

Technical Report

No 19

**An Assessment of the Occurrence and
Effects of Dialkyl**

ortho-PHTHALATES in the Environment

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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 $\mu\text{g}/\text{kg}$ up to $10^5 \mu\text{g}/\text{kg}$ (one higher value, $1.48 \times 10^6 \mu\text{g}/\text{kg}$ dry weight, was recorded by Thuren, 1983);
- iii) concentrations in biota again vary widely, between 1 and 19,000 $\mu\text{g}/\text{kg}$;
- iv) concentrations in air are low, with values up to $3 \text{ ng}/\text{m}^3$ over the sea and up to $130 \text{ ng}/\text{m}^3$ 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 $0.2 \mu\text{g}/\text{l}$, 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-occurring 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/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)

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 $\mu\text{g}/\text{l}$. This discrepancy may be due to the readiness with which DEHP forms colloidal solutions (Klöpffer et al., 1982). These authors prepared "solutions" containing 500 $\mu\text{g}/\text{l}$ but decided that they were colloidal, and believed that the "true solubility in water" is 50 $\mu\text{g}/\text{l}$.

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

<u>Phthalate</u>	<u>Temp.</u> °C	<u>Water-solubility</u> ug/l	<u>Reference</u>
DMP	20	5.0x10 ⁶	Fishbein and Albro (1972)
	-	4.32x10 ⁶	Wolfe et al.(1979)
	20	4.29x10 ⁶	Leyder and Boulanger (1983)
	-	4.0x10 ⁶	Peakall (1975)
	25	4.0x10 ⁶	CMA (1983)
DEP	25	1.08x10 ⁶	CMA (1983)
	20	1.0x10 ⁶	Fishbein and Albro (1972)
	-	1.0x10 ⁶	Peakall (1975)
	20	0.928x10 ⁶	Leyder and Boulanger (1983)
	-	0.896x10 ⁶	Wolfe et al.(1979)
DBP	25	(4.5x10 ⁶)	Fishbein and Albro (1972)
	-	13x10 ³	Wolfe and al.(1979)
	25	11x10 ³	CMA (1983)
	20	10x10 ³	Leyder and Boulanger (1983)
DIBP	20	(1x10 ⁵)	Fishbein et Albro (1972)
	20	2x10 ⁴	Leyder and Boulanger (1983)
	-	6x10 ³	Hollifield (1979)
DEHP	20	(1x10 ⁵)	Fishbein and Albro (1972)
	-	1.3x10 ³	Hirzy et al.(1979)
	-	0.6x10 ³	Branson (1980)
	20	0.4x10 ³	Wolfe et al.(1979)
	25	0.34x10 ³	CMA (1983)
	-	0.28x10 ³	Hollifield (1979)
	-	0.041x10 ³	Leyder and Boulanger (1983)
	15	0.0476x10 ³	OECD (1979)
	25	0.0466x10 ³	OECD (1979)
BBP	-	2.9x10 ³	Hirzy et al.(1979)
	20	2.82x10 ³	Leyder and Boulanger (1983)
	25	2.69x10 ³	CMA (1983)
	-	0.71x10 ³	Hollifield et al.(1979)
DNOP	25	0.9x10 ³	CMA (1983)
DIOP	25	0.09x10 ³	CMA (1983)
DNP	25	below 1x10 ³	CMA (1983)
DINP	25	0.2x10 ³	CMA (1983)
Di-n-decyl	25	0.9x10 ³	CMA (1983)
	-	0.33x10 ³	Hollifield et al.(1979)
DIDP	25	1.19x10 ³	CMA (1983)
	-	0.28x10 ³	Hollifield (1979)
DUP	25	1.11x10 ³	CMA (1983)

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

TABLE 2

<u>Phthalate</u>	<u>Mol.wt.</u>	<u>Vapour press.</u> mm Hg (°C)	<u>Reference</u>	<u>Log. partition</u> coeff.(Pow)	<u>Reference</u>
DMP	194	0.01(20)	Fishbein and Ajro (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. Emission 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 1×10^{-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 ($\mu\text{g/l}$) 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 :