phytotoxic effects from DBP have been observed in closed systems such as greenhouses;

iv) there are undoubtedly elevated levels of certain phthalates in many sediments, but there is virtually no evidence as to whether this may pose a risk to species living in these sediments. Further work is recommended to clarify this;

v) the accumulation of phthalates in certain biota could give rise to a risk of adverse effects on the biota themselves or on predators

which feed on them. In both cases it is concluded, from the limited evidence available, that the risk is likely to be low.

B. INTRODUCTION AND BACKGROUND

Interest in the occurrence and effects of phthalates in the environment has arisen mainly because they have been found to be widely distributed and have been detected in air, water, sediments and a number of living organisms. Thus it has been questioned whether these widely-used, large-tonnage industrial chemicals constitute a risk to animal and plant life, and ECETOC therefore set up a Task Force to examine this topic, with Terms of Reference :

1. To make a critical assessment of the scientific literature concerning the environmental levels and effects of the major industrially-produced phthalates, and identify areas of proven or likely concern.

2. To describe, briefly, current work relevant to the above.

3. To identify any remaining areas in which further investigations would be justified by the existence of legitimate concern.

The work was limited to phthalates in the wider environment, i.e. excluding industrial sites and their immediate vicinity.

The common industrial phthalates have the general structure

(R and R' are alkyl or benzyl)

and are listed in Appendix 1 where the abbreviations used throughout this document are also given. About 2.7×10^6 tonnes/year of total phthalates are produced, of which the non-plasticiser (dimethyl and diethyl) phthalates represent a very small fraction. Of the plasticiser phthalates, DEHP accounts for well over 50% of the tonnage, the contribution of the remaining compounds ranging from about 1 to 10% each (CEFIC, 1984).

There are many extensive reviews of the environmental fate and effects of phthalates, among the most recent being :

U.S.A. - Durkin and Howard (1979), Bogyo and Howard (1980), CMA (1981), Giam et al.(1984).
Canada - Pierce et al.(1980), Dept. of Natl. Health and Welfare (1980).
Germany - Battelle (1982), Kemper and Lüpke (1983).
Japan - Tomita and Nakamura (1980), in Japanese.

The existence of these reviews makes it unnecessary to describe past work in detail. The main purpose of this report is to evaluate the risk to the environment due to the presence of phthalates and, accordingly, it has sections on : the physico-chemical properties relevant to environmental fate and toxicological effects; the degradation (mainly biodegradation) and bioaccumulation of phthalates; recorded environmental concentrations and the possible contribution of naturally-occuring phthalates to these; the evidence regarding toxicity to aquatic species; the evidence regarding exposure and effects; and the risk to animals and plants from environmental phthalates. Finally, gaps in our knowledge which are significant for risk assessment, and further work which could be considered for eliminating them, are noted.

For consistency, and ease of comparison, the following concentration units are used throughout this report :

- in air, ng/m^3 (ppt on a mass/vol basis)
- in water, µg/l (ppb on a mass/vol basis)
- in sediment, soil and biota, µg/kg (ppb on a mass/dry mass basis)

C. PHYSICAL-CHEMICAL PROPERTIES

1. Physical Properties

The main physical properties which are important in considering the environmental fate and effects of phthalates are water solubility, vapour pressure and partition coefficient (between octanol-water or soil-water). Values of water solubility are given in Table 1. Various figures for vapour pressures and partition coefficients were found in the literature and some typical, indicative values are given in Table 2.

It is only in recent years that the difficulties in determining the water-solubility of phthalates seem to have been overcome, in that for some

of the most common compounds a number of values in reasonable agreement have been reported - see Table 1. The value for DEHP is, however, still uncertain, there being two groups of reported solubilities at around 340 and 45 µg/l. This discrepancy may be due to the readiness with which DEHP forms colloidal solutions (Klöpffer et al.,1982). These authors prepared "solutions" containing 500 µg/l but decided that they were colloidal, and believed that the "true solubility in water" is 50 µg/l.

In the CMA (1983) report comment is made on the surprisingly high values for the water solubility of DIDP and DUP, and it is possible that this may again be due to the formation of colloidal solutions.

TABLE 1

Phthalate	Temp. °C	Water-solubility ug/l	Reference
DMP	20	5.0×10^6	Fishbein and Albro (1972)
	-	4.32×10^6	Wolfe et al.(1979)
	20	4.29×10^6	Leyder and Boulanger (1983)
	-	4.0×10^6	Peakall (1975)
	25	4.0×10^6	CMA (1983)
DEP	25	1.08×10^6	CMA (1983)
	20	1.0×10^6	Fishbein and Albro (1972)
	-	1.0×10^6	Peakall (1975)
	20	0.928×10^6	Leyder and Boulanger (1983)
	-	0.896×10^6	Wolfe et al.(1979)
DBP	25	(4.5×10^6)	Fishbein and Albro (1972)
	-	13×10^3	Wolfe and al.(1979)
	25	11×10^3	CMA (1983)
	20	10×10^3	Leyder and Boulanger (1983)
DIBP	20	(1×10^5)	Fishbein et Albro (1972)
	20	2×10^4	Leyder and Boulanger (1983)
	-	6×10^3	Hollifield (1979)
DEHP	20	(1×10^5)	Fishbein and Albro (1972)
	-	1.3×10^3	Hirzy et al.(1979)
	-	0.6×10^3	Branson (1980)
	20	0.4×10^3	Wolfe et al.(1979)
	25	0.34×10^3	CMA (1983)
	-	0.28×10^3	Hollifield (1979)
	-	0.041×10^3	Leyder and Boulanger (1983)
	15	0.0476×10^3	OECD (1979)
	25	0.0466×10^3	OECD (1979)
BBP	-	2.9×10^3	Hirzy et al.(1979)
	20	2.82×10^3	Leyder and Boulanger (1983)
	25	2.69×10^3	CMA (1983)
	-	0.71×10^3	Hollifield et al.(1979)
DNOP	25	0.9×10^3	CMA (1983)
DIOP	25	0.09×10^3	CMA (1983)
DNP	25	below 1×10^3	CMA (1983)
DINP	25	0.2×10^3	CMA (1983)
Di-n-decyl	25	0.9×10^3	CMA (1983)
	-	0.33×10^3	Hollifield et al.(1979)
DIDP	25	1.19×10^3	CMA (1983)
	-	0.28×10^3	Hollifield (1979)
DUP	25	1.11×10^3	CMA (1983)

The present authors believe that values in ( ) are wrong in the light of the later figures quoted.

TABLE 2

Phthalate	Mol.wt.	Vapour press. mm Hg (°C)	Reference	Log. partition coeff.(Pow)	Reference
DMP	194	0.01(20)	Fishbein and Albro (1972)	1.53	Leyder and Boulanger (1983)
DEP	222	0.05(70)	Fishbein and Albro (1972)	2.35	Leyder and Boulanger (1983)
DBP	278	3.5×10^{-5}(25)	Frissell (1956)	4.57	Leyder and Boulanger (1983)
DIBP	278	-		4.11	Leyder and Boulanger (1983)
DEHP	391	3.4×10^{-7}(25)	Frissell (1956)	4.88	Battelle (1982)
BBP	312	-		4.91	Leyder and Boulanger (1983)
DHP	334	1.8×10^{-6}(25)	Frissell (1956)	-	
DNP	419	1(205)	Kemper and Lüpke (1983,p.22)	-	
DIDP	447	3.5×10^{-9}(20)	Kemper and Lüpke (1983,p.23)	-	

2. Chemical Properties

Hydrolysis and phototransformation may influence the environmental fate of phthalates. Evidence on the rates of hydrolysis of phthalates indicates that they are much lower than rates of biodegradation. Wolfe et al.(1980) found half-lives of 4 months for DMP and over 100 years for DEHP, at pH 8 and 30°C. These rates are too low to effect concentrations in the aquatic environment significantly.

There appears to be little information on the photodegradability of phthalates either in air or water. Gledhill et al.(1980) quoted a personal communication indicating that the photolysis of BBP was slow. On the other hand, recent information (Fraunhofer Gessellschaft, 1984) indicates that the atmospheric photodegradation of DEHP is rapid, with a half-life of less than one day.

3. Physical Properties and Environmental Distribution

The release of phthalates to the environment may, in principle, occur during their production and distribution, during the processes by which they are incorporated into a finished article, or by loss from the finished article during its use or following its final disposal. Such release will be either to the air or water, with the subsequent possibility of exchange between water and air, air and water, water and soil/sediment, and water and biota. In this section a qualitative appreciation of the likely significance of these various processes in terms of the environmental distribution of the higher phthalates is given.

3.1. Environmental input

a) Losses during production and distribution. The low water-solubility of plasticiser phthalates and the controlled nature of modern production processes make it unlikely that any significant loss of phthalate to the environment occurs during production, either in aqueous effluents or to the atmosphere, although the older production methods involving sulphuric acid catalysis could result in losses to the aqueous environment of the order of 1% of production.

During distribution, losses may occur during the cleaning of drums and tanks or, exceptionally, by accidental spillage. Estimates of losses to the aquatic environment from drum and tank cleaning (Berndtsson, 1982)

are of the order of 0.05% of production, of which at least part will be to waste-waters receiving biological treatment.

b) Losses during the manufacture of plasticised products. Melt-forming processes are used during the manufacture of plasticised products and thus loss of plasticiser to the atmosphere is likely. However, the extent to which such losses occur depends on the precise nature of the manufacturing process and on the atmospheric purification equipment used by the processor. Emmission estimates range from approximately 2.0% for coating processes to 0.03% for injection moulding, with an overall loss to atmosphere of approximately 0.8% (Berndtsson, 1982).

c) Losses from the plasticised product during use. Although these rates of loss must be low for the plasticisers to be of any use, nonetheless it is apparent from the gradual hardening of plasticised articles that loss does occur. The rate of such loss will depend on the thickness of the article, the temperature, and the nature of the plasticiser. Quackenboss (1953) gives data for the estimated time for 10% loss of plasticiser from a thin (0.01 cm) PVC film. At 20°C the estimated time for dibutyl phthalate is 0.66 years whereas for di-2-ethylhexyl phthalate it is 58 years. Williams and Gerrard (1983) examined the fate of phthalate esters in plasticised PVC during photodegradation. They concluded that some of the phthalate is degraded to lower molecular weight material while some undergoes chemical combination with the polymer chain. Berndtsson (1982) estimated that losses to the atmosphere during use are of the order of 0.35% of annual consumption, except for paint where losses of plasticiser (predominantly DBP) are likely to be about 15% of consumption.

Losses to water, e.g. from plasticised pipes, also occurs, and Graham (1975) described some of the factors, such as water solubility of the plasticiser and its compatibility with the polymer medium, which influence this. From the data of Quackenboss (1953) he calculated that the loss of various plasticisers from PVC discs under standard conditions varied from 0.26% in 24 hr for DBP to 0.01% for DUP. Katase (1972) also showed that DBP is eluted into water in significant amounts from PVC tubing. Berndtsson (1982), using in part the Quackenboss (1953) data, calculated a maximum loss of phthalates to water of 0.15% of the annual consumption in Sweden.

d) Loss from plasticised products after disposal. Most discarded plasticised products are disposed of either by incineration or by dumping in a tip/landfill area. Incineration probably accounts for approximately 30% of the disposal of household waste, and where, as is more usual, this is carried out in a high-temperature incinerator, virtually complete combustion of the phthalate plasticiser is expected. Where incineration is uncontrolled and combustion temperatures are lower, a considerable proportion (say 25%) may be lost to the atmosphere.

After dumping in a tip or landfill, the phthalate plasticiser will be slowly leached from the article and depending on whether it is degraded or absorbed by the soil it could in principle reach the aquatic environment via the tip leachate. However, the low water-solubility of plasticiser phthalates (except DBP) makes it unlikely that major amounts will enter the environment by this route, although Kotzias et al.(1975) have recorded up to 100 µg/l of "di-iso-octyl phthalate" (possibly DEHP) in leachates from 3 Dutch waste tips. Plasticised articles dumped in an uncontrolled manner (litter) seem likely to lose a higher proportion of their plasticisers to the atmosphere, although leaching to surface waters and adsorption by soil may still occur.

It is concluded that most of the phthalate entering the environment is likely to do so by volatilisation to the atmosphere, with only a minor part (perhaps 10%) entering the aquatic environment directly. CEFIC (1984) estimated that world production of phthalate esters was about 2.7×10^6 tonnes, of which the higher, less volatile and very sparingly soluble phthalates probably comprise over 90%. The percentage of these higher phthalates lost to the environment at large is extremely difficult to quantify. However, a yearly emission from production, processing and distribution of around 2.5% of consumption (based on Berndtsson 1982, Swedish data) can be assumed, the remainder being either burnt (say 30%) or largely immobilised in land-fill tips. The lower phthalates, of which DBP is the major material, are both more water-soluble and more volatile and it seems possible that a higher proportion of these escapes to the environment (see also Russell, 1983).

3.2. Environmental distribution

a) Air-water interchange. The above arguments suggest that most phthalates enter the environment via the air, in which case they must reach the aquatic phase by "washing out" via rain. The reverse phenomenon of volatilisation from natural waters to the atmosphere, and the vapour pressure and water-solubility, will determine this behaviour.

Klöpffer (1982), by extrapolating laboratory data on the volatilisation of DEHP from water under defined conditions, obtained a half-life in water of 146 days, although on theoretical grounds a value of only 25 days was calculated. Atlas et al. (1983) reported a value of around $1x10^{-4}$ for the partition coefficient of DBP between air and water, ie. virtually all of the DBP is in the water phase at equilibrium.

b) Soil-water interchange. The plasticiser phthalates all have a high octanol/water partition coefficient, and thus the equilibrium between water and an organic-rich soil or sediment will be very much in favour of the soil or sediment. It is also probable that the presence of the benzene ring and carbonyl group in the phthalate molecules will promote van de Waals type bonds with natural soil minerals, and this, together with the low solubility of the higher phthalates, will again favour the soil or sediment at equilibrium. Thus it is expected that the concentration of phthalate in soils and sediments will be very much higher than that in the body of water with which they are in equilibrium. As shown in Section G, this prediction is confirmed by the actual measurements of phthalate levels in waters and sediments although, as indicated in Section D, the solubilising effects of natural humic and fulvic acids may enhance the levels in waters.

c) Water-biota interchange. Phthalates have high octanol/water partition coefficients - see Table 2. This means that biota living in phthalate - containing water are expected to have a higher phthalate level than does the water itself. However, as pointed out in chapter F, higher organisms can metabolise phthalates, and thus the concentrations found in biota may be lower than expected on the basis of partition coefficients.

D. SOME GENERAL PROBLEMS IN OBTAINING AND ASSESSING DATA

There are substantial difficulties in the analyses required to determine the water-solubility and environmental concentrations of phthalates, and in the preparation of phthalate solutions of a given concentration for laboratory studies. These difficulties are of such general importance that this section is devoted to them.

A major problem in analysing for phthalates is that they occur ubiquitously in laboratory equipment, reagents and atmospheres (see review by Mathur, 1974, and actual measurements on laboratory water, reagents, solvents and equipment by Ishida et al.,1980 and Katase, 1972). Interference from chlorinated hydrocarbons such as DDT and PCBs has also caused analytical difficulties. For an account of how these difficulties have been overcome the reader is referred to papers by Giam (1976), Pierce et al.(1980), Howard (1981), and in particular a thesis by Chan (1975). More recently, Michael et al. (1984) have given a detailed account of the very rigorous precautions necessary to obtain accurate and credible analyses in surface waters and sediments.

Environmental "concentrations" may be enhanced by certain dissolved organic substances, eg. fulvic/humic acids in natural waters, which solubilise these essentially lipid-soluble materials (Ogner and Schnitzer, 1970; Kahn and Schnitzer, 1971; Matsuda and Schnitzer, 1971). It is, however, uncertain whether phthalates which are solubilised in this way are detectable by analysis of the water (Carlberg and Martinsen, 1982), and indeed whether they are bioavailable.

In most laboratory studies of the bioaccumulation and toxic effects of phthalates, the phthalate was administered in water. Standard solutions of very low (µg/l) concentrations are difficult to make up and very often the desired concentrations were obtained by adding to the water a solution of the phthalate in an organic solvent. Results have often been reported at concentrations which are higher than the apparent solubility of the phthalate in water (see Table 1). Insofar as phthalates may be solubilised in natural water (see above), such laboratory solubilisation may be acceptable provided that the phthalate has not separated out as an undissolved phase. Klöpffer (1982) has also noted the tendency of DEHP to form "colloidal solutions" of concentrations above the true solubility, these "colloidal solutions" giving reproducible analytical results on separate samples (see section C.1, above).

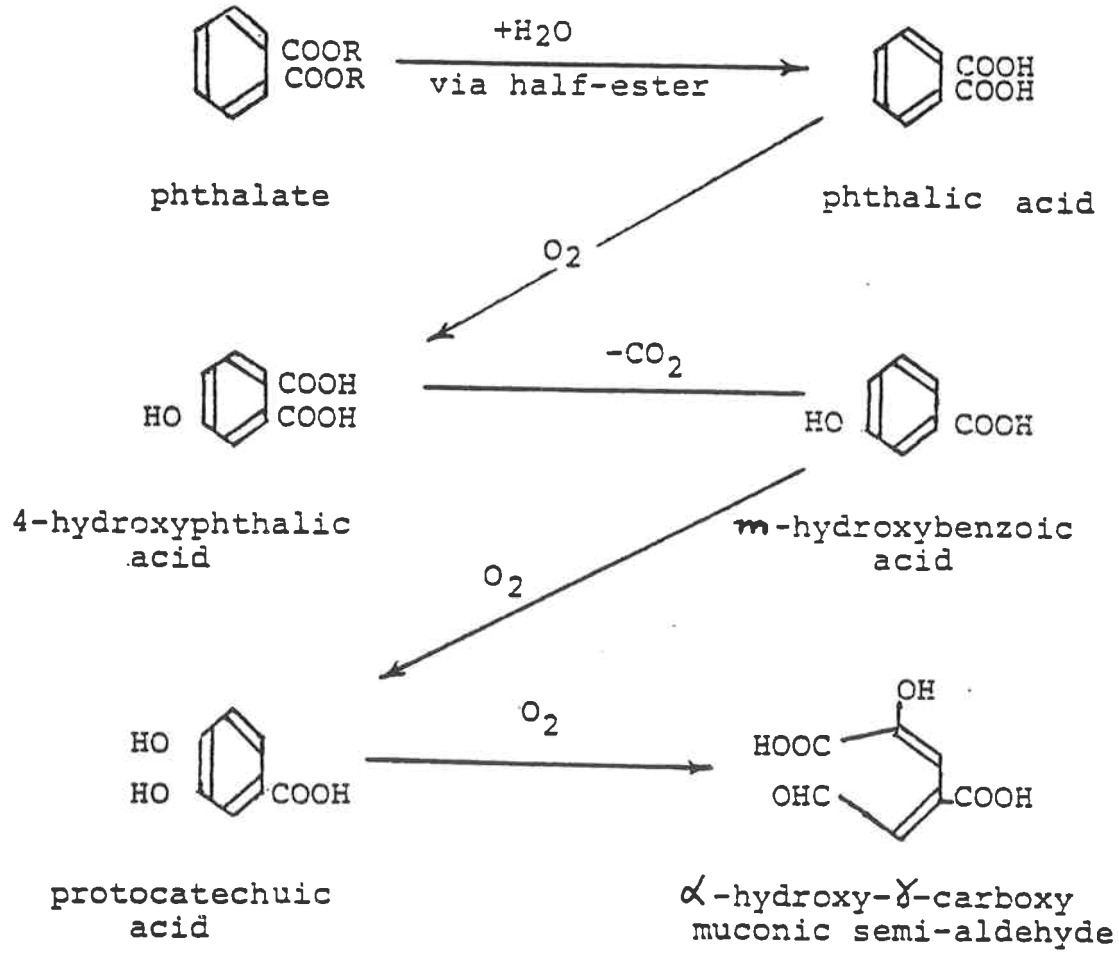
It is not known whether such "colloidal solutions" give rise to toxic effects, or apparent bioaccumulation through sorption onto the surface of biota, blocking of fine gills, etc., which may not be produced by true solutions. Brown and Thompson (1982-b) found a flotation effect on Daphnia magna which they attributed to the fact that the phthalates tested (DEHP and DIDP) were present at above their solubility limit. Södergren (1982) attempted to prepare a solution containing 1470 µg/l of DEHP in a sediment-water ecosystem by adding a concentrated solution of DEHP in acetone to the water. Given the low water solubility of DEHP (see Section C) it is not surprising that he found substantial amounts of the added phthalate on the test vessel walls, in the sediment, and in the surface layer. Södergren also reported that of the test animals in his ecosystem, those which lived in or close to the interfaces showed higher accumulation factors than those living in the bulk solution. As the author notes, this is not surprising since the accumulation factors were based on the very low (approximately 1 µg/l) levels of DEHP found in solution in the water at the end of this experiment, but it does call into question the validity of the very high accumulation factors calculated in his paper.

To summarise : almost any phthalate analysis carried out before the work of Atlas, Chan, etc. in 1975-6 could be in error on the high side. The same could be true of later analyses performed without due precautions.

E. BIODEGRADATION

1. Biodegradation Pathways

Saeger and Tucker (1976) showed that the first stage in the biodegradation of phthalates leads to the half-ester, and the second to phthalic acid. Cleavage of the ester group is slower for longer-chain than for shorter-chain phthalates (see also Keyser et al., 1976; and Engelhardt et al.,1975, 1977 and 1978). One of the possible degradation pathways was elucidated by Nakazawa and Hayashi (1978) who found that degradation by Pseudomonas testosteroni produced the following metabolites :



Other species of bacteria metabolise phthalates via 3,4- or 4,5-dihydroxy-phthalate. The subsequent degradation to the products of complete mineralisation, i.e. CO_2 and H_2O, may proceed via pyruvate or succinate (Eaton and Ribbons, 1982 and Tomita and Nakamura, 1980).

A review of the biodegradation pathways of phthalates has recently appeared (Ribbons et al.,1984), and the reader is referred to it for further details.

2. Micro-organisms

Many species of bacteria, widespread in soils, fresh and salt water, and sediments, have the potential to biodegrade phthalates as shown for example by Sakagami et al.(1982a and b), Engelhardt and Wallnöfer (1978) and Kurane

et al. (1977a, 1977b, 1978, 1979a, 1979b). Forty-four species of bacteria capable of degrading DBP were isolated by Ohta and Nakamoto (1979) from soil samples. Taylor et al. (1981) isolated 56 bacterial cultures capable of degrading 7 phthalates, from river water and sediments in the fresh- and salt-water regions of the Mississippi Delta. Eaton and Ribbons (1982) isolated, from compost, 6 bacterial species of the genus Micrococcus which were capable of degrading a variety of phthalates. The fact that the biodegradation pathways differ according to the genus shows that each genus has a specific genetic potential for the process.

The above findings explain why several authors, using a variety of different micro-organisms, have reported very differing degrees of biodegradation for phthalates - see below.

3. Biodegradability

In this section only post-1974 literature, which contains original data, has been cited. The coverage is not fully comprehensive but it is believed to represent the problem adequately. There is ample laboratory evidence to show that phthalates will completely biodegrade and that, on balance, the rate falls as the alkyl-chain length increases.

3.1. In water and sludges under aerobic conditions. The biodegradability of phthalates at high dilutions, e.g. in river- or sea-water, or in the river-die-away-test, was studied, among others, by Hattori et al.(1975), Kodama and Yoshiharu (1974), Perez et al.(1981), Saeger and Tucker (1976), Tabak et al.(1981) and Wylie et al.(1982). Overall, it appears that phthalates with short alkyl chains, e.g. DMP, DEP, DBP, DIBP, BBP and MBP, undergo rapid degradation which is substantially complete (>90 %) in a few days. Longer-chain phthalates, e.g. DEHP, DOP and DUP, are often only 40-90% degraded after 10-35 days.

Perez et al.(1981) found that the rate of biodegradation of DEHP in a marine microcosm varied with temperature. At 1°C, degradation rates decreased to 50% or less of those at 18°C. Wylie et al. (1982) reported a similar variation with temperature in river water.

Other authors have reported on the biodegradability at higher concentrations of phthalates and/or inoculum in static tests, fill-and-draw tests

(e.g. the SCAS test), or in treatment plants : see papers from Convery et al.(1980), Hollis (1980), Kurane et al.(1977-b, 1979-a), Patterson and Kodukala (1981), Saeger and Tucker (1976), Urushigawa and Yonezawa (1979), Woock (1979) and Petrasek et al.(1983). Under these conditions all phthalates are nearly completely biodegraded, and, again, the esters with shorter alkyl-chains degraded faster than did the long-chain compounds, the extent of degradation being normally greater than 50%.

The most recently-available biodegradability studies (Sugatt et al., 1984) showed that in the acclimatised "shake-flask" (CO_2-evolution) method, 12 phthalates (DMP, DEP, DBP, di-hexyl phthalate, butyl 2-ethylhexyl phthalate, DL610P, DEHP, DIOP, DINP, DL711P, DIDP and diundecyl phthalate) underwent >90% primary, and >55% ultimate, biodegradation. The corresponding figures for BBP were 78% primary and 42.5% ultimate degradation. The half-life for the ultimate biodegradation of all of the above phthalates was less than 28 days.

The primary degradation products, i.e. the half-esters, alcohols and phthalic acid, and the later metabolites, are more soluble in water and more rapidly metabolised than are the parent esters.

3.2. In sediments and/or under anaerobic conditions. Because phthalates are lipophilic they can be readily adsorbed by sediments, or may bioaccumulate in micro-organisms which on dying are incorporated into sediments. Thus knowledge of the degradability of phthalates in sediments is of importance, but rather contradictory information about this is found in the literature.

Johnson and Lulves (1975) followed the biodegradation of DBP and DEHP in hydrosoil samples collected from the shoreline of ponds. Under aerobic conditions, DBP was 97% degraded in 5 days, and DEHP 41% in 30 days. Under anaerobic conditions DEHP did not degrade and DBP degraded somewhat slowly, i.e. 98% in 30 days. Fish et al.(1977) found that after 28 days at 20°C, labelled DEHP in lake sediment samples under aerobic conditions yielded 20% of its ^{14}C as $^{14}CO_2$, having undergone ring cleavage. At temperatures below 20°C no significant degradation occured. In this connection the work of Peterson and Freeman (1982) is interesting. They determined the DEHP content of anaerobic sediment cores taken at successively deeper levels in Chesapeake Bay, Baltimore. The content of DEHP and other phthalates correlated with their production volume in the period corresponding to the

cores. Thus, under the anaerobic conditions in the sediment the degradation of phthalates was very slow. The highest DEHP concentration, 0.18 ppm, occured in the topmost sediment layer. Gledhill et al.(1980) found that BBP in a lake sediment had a half-life of between 2 and 4 days. Schwartz et al.(1979) detected no sign of degradation of DEHP after 14 days in sediment samples from Dutch rivers, but work by Leutzel (1984) showed that it has a half-life in soil of between 31 and 98 days.

Johnson et al.(1984) examined the influence of environmental factors on the biodegradation of several phthalates in water-containing sediments from the Little Dixie Lake in Missouri. Under aerobic and anaerobic conditions the rate of biodegradation was inversely related to the chain-length and degree of branching of the diester alkyl group. At concentrations of about 10^4 µg/l the phthalates disappeared faster than at concentrations in the range 18-100 µg/l. At low temperatures degradation was retarded but not suppressed. The pre-exposure of the sediments to DBP, DEHP, DIOP and DINP produced no detectable adaptation. The authors concluded that the phthalates tested degraded optimally at concentrations near their solubility limit and at temperatures above 22°C, in nutrient-rich aquatic systems such as those in sewage treatment plants, eutrophic lakes and streams in summer. They might be expected to accumulate in sediments during winter.

Steen et al.(1980) found that DNP was degraded more slowly in a sediment-water system as the ratio of sediment to water increased, and they concluded that the adsorption of DNP on suspended sediment rendered it unavailable for degradation.

Laboratory work by Shelton et al.(1984) indicated that DMP, DEP, DNBP and BBP should be mineralised at a significant rate in municipal-sludge, anaerobic digesters, but that DNOP and DEHP would not.

Finally, two papers deal with degradation in the presence of nitrate. Benckiser and Ottow (1982) studied the degradation of DBP under anaerobic conditions and in the presence of nitrate as the only electron acceptor. The sole reaction products were the mono-ester and phthalic acid, and no mineralisation occured. Degradation was slow at low temperatures. By contrast, Aftring et al.(1981) found that under anaerobic conditions and in

the presence of nitrate at 30°C, phthalic acid was rapidly mineralised by mixed bacterial cultures isolated from sediments.

3.3. Summary. A wide range of organisms in nature, including many bacterial species in soil, river- and sea-water, sediments and water-treatment plants have been shown to be capable of biodegrading phthalates. The results of aerobic laboratory tests and studies in treatment plants lead to the conclusion that phthalates are nearly completely biodegradable.

Phthalates with longer alkyl chains seem to biodegrade more slowly than do those with shorter chains. As is usual in biological processes, a decrease in temperature causes a marked decrease in degradation rate, which becomes slow at below about 5°C. It has been demonstrated that phthalates are also biodegradable under anaerobic conditions, albeit at lower rates. The influence of temperature in anaerobic environments may be even more important than in aerobic conditions.

Despite their proven biodegradability, the phthalate esters are found to be widespread in rivers and seas, albeit at very low concentrations (see section G.2.1). This leads to the speculation that there is a balance between continuous input to the aquatic environment (see section C.3.1) and elimination, and/or that the biodegradation observed in the laboratory proceeds much more slowly in the environment. Elimination from natural waters could be by biodegradation, photodegradation, volatilisation or adsorption onto sediments. In the Task Force's opinion, adsorption onto sediments could be a significant route for removing phthalates from natural waters (and indeed concentrations of phthalates in sediments are markedly higher than those in the water above the sediment-strata) and their re-mobilisation could then contribute to the measured levels.

F. BIOACCUMULATION AND METABOLISM

Phthalates will bioaccumulate to a level which depends on their fat-water partitioning behaviour as indicated by the octanol-water partition coefficient, Pow, and by any metabolism of the phthalate occurring in the organism in question (see eg., Geyer et al., 1981 and 1982; and Veith et al.,1980). The Pow of plasticiser phthalates exceeds 1000 (log Pow > 3, see Table 2 on p.8).

Information on the metabolism of phthalates in aquatic organisms has often been obtained as part of accumulation studies in which the exposed species is shown to accumulate phthalate up to a plateau level and/or to lose accumulated phthalate when maintained in clean water. Melancon (1979) has reviewed the metabolism of phthalates in aquatic species. This present review is primarily concerned with reported bioconcentration factors (BCF). (Note: BCF is defined as the ratio of concentration in the animal, on a dry weight basis, to the concentration in water; this term is used in this review even where some other term was used to define the same factor in the original literature).

Wofford et al.(1981) reported that DMP, DBP and DEHP had BCFs in the range 3-42 for oysters, shrimps and sheepshead minnow (Cyprinodon variegatus) after a 24-hour exposure. Although the exposure period is too short to indicate the likely value at equilibrium, the results did show that the extent of bioconcentration did not vary significantly among the three species. After 24 hours the test organisms were analysed for both metabolites and phthalate, and the ratio of metabolites to unchanged phthalate (defined as "biodegradative index") was determined. The results showed the oysters to have the lowest biodegradative index (0.41). The shrimp (8.6) and the fish (11.8) had considerably higher values.

Metcalf et al.(1973) exposed algae, snails, mosquitoes and fish to ^{14}C-labelled DEHP in a model ecosystem by applying it to Sorghum plants and measuring the concentrations of DEHP and various metabolites in water and the various organisms after 33 days. Auto-radiographic analysis showed that algae and mosquito larvae did not appreciably metabolise DEHP, but that snails and fish metabolised it to the mono-ester, phthalic acid and anhydride, and a variety of polar products and conjugates. From the very low level of DEHP found in the water at the end of the experiment (0.34 µg/l) the authors calculated very large accumulation factors for algae (53,900), snails (21,500) and mosquito larvae (107,700), but as already commented in regard to the data of Södergren (see Section D) the validity of this method of calculation in a heterophase system is questionable. Thus Metcalfe et al. suggest that on their evidence DEHP resembles DDT in its rate of uptake, storage and biomagnification (food chain accumulation), but this is contradicted by the results of Macek et al.(1979) who studied a number of chemicals in the food chain: Daphnids to bluegill sunfish, Lepomis macrochirus. They found BCFs of 518 and 112 for DEHP in the above two species, respectively, and noted specifically that it did not accumulate via an aquatic food chain. Indeed, Metcalf et al.'s own data tend to support this evidence for a lack of accumulation, in that the fish in their ecosystem, on the

same calculation basis as for the algae etc., gave an accumulation factor of only 130 times, i.e. a body burden some 830 times less than that of the mosquito larvae.

Sanborn et al.(1975) used ^{14}C-labelled DNOP in studying an ecosystem similar to that of Metcalf et al.. The concentration in the water at the end of the 33-day experiment was 0.064 µg/l, and accumulation factors as calculated by Metcalf's procedure were 28,500 for algae, 2,600 for Daphnia, 9,400 for fish and mosquito larvae, and 13,600 for snails. Sanborn also compared the accumulation factors for fish from 3-day and 33-day experiments in the ecosystem. He concluded that the high ratio of the 33-day to the 3-day factor (ie. 8,100) is evidence for the accumulation and persistence of DNOP. However, a comparison of the absolute amounts of DNOP and metabolic products from these two experiments shows that the quantities present in the fish were virtually identical. Furthermore, Sanborn's own evidence shows that the DNOP was extensively metabolised in the the fish such that only 4.4% of the original ^{14}C remained as intact DNOP. In the Task Forces' opinion this reinforces the view that it is misleading to base the calculation of accumulation factors on the residual quantity of a substance present in the water at the end of such an experiment.

Mayer and Sanders (1973) have given depuration rates in clean water for the loss of accumulated ^{14}C-labelled phthalate from various organisms. For example, Daphnia which had been exposed to 100 µg/l (as C-14 activity) lost half this activity in 3 days. Fathead minnows, Pimphales promelas, exposed to 1.9 µg/l of DEHP reached an equilibrium body load at 28 days corresponding to an accumulation factor of 1,380 as ^{14}C activity. After transference to clean water, the fish lost half this activity in 7 days.

Brown and Thompson (1982a), using ^{14}C-labelled phthalates, found that after 21 days exposure, Daphnia magna had bioconcentration factors of 209 for DEHP and 116 for DIDP. The same authors (1982b) exposed mussels (Mytilus edulis) to DEHP and DIDP for 28 days, and recorded bioconcentration factors of 2,500 and 3,500, respectively. The depuration half-life for the mussels in clean water was about 3.5 days for both phthalates.

Mehrle and Mayer (1976) hatched rainbow trout (Salmo gardineri) eggs in the presence of ^{14}C-labelled DEHP and analysed the ^{14}C residues in the fry after 24 days of continuous exposure. The overall bioaconcentration factor varied from 42 to 113, depending on the exposure concentration. The ^{14}C activity was approximately 50 % as conjugate metabolites, 20 % unchanged DEHP, 20 %

mono-ester and 10 % phthalic acid. The same authors exposed 7-month old fathead minnows, Pimphales promelas, to concentrations of DEHP between 1.9 and 62 ug/l for 56 days. The bioaccumulation factors varied between 856 at the lowest exposure level and 155 at the highest which, the authors suggested, may indicate an increase in DEHP degradation and elimination due to the induction of detoxifying enzymes in the liver.

Streufert (1977) examined the uptake of ^{14}C-labelled DEHP by midge larvae and found a plateau concentration of ^{14}C corresponding to a bioaccumulation factor of 450. On depuration, a ^{14}C half-life of about 5 days was found.

Austerberry et al. (1979) found that brine shrimp (Artemia salina) larvae rapidly accumulate DBP and that the subsequent onset of death is accompanied by in vivo hydrolysis of the DBP to the mono-ester. However, they ruled out the mono-ester and n-butanol as the toxic agents.

A potentially useful in vitro technique for studying the likely metabolic rates of phthalates has been described by Johnson et al. (1977). They used a system containing a liver extract from channel catfish, Ictalurus punctatus, and found that DBP was degraded/metabolised 16 times faster than was DEHP. Similar studies on the metabolism of DEHP by liver extracts from rainbow trout, Salmo gardineri, have been reported by Melancon and Lech (1976).

To summarise : most of the work on the bioaccumulation and metabolism of phthalates has been done on DBP and DEHP, and indicates that they will accumulate in aquatic organisms, although the degree of accumulation is species-dependent. For fish, the evidence indicates that the accumulation occurs predominantly from the water rather than via the food-chain. Bioconcentration factors can be high, but their magnitude depends on whether the criterion for accumulation is the content of phthalate itself or the ^{14}C-content arising from a labelled material. The factors also depend on the experimental design in that some authors used a static method and based their calculations on the residual concentration of phthalate in the water. The Task Force does not believe that this method of calculation is valid - see comments in the text. In most flow-through studies a plateau level was reached suggesting that many organisms are able to metabolise phthalates, as is confirmed by a rather rapid loss of ^{14}C during depuration.

G. ENVIRONMENTAL CONCENTRATIONS

For consistency, and ease of comparison, the following concentration units are used throughout this report :

- in air, ng/m³ (ppt on a mass/vol basis)
- in water, µg/l (ppb on a mass/vol basis)
- in sediment, soil and biota, µg/kg (ppb on a mass/dry mass basis)

This necessitated the conversion of some of the reported values from ppm, ppb, etc. into the above units on the assumption that the original values were, indeed, on a mass/vol basis for water and a mass/dry mass basis for sediment, soil and biota.

It is not intended to make an exhaustive compilation of all of the literature data on environmental concentrations, but to refer to the major reviews and papers which give typical results. Much of the data can be found in publications by Giam, Chan, Howard, and Pierce mentioned below, and in reports from the Commission of the European Communities (1976 and 1979).

Because it has been questioned whether the recorded environmental phthalates are really of industrial origin or could arise partly from natural sources, the natural occurrence of phthalates is discussed in the next section before reviewing the actual concentrations found.

1. Naturally-occurring Phthalates.

There have been many reports that phthalates or phthalic acid occur naturally in plant or animal tissues, but their reliability must always be questioned because of possible artefacts arising either during the analytical procedure or from prior contamination of the organisms by contact with synthetic phthalates. Mathur (1974) critically reviewed this problem and the problem of contamination during the isolation and analysis of samples. He concluded that "the possibility of the phthalic acid esters found in biological and geochemical samples being of biosynthetic origin cannot be ruled out". Peakall (1975) was of the opinion that most phthalates detected in living tissues originated from contact with contaminated water, or the ingestion of contaminated food or plants.

The Mathur (1974) and Peakall (1975) papers mention many organisms in which various phthalates or phthalic acid have been found. The detection of phthalic acid in Azobacter chroococcum by Aso et al. (1932), and in Papaver somniferum by Schmid and Karrer (1945), and of "phthalates" in dry tobacco (Nicotiana tabacum) leaf by Swain et al. (1961) seem to be well authenticated. Hyashi et al.(1967) found several phthalates, including DMP and DEHP, in the leaves of the plant Japonica in Japan.

Since the reviews by Mathur and Peakall, a number of other cases have been reported for which the experimental methods and precautions strongly suggest, or prove, that artefacts were excluded. Manandhar et al. (1979) isolated di-(2-n-propyl)-pentyl phthalate from Cryptocarya amygdalina ; Paré et al (1981) found as much as 0.2-0.7% dry weight (of the whole plant) of n-butyl-4-ol n-propyl phthalate in a common house plant, Sansevierea trifaciata ; and Jones et al.(1973) detected 1750 µg/kg of DBP in the cockroach Periplaneta americana, reared under conditions which, according to the authors, excluded contamination.

Ehrhardt and Derenbach (1980) identified the mixed ester, n-butyl iso-butyl phthalate, in water from the Kiel Bight in Germany and suggested that it was of natural origin since it is not a manufactured product. Peterson and Freeman (1982) have suggested that some of the phthalates found in older samples of sediment cores from Chesapeake Bay, corresponding to the period 1924-1979, may have been of natural origin.

Philips and Breger (1958) reported the isolation of a di-octyl phthalate representing 0.15% of a crude oil. Subsequent analysis of the same crude oil (Pugh, 1984) by GC and MS techniques showed that only about 10^{-3}µg/l of DBP and DEHP were present.

From the above evidence the Task Force concludes that although our knowledge of naturally-produced phthalates is limited or uncertain, and the significance of their contribution to environmental levels cannot be determined at present, it seems unlikely that this contribution is of significance except, possibly, in very localised areas where there are dense populations of phthalate-producing organisms.

2. Recorded Environmental Concentrations.

There are many publications in which the concentrations of phthalates in various parts of the environment are recorded. Those which do not take account of the sources of analytical error described in chapter D may be inaccurate, and are likely to be conservative, ie. on the high side.

2.1. In waters

2.1.1. Fresh water. Most data are on DBP, DEHP and BBP, the reported concentrations of which cover an extremely wide range depending on the source and location of the sample, and possibly on the analytical procedure.

a) DBP. Concentrations of DBP in fresh water range from non-detectable (ND), through fractions of a µg/l, eg. as in Lake Huron (Stalling, 1973), up to 350 µg/l in a Japanese river (Katase, 1972). Much lower values, from 0.16-3.06 µg/l, were recorded by Goto (1979) in Japanese rivers. He also found rather similar values, 0.12-8.6 µg/l, in rainwater. Kodoma et al. (1975) found levels of DBP ranging from ND to 4.4 µg/l in other Japanese rivers. In industrialised US water basins, Ewing et al. (1977) recorded 1-10 µg/l of DBP, with outlying values of 14, 20 and 60. Van Vliet et al.(1979) found less than 0.05 µg/l in the Rhine.

b) DEHP. Recorded levels of DEHP are generally similar to those of DBP. Goto (1979) reported a range of 0.1-2.19 µg/l in Japanese rivers and 0.65-3.16 µg/l in rainwater. Ewing et al. (1977) found DEHP concentrations of between 1 and 85 µg/l (one outlying value at 2,347) in industrialised US water basins. Van Vliet et al. (1979) reported finding 0.2 µg/l in the Rhine, and Stalling (1973) reported 5 µg/l in Lake Huron and the Mississippi river, and 300 µg/l in Lake Superior. Weber and Ernst (1983) found DEHP concentrations of between 0.02 and 0.5 µg/l in 3 German estuaries.

Kotzias et al. (1975) analysed surface waters from a Dutch waste tip and found 5,000-12,000 µg/l of DBP but only traces of DEHP. The detection limit was probably a few µg/l.

c) BBP. Michael et al. (1984), who used a very rigorously-controlled technique of sampling, analysis and statistical examination, determined the concentrations of BBP in 31 rivers, estuaries or lakes

in the USA during 1980-1982. They found concentrations of between 0.3 and 0.9 µg/l at 3 locations, the amounts being "not detectable" (limit of detection 0.3 µg/l in 1982) at the remaining sites.

d) van de Meent (1982) measured monthly values of the total phthalates concentration in 5 Dutch surface waters during 1978. The values lay consistently between 2 and 11 µg/l. All sampling and analytical equipment was free of phthalates, and none were present in the blanks.

e) It is concluded that, in general, the concentrations of DBP, BBP and DEHP in freshwaters lie between fractions of a µg/l and 10 µg/l, with isolated examples at much higher concentrations. Pierce et al. (1980) have suggested that the higher concentrations may arise from the complexing of phthalates by humic/fulvic acids (see Matsuda and Schnitzer, 1971) present at elevated levels in certain waters.

2.1.2. Estuarine and sea water. Much of the data on these waters have been reported by Giam and co workers, eg. Giam et al. (1978) and Murray et al. (1981). Most reports are of DBP and DEHP levels.

a) DBP. Giam et al. (1978) found about 0.1 µg/l in waters of the Mississippi Delta and the Gulf of Mexico, but it was not detectable in the northern Atlantic. In Japanese marine waters, Kodama et al. (1975) reported levels between ND and 1.2 µg/l; in a UK estuarine water, Waldock (1983) recorded levels of 0.024-0.058 µg/l; and in the Baltic, Ehrhardt and Derenbach (1980) detected between 0.06 and 0.2 µg/l of DBP. These last authors noted that the levels of phthalates were "amazingly high", exceeding the concentration of chlorinated hydrocarbon pesticides measured on the same samples by a factor of 100. It should, however, be noted that their butyl phthalates contained a non-industrial material, n-butyl iso-butyl phthalate. Weber and Ernst (1983) recorded levels of between 0.02 and 0.5 µg/l in 3 German estuaries.

b) DEHP. In the Mississippi Delta and Gulf of Mexico, Giam et al. (1976, 1983) found up to about 0.3 µg/l, and in the northern Atlantic 0.005 µg/l (Giam et al.,1978). Values between ND and 0.7 µg/l were reported in Japanese sea waters by Kodama et al. (1975), and 0.058 to 0.078 µg/l was found in a UK estuarine water by Waldock (1983).

c) The general conclusion is that in estuarine and marine waters the concentrations of DBP and DEHP are usually in the range from ND up to values approaching 0.7 µg/l.

2.2. In sediments

Sullivan et al. (1982) have shown that phthalates may be adsorbed by clay minerals and a natural sediment, and that the amount adsorbed is influenced by the nature of the phthalate and the salinity of the aqueous phase. The adsorption and desorption will also be strongly affected by the organic matter on the sediment.

Malisch et al.(1981) measured phthalate levels in sediments in the Rhine, from Rüdlingen near Lake Constance to Wesel near the Dutch border, and also in the Neckar, from Schwennigen in the upper reaches to Feudenheim near its entry to the Rhine. In general the highest concentrations were at Wesel : DEHP (14,600 µg/kg), DNP (1,250 µg/kg), DINP (1,460 µg/kg), DBP (115 µg/kg) and DIBP (21 µg/kg). In the same work the concentration of chlorinated benzenes and of DDT and metabolites were also measured and found to be 2-3 orders of magnitude lower than that of DEHP.

Eder (1984) analysed sediments from the Ems estuary and found concentrations of DEHP of between 32 and 60.5 µg/kg and of DBP between 25.5 and 48.4 µg/kg, based on sediment wet-weight. These correspond to about 320, 605, 255 and 484 µg/kg on a dry-weight basis.

Field data for phthalate concentrations in sediments (all values based on dry weight) show that the levels are about 1000 times those found, or expected, in the associated water. Giam and Atlas (1980) have summarised data from their own and other author's work. They cite DBP-in-sediment levels ranging from 3 µg/kg (Gulf of Mexico), to 15,000 µg/kg (Rhine and Ijssel rivers) and 100,000 µg/kg (Lake Superior). The DEHP levels were of the same order.

Goto (1979)found Japanese river sediments to contain between 300 and 600 µg/kg of DBP (associated water, 0.16 to 3.06 µg/l), and from 80 to 1,360 µg/kg of DEHP (associated water, 0.1 to 2.19 µg/l). In sediments from the estuary of the River Crouch (UK), Waldock (1983) reported 3.9-14.5 µg/kg of DBP wet weight (say, 39-115 µg/kg dry weight), and 11.2-26.2 µg/kg wet

weight (say, 112-262 µg/kg dry weight) of DEHP. The associated waters contained about 0.04 µg/l of DBP, and 0.07 µg/l of DEHP.

Michael et al. (1984) measured BBP in sediments in the USA - see 2.1 above for details of locations and comments on technique. Only at 4 out of 31 sites was BBP detected (limit of detection in 1982 : 60 µg/kg), the concentrations ranging from 100 to 420 µg/kg). It was not clear from the paper whether the results were expressed on a wet or dry sediment basis.

Total, and some individual, phthalate levels in sediments from Galveston Bay were reported by Murray et al. (1981) as follows (in µg/kg) :

- total phthalates, average 159 (cf. 82 in the Mississipi Delta, and 14 in the Gulf Coast) ;
- DEHP, average 94;
- DBP, average 60;
- DEP, average 5.

In comparison, the concentration of benzo-α-pyrene averaged 2.2 µg/kg, and that of hexachlorobenzene, PCBs and some other pollutants was even lower.

Thurén (1983) measured DEHP concentrations in fresh-water sediments near two Swedish phthalate-using factories. Two values at points nearest to the factories (6.28×10^5 and 1.48×10^6 µg/kg dry weight) were the highest found by the Task Force in the literature. The remaining 9 concentrations were in the range 149 µg/kg to 7.92×10^4 µg/kg.

Two groups have studied the phthalates distribution in sediment cores as a function of depth (age). The results of Giam and Atlas (1980) on Lake Constance sediments were anomalous in that high levels of DBP (400 µg/kg) were found in core samples corresponding to the early 1800s, and DEHP peaked at 1100 µg/kg in those corresponding to 1940. The authors attribute the anomalies to (undefined) contamination, but concluded that the overall results (DBP, 100-300 µg/kg ; DEHP 200-700 µg/kg) showed that concentrations had increased over recent decades. This would correspond to increases in production and use in the same period. In a similar study of sediments cores from Chesapeake Bay, Peterson and Freeman (1982) found, in one sample, a good correlation of measured levels of DEHP (20-180 µg/kg) with the increase in production over the period 1924-1979. Over the same

period, DBP levels in the corresponding sediments were 30 to 90 µg/kg. They suggested that some of the material in the deep (older) cores may have arisen from natural sources.

The general conclusion is that the concentrations of phthalates in sediments vary widely over the range of a few µg/kg up to 100,000 µg/kg, and that the levels are, in general, several orders of magnitude higher than in the associated waters.

2.3. In biota.

Much of the data on concentrations of phthalates in biota of the natural environment has been summarised by Howard (1981) and Pierce et al. (1980). DBP and DEHP were the most commonly found, the reported levels varying widely from ND up to a few tens of thousand µg/kg.

a) DBP. Mayer et al. (1972) found 200-300 µg/kg in channel catfish (Ictalurus punctatus), dragonfly naiads and tadpoles at an Iowa fish hatchery, but none in channel catfish from Mississippi and Arkansas. Japanese workers have given the following values for fish (in µg/kg) : Kodama and Takai (1974), 60-530; Kamata et al. (1978), less than 20 to 170; Goto (1979), 40-230. Freshwater fish caught around Lake Michigan were found by Schacht (1974) to contain levels of DBP from ND to 100 µg/kg.

Musial and Uthe (1980) detected 10-220 µg/kg of DBP in plaice (Pleuronectes platessa), redfish (Sebastes marinus) and herring (Clupea herengus) caught in the Bay of Fundy and the Gulf of St. Lawrence.

Rather lower values have been reported by Waldock (1983) for species in the UK. Molluscs caught near the River Crouch contained DBP concentrations from ND to 8 µg/kg above blank levels, on a wet weight basis. Dab (Limanda limanda), plaice (Pleuronectes platessa) and whiting (Merlangius merlangus) from the Crouch estuary and Tees Bay contained DBP levels similar to the blank values (a few µg/kg), although some liver samples contained amounts somewhat higher than the blanks.

Zitko (1973) reported that lipid from birds eggs contained 11,000 - 19,000 µg/kg of DBP.

b) DEHP. Mayer et al. (1972) found 3,200 µg/kg in channel catfish (Italurus punctatus) from Mississipi and Arkansas, and 200-300 µg/kg in channel catfish, dragonfly naiads and tadpoles of an Iowa fish hatchery. They noted the occurrence of 2,000-7,000 µg/kg of DEHP in a commercial fish food.

Musial and Uthe (1980) found DEHP concentrations from less than 1 µg/kg up to 7,240 µg/kg in plaice (Pleuronectes platessa), redfish (Sebastus marinus) and herring (Clupea harengus) from the Gulf of St Lawrence and the Bay of Fundy. In Japanese fish, Kodama and Takai (1974) found 70-450 µg/kg, Kamata et al. (1978) reported values of less than 50 up to 1,800 µg/kg, and Goto (1979) 40-720 µg/kg. Fish caught around Lake Michigan contained levels between ND and 1,300 µg/kg (Schacht, 1974).

The DEHP levels in the livers of fish caught in Tees Bay, which receives a large amount of industrial effluent, were reported to be up to 80 µg/kg wet weight (Waldock, 1983). The same author also found between 2.2 and 212 µg/kg wet weight in the digestive gland of molluscs caught in the river Crouch. Burns et al. (1981) found up to 10^4 µg/kg (wet basis) of DEHP in the tissues of five species of fish, and one of eels, caught in Canada. The levels in several species of biota from various locations in the Gulf of Mexico were found by Chan (1975) to be from 1 to 135 µg/kg wet weight (see also Giam et al.,1978).

Persson et al. (1978) found DEHP in a variety of organisms and in soil from an industrial area in Finland. The following levels were recorded (µg/kg) : soil anthropods 2800; fry and sticklebacks (Gasterosteus aculeatus), freshwater anthropods, molluscs and perch (Perca fluviatilus), 100; bream (Abramis brama) 500; roach (Rutilus rutilus) 110; pike (Esox lucius) liver, 2300; plankton, 0. Zitko (1973) detected DEHP at concentrations between 11 and 19 µg/kg in seal pup blubber and juvenile Atlantic salmon (Salmo salar) from a hatchery.

c) Phthalic acid. Morris (1976) found 10^5 µg/kg in the deep-sea jelly fish, Atolla. This does not seem to be an artefact of the analysis or sampling procedures since other biota sampled and analysed at the same

time contained no phthalic acid. It cannot be ruled out that the acid was of natural biosynthetic origin.

d) Conclusion : the levels of phthalates detected in biota vary from 1 up to 19,000 µg/kg. There are insufficient data to enable a correlation to be established between concentrations of phthalates in water and recorded levels in biota.

2.4. In air and rainwater

Few quantitative measurements have been recorded.

a) In air over the Gulf of Mexico, the N. Pacific and the N. Atlantic, concentrations of DBP and DEHP of around 1-3 ng/m³ have been recorded (Atlas and Giam, 1981). Some of the values reported were of phthalates adsorbed on atmospheric particulate matter (Giam et al.,1980).

b) In city air, values are available only for phthalates in atmospheric particulate matter (Bove et al.,1978; Cautreels et al.,1977). The values ranged from 0.14 to 74 ng/m³ of air for DBP, and from 5 to 132 ng/m³ for DEHP. The biological and physical availability of such adsorbed phthalates is unknown.

c) In rainwater. Atlas and Giam (1981) have given some interesting figures, measured in the N. Pacific, for the concentration of DBP and DEHP in rainwater and in the air at the same location.

- rainwater (ng/l)	DBP	2.6 - 72.5	(average 31)
	DEHP	5.3 - 213	(average 55)
- air (ng/m³)	DBP	0.4 - 1.8	(average 0.87)
	DEHP	0.3 - 2.7	(average 1.4)

The main interest in atmospheric and rainwater concentrations is that phthalates can be transferred from the air to the water compartment by "wash out". If the average DEHP values, above, are taken as an example, the degree of concentration in passing from air to rain can be calculated. Thus, 1.4 ng/m³ (= 1.4×10^{-3} ng/l) in air gives rise to a concentration in rain of 55 ng/l, a concentration factor of 4×10^{4}. The concentration factor for DBP is, similarly, 3.5×10^{4} despite the fact that it is considerably more soluble in water than is DEHP (see Table 1). The partition coefficient air/water of DBP is 7.4×10^{-5} (Atlas and Giam,

1983), and leads to an expected concentration factor of around 10^4 at equilibrium, in good agreement with the value calculated as above.

2.5 Variation with time

From the above information it is not possible to deduce whether the environmental concentrations of phthalates are increasing with time since no systematic monitoring has been carried out with a standardised analytical procedure. Although in principle information on the trend in phthalate concentrations is important for risk evaluation, in practice the selection of appropriate samples to monitor and the performance of this monitoring over the period (many years) required to establish a trend is virtually impossible (except for sediment cores which, however, seem able to reveal changes only over decades).

H. TOXICITY TO ENVIRONMENTAL SPECIES

Concern about the potential effects of phthalates on environmental species has been mainly directed towards aquatic organisms. Data on toxicity to aquatic species, soil organisms and plants are presented in this chapter.

Some of the problems in assessing toxicity data have been described in section D. One further problem is especially associated with toxicity studies on products of low solubility in water. For example if, from Table 1, it is assumed that the solubility of DEHP in water is, e.g. 340 µg/l (CMA,1983), this is the maximum attainable, realistic environmental concentration. It is also the highest, realistic concentration attainable in determining LC_{50}s for aquatic species, but at this low concentration there may be less than 50% deaths. In this case the LC_{50} cannot be determined, although it is sometimes quoted as being above the solubility. As is seen from the results presented below, LC_{50}s have been quoted at much higher concentrations, possibly attained by solubilising the DEHP by the use of water-miscible solvents or dispersants. The significance of LC_{50}s obtained by such means needs cautious interpretation.

1. Micro-organisms

Indirect evidence that phthalates are generally of low toxicity to micro-organisms is provided by the fact that many are known to degrade

phthalates - see E.2.2. Tomita and Nakamura (1980), indeed, have suggested that micro-organisms play a role in removing phthalates from the environment.

Perez et al. (1976) found that the bacterium Pseudomonas aeruginosa, used DMP as a carbon source, and that its growth was not inhibited at concentrations of up to 10^6 µg/l.

Mutz (1978) reported that neither DEHP, 2-ethylhexanol, or phthalic acid interfered with nutrient cycling or microbial processes in a hydrosoil microcosm.

DBP had no effect on the growth of the marine alga Skeletonema costatum at concentrations of up to about 5×10^5 µg/l, except in water of low salinity where there was some effect at 5×10^5, but not 2×10^5 µg/l (Medlin, 1980). These concentrations are well above the most recent values of about 0.1×10^5 µg/l for the solubility of DBP - see Table 1. With the same alga, the EPA (1978b) reported EC_{50}s of 30,000, 85,000 and 200 µg/l for, respectively, DMP, DEP and BBP, and Gledhill et al. (1980) obtained a value of 600 µg/l for BBP, close to the EPA figure. They also found EC_{50}s ranging from 400 to 1000 µg/l for the action of BBP on a number of other algae.

2. Aquatic Organisms

This has been reviewed by the EPA (1978-b). The highlights from this review and more recent work are given below.

2.1. Acute toxicity

a) Fish. For lower phthalates, reported LC_{50}s (usually 48 or 96 h.) range from 35×10^4 (DMP, bluegill sunfish, Lepomis macrochirus; Buccafusco et al. 1981) to 700 µg/l (DBP, bluegill sunfish, ; Mayer and Sanders, 1973). The bluegill sunfish seems to be marginally more sensitive than the fathead minnow, Pimphales promelas, or rainbow trout, Salmo gardineri (Gledhill et al., 1980; Mayer and Sanders, 1973). Zitko (1972) described "preliminary" bioassays with juvenile Atlantic salmon, Salmo salar, in which DMP caused no deaths at 10^4 µg/l over 96 h., and DBP at the same concentration caused 100 % deaths in 3 h., but none at 10^3 µg/l over 96 h.

Data on the acute toxicity of higher phthalates to fish are scarce. Zitko (1972) found that DEHP caused no deaths among juvenile Atlantic

salmon at 10^4 µg/l over 96 h. Mayer and Sanders (1973) quote 96-hour LC_{50}s of above 10^4 µg/l of DEHP for a range of fish. Buccafusco et al. (1981) quoted 24 and 96 h. LC_{50}s of above 77×10^4 µg/l for DEHP with respect to the bluegill sunfish (Lepomis macrochirus). Given that these concentrations were well above the water solubility, the results are somewhat suspect.

The most recent data, from studies performed for the US Chemical Manufacturers Association, are of 96 h. LC_{50}s for fathead minnows, Pimphales promelas, exposed to 14 phthalates in a static test (EG and G Bionomics, 1983a). DMP, DEP and DBP were the only ones to have no-observed-effect levels below their water solubility, the NAELs being 35,000, 3,000 and 940 µg/l, respectively. BBP, di-hexyl phthalate, butyl 2-ethylhexyl phthalate, DL610P, DEHP, DIOP, DINP, DL711P, DIDP, di-undecyl phthalate and DTDP had no toxic effect at concentrations equal to their water solubility. Similar results were obtained under flow-through conditions (EG and G Bionomics, 1983-b).

Randall et al.(1983) found that BBP killed English sole, Parophrys vetulus, at concentrations down to 300 µg/l and had sub-lethal effects at 100 µg/l, the lowest concentration tested. Ozretich et al.(1983) in further work with BBP reported a 165-hour LC_{50} of 490 µg/l, and slight behavioural effects at 80 µg/l in the estuarine fish, shiner perch (Cymatogaster aggregata).

b) Invertebrate aquatic species. Data are scarce but suggest that LC_{50}s for the effect of DBP and DEHP on scud (Gammarus pseudolimnaeus), midges (Chiromonidae) and Daphnia are similar to those for fish - see Mayer and Sanders (1973), Streufert (1980), EPA (1978-b) and Gledhill et al.(1980).

EG and G Bionomics (1984a) reported 24- and 48-hour LC_{50}s for larvae of the midge, Paratanytarsus parthenogenica, exposed to 12 phthalates. Only DMP, DEP and DBP were toxic at concentrations below their water solubility, having 48 h. LC_{50}s of 390,000 , 140,000 and 5800 µg/l respectively. Of the remainder (DINP, DIOP, di-tridecyl phthalate, butyl 2-ethylhexyl phthalate, di-hexyl phthalate, DL610P, DEHP, DUP and DIDP), only DIDP had a discernible effect at a concentration (960 µg/l) below its solubility. However, this effect comprised 1 death in

5 animals, a mortality rate which also occurred in some of the control groups.

Linden et al. (1979) measured the 96-hour LC_{50}s of five phthalates, of increasing alkyl-chain length, against the marine crustacean Nitocra spinipes, and noted a peak in acute toxicity at DBP :

	µg/l
DMP	62,000
DBP	1,700
DIBP	3,000
DEHP	$>3x10^5$*
DNP	$>3x10^5$*

* well above the water-solubility.

With Daphnia magna, Le Blanc (1980) found that the 48-hour LC_{50} peaked at DEHP in the series :

	µg/l
DMP	33,000
DEP	52,000
BBP	92,000
DEHP	11,000*

* well above the water-solubility

Hobson et al.(1984) fed diets containing between 40 and 50,000 ppm of DEHP to the shrimp, Penaeus vannamei, for 14 days at 4% body weight per day. At the highest dose the DEHP accumulated to give a whole-body concentration of 18,000 µg/kg. The concentration of DEHP found in the water was equal to or less than 1.7 µg/l at all dietary dose levels. Under these conditions there was no increase in mortality and no histopathological alterations were observed.

In general, LC_{50}s for organisms other than micro-organisms are above 10^4 µg/l with a few values in the range 0.7 to 10.

.2. Longer-term toxicity including reproductive effects

a) Fish. Mehrle and Mayer (1976) exposed fathead minnows, Pimphales

promelas, to DEHP at concentrations of up to 62 µg/l for 56 days and found no effect on growth or survival. They also exposed rainbow trout (Salmo gardineri) eggs to DEHP at concentrations of up to 54 µg/l for 12 days prior to hatch, and 90 days thereafter. The DEHP did not alter egg hatchability or survival of the fry following the first five days after hatch. However, the two highest concentrations (14 µg/l and 54 ug/l) did cause an increase in mortality during the first five days following hatch, though we note that the 14 µg/l level gave 15 per cent mortality whereas the 54 µg/l gave only 9 per cent mortality. At 5 µg/l there was no significant difference (p less than 0.05) between exposed and control organisms.

Birge et al.(1978) compared the toxicity of dioctyl phthalate, DINP and PCBs to channel catfish, (Ictalurus punctatus), red-ear sunfish (Lepomis microlophus) and amphibia at the embryolarval stage. The PCBs were very toxic (LC_{50}s between 1 and 30 µg/l) and gave rise to a significant number of teratogenic effects. By contrast, the phthalates had LC_{50}s in the range 10^3-10^5 µg/l, and the incidence of teratogenic effects was low.

The synthesis of vertebral collagen and of its most important building block, hydroxyproline, can be used as a sensitive indicator of the chronic effect of chemicals on growth. If growth is retarded, lower vertebral collagen and hydroxyproline levels are expected. Mayer et al.(1977) studied the effect of a number of chemicals on the vertebral collagen metabolism and growth rate of fish species, and indeed found that, except for DEHP, they caused a reduction in collagen synthesis and growth rate. Significantly lower collagen levels were found after long-term exposure to DEHP (levels in brackets) of adult brook trout, Salvelinus fontinalis (3.7 µg/l), fathead minnow fry, Pimphales promelas (11 µg/l) and rainbow trout fry (5 µg/l) for 150, 127 and 90 days, respectively. However, DEHP had no effect on fish growth, and produced either no effect on, or an increase in, hydroxyproline content. No satisfactory explanation could be given for these contradictory findings. In this case, effects on the vertebral collagen metabolism were not found to be valuable indicators of chronic effects on fish growth.

DEHP feeding studies on zebra fish (Brachydanio rerio) and guppies (Poecilia reticulata) were reported by Mayer and Sanders (1973). At 50 and 100 ppm of DEHP in the food, the number of zebra fish spawns increased compared with the control, but the survival rate of the fry decreased. Some of the fish died in tetany (muscle spasm) during exposure, and the authors suggested that their calcium metabolism may have been affected. In support of this hypothesis, Grant (1970) found that DEHP injected intra-peritoneally into Coho salmon (Oncorhynchus kisutch) at a dose of 3 µg/kg gave rise to an increase in serum calcium. On the other hand, Ozaki and Ikeda (1976) found that dioctyl phthalate (probably DEHP) had no such effect in yellowtail fish (Seriola quinqueradiata).

b) Daphnia and midges. Mayer and Sanders (1973) studied the effect of DEHP on the reproduction of Daphnia magna and found that at 3 µg/l, the lowest concentration tested, the number of young produced was only 40 % of that of the control. By contrast, Brown and Thompson (1982-a) found that at 100 µg/l, the highest concentration used, neither DEHP nor DIDP had any effect on the reproduction of the Daphnia magna. Commenting on these two sets of results, Brown and Thompson noted the very large differences between the numbers of young per parent Daphnia in their work (170) and in the control animals in the earlier work (11).

Gledhill et al. (1980) in studies on BBP found that the reproduction of Daphnia sp. was affected only at the highest concentration studied, ie. 760 µg/l.

Streufert (1977) found that neither DBP nor DEHP affected the life cycle of the freshwater midge, Chironomous plumosus. Midges were exposed to concentrations in "hydrosoil" (water and river sediment) of up to 695 µg/l of DBP, and up to 240 µg/l of DEHP, but there was no effect on their emergence. DEHP had no effect on egg hatchability, or the number of eggs per egg case, in concentrations of up to 193 µg/l in hydrosoil and 362 µg/l in sand (in this case the units as quoted in the paper are given).

c) Marine organisms. Rather few marine organisms have been studied.

Laughlin et al. (1977) found that DMP and DBP did not significantly affect the development of mud crab (Rhithropanopens harrisi) larvae at concentrations of up to 1,000 µg/l. They (Laughlin et al., 1978) also studied the effect of DMP, DBP and DEHP on the survival and development of the grass shrimp, Palaemonetas pugio. DEHP had no effect at concentrations of up to 10^3 µg/l. DMP and DBP were acutely toxic to the larvae at rather high concentrations, ie. 10^5 and (1-5) x 10^4 µg/l, respectively, and the authors concluded that the phthalates were of low toxicity and had little effect on larval development.

Brown and Thompson (1982b) during bioconcentration studies on mussels (Mytilus edulis) found no apparent adverse effects of exposure to DEHP and DIDP, at nominal concentrations of 50 µg/l, during a 28-day accumulation and 14-day depuration period.

Sugawara (1974) examined the effect of DMP, DEP, dihexyl and dioctyl phthalates on the hatching of brine shrimp (Artemia salina) eggs. DBP was the most toxic, but its effect at 10^4 µg/l was only marginal. The 24-hour LC_{50} of DBP for the same species was about 6,000 µg/l (reported as 20 µM) according to Hudson and Bagshaw (1978).

d) Macrobenthic species. Tagatz et al. (1983) studied the effect of DBP on a number of macrobenthic species (Chordata, Mollusca, Arthropoda, Annelida, Echinodermata and Coelenterata) in a laboratory aquarium. At DBP concentrations of 3,700 and 340, but not at 44 µg/l, there were effects on the community structure and population density.

e) Summary. The available information suggests that a number of aquatic organisms at certain stages in their life cycle may be sensitive to some phthalates at the µg/l level. One of the most obvious of the effects reported is the 60 % decrease in the production of young by Daphnia magna in the presence of 3 µg/l of DEHP, although this result was not confirmed in later work in which no such effects were seen at 100 µg/l of DEHP. This type of study, together with a fish egg-and-fry study, seems to be a useful indicator of whether a particular phthalate is likely to have adverse long-term effects.

3. Plants

In 1983 (Anon) it was reported that certain crops (tomato, cabbage, radish) were severely damaged by the release into the atmosphere of DBP and DIBP from PVC glazing used in greenhouses. The volatility of these phthalates apparently led to atmospheric concentrations causing photosynthesis to be inhibited, especially when ventilation was restricted. This effect had been noted somewhat earlier by Lokke and Bro-Rasmussen (1981) and Lokke and Rasmussen (1983). During growth-chamber experiments it was found that DBP caused chlorosis when applied to the young leaves of Sinapsis alba (white mustard) and Brassica napus (rape seed), but not Achillea millifolium (milfoil). DIBP and DEHP caused no visible effects on these species. The lowest concentration causing an effect was expressed as 1-2 µg of phthalate per cm^2 of leaf area.

Lokke and and Rasmussen (1983) calculated the dose expected to arise from the likely atmospheric concentration of DBP and DEHP in the open environment and concluded that "any significant effect or accumulation of DBP and DEHP on naturally-growing higher plants is unlikely to occur even in industrial areas".

Virgin et al. (1981) reported that when two species of house plants (Browallia speciosa and Raphanus sativus) were exposed to the vapour of DBP at concentrations between 1.7×10^3 and 1.6×10^4 ng/m^3, chlorophyll deficiency, seemingly due to an effect on carotenoid synthesis, led to the formation of pale or white leaves. The same authors (1984) later reported similar effects in sprouts (Brassica sp.).

Stanley and Tapp (1982) found that DEHP at a dose level of 10^6 µg/kg in soil had no effect on the growth of Brassica rapa (rape) and only a slight effect on that of Avena sativa (oats).

I. EVALUATION OF RISK TO ENVIRONMENTAL SPECIES FROM PHTHALATES

In this section the term "risk evaluation" is used to mean a comparison of effect or no-effect levels of a particular phthalate, as determined in laboratory experiments on specific organisms, with the measured levels of these phthalates in the environment. Based on these data a qualitative statement is then made about the likelihood of adverse effects. When there are no data on

chronic effects the following generalisation is often used : if environmental levels of a substance are less than 1% of the acute toxic effect level the risk of chronic effects is low (see ECETOC, 1984). A more direct comparison with environmental levels can be made if data on chronic effects are available, in which case it may be prudent to use a margin of 10% between laboratory chronic effect levels and acceptable environmental levels (EPA, 1984).

As indicated in Chapter G, most data on environmental levels are on DBP and DEHP with little or none on most of the other phthalates. A somewhat similar situation applies regarding the toxicity data (see Section H), although the studies recently carried out for the CMA (EG and G Bionomics, 1983a and b; 1984a and b) and other CMA-sponsored studies yet to be reported are now providing, or will provide, data for other phthalates. It may be assumed that the lack of data on environmental levels of most phthalates is due to the low level of use, and hence low environmental concentrations, of these materials, rather than to a failure to detect significant amounts actually present. Thus, although the evaluation of risk made in this Section strictly applies only to DBP and DEHP, it follows from the above argument that unless other phthalates are very significantly more toxic, any risk to the environment from them will be less than that from DBP and DEHP.

1. Risk to Freshwater Species

In section G.2.2. d) it was concluded that the concentration of DBP and DEHP in fresh waters normally lies between fractions of a µg/l and 10 µg/l. For the purposes of risk evaluation we have taken 10 µg/l as a conservative value at the upper end of the range. As indicated above, it seems entirely reasonable to assume that the levels of other phthalates will be significantly below this value. If phthalates other than DBP and DEHP were present in similar concentrations it seems likely that such concentrations would have been recorded by the analytical techniques used for DBP and DEHP.

1.1. Risk to micro-organisms

This seems to be negligible on the limited evidence available - see section H.1 - and is not discussed further.

1.2. Fish. As indicated in chapter H, the upper level at which the acute toxicity of most phthalates can be realistically determined is governed by their low solubility in water. From the data in section H.2.1 it is

possible to conclude that there is a negligible risk of acute effects on freshwater fish from the less soluble materials (DEHP and higher) among the phthalates tested (DMP, DEP, DBP, BBP, DEHP, DHP, butyl 2-hexyl phthalate, DL610P, DIOP, DINP, DL7IIP, DIDP, DUDP and DTDP). Application of the above-mentioned 1% factor to the lower of the acute LC_{50}s gives a value of about 10 µg/l against which the likelihood of chronic effects has to be assessed. On this basis it is not possible to reach a firm conclusion that chronic effects are unlikely. However, the maximum levels tested for acute effects had, in fact, no effect, and 10 µg/l is very much at the top of the likely range of concentration of the most common phthalates in freshwaters. Thus it seems reasonable to conclude from the acute toxicity data that chronic effects are not likely.

However, there is some evidence suggesting a risk of chronic effects from DEHP at around 10 µg/l in that, i) DEHP caused a slight increase in mortality of rainbow trout fry at 15 µg/l, with an NAEL at 5 µg/l, and ii) exposure to DEHP led to a reduction in vertebral collagen and hydroxy-proline synthesis in 3 species of fish at concentrations of 3.7 to 11 µg/l. Although, in theory, this should have affected the growth of the fish, no such effect was observed and the observation seems to be of marginal toxicological significance.

Embryo larval studies planned by the CMA (1981) should give valuable information on whether low levels of the phthalates to be tested do, in fact, pose a risk of chronic effects to fish.

1.3. Daphnia and midges. Mayer and Sanders reported that DEHP at 3 µg/l affected the reproduction of Daphnia magna, although Brown and Thompson found no such effect at 100 µg/l of DEHP or DIDP (see section H.2.2.b). Studies in hand by the CMA on the effect of a range of phthalates on Daphnia reproduction should resolve this contradiction. The present conclusion is that there is no credible evidence that phthalates will adversely affect freshwater invertebrate species at current environmental levels.

2. Risk to Marine Species

In section 2.1.2 c) it is concluded that the concentration of DBP and DEHP (the only phthalates for which measurements are available) does not exceed 0.7 µg/l in estuarine and sea waters. As explained above, the concentrations of the other phthalates are likely to be significantly below this.

2.1. Fish. Data on acute toxicity are available for two species of marine fish

exposed to DMP, DBP and BBP. The lowest recorded acute-effect concentration is at 100 µg/l, well above any likely environmental level. Although no information was found on chronic effects on marine fish, the acute toxicity levels are such that chronic effects seem unlikely (1% of 100 µg/l is 1 µg/l, i.e. just above the maximum expected concentration in marine waters).

2.2. Other species. The acute or chronic toxicity of several phthalates (DMP, DEP, DBP, DIBP, DEHP, dihexylphthalate, DOP and DNP) to one or more of a variety of other species has been reported. The LC_{50}s or NAELs were all several orders-of-magnitude above the likely concentration of phthalates in marine or estuarine waters. There is thus no evidence that the above species are at risk from the various phthalates to which they may have been respectively exposed.

3. Risks to Plants

Although DBP and DIBP affect the growth of plants in a closed environment, the effect appears to be specific to these phthalates, probably because of their high volatility from the plasticised PVC used in the glazing bars, etc. Lokke and Rasmussen (1983) concluded that at the current atmospheric levels of DBP and DEHP, even in industrial areas, they are unlikely to affect plants (section H.3). This seems to be a sound conclusion given the minute concentrations recorded (section G.2.4).

DEHP at a concentration of 10^6 µg/kg in soil had a marginal effect on the growth of oats. There are no reports of DEHP concentrations in soil in the environment, but figures for sediment may be taken as a comparison. The highest recorded value for DEHP is in a Lake Superior sediment which contained 10^5 µg/kg. As can be seen from section G.2.3, this is a quite exceptional value, but is still ten times less than the above DEHP "slight-effect" level. It thus seems unlikely that DEHP will reach levels in soil to constitute a risk, at least to plant species of sensitivity equal to or less than that of oats.

4. Risk from Phthalates in Sediments

There is much information in the literature on the concentrations of several phthalates in sediments, and levels can be high, i.e. up to 10^5 µg/kg (section G.2.2). To the Task Force's knowledge there is no published account of studies to investigate whether sediments containing significant amounts of phthalates are in any way deficient in animal numbers or species diversity.

Apart from the midge larval studies of Streufert (see H.2.2.b) there appear to be no published laboratory studies to determine whether the presence of phthalates in sediments affects benthic organisms - indeed there are no generally-accepted methods for carrying out such investigations.

In this situation it is not known whether phthalates in sediments pose a risk to benthic species.

5. Risk from Accumulation of Phthalates in Biota

DBP and DEHP have been found in a wide variety of biota at concentrations up to 10^5 µg/kg. Two questions thus arise : does the phthalate harm biota in which it is present; and if the phthalate-containing biota are subject to predation will the phthalate harm the predator ?

No published reports were found suggesting that phthalate-containing biota in the natural environment were showing any adverse effects at the time of their collection. In the quite numerous laboratory studies on the bioconcentration of phthalates, the only evidence of an adverse effect was that reported by Austerberry et al. in relation to DBP and the brine shrimp (see section F). Since observations of any toxic effects would have been made in laboratory bioconcentration studies it may be concluded that on the limited evidence available it seems unlikely that biota which accumulate phthalates in the environment will suffer adverse effects.

Regarding risk to predators, e.g. fish-eating birds, there is no direct evidence, but the rather low oral toxicity of phthalates to higher animals (Kemper and Lüpke, 1983) suggests that the risk is negligible.

6. Risk from Phthalates in the Atmosphere

Data on atmospheric concentrations have been reported only for DBP and DEHP - see section G.2.4. The values range from below 1 up to 74 ng/m^3. Of the environmental species exposed, only plants are likely to be affected, but the risk of adverse effects is negligible at the above concentrations - see section 3, above.

J. RECOMMENDATIONS

1. Measurement of environmental levels.

   The assessment of risk from environmental phthalates depends critically on a correct measurement of exposure levels. Thus, it is recommended that the analysis of environmental levels of phthalates continues and that the analytical methods incorporate the stringent precautions referred to in section D, para.2.

   In such environmental analyses, particular emphasis should be placed on sediments since, in general, they provide the best indicator of changes in phthalate levels in the aquatic environment. (By adsorption they concentrate phthalates in relation to the overlying water, and the adsorbed phthalate seems to be only slowly degraded). Where sediment layers are stable, a core sample may provide an historical record of phthalate deposition.

2. Determination of toxic effects.

   a) The available data, and those which will result from CMA-sponsored studies in hand, seem likely to provide enough information to enable satisfactory risk evaluations for phthalates in most environmental compartments. The exception is for sediments, where evidence for the existence or absence of toxic effects is lacking. It is recommended that such evidence be sought.

   b) Unfortunately there are very few experimental procedures (and no generally-accepted ones) for assessing the possible toxic effects of phthalate-containing sediments on animals which live in them, and it is recommended that such procedures be developed. Phthalates which have been identified in sediments, such as DBP and DEHP, should be tested in such procedures.

   c) Where phthalate-rich sediments are found in the environment it is recommended that their animal population is monitored to determine whether the numbers and species-diversity are those normally expected in the sediments.

3. Use and disposal practices.

   The findings reviewed in this report provide no evidence suggesting that there is a high risk to environmental species from phthalates at the levels corresponding to current use and disposal practices. Thus there appears to be no need to make any recommendations regarding these practices.

K. APPENDIX

Main Industrial Pthalates

Phthalate	Abbreviation	Comments
dimethyl	DMP	
diethyl	DEP	
di-n-butyl	DBP	
di-iso-butyl	DIBP	
di-2-ethylhexyl	DEHP	(often referred to as di-octyl phthalate, DOP)
di-n-octyl	DNOP	
di-iso-octyl	DIOP	mainly dimethylhexyl
di-nonyl	DNP	mainly 3,5,5-trimethylhexyl
di-iso-nonyl	DINP	mainly dimethylheptyl
di-iso-decyl	DIDP	dimethyloctyl and trimethylheptyl
di-undecyl	DUP	
di-iso-tridecyl	DTDP	tridecanols from carbonylation of propylene tetramer
butyl-benzyl	BBP	
di-C_6C_{10} alkyl	DL610P	mainly n-alkyl
di-C_7C_9 alkyl	DL79P	mainly n-alkyl
di-C_7-C_{10}alkyl	DL710P	mainly n-alkyl
di-C_7-C_{11} alkyl	DL711P	mainly n-alkyl
di-C_8-C_{10} alkyl	DL810P	mainly n-alkyl

(Note : abbreviations are taken from a British Plastics Federation publication No.301, July 1st, 1984)

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