Environmental Fate and Aquatic Toxicology Studies on Phthalate Esters

by Edward F. Group, Jr.*

A comprehensive environmental fate and effects testing program, sponsored by the Chemical Manufacturers Association (CMA) Phthalate Esters Program Panel, has been completed. Based on the results, a preliminary safety assessment has shown that all of the 14 commercially important phthalates tested have sufficiently high safety factors to demonstrate low potential for adverse environmental effects.

This program comprised acute toxicity studies on nine representative species of aquatic life, chronic reproduction studies on Daphnia magna, biodegradation (fate) testing, and physicochemical property (mobility) determinations on 14 phthalate esters. The objectives of this program were to determine for each test compound: The concentration at which effects on aquatic life might occur, the potential for bioconcentration in aquatic life, and the relative persistence in the environment. These data would provide the basis for an environmental safety assessment and would identify potential effects that might require further investigation.

A total of 195 individual studies were carried out.

Tests on a wide variety of aquatic organisms representing different food chain levels in both fresh and salt water environments showed that no single test species was unusually sensitive to the test materials. The higher molecular weight (longer side-chain) phthalates exhibited no toxic effects up to their limits of water solubility in the test systems. Even though the lower molecular weight, more water-soluble phthalates produced toxic effects below their limits of water solubility, no product exhibited unusually severe effects of concern.

Data from the Daphnia magna (water flea) chronic studies, coupled with recent data published outside of the CMA program, show that effect levels for DEHP and other phthalates are one or two orders of magnitude (10 x to 100 x) above the 3 ppb reproductive effect level for DEHP reported in 1973.

Phthalates were shown to be practically nonvolatile and only sparingly soluble in water. The high molecular weight phthalates can be expected to partition preferentially from water to organic matter.

All phthalates tested were readily biodegraded under the aerobic/high microbial population test conditions.

The CMA Phthalate Esters Panel believes the scientific data support a conclusion that phthalates do not pose a significant threat to the environment.

Introduction

A comprehensive environmental fate and effects testing program on phthalate esters, sponsored by the Chemical Manufacturers Association (CMA) Phthalate Esters Program Panel, has been completed. Initiated in 1981, the program's overall objective was to determine if phthalate esters are capable of causing adverse effects at concentrations likely to be present in the environment. The safety assessment based on test results demonstrates that phthalates have a low potential for adverse environmental effects.

Phthalate esters represent a large production volume class of compounds with potential for environmental release. Their occurrence in the environment is reportedly widespread, although much of the analytical data is suspect due to sampling and laboratory contamination problems. Because of their low water solubility and perceived persistence in the environment, the potential for bioconcentration has been recognized. Also, there have been scattered literature reports of adverse effects on aquatic life at low concentrations in laboratory test waters.

The CMA Phthalates Panel was established in the mid-1970s to investigate the potential environmental impact of phthalate esters. Initially, the Panel sponsored literature surveys and aquatic toxicity studies. In 1980, this activity was expanded in concert with the U.S. Environmental Protection Agency (EPA), into a comprehensive testing program to broaden the environmental data base on phthalate esters, comprising two types of testing: environmental fate studies (biodegradation and mobility),

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and biological effects on aquatic organisms. The objectives of this program were to identify concentrations at which effects on aquatic life might occur, to assess the potential for bioconcentration in aquatic species, and to ascertain relative persistence in the environment.

Phase I of this program was designed to develop a broad data base on 14 commercially important phthalate esters (Table 1). Included were acute toxicity studies on nine representative aquatic species, life-cycle (chronic) survival/reproductive studies on the invertebrate species *Daphnia magna* (water flea), primary and ultimate biodegradation tests, and physicochemical testing to assess the mobility of phthalates in the environment. An outline of the program elements and rationale for test selection are shown in Table 2. The intent of this approach was to develop a broad data base which could be used for safety assessment and to determine if additional testing might be justified.

A total of 18 complete Phase I test reports have been issued and are available from CMA. In addition, a summary report of Phase I testing, which contains a tabulation of all results, has been issued (1). The sections that follow present a condensation of the results and conclusions from the Phase I study.

### Biological Testing Results: Acute

Results of studies on nine different aquatic species representing different food chain levels in both freshwater and saltwater environments can be summarized as follows.

#### Fish

No single test species was unusually sensitive to any of the test compounds in either fresh or salt water environments. The higher molecular weight (C₁₀ and higher side-chain) phthalates exhibited no toxic effects up to their limits of water solubility in the test systems. The lower molecular weight, more water-soluble, phthalates produced toxic effects below their limits of water solubility, with LC₅₀ values ranging from 0.8 to 120 mg/L. These effect levels are far above concentrations likely to be encountered in the environment. Results of studies conducted in the dynamic versus static testing mode did not differ significantly.

#### Invertebrates

Acute toxicity tests on *Daphnia magna* (fresh water) and mysid shrimp (salt water) gave results similar to tests on fish. The lower molecular weight phthalates produced effects for mysid shrimp at concentrations below the water solubility. Only DEP and DBP had definitive EC₅₀ values in daphnid testing. The 48-hr EC₅₀ values for C₆-C₁₃ side-chain phthalates were all “greater than” for both daphnid and mysid shrimp, indicating no toxic effects at the water solubility limit attained in test waters.

#### Benthos

Results on the midge, a benthic filter-feeder organism, showed this bottom-dwelling species to be the least sensitive to low molecular weight phthalates. For the remaining phthalate esters, EC₅₀ values were all “greater than,” indicating no toxic effects up to the water solubility limit attained in test waters.

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**Table 1. Phthalate esters selected for CMA Phase I environmental effects testing.**

| Common designation | Chemical name |
|--------------------|---------------|
| DMP                | Dimethyl phthalate |
| DEP                | Diethyl phthalate |
| DBP                | Di(n-butyl) phthalate |
| BBP                | Butyl benzyl phthalate |
| DHP                | Dihexyl phthalate |
| BOP                | Butyl, 2-ethylhexyl phthalate (mixed esters) |
| 610P               | Di(n-hexyl, n-octyl, n-decyl) phthalate |
| DEHP (or DOP)      | Di(2-ethylhexyl) phthalate |
| DIOP               | Diisooctyl phthalate |
| DINP               | Diisoundecyl phthalate |
| 711P               | Di(heptyl, nonyl, undecyl) phthalate |
| DIPD               | Diundecyl phthalate |
| DE2D               | Ditridecyl phthalate |

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**Table 2. CMA Phase I environmental effects test program.**

| Tests                        | Rationale                                      |
|------------------------------|------------------------------------------------|
| Aquatic toxicity             |                                                |
| Static acute LC₅₀            | Different trophic levels in the aquatic food chain; variety of test species and habitat |
| *Daphnia Magna*              |                                                |
| Fathead minnow               |                                                |
| Freshwater algae             |                                                |
| Midge (insect)               |                                                |
| Mysid shrimp                 |                                                |
| Bluegill                     |                                                |
| Dynamic acute LC₅₀'s         | Confirmation of static acute data in flow-through system |
| Rainbow trout                |                                                |
| Fathead minnow               |                                                |
| Sheepshead minnow            |                                                |
| Chronic *Daphnia Magna* study| Life-cycle survival, reproduction study on species reportedly sensitive to phthalates |

**Environmental fate**

| Biodegradation               | Relative persistence                           |
|------------------------------|------------------------------------------------|
| Shake flask                  | Measure of ultimate degradation to CO₂ and water |
| Activated sludge (SCAS)      | Standard test for parent compound degradation — simulated sewage treatment plant conditions (high microbial population) |
| Water solubility             | To determine test concentrations for aquatic toxicity testing |
| Octanol–water partition      | Predictor of bioconcentration potential (lipophilic hydrophilic tendencies) |
| Vapor pressure               | Measure of mobility in terms of volatility    |

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Algae

Toxicity was observed for the lower molecular weight phthalates below their limits of water solubility; EC50 values ranged from 0.2 to 145 mg/L, not significantly different from fish. For higher molecular weight phthalates no toxic effects were observed at the solubility limits attained in test waters.

Biological Testing Results: Chronic

Since Daphnia magna have been reported to be among the most sensitive species for phthalate esters, it was felt that a chronic daphnid study on all 14 phthalates should be a part of Phase I testing. Maximum acceptable toxicant concentrations (MATC's) for the lower molecular weight products ranged from 0.6 to 38 mg/L. The MATC’s for C6-C13 dialkyl phthalates range from 0.62 to 0.15 mg/L (42-150 ppb); these values were largely dictated by the very low water solubility of the test compounds. The study was also confounded by surface film entrapment of test organisms. Observed results were in some cases attributable to physical effects not likely to occur in the environment.

Conclusions: Biological Testing

Based on acute toxicity test results, no single species can be considered particularly sensitive to phthalate esters. Although the lower molecular weight phthalates produced effects below maximum water solubility, they are unlikely to be present in the environment at these levels since they are rapidly biodegraded.

Results for the higher molecular weight phthalates were indeterminate, since no acute toxic effects were observed at the limits of water solubility attained in the tests. Therefore, the relatively low values obtained do not indicate true toxic effect concentrations; rather, they reflect experimental difficulties in attaining true solubilities in test waters.

Toxicity data obtained in the multigeneration algal studies, compared with data for all other aquatic species tested, indicate that algae are not an unusually sensitive test species.

Daphnid chronic data showed that Daphnia magna are not unusually sensitive to phthalates as previously believed. The effect levels (MATCs) obtained in this study for DEHP and other phthalates, combined with data from similar studies reported in the literature (2,3), indicate that safe levels are at least one to two orders of magnitude (10 × to 100 ×) higher than the 3 ppb reproductive effect level reported for DEHP in 1973 (4).

Static vs. dynamic testing gave essentially the same results. Freshwater and saltwater species are about equally sensitive.

The general pattern of the aquatic toxicity of phthalate esters to all organisms tested was primarily a function of relative molecular weight/side chain length/water solubility. Phthalate esters with side chains C8 or greater exhibited no toxic effect up to their limits of water solubility in the test systems. Even though the lower molecular weight, more water-soluble phthalates exhibited toxic effects below their limits of water solubility, no ester exhibited unusually severe effects of concern.

Environmental Fate Testing Results

Partitioning

Water solubility determinations showed that even the lower molecular weight phthalates are only slightly soluble. The higher molecular weight phthalates are practically insoluble, with solubilities in the 0.1 to 1.2 mg/L range. Phthalates were even less soluble in salt water.

Octanol–water partition coefficient (Kow) data showed the expected molecular weight-related preferential partitioning of phthalates into the organic phase. Determination of Kow for the higher molecular weight phthalates was not possible in these studies because the partitioning resulted in lower water concentrations than could be measured with existing analytical methods. Therefore, Kow values for these phthalates were calculated from water solubilities.

Vapor pressure measurements verified that phthalates as a class are practically nonvolatile. Only those in the low molecular weight range can be expected to volatilize significantly at ambient temperatures. As would be predicted, the higher molecular weight, plasticizer-range phthalates were essentially nonvolatile.

Transformation

Semicontinuous Activated Sludge (SCAS) testing showed the primary degradation rate of all phthalates to be very rapid under the high microbial, sewage treatment plant simulated conditions. For most phthalates, >50% primary degradation occurred within 24 hr.

Shake flask studies were used to measure ultimate degradation of phthalates to CO2 and water. In these studies, phthalates were found to degrade readily, with degradation half-lives of 1.9 to 27.7 days. The average t1/2 for all 14 phthalates tested was about 8 days.

Conclusions: Environmental Fate Testing

Phthalate solubilities in water decrease with increasing molecular weight in general. Higher molecular weight phthalates are practically insoluble, making detection in the water column extremely difficult. Phthalates are generally less soluble in salt water than in fresh water.

Vapor pressure decreases with increasing molecular weight; at C9 carbon side-chain length and higher, vapor pressures are essentially nil at ambient temperatures. Therefore, volatilization of phthalates into the atmosphere is practically nonexistent.

Octanol–water partitioning data verified the tendency of phthalates to preferentially partition to organic matter (biota) and to soil or sediment.

There was a general correlation between biodegradation half-lives and the length of alkyl sidechains in both
shake flask and SCAS studies. Phthalates as a class are readily degraded under high microbial/sewage treatment plant simulated conditions.

Based on these data and on published literature studies for five representative phthalates, only low to moderate potential for biocorcentration is indicated.

Safety Assessment

Environmental safety assessment is based on the concept of the magnitude of difference, or safety factor, between the exposure concentration in the environment and the effects concentration using the most sensitive species tested under laboratory conditions to represent the most sensitive organisms in the environment. This concept (5) has been accepted within the environmental science community for many years. The larger the safety factor, the lower the risk to aquatic life. A safety factor of 1 to 10 can be considered adequate if based on toxicity values for a variety of species and measured environmental concentrations. Factors of 10 and higher are defensible based on aquatic toxicity data from a variety of species, as in this study, and on estimated environmental concentrations.

Environmental exposure concentrations for phthalates where no data exist can be derived from reported monitoring data on other phthalates by factoring in estimated production volume and correcting for biodegradation rate.

A discussion of the details of this calculation scheme is beyond the scope of this paper, but has been reported elsewhere (1).

Based on this scheme, developed by the CMA Phthalates Panel's Environmental Research Task Group, the four low molecular weight phthalates have very comfortable safety margins (all well above 100). Factors above 100 are generally considered safe, especially if based on testing data for a variety of species, as is the case in this program, even though environmental concentrations were estimated for two of the four lower molecular weight phthalates tested.

For the higher molecular weight phthalates, safety factors ranged from 90 to 4200, based on DEHP as the reference compound (for which monitoring data exist). Safety factors in the range of 10 to 100 are regarded as safe if based on multispecies test data and estimated environmental concentrations.

Therefore, based on the CMA test program data and calculations scheme, all of the 14 test compounds had sufficiently high safety factors to demonstrate low potential for adverse effects on the environment.

Future Work

The CMA Phthalates Panel is studying Phase I results to determine what additional testing might be required to fill out the scientific data base for environmental effects of phthalates. Based on the CMA safety assessment, and on additional environmental studies on phthalates published in recent years, it is becoming evident that very little additional data will be required for a definitive analysis of the impact of phthalate esters on the environment.

This program was sponsored by the Chemical Manufacturers Association (CMA) Phthalate Esters Program Panel, comprised of manufacturers of phthalate esters, suppliers of raw materials used to produce phthalate esters, and companies that process compounds containing phthalates into commercial plastic products. Program Administrator for the CMA was Dr. Elizabeth J. Moran. The Panel's Environmental Research Task Group (ERTG) provided the technical assistance for developing the program and monitoring the studies. Current ERTG members were: E. F. Group, Jr., (Chairman), Exxon Chemical Company; R. K. Arisman, General Electric Company; H. B. Lockhart, Jr., Eastman Kodak Company; A. W. Mald, Exxon Corporation; D. E. Simanek, U.S. Steel Corporation; A. F. Werner, Monsanto Company.

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