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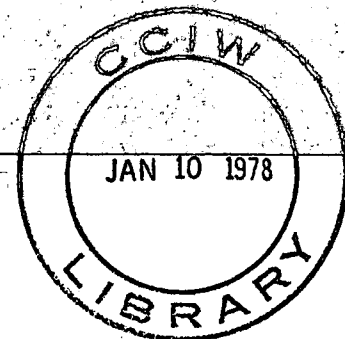
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Environmental Contaminants Inventory Study No. 4

The Production, Use and Distribution of Phthalic Acid Esters in Canada

T. D. Leah



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(Résumé en français)

**INLAND WATERS DIRECTORATE, ONTARIO REGION,
WATER PLANNING AND MANAGEMENT BRANCH,
BURLINGTON, ONTARIO, 1977.**



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Cat. No. : En 36-508/47

ISBN - 0-662-01251-8

CONTRACT NO. 08KX.KL229-7-1040

THORN PRESS LIMITED

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Abstract

This study is the fourth in the Environmental Contaminants Inventory Series. The first chapter contains an introduction to and summary of the material detailed throughout the report. The second and third chapters review the literature on ortho-phthalic acid esters (PAEs) in the environment and their effects on human health. By combining information on exposure and toxicity, an attempt is made to assess the present hazard to human health and the environment posed by observed levels of PAEs in the environment. In the fourth chapter, the production and use of PAEs in Canada is analyzed for the year 1973. The fifth chapter covers the releases of PAEs to the environment from production and processing, and from the use and disposal of articles that contain PAEs. Estimates indicate that in 1973 releases from production and processing activities comprised approximately 20% of the total, whereas use and disposal activities accounted for the remaining 80%. These releases have been presented in terms of major drainage basins to give the data more regional significance. The sixth chapter reviews the chemistry and properties of PAEs, the major processes used in producing and fabricating flexibilized (plasticized) poly (vinyl chloride) and the use of related chemicals such as phthalic anhydride and terephthalic acid. The final chapter summarizes the conclusions and recommendations based on the findings of this study.

Throughout the report, the data are clarified through the use of a material flow chart, tables, and maps.

Résumé

La présente étude est la quatrième dans le cadre de l'Inventaire des contaminants de l'environnement. Le premier chapitre comprend une introduction et un résumé portant sur la substance dont traite en détail le rapport. Aux deuxième et troisième chapitres, on passe en revue les ouvrages traitant de la présence des esters de l'acide ortho-phthalique (EAP ou phtalates) et de leurs effets sur la santé de l'homme. En combinant les données relatives à l'exposition et à la toxicité, on essaie d'évaluer le danger que représentent actuellement, pour l'homme et l'environnement, les taux de phtalates, observés dans l'environnement. Au quatrième chapitre, on analyse la production et l'utilisation des phtalates au Canada, pour l'année 1973. Le cinquième chapitre traite du déversement de phtalates dans l'environnement, à partir des installations de production et de traitement, ainsi que de l'utilisation et de l'élimination d'articles contenant des phtalates. Les estimations indiquent qu'en 1973 le déversement provenant des installations ci-dessus représentait 20 pour cent du déversement total, l'utilisation et l'élimination comptant pour 80 pour cent. Ces déversements sont présentés en fonction des principaux bassins de drainage, pour que les données aient une signification de caractère plus régional. Au sixième chapitre, on étudie les propriétés chimiques et autres des phtalates, les principaux procédés de production et de fabrication de chlorure de polyvinyle plastifié, et l'utilisation de substances chimiques connexes, comme l'anhydride phthalique et l'acide téréphthalique. Le dernier chapitre est un résumé des conclusions et des recommandations, fondées sur les résultats de la présente étude.

Tout au long du rapport, les données sont accompagnées de diagrammes des débits du produit, de tableaux et de cartes.

Introduction and Summary

Phthalic acid esters (PAEs) are a family of organic chemicals produced by reacting phthalic anhydride (PA) with various alcohols. Their largest use by far is as plasticizers, the purpose of which is to impart flexibility to certain plastics, notably poly (vinyl chloride), or PVC. They are also used in cosmetics, inks, insect repellents and other miscellaneous applications. In the United States, some PAEs are being considered for use in electrical capacitors as substitutes for polychlorinated biphenyls (PCBs).

In recent years, phthalate residues have been detected in the environment, and in human and animal tissue. Concern originated with the discovery that blood is capable of extracting PAEs from plastic storage bags and other plastic medical devices. As a result, the possibility that PAEs might constitute a hazard to the environment and/or human health came to light. Questions were raised about the effects of continued long-term exposure to low levels of PAEs from the vast array of plastics and other PAE-containing products in use today.

In September 1972, the National Institute of Environmental Health Sciences held a conference in Pinehurst, North Carolina, to draw together the available information on the effects of PAEs on the environment and human health. Much of the data reviewed in this report was presented at that conference.

The purpose of this study is to develop an internally consistent inventory of PAEs in Canada. This requires examination of domestic production, imports and exports of PAEs, the use of PAEs in manufacturing, and the import and export of products containing PAEs. One must also consider the quantities of PAEs released to the environment from the production and processing of PAEs, and from the use and disposal of products containing them. The recycling of scrap plastics is another factor in the material balance.

The second chapter reviews the literature on PAEs in the environment. Information on environmental levels is by no means extensive. Data on atmospheric levels of PAEs are virtually non-existent. Observed water and sediment concentrations range from non-detectable to hundreds of parts per billion (ppb). Various species of plants have been found to contain phthalates, although the origin of these is unconfirmed. A wide range of PAE residues, some as high as 3,200 ppb of di-(2-ethylhexyl) phthalate have been found in fish. These levels vary greatly with species and location. Invertebrates and fish have been shown to accumulate PAEs, however, these residues are rapidly cleared on transfer to phthalate-free water. There is evidence to suggest that some species of microorganisms are able to biosynthesize and biodegrade PAEs. The known toxicities and physiological effects of PAEs are summarized and, on the basis of toxicity and exposure, an estimate of the potential hazard associated with current environmental levels has been made. The immediate hazard to most terrestrial organisms, fish and aquatic organisms appears to be low, however, fish-eating birds and mammals could conceivably sustain effects due to bioaccumulation, and current water levels may pose an immediate threat to water flea reproduction.

The third chapter covers the literature on PAEs and human health. The acute oral toxicities (LD_{50}) of PAEs to test animals are generally quite low. The Acceptable Daily Intake (ADI), a figure which extrapolates the observed acute

toxicities of PAEs for test animals to humans, has been determined for some PAEs to be in the same range as those of some common food additives. Phthalates in the work place are generally no problem where good industrial hygiene is practiced, however, no Threshold Limit Values (TLVs) have yet been established for PAEs. Some researchers have reported teratogenic and mutagenic effects in test animals.

Humans are exposed to PAEs through air, water, food and skin contact. Some hospital patients may be exposed to PAEs in plastic biomedical devices during blood transfusion or hemodialysis. A rough estimate shows the daily adult intake of PAEs from common sources to be approximately two to four orders of magnitude smaller than the acceptable daily intake values. This suggests that there is no immediate toxicity threat to humans from present levels of PAE ingestion. However, the effects of prolonged exposure to low levels of PAEs are unknown and should be investigated.

The fourth chapter analyzes the production and use of PAEs in Canada for the base year 1973. Some 78 million pounds of PAEs were processed in Canada in that year. Domestic production supplied 75% of this total, with the rest being imported from Europe and the United States. Ninety-seven percent of the total was used as plasticizer in the production of flexible PVC. An estimated additional 11.5 million pounds of PAEs were contained in imported vinyl compounds. Examination of the data shows that virtually all activities involving the production and processing of PAEs are confined to specific geographical areas, namely, the Lower Great Lakes and mid-St. Lawrence drainage basins. The degree of use and disposal of items containing PAEs is assumed to be proportional to population.

The fifth chapter describes the releases of PAEs to the environment in terms of routes and quantities. The sources of PAE releases have been divided into the following two categories:

1. the production and processing of PAEs; and
2. the use and disposal of items containing PAEs.

The routes of PAE entry to the environment are described for both categories (e.g., volatilization, industrial waste disposal, incineration, leachate from landfill, etc.). Because of insufficient data, however, there has been no attempt to provide a breakdown of releases by route of entry. By the same token, the release figures represent totals only and do not indicate the quantities of PAEs released directly to the aquatic environment as opposed to the atmosphere. To gain insight into the localized nature of PAE releases, the country has been divided into suitable watershed basins, and releases to the environment have been estimated for each basin. One finds that releases from production and processing activities are confined to the Southern Ontario and mid-St. Lawrence basins. Releases from the use and disposal of items containing PAEs have been assumed proportional to the population of the watershed. Again, the Southern Ontario and mid-St. Lawrence basins, having the largest populations of any of the watersheds, account for the greatest releases from use and disposal activities. In 1973, releases of PAEs to the environment in Canada totalled between 9.9 and 11.9 million pounds. Approximately 22% of the total resulted from production and processing activities.

The sixth chapter summarizes the relevant background information regarding PAEs and their use as plasticizers. The physical and chemical properties of PAEs are outlined. Plasticizer technology is reviewed, along with some of the processes employed in formulating and fabricating flexible PVC. In addition, the uses of phthalic anhydride, other than in the production of PAEs, are described. In 1973, the manufacture of PAEs accounted for 33% of phthalic anhydride consumption in Canada. Fifty-eight percent was used in the production of alkyd and polyester resins, nine percent was exported, and a small amount was used in the making of chemical derivatives. The production of polyester fibre from terephthalic acid

(TPA) and dimethyl terephthalate (DMT) is outlined in this chapter. DMT is a para-phthalate, different in chemical structure from the ortho-phthalates (PAEs).

In conclusion, phthalic acid esters (PAEs) are a group of chemicals which display reasonably low acute toxicities. At current levels of exposure, they seem to pose no immediate threat to the environment (with the possible exception of water flea reproduction) or human health (with the possible exception of patients receiving blood transfusions or hemodialysis therapy). These conclusions, however, must be taken with emphasis on the following. First, the data on environmental levels of PAEs, especially in areas of known environmental discharges of PAEs, is far from complete. Second, information concerning pathways of PAE movement in the environment is equally lacking, if not more so. Third, virtually nothing is known about the effects of long-term exposure to varying levels of PAEs. It is conceivable that when a better state of knowledge in these areas is achieved, the presence of PAEs in the environment and the resulting exposure sustained by living organisms may prove worthy of considerably greater concern than present information would indicate.

Phthalic Acid Esters in the Environment

INTRODUCTION

The issue of phthalic acid esters (PAEs) as environmental pollutants and as a human health hazard has become increasingly important to those charged with preserving the quality of our air, water and environment in general. To determine the environmental hazard posed by these compounds, one must consider not only their toxicity, but the degree of exposure involved; that is, the quantities to which the environment and various biota are exposed. For the most part, these chemicals display low acute toxicities. On the other hand, the consumption of these compounds is extremely high (in excess of one billion pounds annually in the U.S., 78 million pounds in Canada in 1973) and all of this will sooner or later be released to the environment by the various means discussed in Chapter 5.

The following sections summarize some of the pertinent literature on the subjects of environmental levels of phthalates and the toxicity of phthalates to biota.

ENVIRONMENTAL LEVELS

Peakall (1) has summarized much of the data on phthalate levels in environmental samples. Residues of phthalates and phthalic acid have been found in various substances (soil, plants, animals, etc.) and in many cases there is speculation as to the origin of the PAEs. Considerable uncertainty exists as to whether the phthalate contamination measured in samples is truly native (naturally occurring) or exogenous (absorbed from the ambient environment) or whether it originates with the equipment used in the laboratory, for example, plastic tubing containing plasticizer. Several authors (2,3,4) refer to contamination during collection and analysis as the likely source of phthalates in some environmental samples. Peakall states that this possibility may be eliminated if suitable precautions are taken and proper controls run. It is often unclear, however, whether or not suitable precautions were taken. The question of exogenous origin versus natural occurrence is more difficult to resolve.

The following is a summary of the information contained in the literature on phthalate levels in the environment. The information provides an indication of phthalate levels in air, water, soil and living organisms. It must be noted, however, that the type of detailed information presented by Woodwell *et al.* (5) for DDT and Nisbet and Sarofim (6) for PCBs is not yet available for PAEs.

Air

Thomas (7) reported levels of 300 ng/m³ of di-2-ethylhexyl phthalate (DEHP) and 700 ng/m³ of di-n-butyl phthalate (DnBP) in air in Hamilton, Ontario. One would expect ambient air levels to be considerably lower in rural areas, but at present very little information, if any, is available.

Water and Sediments

The data available on PAEs in water is considerably greater than that for air. Hites (8) reported phthalate levels in the Charles River in Boston, Massachusetts, ranging from 0.88 to 1.9 ppb. The author suggests that as the contaminated water

flows downstream from the phthalate source, more water is added from runoff and other sources, thus diluting the phthalates. Biological activity may also tend to reduce the phthalate concentration as the water moves downstream. The Michigan Water Resources Commission (9) measured the level of DEHP in the settleable solids collected from three Michigan rivers in the spring of 1973. On an over dry basis, levels ranged from 17.6 mg/kg to 25.0 mg/kg for the Grand River, 8.3 mg/kg to 12.5 mg/kg for the St. Joseph River, and <1 mg/kg for the Kalamazoo River. No data were reported on DEHP levels in the water itself. Mayer *et al.* (10) analyzed samples from the Great Lakes. For the Black Bay Region of Lake Superior, Ontario (a rural and industrial area), water contained no detectable DnBP and 300 ppb DEHP. Sediments from the bay contained 100 ppb DnBP and 200 ppb DEHP. The authors do not speculate about why the sediments contain lower levels of DEHP than the water, which is contrary to what might be expected. Water from Hammond Bay, Lake Huron, Michigan (a forested area), contained 0.04 ppb DnBP but no detectable DEHP, whereas Lake Huron, Michigan, water (presumably open lake) had 5.0 ppb. Working Group C of the International Joint Commission Upper Lakes Reference Group has determined the loadings from the State of Michigan to Lake Superior to be 0.6 kg/day and 2.23 kg/day of DEHP and DnBP respectively. No data are available for the other lakes.

In general, little information is available on PAEs in Canadian waters. No surveillance program has been implemented by Fisheries and Environment Canada to gather information on PAEs, and there are currently no plans to set up such a program (Dr. D.B. Carlisle, Water Quality Branch, Fisheries and Environment Canada, Ottawa, personal communication). Some data have been collected for Ontario at the provincial level. In 1975 drinking water samples in Ontario were analyzed for plasticizer materials including five phthalates; dimethyl phthalate (DMP), dipropyl phthalate (DPP), dibutyl phthalate (DBP), dioctyl phthalate (DOP), and dinonyl phthalate (DNP) (Dr. O. Meresz, Ministry of the Environment, Ontario, personal communication). Samples of raw and treated water were collected from 30 treatment plants throughout Ontario. Of the 79 samples analyzed, 38 showed detectable levels ranging from 0.05 to 9.0 ppb total phthalate, with no observable trend. Four samples contained above 4 ppb, five contained between 2 and 4 ppb, and the remaining samples registered below 2 ppb. In the case of treated water, likely sources of phthalates include plastic tubing and chemical storage containers used in the plant, whereas levels in raw water result from phthalate contamination of the general environment.

Soil

Ogner and Schnitzer (11) studied a humus from Prince Edward Island and found phthalate-fulvic acid complexes with levels of 13 mg phthalate per 100 g fulvic acid, up to 0.03% (300 ppm) dry weight. The origin of this contamination was uncertain. Matsuda and Schnitzer (12) found that such fulvic acid complexes make phthalates more water soluble. They observed that 125 mg of fulvic acid solubilized 203 mg of DEHP, 65 mg of dicyclohexyl phthalate, and 35 mg of DBP at pH = 2.45, and approximately 25% less at pH = 7.

Phillips and Breger (13) extracted DOP (0.15%) from a petroleum crude oil in Utah, but no mention was made of possible contamination. Breger (14) stated that DOP was also found in an Italian crude oil, and in this case the possibility of contamination was reportedly eliminated.

Biota

Levels of PAEs in biological samples have been studied by Mayer *et al.* (10) and Zitko (15). Data assembled by Stalling *et al.* (16) on PAEs are presented in Table 1. Observed levels of PAEs in fish vary greatly with location. In Mississippi and Arkansas, DEHP residue in channel catfish ranged from 1,000 to

7,500 ppb. A walleye from Black Bay, Lake Superior, contained 800 ppb DEHP, whereas yellow perch from Iowa and brook trout from California contained no detectable DEHP. Zitko (15) found 14.1 ppm (lipid basis) of dibutyl phthalate in an egg of a double-crested cormorant (Phalacrocorax auritus) and 10.9-19.1 ppm in three eggs of herring gulls (Larus argentatus). Two hatchery-reared juvenile Atlantic salmon (Salmo salar) contained 12.9 and 16.4 ppm DEHP and the blubber of a common seal pup (Phoca vitulina) contained 11 ppm. The collection sites of the eggs and seal were not indicated, but Peakall (1) states that they were probably in New Brunswick.

Table 1. Phthalate Ester Residues Found in Selected Samples from North America

Source	Sample	Residue, ng/g (ppb)	
		DnBP ¹	DEHP ²
Mississippi and Arkansas (agriculture and industrial areas)	Channel catfish	Trace	3,200
Fairport National Fish Hatchery, Iowa (water supply from industrial area of Mississippi River)	Channel catfish ³	200	400
	Dragonfly naiads	200	200
	Tadpoles	500	300
Black Bay, Lake Superior, Ontario (rural and industrial area)	Walleye	—	800
	Water	—	300
	Sediment	100	200
Hammond Bay, Lake Huron, Michigan (forested area)	Water	0.040	—
Lake Huron, Michigan	Water	—	5.0
Spirit Lake, Iowa (agriculture area)	Yellow perch	—	—
Clover Leaf Lake, California (10,300 ft elevation)	Brook trout	—	—
Missouri River McBaine, Missouri	Water (turbid)	0.09	4.9
Fish food and components	Total diets	—	2,000
	Total diets	—	7,000
	Casein	20	190
	Corn starch	20	170
	Gelatin	20	140
	Bone meal	30	400
	Wheat middlings	30	200
	Carboxymethyl cellulose	—	—

SOURCE: Stalling *et al.* (16).

¹ Di-*n*-butyl phthalate.

² Di-2-ethylhexyl phthalate.

³ Residues presented for this group are the means of 40 fish. Di-2-ethylhexyl phthalate residues ranged from 1,000 to 7,500 ng/g.

Morris (17) analyzed specimens of the deep sea jellyfish (Atolla) from the North Atlantic and found phthalic acid to be 13% of total lipid weight and 26% of total fatty acid weight. These concentrations were considered to be a result of accumulation.

Taborsky (18) found DOP at about 700 ppm in bovine pineal glands, and claimed that this was not due to contamination after collection. Nazir et al. (19) detected 35-135 μg DEHP/100 g original heart muscle mitochondria of dog, rat, rabbit and cattle, with the same qualification. It seems likely that the DOP and DEHP present in certain animal organs were ingested rather than biosynthesized in situ.

The occurrence of phthalates in a wide variety of plants suggests natural occurrence. Through detailed studies of plants from areas likely to be exposed to phthalate contamination and from remote areas, it should be possible to determine a baseline for the presumably natural occurrence of phthalates in plants. Hayashi et al. (20) found several dialkyl phthalates in umbelliferae (a perennial vegetable grown in Japan) but did not state whether they believed the esters were biosynthesized or were artifacts. Zinfandel grapes (Vitis vinifera) were found to contain 2.25 ppm n-butyl phthalate on a fresh weight basis (21). Again, the likelihood of artifacts was not mentioned. Swain et al. (22) analyzed tobacco leaves containing phthalates in the order of 0.02% (200 ppm) of dry leaf weight. Stedman and Dymicky (23) emphasized that the PAEs they detected in tobacco leaf extract did not originate in solvents or laboratory equipment. With regard to plant products, Beroza et al. (24) found DEHP in corn oil, and Covello et al. (25) detected 1 to 5 ppm phthalates in olive oil.

BIOSYNTHESIS AND BIODEGRADATION OF PAES

It seems that some biological species, notably microorganisms, may be able to biosynthesize some phthalate esters, although information is limited. Sugiyama et al. (26) isolated a phthalate from the fungus Alternaria kikuchiana, which causes black spot disease in pears. They concluded that the ester was a normal metabolite of the fungus. They did not mention whether the possibility of contamination was considered. Miyoshi and Harada (27) isolated DBP in a culture of soil bacterium strain BD34. Mathur (28) states that care must be taken when extrapolating the results of such laboratory culture studies to a natural system.

Aebi et al. (29) isolated phthalic acid and a phthalate, most probably DOP, from the lipid fraction of the bacterial pathogen Mycobacterium tuberculosis. These findings were considered not to be artifacts. Asselineau (30) found DBP in another bacterial pathogen, Corynebacterium diphtheriae, but did not exclude the possibility of contamination. Etemadi (31) concluded that the findings in the above two studies were indeed artifacts.

Several authors have reported on the biodeterioration of plastics, including plastic additives such as PAEs, by microorganisms. Interest in this field was aroused during World War II, when plastics were first exposed to tropical climates. It was observed then that the loss of plasticizers was mainly responsible for making the plastics brittle.

Berk et al. (32) tested 24 species of fungi and found them unable to utilize PAEs as a carbon source. Stahl and Pessen (33) reported that two yeasts were unable to utilize DOP and DEHP, and that two bacteria often found on degraded plastic films utilized DEHP and DOP only to a negligible extent. Booth and Robb (34) reported that the DEHP in plasticized film was resistant to attack by soil microorganisms (species of Pseudomonas and Brevibacterium). The susceptibility of other plasticizers depended on the stabilizers used in the PVC formulation. De Coste (35) observed that the loss of plasticizer in PVC cable jackets after 4 years of burial was the same order of magnitude in the subsoil as in the biologically active topsoil. The author thus felt that the loss mechanism may not have been biological. Mathur (28) states that the common presence of PAEs

in the environment, notably DEHP and its isomers, may be explained in part by the lack of microorganisms that are capable of utilizing them under natural conditions. This also suggests that DEHP is not biosynthesized in nature.

TOXICITY AND PHYSIOLOGICAL EFFECTS OF PAEs

In recent years, many researchers have investigated and reported upon the acute and chronic toxicity aspects of PAEs to aquatic and terrestrial biota. Much of the literature has been summarized by Peakall (1), Autian (36) and Krauskopf (37). The acute toxicities of most of the phthalates are generally quite low [0.7->10 ppm of DnBP, for fish (38)]. On the other hand, concentrations as low as 3 ppb of DEHP significantly inhibit reproduction in water fleas (Daphnia magna) (38). Some of the more representative studies and findings are outlined in the following.

Aquatic Organisms

Toxicity

Using standard static and flow-through bioassay procedures (39), Mayer and Sanders (38) showed that the acute toxicity of DnBP to fish is relatively low (1-7 ppm, Table 2) as compared with DDT (7-19 $\mu\text{g}/\text{l}$ (ppb), acute 96-hr LC_{50}). The 96-hr LC_{50} (the concentration required to kill 50% of the test organisms in 96 hr) to scuds (Gammarus pseudolimnaeus) and crayfish (Orconectes nais) was 2.1 mg/l and >10.0 mg/l respectively. The 96-hr LC_{50} values of DEHP were >10 mg/l for both fish and invertebrates. Zitko (40) observed no mortality in 96 hr in preliminary bioassay experiments with juvenile Atlantic salmon using 10 mg/l of DMP and DEHP. At this concentration DBP caused 100% mortality in 3 hr ($\text{LT}_{50} = 1.25$ hr) but no mortality in 96 hr occurred at 1 mg/l.

Table 2. Acute Toxicity of Di-n-butyl Phthalate to Aquatic Organisms

Species	LC_{50} value, mg/l		
	24 hr	48 hr	96 hr
Fathead minnow (<u>Pimephales promelas</u>)	—	1.49	1.30
Bluegill (<u>Lepomis macrochirus</u>)	1.23	0.73	0.73
Channel catfish (<u>Ictalurus punctatus</u>)	3.72	2.91	2.91
Rainbow trout (<u>Salmo gairdneri</u>)	—	—	6.47
Scud (<u>Gammarus pseudolimnaeus</u>)	7.00	—	2.10
Crayfish (<u>Orconectes nais</u>)	—	—	>10.0

From: Mayer and Sanders (38).

In vitro studies with channel catfish (Ictalurus punctatus) liver indicate that DnBP is degraded 16 times more rapidly than DEHP (41). The large difference in toxicity between the two esters may be due to the rate of degradation of the parent compound, the ester, to a more toxic substance such as phthalic acid.

Accumulation, Metabolism, Excretion

Mayer and Sanders (38) exposed invertebrates to ^{14}C -DnBP (di-n-butyl phthalate containing radioactive carbon-14), and ^{14}C -DEHP. The initial rapid uptake and accumulation of radioactive residues was several hundred times greater than the concentration in the water. DEHP residues were accumulated and stored by scuds

during a 14-day exposure at levels 3600 times greater than the 0.1 µg/l concentrations in the surrounding water, whereas the same exposure to DnBP caused accumulated total body concentrations 1400 times that of the water. Daphnia accumulated DBP residue at levels of 6000 times the 0.1 µg/l in the surrounding water (42).

The metabolism and excretion of PAEs have been studied by Mayer and Sanders (38) and Metcalf et al. (43). Mayer and Sanders (38) exposed water fleas to 0.01 µg/l of DnBP for 7 days. The organisms were then transferred to fresh water and after 7 days, 25% of the phthalate activity was still present. In a similar experiment, scuds were exposed to 0.1 µg/l DEHP for 7 days and transferred to fresh water. After 10 days, 6% of the total activity remained. Metabolism of the esters was not determined and the loss in radioactive residues may have been due to metabolism and/or excretion of the parent compound. Fathead minnows (Pimephales promelas) exposed to 1.9 µg/l ¹⁴C-DEHP accumulated 1380 times the water concentration in 28 days. The amount accumulated was comparable to that of DDT over the same period of time. After placing the fish in fresh water, the time required for 50% elimination of DEHP and its degradation products was 7 days. Residues consisted of DEHP, the monoester mono-2-ethylhexylphthalate, MEHP, free phthalic acid, the conjugated monoester and conjugated phthalic acid.

Metcalf et al. (43) studied the uptake and degradation of ¹⁴C-DEHP by several aquatic organisms. In guppies (Lebistes reticulatus) DEHP represented 88.5% of the total observed radioactivity after 1 day and 16.8% after 7 days. Uncontaminated guppies fed Daphnia with a 1-day uptake of ¹⁴C-DEHP showed the same degradation pattern. Metabolites identified included phthalic acid and phthalic anhydride. Organisms such as the fingernail clam (Sphaerium striatinum), the water flea (Daphnia magna), and the aquatic plant (Elodea canadensis) accumulated large amounts of ¹⁴C-DEHP but degraded it more slowly than the guppy. The mosquito larva (Culex pipiens quinquefasciatus) accumulated ¹⁴C-DEHP to much higher levels than the other organisms (Fig. 1).

In the same study Metcalf et al. used a model ecosystem with a terrestrial-aquatic interface to observe the distribution of DEHP in various elements of the food chain. The distribution of the ¹⁴C-DEHP and metabolites in the various organisms is shown in Table 3. These data show that the mosquito larva had the highest bioconcentration factor (107,670X) and the fish, the least (130X). Under identical conditions (44), DDT was biomagnified in the mosquito larva 8200 times and in the fish 84,500 times. It appears that only the fish is able to degrade the DEHP and slowly excrete its metabolites. The major degradative pathways seem to be through hydrolysis of the ester groups to produce MEHP, then phthalic acid, then phthalic anhydride.

Table 3. Distribution of ¹⁴C-DEHP and Metabolites in Laboratory Model Ecosystem

	R_f^*	Concentration, ppm as DEHP equivalents				
		H ₂ O	<i>Oedogonium</i> (algae)	<i>Physa</i> (snail)	<i>Culex</i> (mosquito)	<i>Gambusia</i> (fish)
Total ¹⁴ C		0.0078	19.105	20.325	36.609	0.206
DEHP	0.79	0.00034	18.322	7.302	36.609	0.044
MEHP	0.70	0.00099	0.325	2.541	—	0.021
Phthalic anhydride	0.65	0.00363	0.108	5.772	—	0.113
Unknown I	0.50	0.00136	—	—	—	—
Phthalic acid	0.35	0.00077	0.094	2.724	—	0.018
Unknown II	0.13	0.00054	0.029	0.768	—	—
Polar metabolites	0.0	0.00016	0.155	1.218	—	0.010

SOURCE: Metcalf et al. (43).

*Thin layer chromatography in solvent system of benzene: Skellysolve B: acetone: acetic acid, 65:25:25:5 by volume.

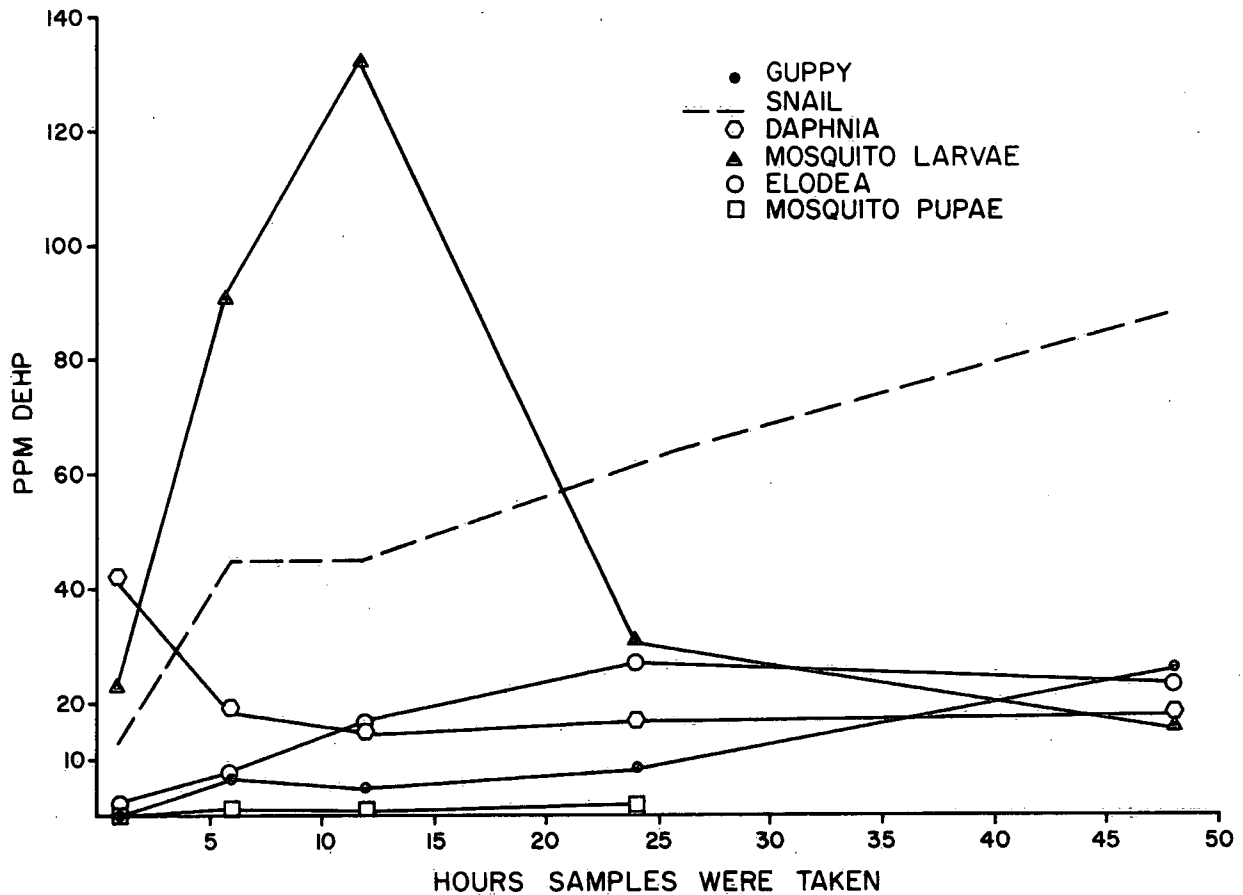


Figure 1. Time course study of uptake of DEHP by aquatic organisms from water containing 0.1 ppm DEHP. Source: Metcalf *et al.* (43).

Effects on Reproduction

Mayer and Sanders (38) studied the reproduction of water fleas which were continuously exposed to 3 $\mu\text{g}/\text{l}$, 10 $\mu\text{g}/\text{l}$, and 30 $\mu\text{g}/\text{l}$, of DEHP for a complete life cycle (21 days). Reproduction was inhibited 60%, 70% and 83% in the respective treatment levels. The observed toxicity values (LC_{50}) for aquatic invertebrates are 700 to 3300 times that which inhibited reproduction in water fleas.

Table 4. Reproduction in Zebra Fish (*Brachydanio rerio*) and Guppies (*Lebistes reticulatus*) Fed Di-(2-ethylhexyl) Phthalate

Species	Reproductive variable	Dietary di-(2-ethylhexyl) phthalate concentration, $\mu\text{g}/\text{g}$		
		0	50	100
Zebra fish (<i>Brachydanio rerio</i>)	Number of spawns	6	8	14
	Eggs per spawn	20.3	15.2	10.1
	Percent fry survival	51.1	31.7	11.5
Guppies (<i>Lebistes reticulatus</i>)	Fry per female	33	—	29
	Percent abortions	0	—	8

SOURCE: Mayer and Sanders (38).

The effects of DEHP on reproduction of zebra fish (Brachydanio rerio) and guppies (Lebistes reticulatus) were determined with 90-day dietary exposures of the phthalate (Table 4). The number of spawns were greater in the treated zebra fish, but the control fish produced more eggs per spawn. Fry survival was significantly reduced by phthalate exposure. The least number of guppy fry were born to parents fed DEHP, and an 8% incidence of abortions was noted. Coho salmon (Oncorhynchus kisutch) injected intraperitoneally (into the abdominal cavity) with 3 μ g DEHP/kg of fish demonstrated increased serum calcium (45). This finding, combined with the tetany observed in the zebra fish fry, suggests that DEHP may alter normal calcium metabolism in fish.

Sugawara (46) studied the relative effects of three phthalates (DMP, DEP, DBP) on the hatching of eggs of brine shrimp (Artemia salina). The toxic order of the PAEs was DBP>>DEP>DMP. The toxic order was inversely proportional to their solubility in water.

Terrestrial Organisms

Studies indicate that the acute toxicity of phthalates to mammals is low (Table 5). The data on birds appear to be limited to one species and one phthalate (47) and in this case the acute toxicity was of the same order as that found for mammals. Most of the data on acute toxicity have been gathered using rat, mouse, rabbit and guinea pig as test species.

In ingestion studies, the dibutyl phthalates and DEHP were the most widely used. Rats were the most common test animals. Prolonged ingestion studies generally involved daily dosages well below the LD₅₀ values. Autian (36) has summarized the literature on such long-term feeding studies. Over a period of 2 years, the effects of dimethyl phthalate (DMP) in the diet of female rats ranged from none (at 2% in diet) to some chronic nephritic changes (at 8% in diet) (48). Rats fed 0.01, 0.05 and 0.25% DBP in the diet showed no toxic reactions after 1 yr (52). Of those fed 1.25%, half died within the first week, whereas the survivors grew normally. Lefaux (53) reported on feeding studies where several generations of rats were fed 100, 300 and 500 mg DBP/kg body weight. Both male and female rats showed normal weight gains and reproductive patterns. Shaffer et al. (55) exposed rats to dietary concentrations of 3.0, 1.5, 0.75 and 0.375% DEHP for 90 days. They concluded that no injury resulted from oral administration of 0.2 g/kg/day or less, whereas a slight retardation in growth occurred at 0.4 g/kg/day.

Autian (36) describes the unpublished data of Lawrence on the subacute toxicity of DEHP. In one experiment, DEHP was administered subcutaneously (under the skin) at three dose levels (5.0 g/kg, 100 mg/kg and 25 mg/kg) once a week for 12 weeks. No significant differences from controls were noted in gross and histopathologic examination of tissues and organs. At the highest dose levels, DEHP was found in the liver and kidney. Lawrence also found that the toxicity of DOP and DEHP to mice increased over repeated administrations. The LD₅₀ of DOP and DEHP decreased by factors of 4.6 and 8.3 respectively (i.e., toxicity increased by these factors) over 11 weeks of intraperitoneal (abdominal) administration. In a study where mice were exposed to DEHP vapours for 1 hr three times a week for 12 weeks, the only pathologic response observed by Lawrence was signs of diffuse chronic inflammation of the lungs, similar to a burn reaction. Shaffer et al. (55) exposed rats to mists formed by cooling air saturated with di-(2-ethylhexyl) phthalate. None were killed in 2 hr but all died within 4 hr.

Peakall (60) studied the effects of DnBP and DEHP on the eggs of ring doves (Streptopelia risoria). No significant effects were noted with DEHP, whereas a diet containing 10 ppm DnBP caused a decrease in eggshell thickness and an increase in permeability to water. Eggshell thickness recovered rapidly on a phthalate-free diet, whereas the clearance rate for organochlorines was slow. The evidence

suggests that only where DnBP is continually available in the diet could it be of importance in eggshell thinning. The species at greatest risk would be the avian fish-eaters, since cold-blooded creatures, such as fish, metabolize phthalates much more slowly than do warm-blooded ones.

Table 5. Acute Oral Toxicity of Phthalates

Phthalate	Species	LD ₅₀	References
Symmetrical dimethyl	Guinea pig	2.4 g/kg	48
	Mouse	7.2 g/kg	48
	Rabbit	4.4 g/kg	48
	Rat	6.9 g/kg	48
	Rat	6.7 g/kg	49
	Rat	6.8 g/kg	50
Diethyl	Rat	8.2 ml/kg	51
Dibutyl	Rat	>20 g/kg	48
	Rat	ca. 8 g/kg	52
	Rat	8-10 g/kg	53
	Rat	10 g/kg	53
Di-n-butyl	Rat	12.6 g/kg	54
	Rat		
Di-n-hexyl	Rat (males)	29.6 ml/kg	49
	Rat (females)	38.9 ml/kg	49
Dicyclohexyl	Rat	30 ml/kg	53
Diisooctyl	Rat	22.6 ml/kg	54
Di-2-ethylhexyl	Guinea pig	26.3 g/kg	49
	Mouse	34.0 ml/kg	49
	Rabbit	33.9 g/kg	55
	Rat	30.6 g/kg	55
	Rat	34.3 ml/kg	49
Diisononyl	Rat	>10 g/kg	56
Diisodecyl	Rat	>64 ml/kg	57
Ditridecyl	Rat	>64 ml/kg	57
Coesters of alcohol mixtures			
Butyl, octyl	Rat	>63 ml/kg	54
Butyl, decyl	Rat	20.8 ml/kg	57
Hexyl, decyl	Rat	49.4 ml/kg	57
n-Hexyl, n-octyl, n-decyl	Rat	45.2 ml/kg	54
Heptyl, nonyl	Mouse	>19.3 g/kg	58
	Rat	>19.3 g/kg	58
Heptyl, nonyl, undecyl	Mouse	>20 g/kg	58
	Rat	>20 g/kg	58
	Rat	>64 g/kg	54
Octyl, decyl	Rat	45.2 ml/kg	57
	Rat	>63 ml/kg	54
2-Ethylhexyl, benzyl	Rat	60.3 g/kg	59
Nonyl, undecyl	Mouse	>19.7 g/kg	58
	Rat	>19.7 g/kg	58
o-Phthalic acid	Rat	7.9 ml/kg	55

After: Krauskopf (37).

HAZARD POTENTIAL OF PAES

In any estimate of the risk posed by current environmental levels of PAEs to the health and stability of the ecosystem, one must consider the exposure involved, i.e., the quantities to which the biota are exposed, and the toxicities of the PAEs to these biota. In addition, the pathways by which the PAEs become available to exert a toxic action must be considered.

The organism most sensitive to PAEs so far studied is the water flea (Daphnia magna). Its reproduction is impaired by DBP and DEHP concentrations of 20 and 3-5 ppb, respectively (38, 61). The emergence of adult midges (Chironomas tentans) is significantly reduced at DEHP concentration of 14 ppb (62). Observed LC_{50} 's for aquatic invertebrates are 700-3300 times the concentration which inhibits reproduction in water fleas. Observed water concentrations in some areas (1-5 ppb) then, may pose an immediate threat to water flea reproduction, but no immediate hazard to fish and other organisms. On the basis of these data and the application of a general safety factor of 0.2, maximum levels recommended by the International Joint Commission Great Lakes Water Quality Board (63) are 4 $\mu\text{g}/\text{l}$ (ppb) for DBP and 0.6 $\mu\text{g}/\text{l}$ for DEHP. The Board further recommended that until such time as chronic data on other PAEs become available, concentrations of other individual PAEs in water be restricted to the recommended quantification level of 0.2 $\mu\text{g}/\text{l}$. Such action should minimize the hazard posed by PAEs to water fleas, and since this is one of the most sensitive organisms, other species of aquatic organisms should be protected as well.

The immediate danger to terrestrial organisms of environmental levels of PAEs appears to be low, considering the low acute toxicities of most PAEs. However, avian fish-eaters, such as gulls, and mammals, such as mink and otter, are exposed to PAEs from the aquatic ecosystem and their reproductive mechanisms may be affected, as was the case with DDT and PCBs. Although the toxicity of DDT and PCBs is generally much greater than that of PAEs, the vast quantity of the latter in use suggests that an indicator species should be selected and routinely monitored for deleterious effects.

Phthalic Acid Esters and Human Health

INTRODUCTION

In dealing with the effect of PAEs on human health, two factors must be considered. These are:

- a) exposure, i.e., sources of phthalates to which humans are exposed, the routes by which exposure occurs and the quantities involved; and
- b) toxicity, i.e., the acute and chronic toxicities of PAEs to humans, and the behaviour of PAEs in the human body.

By combining these two factors, one may assess the hazard to human health posed by exposure to PAEs from the various sources. The following sections summarize the literature pertaining to the above factors.

HUMAN EXPOSURE TO PAES

What are the sources of human exposure to phthalates, by what routes does exposure occur, and what are the quantities to which humans are exposed?

The direct sources of human exposure to PAEs are many and increasing yearly. They are used in common household articles such as shoe soles, garden hose, food packaging, wall covering, flooring, furniture, upholstery and host of other products containing flexible PVC and other plastics. They are found in widely used PVC biomedical devices such as transfusion tubing and PVC blood storage bags.

Indirect exposure occurs through contamination of the environment by PAEs. Environmental residues result from releases of PAEs to the environment during the manufacture and formulation of phthalate plasticizers, and during the production, use and disposal (incineration and landfill) of products containing PAEs. Chapter 5 deals with releases of PAEs to the environment.

The routes by which humans are exposed to PAEs are air, water, food, skin contact and the use of PVC biomedical devices in blood transfusion and hemodialysis. An attempt has been made to establish, within the limits of available data, the average adult's daily intake of PAEs from these routes. Nothing is known about the daily exposure of the population to PAEs through skin contact. Exposure of PAEs in the work place and from biomedical devices affects only a small fraction of the population. The estimates ("guestimates" is perhaps a better word because of their arbitrary nature) are therefore based solely on PAE intake from food, water and air. The arbitrary nature of the guestimates derives from the following factors. First, data on PAE residues are, at best, sporadic for food and water, and virtually non-existent for air. At present, it is impossible to say what percentage of all food and water consumed by the average Canadian is contaminated with detectable, let alone non-detectable, amounts of PAEs. By assuming for simplicity of calculation that foods such as meat, fish, poultry and dairy products, in addition to potable water, all contain detectable levels of

PAEs, there exists a good possibility that any estimate of PAE intake from these sources is high. This will apply to similar assumptions concerning PAEs in the atmosphere, since it is quite likely that PAEs reach detectable levels only in industrial areas and incineration sites, which represent a small percentage of Canada's total geographic area.

Secondly, the metabolism, distribution and fate (accumulation, excretion) of PAEs ingested in food and water remain unclear. In addition, the behaviour of inhaled PAEs in the lungs is unknown beyond observation that airborne PAEs are lethal to rats in sufficiently high concentrations (55). It is very probable that PAEs are absorbed by human lung tissue, although the extent is unknown.

In light of these information gaps, it must be emphasized that the "gestimates" developed below are largely arbitrary and quite likely in excess of the actual quantities involved.

Air

The air undoubtedly contains trace quantities of PAEs that have volatilized from plastic articles of various kinds, although little information is available. Aside from occupational exposure, the highest atmospheric concentrations to which humans are exposed seem to occur in automobiles. Dashboard coverings, side-panels, interior linings and seats are all sources of plasticizing compounds. As described by Shea (64), the "new-car smell" is largely the result of volatilized plasticizers, as is the film of sticky material deposited on the inside of auto windshields (fogging). The degree and significance of exposure from these sources are as yet unknown.

Airborne levels of PAEs are in all likelihood considerable in factories where PAEs and flexible plastics are produced and fabricated. The actual levels will depend on industrial hygiene practices, particularly ventilation. There are currently no occupational Threshold Limit Values (TLVs) in effect for PAEs in Canada or the United States.

It is difficult to arrive at a realistic estimate of phthalate exposure through respiration. As was mentioned above, virtually nothing is known about the ambient air levels to which the general population is exposed. Similarly, the absorption of inhaled PAEs in the lungs is unexplored beyond observations that DEHP mists in sufficiently high concentrations are lethal to rats (55) and that DBP vapours may damage the upper respiratory tracts of test animals (65). It is almost certain, however, that PAEs are absorbed to some extent by human lung tissue. If an ambient air level of $1 \mu\text{g}/\text{m}^3$ is arbitrarily assumed [greater than reported levels of DEHP and DnBP in Hamilton, Ontario (7)], and the volume of air breathed per day is 15 m^3 (66), the daily intake of PAEs into the lungs will be $15 \mu\text{g}$. If one further assumes arbitrarily that 20% of the inhaled PAEs are retained (80% exhaled) and that all of this is absorbed into the blood, daily exposure from respiration becomes $3.0 \mu\text{g}$. The exposure is undoubtedly higher for persons exposed to occupational levels of PAEs.

Water

In some areas of Ontario, drinking water samples have been found to contain phthalates ranging from 0.05 to 9.0 ppb, with most less than 2 ppb (Dr. O. Meresz, Ministry of the Environment, Ontario, personal communication). In the samples where PAEs were detected, the sources were suspected to be plastics in the water treatment facilities as well as general environmental levels. There is currently no established drinking water standard for PAEs in any Canadian jurisdiction.

An average adult man's intake of water-based fluids is about 1.5 litres per day (67). If one arbitrarily assumes, for simplicity of calculation, that this is all

treated water containing 2 ppb PAEs, the daily intake of PAEs from this source becomes 3.0 μg . It should be noted that about one-half of the finished water samples tested in the Ontario study did not contain detectable levels of PAEs. For this reason, the figure is arbitrarily lowered to 2 $\mu\text{g}/\text{day}$.

Food

Phthalate esters are not analyzed for in-market basket surveys as are certain heavy metals. The monitoring of foods for PAE contamination seems to be sporadic and data are, at best, scarce. Williams (68) surveyed 21 samples of fish as available to the Canadian consumer and found DBP levels of 0-78 ppb (10 ppb mean value) and DEHP levels of 0-160 (15 ppb mean value). The highest levels were found in samples of processed canned fish, whereas only one sample in the unprocessed fish category, eel, contained a high level.

A major source of PAEs in food is packaging. Phthalates may migrate from some flexible PVC food wraps into certain foods, notably, those with a high fat content, such as meat and dairy products. Foils coated with plasticized nitrocellulose or vinyl chloride/vinyl acetate copolymer released DBP and DEHP into lard and cheese samples wrapped therein (69).

In Canada, meat and produce are the only foods of which great quantities are packaged in PVC. Meat wraps contain adipate (non-phthalate) plasticizers, whereas produce wraps contain phthalates. The migration potential of PAEs is low in the case of produce, since the water content of produce is generally high and fat content low. Milk bags and jugs are made of polyethylene which contains no phthalate plasticizers. On the other hand, food wraps used in the household may contain phthalates, and migration is possible if high fat content foods are wrapped therein. It may be that the greatest likelihood of contamination is by the unaware consumer rather than at the retail level.

A unique aspect of PAEs in food is brought to light by the migration of PAEs to milk from flexible PVC collection tubing. After an extended period of use (70), such tubing loses its originally smooth inner surface and develops fine tears. Bacteria and other contamination are difficult to remove from such surfaces, and effective cleaning and sterilization become impossible. Wildbrett (71) examined the migration of PAEs into milk and cleaning solutions and found milk to be a more effective extracting agent than any of the cleaning solutions tested. Dinonyl phthalate (DNP) was more prone to migration than DEHP. Milk at 56°C extracted 7.0 and 3.1 mg/100 ml of DNP and DEHP, respectively, and at 38°C (the body temperature of a dairy cow is 38.6°C) the figures were 4.6 and 2.0 mg/100 ml of milk. It should be noted that the contact time used was 24 hr. In real situations the contact time is in the order of seconds and phthalate migration per unit volume would likely be negligible. No Canadian data are available on PAE levels in milk.

It is appropriate here to outline the regulations that exist to mitigate phthalate in food.

Regulations on the use of PAEs in food packaging in the United States have been described by Shibko and Blumenthal (72). Some PAEs are listed in the Food and Drug Act as suitable for use in packaging for certain foods, notably those foods with a high water content, such as produce. Some are permitted for use in products where migration to the food may occur (the "possible migration" products), whereas others are allowed only where migration is essentially nil (the "no migration" products). "Possible migration" products often have direct contact with food and include cellophane film and food container gaskets. Most phthalates permitted for use here are also allowed in "no migration" products, which have no direct contact with the food. Examples include adhesives and defoaming agents used in paper and paperboard manufacture. Phthalates regulated for "no migration" products are not permitted in

"possible migration" products. The safe use of PAEs regulated for "possible migration" products is based on available toxicity data as well as regulations which specify the maximum extractable fraction of plasticizer that may enter the food. The amount available for migration is limited by good manufacturing practice for food packaging materials, which restricts the quantity of phthalate used to the least amount reasonably possible. In Canada, the Food and Drug Act does not presently regulate the composition of food wraps, although it is planned to prescribe the formulations of all packaging in the future, including PVC types which contain phthalate plasticizers. In the meantime, it is the responsibility of the food processor to see that the wrapping used is appropriate for the food, and as a result the processors require information from the wrap manufacturers regarding the phthalate content of their products. However, these PAEs would be controlled under a section of the Food and Drug Regulations which states that "no person shall sell a food in a package that may yield to its contents any substance that may be injurious to the health of the consumer of the food" (73). Certain other plastic additives, such as dioctyl tin stabilizer, and contaminants such as vinyl chloride monomer, have considerably high toxicities and are currently regulated by the Food and Drug Act (74).

It is difficult to estimate the daily intake of PAEs from food. This is due to the lack of comprehensive data on the PAE content of Canadian total diet composites. Therefore, some assumptions must be made to arrive at an estimate. It is reasonable to assume that the highest levels of PAEs will be in those foods with high fat content, such as meats, dairy products, oils and fats. The daily consumption of these foods (66) is: Meat, fish and poultry, 276 g/man/day; milk and dairy foods, 495 g/man/day and oils and fats, 27 g/man/day. If we assume a PAE level of 0.1 ppm in all meat, fish and poultry consumed [the same order as Williams (68) observed in the most contaminated fish samples], daily PAE intake from this source is roughly 28 μ g. If we further assume an arbitrary level of 0.1 ppm PAEs on dairy foods, oils and fats, daily intake from these sources becomes approximately 52 μ g. The total intake from food is therefore "guessed" to be in the range of 80 μ g/man/day.

Skin Contact

In experiments with animals, dermal absorption is low with the higher molecular weight PAEs, whereas recent data on rabbits (75) indicate that diethyl phthalate (DEP) is absorbed through the skin more rapidly than originally expected.

In the case of humans, Patty (76) has stated that PAEs, presumably in pure form, are not absorbed through the skin in occupational situations. Products used by the general population, such as some insect repellents, cosmetics and rubbing alcohol are known to contain phthalates. The possibility that dermal absorption of PAEs occurs when applied with other chemical components in cosmetic formulations should be investigated. For purposes of this estimate, however, the contribution to daily intake from these sources is assumed to be negligible.

Biomedical Devices

Concern for PAEs as potential health hazards was initiated by the discovery that they were readily extracted into blood from plastic storage bags and other medical devices. Much of the literature in this area has been summarized by Hugos (77), Autian (36) and Hartung (78). Some of the major aspects are described in the following paragraphs.

It has been definitely established that blood (particularly lipids, proteins and platelets) is able to extract PAEs from PVC plastic. Jaeger and Rubin (79) showed that several plasticizers may be extracted from PVC tubing by human and animal blood alike, and that the rate of accumulation of DEHP in blood stored in

plastic blood bags was 0.25 mg/100 ml/day over a storage period of 21 days. Hence, DEHP may be transfused into humans. Jaeger and Rubin (80) reported that an average-sized man needing a total transfusion of 14 pints (not uncommon in the treatment of severe hemorrhage) could receive intravenously as much as 350 mg of plasticizer at one time.

The significance of the contribution of transfusion and dialysis fluids to the total body burden of PAEs is uncertain. Rubin and Nair (81) found DEHP in tissues from transfused as well as non-transfused persons. Although blood is able to solubilize DEHP from biomedical plastic devices, the DEHP rapidly disappears from blood in vivo (82).

Total Daily Intake of PAEs

Total daily intake of PAEs will vary according to individual life habits. Individuals exposed at the work place, through blood transfusions or hemodialysis therapy will be subject to higher intakes than the average Canadian.

A "guestimate" of daily intake of PAEs for the average Canadian, based on consumption of food, water and air, is made up of 80 μg from food, 15 μg from air and 2 μg from water for a total of 97 μg . The amount estimated to be absorbed (not exhaled or excreted in unchanged form) is 80 μg from food, 3.0 μg from air and 2 μg from water for a total of 85 $\mu\text{g}/\text{day}$. An average person of 60 kg (132 lb) thus absorbs daily 1.4 $\mu\text{g}/\text{kg}$ body weight from these sources.

TOXICITY OF PAES TO HUMANS

What is the behaviour of PAEs once inside the human body? What are the acute and chronic toxicities of PAEs to humans?

The behaviour of PAEs in humans can be described by considering four aspects: absorption, distribution, excretion and metabolism. These are described in the following paragraphs.

Absorption

Autian (36) states that phthalate esters can be absorbed from the intestinal tract, the intraperitoneal (abdominal) cavity and the lungs. Dermal contact with products containing PAEs may result in PAE intake, but this has not been confirmed in man. Phthalate absorption from ingestion and respiration has been estimated in the previous section entitled "Human Exposure to Phthalates."

Distribution

Jaeger and Rubin (79) analyzed tissues from organs of expired patients with varying disease and treatment histories. Levels of DEHP ranged from 25 $\mu\text{g}/\text{g}$ dry weight in the spleen to 270 $\mu\text{g}/\text{g}$ dry weight in abdominal fat. In one patient, high levels were found in the lung, liver and spleen, but none in the abdominal fat. All had been administered blood from PVC storage bags and tubing containing phthalate plasticizers and this was presumed to be the source of the PAEs. The distribution of orally ingested phthalates is unknown.

Excretion

Shaffer et al. (55) reported phthalates (as phthalic acid) in the urine of man, dogs and rabbits after single oral doses of DEHP, indicating absorption from the

intestine. Two human males who received single doses of 10 g and 5 g of DEHP excreted 4.5% and 2.0% respectively of the total dose in the urine over 24 hr. The remainder was presumably metabolized or retained.

Metabolism

Shaffer et al. (55) noted that the urine of man, dogs, rabbits and rats contained phthalic acid after oral administration of DEHP. By their methods they were unable to identify the esters as such in the urine. In light of this, Autian (36) raises the question whether, if DEHP is metabolized in the body, the acute toxicity of the administered ester would be due to the alcohol, phthalic acid or a combination of alcohol, phthalic acid and esters. Shaffer and associates concluded that the toxicity of the original ester is most likely due to the alkyl portion of the molecule rather than to the ester or acid. There is no indication of whether "ester" refers to the monoester (MEHP) or diester (DEHP), although the monoester occurs more commonly as the conjugated metabolite. The toxicities of these may vary. Metcalf et al. (43) have suggested that MEHP is one of the stable intermediates formed during the degradation of DEHP in fish.

In experiments with isolated rat liver preparations, Jaeger and Rubin (83) concluded that butyl glycolylbutyl phthalate (BGBP) can be metabolized by the liver, whereas DEHP cannot. Autian (36) points out that these experiments were run in isolated rat liver preparations and that if deesterification takes place in the kidney in the process of excretion, the results are not incompatible.

An important subject which needs to be examined is the possible accumulation of PAEs in the body. If the esters accumulate in some specific organ or tissue, the tolerable body burden may be exceeded, bringing about subtle toxic effects. At present, no information is available to indicate that tolerable body burdens are being exceeded or even what may be considered a tolerable body burden.

Toxicity and Ingestion of PAEs

Most toxicity data have been derived from studies of laboratory test animals. Some studies mention isolated cases of human ingestion. Krauskopf (37) has summarized much of the data gathered through ingestion studies on phthalates and related materials. In general, experiments were carried out on rats, mice, guinea pigs and dogs. A very low order of toxicity was indicated for these animals. No carcinogenic, adverse histological or pathological effects were found.

In his review, Krauskopf mentions three cases of single-dose human ingestion. Shaffer et al. (55) reported that an adult male intentionally took 10 g of DEHP and experienced mild diarrhea, whereas another adult male showed no effects after taking 5 g. Lefaux (53) reported that a young adult male mistakenly ingested about 10 g of DBP. He experienced nausea and vertigo, and signs of keratitis and toxic nephritis (excess albumen in the urine, together with red and white corpuscles) were observed. He was treated and released from hospital after two weeks observation with no after-effects.

The Joint FAO/WHO Expert Committee on Food Additives (84) has determined acceptable daily intake (ADI) zones for various substances, expressed as mg/kg of man body weight. The ADI, which extrapolates the observed toxicities of PAEs for test animals to humans, is determined by the equation $ADI (mg/kg) = N/F$ where N denotes the maximum "no effect" level of substance based on the most sensitive test with the most sensitive test species, in mg/kg/day, and F is a safety factor to convert from animal species to man. Table 6 shows the calculated ADI values for phthalates, where the cited reference provided the pertinent information. Values range from 0.04 mg/kg (29) to >8.4 mg/kg (85). From these data Krauskopf (37) has estimated that a typical adult of 60 kg (132 lb) weight could survive daily doses

of phthalates ranging from 2.4 mg to 480 mg (0.48 g). For further comparison, Table 7 lists the ADI values of some common food additives. The acceptable limits of these chemicals have ADI values of the same order of magnitude that has been calculated for the phthalates.

Table 6. ADI Calculated from Various Investigations

Phthalate	Species	Period, days	Maximum no-effect level, mg/kg/day	ADI mg/kg ¹	Reference
Di-(2-ethylhexyl)	Rat	365	400	4.0	86
	Rat	730	80	8.0	86
	Dog	98	100	0.2	86
	Rat	90	200	0.4	55
	Dog	98	100	0.2	87
	Rat	365	>60, <200	>8.4, <28	85
				>0.6, <2.0	
Dibutyl	Guinea pig	365	ca. 60	ca. 0.6	85
	Dog	365	ca. 60	ca. 0.6	85
	Rat	365	350-110	3.5-1.1	52
	Rat	450	4.3	0.04	53
Diisononyl	Rat	91	150	0.3	56
	Dog	91	37	0.07	56
Heptyl nonyl	Rat	90	ca. 60	ca. 0.12	88
	Mouse	90	ca. 60	ca. 0.12	88

SOURCE: Krauskopf (37).

¹ADI = N/F, where F = 500 for <365-day period; 100 for ≥ 365-day period.

Table 7. Acceptable Daily Intakes for Man of some Antimicrobials, Antioxidants, and Antioxidant Synergists*

	Overall daily intake zone, mg/kg body weight†	
	Unconditional	Conditional
Benzoic acid Benzoate, potassium Benzoate, sodium	0-5‡	5-10‡
Benzoate, butyl p-hydroxy	Decision postponed	
Benzoate, ethyl p-hydroxy Benzoate, methyl p-hydroxy Benzoate, propyl p-hydroxy	0-2§	2-7§
Butylated hydroxyanisole Butylated hydroxytoluene	0-0.5	0.5-2
EDTA, calcium disodium	0-1.25	1.25-2.5
Isopropyl citrate mixture	0-7	7-20

* Source: FAO Nutrition Meeting (89).

† The first part of the overall acceptable daily intake zone is termed unconditional, and this represents levels which can be safely used without further expert supervision and advice. The second part is termed conditional and represents levels of use that can be safely employed but at which it is thought desirable that some degree of expert supervision and advice should be readily available.

‡ As sum of benzoic acid and sodium and potassium benzoate (calculated as benzoic acid).

§ As sum of methyl, ethyl and propyl esters of p-hydroxybenzoic acid.

|| As sum of butylated hydroxytoluene and butylated hydroxyanisole.

Toxicity of PAEs in the Work Place

Human exposure to PAEs appears to be potentially significant in occupations involving the production and processing of phthalates and PVC plastics. Patty (76) has summarized the toxicity data of many of the commonly used phthalate esters. He states that, in general, the phthalate esters are among the most inert of all industrial materials. They are rarely the cause of skin difficulties and are not absorbed through the skin. Their low vapour pressures usually preclude the inhalation of a toxicologically significant amount.

Some of the starting materials used in PAE production may exert toxic effects under certain conditions. For example, the toxic nature of phthalic anhydride is considerable. It has a characteristic choking odour and can be a moderate fire hazard. It acts as an irritant on skin, eyes and mucous membranes of the nasal passage and upper respiratory tract. In susceptible workers, repeated contact with the chemical may lead to allergic dermatitis and possibly asthmatic attacks. The Threshold Limit Value (90) for phthalic anhydride in air is presently 12 mg/m³, but it is proposed to lower this to 6 mg/m³. Alcohols used in the manufacture of PAEs may also pose health problems if proper safety precautions are not taken. The toxicity and irritant effects on eyes and membranes depend on the specific alcohol being used. For the most part, however, the alcohols have not presented serious industrial hazards.

Milkov et al. (91) studied the health status of workers exposed to phthalate plasticizers used in the manufacture of artificial leather and PVC films. The authors reported several effects, the frequency and degree of which increased with the length of stay on the job. They observed polyneuritis comprised of pain and weakness in the upper and lower extremities, functional disturbance of the nervous system, and decreased sensitivity in various sensory nerve endings. They also noted a slight lowering of platelets, leukocytes and hemoglobin in the blood. Hartung (78) observed that the exposure included triaryl phosphates, which are known to produce symptoms such as those noted by Milkov et al. (91). Thus, he states that the investigators were probably in error when they ascribed the observed polyneuritis to PAEs.

Toxic Effects of PAEs Leached from Plastic Biomedical Devices

In a study involving the leaching of plasticizers into blood from plastic biomedical devices, Rubin and Jaeger (92) indicated that blood platelets form microaggregates (tiny clusters) after storage in PVC bags, and that the extent of this formation was directly related to the amount of DEHP in the plastic. Further studies were reported necessary before a cause and effect relation could be established. When DEHP was administered intravenously without regard to complete solubilization, the amount stored in the lung was significant (79), whereas little DEHP appears to be stored in the lung when it is in solution (93).

Evidence regarding the relation of PAEs to shock lung (a congestive lung disease which occasionally occurs after repeated transfusions) is controversial. Jaeger and Rubin (79) have speculated that blood platelet microaggregates may play a role in the etiology (development) of shock lung. At high levels of infusion, lung damage can be produced which is similar, but not identical, to shock lung. It is unclear whether the shock lung is due to PAEs leached from medical devices, exposure to other compounds during transfusion, a reaction to repeated transfusions per se or a combination of these.

It seems reasonable to state that phthalates display a considerably low order of oral toxicity. The ADI values of phthalates are the same order of magnitude as those of common food additives such as antimicrobials and antioxidants. The dermal toxicity and irritant potential of PAEs are low, whereas the toxic nature of

phthalic anhydride, one of the starting materials in PAE manufacture, is considerable. The effects exerted by phthalates received intravenously during blood transfusions and hemodialysis are not yet confirmed and warrant further investigation. Virtually nothing is known about the long-term effects of low-level phthalate intake.

Carcinogenic Effects

Summaries of chronic toxicity studies (1,37) give no indication that phthalates are carcinogenic. Oppenheimer *et al.* (94) reported on malignant tumours in rats caused by inserting small pieces of PVC film beneath the skin. It was concluded (95,96) after investigations of many films that the cancer-causing agent is the plastic macromolecule itself rather than any additive or impurity which might be present in the commercial film.

Teratogenic Effects

Several investigators have studied the teratogenic effects of phthalates by injection into developing chicken eggs. Butyloctyl phthalate (BOP) and butyldecyl phthalate caused deformities in the legs and neurological disorders (97,98). Bower *et al.* (99) noted abnormalities such as tremors, swaying and impairment in the ability to stand or walk in chicks whose eggs were injected with dibutoxyethyl phthalate, di-(2-methoxyethyl) phthalate, and n-octyl-n-decyl phthalate. Congenital malformations were noted with dibutoxyethyl phthalate. Increased mortality was noted with several PAEs, but mortality rates were too high in both inoculated and uninoculated controls to give confidence in this experiment.

The teratogenicity of PAEs in rats has been examined by Singh *et al.* (100). Six phthalates were administered intraperitoneally (injected into the abdominal cavity) to pregnant rats at varying doses up to one third of the acute LD₅₀, and at varying stages of gestation. It was found that the administration of the PAEs did not interfere with fertility, but there were significant effects on embryonic and/or fetal development. All PAEs studied showed a deleterious effect on the developing embryo and/or fetus. In all cases, fetus weight was decreased relative to controls. Dimethoxyethyl phthalate (DMEP) was the most embryotoxic and the most water soluble of the PAEs studied. DOP and DEHP were the least water soluble and had the least overall adverse effect on embryo-fetal development. The intensity of gross abnormalities, skeletal malformations, fetal death and decreased fetal size were found to be dose-related.

It is clear that phthalates are teratogenic to rats at high dosages [up to one third of the LD₅₀ (100)]. It is extremely unlikely, however, that humans would ever undergo such exposure under normal circumstances. Research on teratogenicity is therefore needed using blood concentrations of PAEs to which humans may be realistically exposed, such as those encountered after massive blood transfusions. In addition, the significance of exposure from current environmental levels should be assessed in terms of teratogenicity. Autian (36) states that although it is unlikely that expectant female humans will be exposed to sufficiently high levels of PAEs to produce embryotoxic effects and birth defects, they should nevertheless be afforded maximum protection against these esters, particularly during the early stages of pregnancy.

Mutagenic Effects

Dillingham and Autian (101) described the preliminary unpublished work of Singh *et al.* in which were studied the mutagenic effects of DEHP and DMEP on mice. The investigators observed a decrease in implants and the number of live fetuses for both phthalates at the highest doses tested. These were single intraperitoneal injections into male mice of 25.6 ml/kg DEHP and 2.4 ml/kg DMEP. After a series of

matings, fetal deaths were noted at all concentrations of DEHP and at the highest concentration of DMEP. The mutagenic effect of DEHP was significantly greater than for DMEP in contrast with the teratogenic effects of those compounds (DMEP was the most embryotoxic of all the PAEs tested).

PAEs may act as mutagenic agents in man, but this cannot be confirmed until further research is conducted. The need for such research cannot be overemphasized considering the implications for human health and reproduction.

HAZARD POTENTIAL OF PAES

It would appear that the short-term health hazard posed by PAEs is low in light of the information presented on exposure and toxicity. Estimated daily intakes for the average Canadian (from food, water and air) are in the order of 0.001 mg/kg/day, whereas the ADI values presented by Krauskopf (37) are in the order of 0.1 to 10 mg/kg/day.

Certain segments of the population face additional exposure beyond that of PAEs in food, water and air. Workers in factories where PAEs and PVC plastics are produced and fabricated are exposed to above-normal atmospheric levels of PAEs. The short-term industrial hazard of PAEs appears to be low when proper industrial hygiene, including ventilation, is practiced, whereas the long-term effects of exposure to occupational levels are unknown. In addition, it is not known to what extent workers may still be exposed to unacceptable conditions of industrial hygiene.

A percentage of hospital patients are exposed to phthalates through blood transfusions and hemodialysis therapy. Phthalate intake from blood transfusions can be significant, but is generally irregular and infrequent. Hemodialysis, on the other hand, is required on a regular long-term basis, often for the duration of the patient's life. Exposure to PAEs is likewise regular and long-term, and the resultant health hazard is unknown.

In the case of individuals exposed to PAEs at the work place and through biomedical devices, the ADI may be exceeded. It should be noted, however, that ADI's are calculated from feeding studies only and do not take into account phthalate intake from other sources (e.g., respiration and intravenous injections of blood).

The need for further research on the long-term toxic effects of PAEs from sources other than oral ingestion is obvious. In the meantime, efforts should be made to minimize the exposure at the work place and from biomedical devices. Although a good many factories already practice an effective level of industrial hygiene, this could be enhanced by the establishment of Threshold Limit Values (TLVs) for phthalates at the work place, followed by strict adherence to these regulations. While plasticized PVC is presently used in blood pouches and tubing, alternative materials are being sought which may replace plasticized PVC in such medical devices before the end of the decade (Dr. R.W. Campbell, Bureau of Medical Services, Health and Welfare Canada, personal communication). In the development of alternatives, caution should be exercised to avoid materials which may pose new hazards to human health. During the interim, the toxic effects of PVC medical devices are being further investigated by the Department of National Health and Welfare.

The Structure of Phthalic Acid Ester Production and Use in Canada

INTRODUCTION

There is a growing concern that PAEs may constitute a threat to human health and the natural ecosystem. An essential part of the assessment of this threat is the analysis of the sources of PAEs. Some evidence suggests that certain specific phthalates are biosynthesized in nature, but it is reasonable to assume that the primary sources of these chemicals are man's activities. The quantification of these sources, i.e., the production, use and distribution of PAEs in the Canadian economy, is necessary to evaluate the quantities of PAEs to which the ecosystem and its constituent biota, including man, are exposed. This follows from the fact that the environment is the ultimate sink for all man-made materials, including PAEs.

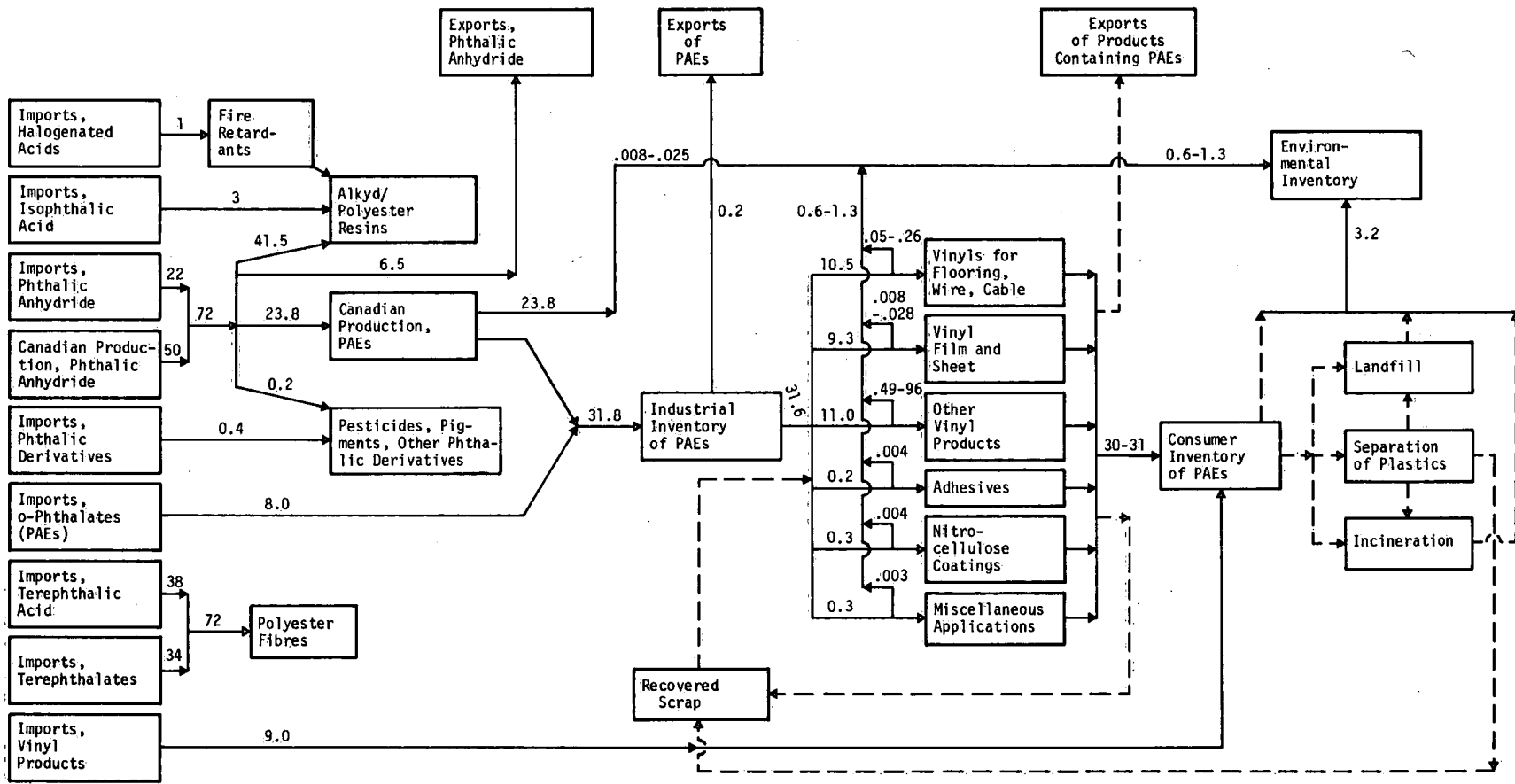
Chapter 4 is an analysis of the production, use and distribution of PAEs in the Canadian economy. The bulk of the production (manufacturing, processing and fabrication) activities are confined to a very small area of the country, whereas the geographical use, distribution and disposal of products containing PAEs are assumed to be proportional to population distribution.

The detailed analysis of the production and use of phthalates was performed by Corpus Publishers Services, Toronto, under contract to the Inland Waters Directorate, Ontario Region. Their report constitutes the main source of the data presented in this and subsequent chapters. Some information was obtained from government sources, primarily Statistics Canada.

PRODUCTION, IMPORTS, AND EXPORTS OF PAEs

In 1973, the PAE production of the four major Canadian producers totalled 61.5 million pounds (23.8 million pounds PAQ)*. Canadian producers of PAEs are listed in Appendix A. Import of PAEs totalled 17.0 million pounds (8 million pounds PAQ). In addition 40 million pounds of terephthalates were imported. An estimated 11.5 million pounds of PAEs (4 million pounds PAQ) were contained in imported vinyl compounds, film and sheet, whereas an estimated 14 million pounds (5 million pounds PAQ) were contained in imported fabricated vinyls. The supply and demand of PAEs is presented in Table 8. Figure 2 is a flowchart illustrating the use and distribution in the Canadian economy of PAEs and one of the starting materials, phthalic anhydride, for 1973. All quantities have been converted to PAQ for simplicity.

*PAQ = Phthalic Acid Equivalent, the amount of phthalic acid which is made from or is required to make the indicated amount of phthalate, phthalic anhydride, etc.



Note: Dotted lines indicate unknown quantities.

Figure 2. Material flowchart of phthalic anhydride and phthalic acid esters (PAEs) in Canada, 1973 (10^6 lb phthalic acid equivalent).

Table 8. Phthalates Supply and Demand, 1973

	PAEs (million lb)	PAQ (million lb)	% of total
<i>Supply</i>			
Domestic production	61.5	23.8	78.3
Imports	17.0	8.0	21.7
Total	78.5	31.8	100.0
<i>Demand</i>			
(a) As plasticizers in:			
Flooring	12.8	6.5	15.3
Extruded film and sheet	24.1	9.3	30.7
Wire and cable insulation	10.4	4.0	13.2
Plastisols	24.5	9.3	31.2
Other vinyl extrusions and mouldings	4.5	1.7	5.7
Adhesives	0.5	0.2	1.7
Cellulose film coatings	0.5	0.3	0.6
(b) Other applications	0.7	0.3	0.9
(c) Export	0.5	0.2	0.6
Total	78.5	31.8	99.9

GENERAL APPLICATIONS

Phthalic acid esters are used in a wide variety of applications. Their largest use by far is as plasticizing agents for resins and polymers such as poly(vinyl chloride) (PVC), the cellulose and certain types of elastomers. They are also used as defoaming agents in paper manufacture; in cosmetic products as a vehicle for perfumes; in lubricating oils; in insect repellent formulations and in numerous other products. The use of PAEs in these applications is described in the following sections.

PAES AS PLASTICIZERS IN VINYL CHLORIDE RESINS

A plasticizer is a material incorporated in a plastic to increase its workability and distensibility. The major use of all types of plasticizers is in poly(vinyl chloride) (PVC) and other resins. They are not chemically bound to the resin polymer, but are dispersed in the matrix of polymer chains to decrease the interaction forces of adjacent chains, thereby promoting chain mobility and flexibility (Chapter 6). In Canada, one group of plasticizers, the esters, which include PAEs, accounts for more than 75% of all plasticizer consumption. In 1973, 95% of all phthalate plasticizer (representing 25% of all phthalic anhydride) consumed was used in PVC resins. By 1980, PVC systems are expected to account for 75% of all phthalate plasticizer use, with the remainder being used in other resins and non-plasticizer uses.

Major End Uses of Flexible PVC

This section describes the major products made from flexible PVC in Canada, and the quantities of PAEs used in each case in 1973.

Vinyl Flooring

The term vinyl flooring includes homogeneous vinyl tile, vinyl asbestos tile, vinyl chloride carpet backing, and vinyl roll goods (foamed and non-foamed). Vinyl tile and roll goods are processed from flexible vinyl compounds using calendaring techniques.

Diethyl phthalate (DOP) is the main plasticizer used in the homogeneous vinyl flooring product, and is used to a lesser extent in vinyl asbestos flooring. In the latter product, the higher speed solvating (see Chapter 6, p. 48) plasticizer types [butylbenzyl phthalate (BBP); butyloctyl phthalate (BOP); butyldecyl phthalate (BDP); and benzoates] are the main ones used. Vinyl asbestos tile typically contains 40% phthalate by weight, although some formulations contain as little as 6.5% phthalate by weight (7 parts per hundred parts resin, phr). These require mixtures of BBP and DOP or DIOP.

Four companies manufacturing floor tile and roll goods consumed a total of some 13 million pounds of phthalate plasticizers (6.5 million pounds PAQ) in 1973. These companies are listed in Appendix A.

Sheeting and Film

Vinyl sheeting and film are produced by three techniques in Canada:

- a) calendaring;
- b) extrusion; and
- c) plastisol spread coating on supporting fabrics.

Sheeting generally refers to PVC thickness of 10 mils (0.01 inch) or over, whereas film refers to sheet of less than 10 mils thickness. Food packaging constitutes a major end use for PVC film (Chapter 3). DOP and DIOP dominate the market for sheeting and film and are used interchangeably or in combination. Secondary (less costly) plasticizers are also used.

In 1973, a total of 36.7 million pounds of phthalate plasticizers (14.0 million pounds PAQ) were used in the production of PVC sheet and film. Calendaring and extrusion operations processed 42 to 44 million pounds of PVC resin and 24.2 million pounds (9.3 million pounds PAQ) of phthalate plasticizers, while plastisol formulations used in the manufacture of supported film consumed some 14.0 million pounds of PVC resin and 12.5 million pounds (4.7 million pounds PAQ) of plasticizers. This latter figure is included in the section entitled "Plastisols." Companies producing extruded film and sheet in 1973 are listed in Appendix A.

Wire and Cable Insulation

Electric wire and cable insulation varies in its formulation depending on temperature and other characteristics of the end-use environment. There are five wire ratings in Canada: 125°C, 105°C, 90°C, 75°C and 60°C, with the latter rating becoming obsolete.

In the total wire and cable requirement for PVC, 80% of the phthalate used is dinitridecyl phthalate (DTDP), octyldecyl phthalate (ODP), or diisodecyl phthalate (DIDP), since these exhibit better permanence properties. The higher temperature coatings utilize non-phthalate plasticizers (polymeric and epoxies) to some 8-10%

of the plasticizer blend, since these are less volatile than the phthalates. Secondary plasticizers are not used, since they are generally volatile and present a fire hazard. The average plasticizer ratio for all categories is approximately 50 phr.

In 1973, the production of wire and cable consumed between 10.0 and 10.5 million pounds (4.0 million pounds PAQ) of phthalate plasticizers. Eight companies accounted for greater than 85% of all Canadian wire and cable production. They are listed in Appendix A.

Plastisols

Plastisols are paste-like suspensions of PVC polymer particles in plasticizers. These are not to be confused with organosols, which contain volatile solvents in addition to plasticizers as part of the suspension medium. Most plastisol is processed in one of three ways:

- a) as "spread" or "doctor blade" coatings on textile or paper substrates; e.g., in production of vinyl wallpapers;
- b) dipping of heated forms; e.g., dish drainers; and
- c) slush moulding (hot and cold forms); e.g., footwear, toys.

Because of low cost and high efficiency, DOP and DIOP are the principal plasticizers consumed in this end-use area. DIOP possesses better viscosity characteristics for coating operations. DIDP is less volatile and exhibits better viscosity over varying temperature, but is higher in price and is, therefore, not used widely; i.e., only 10% of all plasticizer usage. Secondary plasticizers are used as diluents and contribute some viscosity control of the molten PVC coating material. Polymeric and epoxy type plasticizers are used only to a small extent in textile and paper coating.

At least 55 million pounds of PVC were used by Canadian plastisol producers in 1973. Consumption of plasticizer has been estimated at 24.5 million pounds (9.3 million pounds PAQ) within a range of 22-40 million pounds. Some formulators and consumers of plastisols are listed in Appendix A.

Other Vinyl Extrusion and Moulding

Companies engaged in injection moulding and vinyl extrusion processing generally work with supplier mixed compounds. In 1973, 15 million pounds of plasticized PVC were used, containing 4.5 million pounds of phthalates (1.7 million pounds PAQ). Three of the companies included in this category are listed in Appendix A.

PAES AS PLASTICIZERS IN OTHER MATERIALS

Adhesives

Phthalates represent the bulk of the plasticizer used in formulating polyvinyl acetate adhesives, which are produced by emulsification techniques. The plasticizer blend, which constitutes approximately 10% by weight of the adhesive, also contains non-phthalate chemicals such as benzoates (preservatives which inhibit mildew), chlorinated paraffins, and tricresyl phosphates (which impart fire retardancy).

Approximately one-half million pounds of phthalate plasticizers (0.2 million pounds PAQ) were used in adhesive formulations in Canada in 1973. Some manufacturers of adhesives are listed in Appendix A.

Nitrocellulose Film Coating

Approximately 400,000 pounds of dibutyl phthalate (DBP) and 260,000 pounds of dicyclohexyl phthalate (DCHP) (a total of 0.3 million pounds PAQ) were used in Canada in 1973 to coat nitrocellulose film to reduce water vapour transmission. The main use of this film is in cigarette and sundries packaging. Although some of the film is exported or goes into miscellaneous use, it is estimated that 60% goes to Canada's municipal refuse in the year of manufacture. Some manufacturers of nitrocellulose film are listed in Appendix A.

OTHER USES OF PAEs

Several miscellaneous applications for PAEs have been identified but not quantified individually. The total consumption of phthalates for these applications has been estimated at 700,000 pounds (0.3 million pounds PAQ) for 1973. These applications include:

- a) the use of DEP in insect repellent formulations;
- b) the use of DMP in defoaming agents used in the manufacture of paper and paperboard;
- c) the use of DEP in the production of denatured ethyl alcohol for use in cosmetics, rubbing alcohol, liquid soap and detergents;
- d) the use of DBP in inks for decorative packaging;
- e) the use of DOP and DBP in lacquers for industrial flooring and for applying phosphor to fluorescent lamps;
- f) the use of DEP and DBP as cooling agents in military propellants;
- g) the use of DMP as a carrier for peroxide catalysts in the production of polyester fibreglass reinforced plastics;
- h) the use of phthalates as additives in industrial and lubricating oils; and
- i) the use of phthalates as carriers in pesticide formulations, although this is now minimal because of the costs involved.

Release of Phthalic Acid Esters to the Environment

INTRODUCTION

The release of PAEs to the environment originates with the production and compounding of PAEs, and the production, use and disposal of products that contain them. These sources have been divided into two major categories. In both categories, the information necessary to quantify accurately the releases of PAEs is either in the very early stages of development, or completely lacking. Many assumptions have been made in the development of reasonable estimates, and these are specified throughout the chapter where appropriate. The categories are:

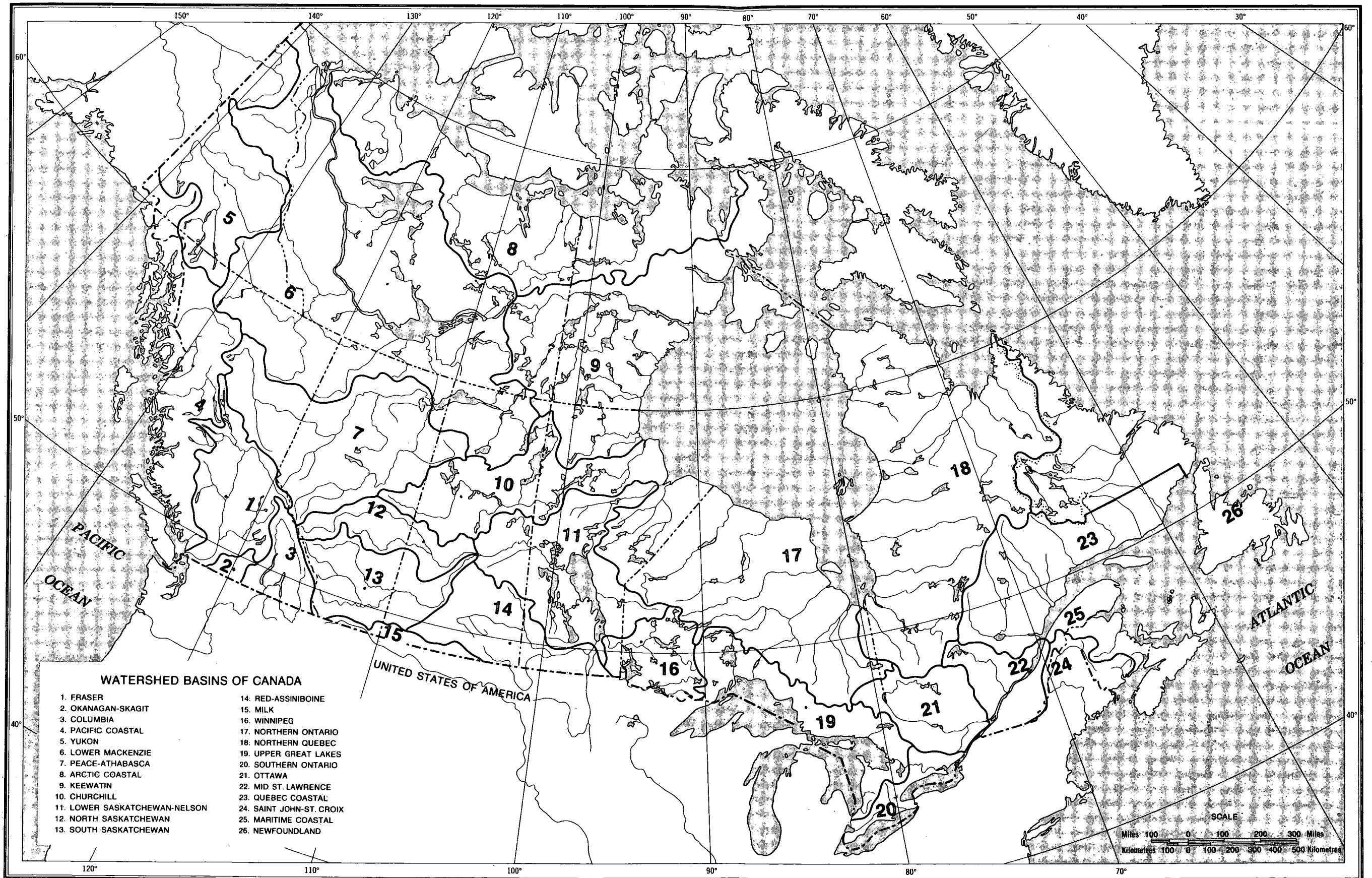
- a) releases of PAEs from production and processing activities, which include losses from the production of PAEs, the compounding of plasticizers and PVC resins to make flexible PVC, the fabrication of flexible PVC into products, and the production of adhesives, plastisols, nitrocellulose lacquer coatings and miscellaneous products; and
- b) releases of PAEs from use and disposal activities, which include the loss of PAEs from PVC products during the useful life of those products, and the final disposal of the products by landfill and incineration, processes whereby the PAE content gains access to the environment.

In the first category, PAE releases, or losses, have been calculated using loss factors estimated by the industries involved. For the most part, no actual monitoring of these loss rates has been carried out and the data must be considered subject to verification by surveillance procedures.

In the second category, the quantification of PAE releases during the useful life of products, notably those made of flexible PVC, is made difficult by the variety of use environments as well as the lack of information on loss rates at the point of end use. In almost all cases, some loss of plasticizer is likely to occur, be it by physical or biological routes. The loss of PAE plasticizer results in brittleness and inflexibility and is therefore a major reason for disposing of the item. An accurate calculation of PAE release through the disposal of refuse requires analysis of the composition of the refuse, the methods of disposal and quantities disposed of by each method. Available information in these areas, although far from complete, has been used in conjunction with demographic (population) data to estimate PAE releases by drainage basin from use and disposal activities. The drainage basins of Canada are shown in Map 1.

SUMMARY

Canadian releases of PAEs in 1973 from production, processing, use and disposal activities totalled between 9.9 and 11.9 million pounds (3.7 and 4.4 million pounds PAQ). Of the national total, approximately 22% originated with production and processing activities. In all drainage basins other than the Southern Ontario and mid-St. Lawrence, virtually all releases resulted from use and disposal activities.



Map 1. The drainage basins of Canada.

In the Southern Ontario and mid-St. Lawrence basins approximately 38% and 35% respectively of the total releases resulted from production and processing activities.

RELEASES TO THE ENVIRONMENT OF PAEs DURING PRODUCTION AND PROCESSING ACTIVITIES

Introduction

Phthalates released during production and processing activities may leave the plant in liquid or gaseous effluents. Information concerning the quantities of PAEs which leave the plant by each of these routes is currently unavailable and can be determined only through comprehensive monitoring of stack, sewer and ventilated effluents. To date, it seems that PAEs have not been analyzed in any systematic program by industry or government. The loss factors used throughout this section are primarily estimates by the industries involved, and must be considered subject to verification by monitoring.

The main source of work place concentrations of PAEs is volatilization during the production, compounding and processing of plasticizers and plasticized polymers, mainly PVC.* Where open kettles, calenders, and moulds are used, the plant atmosphere is the direct receptacle for volatilized material. PAEs may in some cases be released to liquid media, for example, the water baths used for cooling in the production of PVC insulated wire and cable. PAEs may be lost through the disposal of scrap plasticized PVC, although the price of the polymer resin is dictating a high degree of scrap reclamation.

Some establishments have installed pollution abatement equipment to remove organics, including PAEs, and other contaminants from their liquid and gaseous effluents. Removal efficiencies are generally known for parameters such as chemical oxygen demand (COD) and suspended solids, but are as yet unknown for many specific components of the effluent stream, including PAEs.

Establishments practicing reasonable industrial hygiene will use some method of removing PAEs from the plant atmosphere. This is notably the case with PVC compounding and fabricating plants where efforts are made to minimize the work place concentration of vinyl chloride monomer. Methods include venting the contaminated air directly to the outside, and the collection and disposal of fumes on site. In the latter case, fumes are collected in mist eliminators and disposed of as sludges in chemical dumps, or they may be diluted with water and sewerred to an on-site treatment lagoon or directly to a municipal treatment facility. In some cases, collected fumes are incinerated on the spot. This presumably oxidizes the PAEs to some extent, although no information is available on the resulting combustion products.

Summary

In 1973, releases of PAEs totalled between 1.6 and 3.5 million pounds (600 thousand and 1.3 million pounds PAQ). Losses occurred during production of PAEs, the manufacture of polyester fibre, the preparation and fabrication of plasticized PVC and the preparation of miscellaneous products containing PAEs. Quantities released from these sources are listed in Table 9.

*The techniques employed in the processing of PVC are outlined in Chapter 6 in the section entitled "PVC compounding, Processing and Fabrication."

Table 9. Releases of PAEs from Production and Processing Activities, 1973 ('000 lb)

Activity	As PAEs	Release ¹	As PAQ ²
<i>PAE Production</i>	61-185		24-71
<i>PVC Compounding and Processing</i>			
Compounds preparation	41		16
Flooring products processing	130-650		50-250
Sheet and film, calendered/ extruded	24-72		9-28
Wire and cable extrusion	10-21		4-8
Plastisols	1275-2525		484-959
Other vinyl extrusion and moulding	5		2
<i>Other</i>			
Adhesives formulating	10		4
Cellulose film coating	7		4
Miscellaneous	7		3
<i>Total</i>	1570-3523		600-1345

¹ All figures rounded to nearest thousand.

² Phthalic acid equivalent.

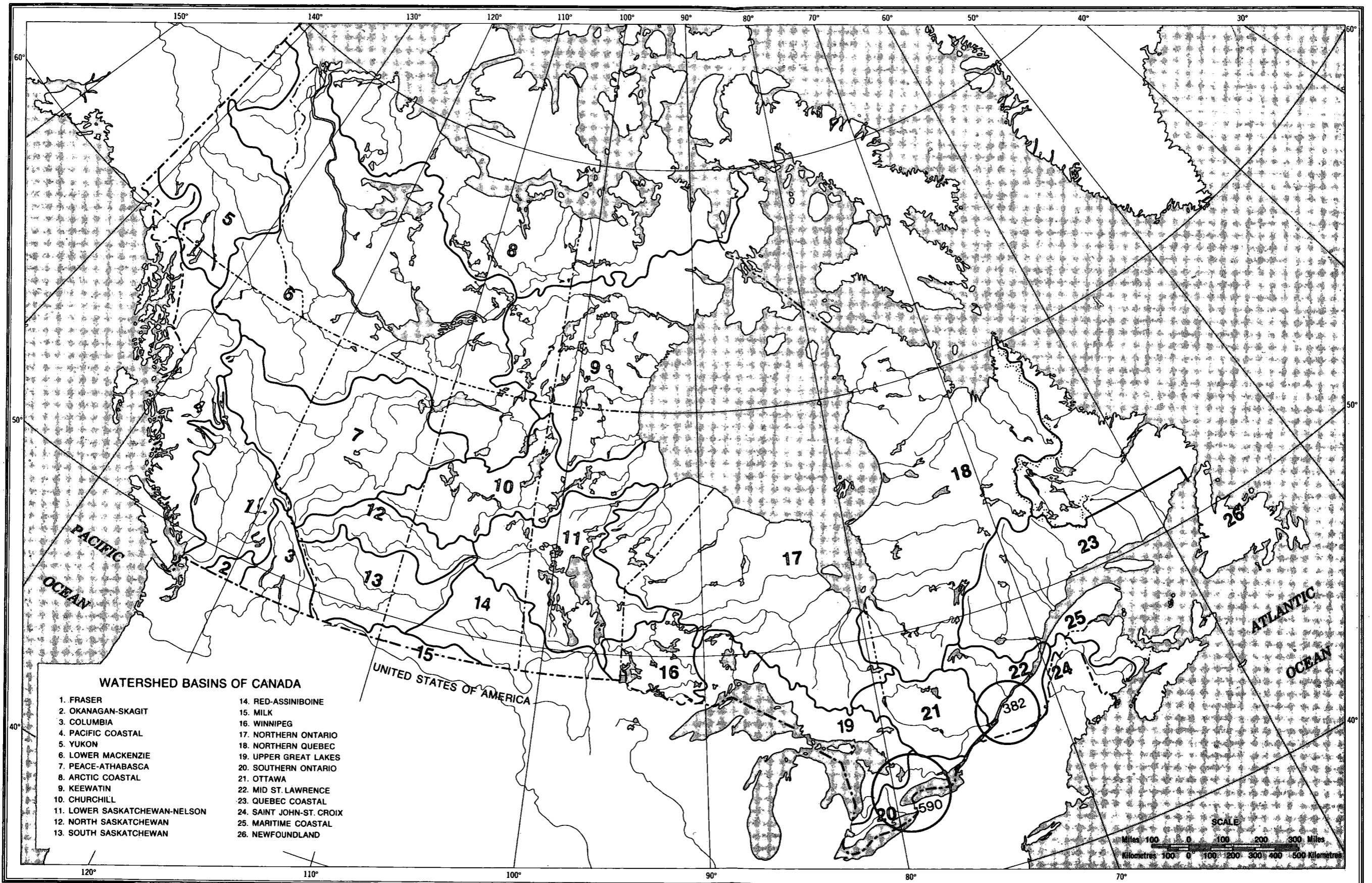
In the following sections, the releases of PAEs from production and processing activities are described and quantified in terms of the major drainage basins depicted in Map 1. These quantities are listed in Table 10 and illustrated in Map 2. In the case of production and processing activities, releases of PAEs are confined to two drainage basins: the Southern Ontario drainage basin and the mid-St. Lawrence drainage basin.

Table 10. Releases of PAEs from Production and Processing Activities by Drainage Basin, 1973 ('000 lb PAQ)

Activity	Releases		Total, Canada
	Southern Ontario Drainage basin (20)	Mid-St. Lawrence Drainage basin (22)	
<i>Production of PAEs</i>	*	*	24-71
<i>PVC Compounding and Processing</i>			
Compounds preparation	*	*	16
Flooring products processing	*	*	50-250
Sheet and film, calendered extruded	7-21	2.3-7	9.3-28
Wire and cable extrusion	2.7-5.4	1.3-2.7	4-8
Plastisols	347-687	137-273	484-960
Other vinyl extrusion and moulding	0.25	1.45	1.7
<i>Other</i>			
Adhesives formulating	2	2	4
Cellulose film coating	4	—	4
Miscellaneous	1.3	1.3	2.6
<i>Total</i>	388.4-792 (590)†	211.4-553 (382)†	600-1345

* Confidential.

† See Map 2. These figures are the simple averages of the maximum and minimum estimated releases.



Map 2. Releases to the environment of PAEs from production and processing activities, 1973 ('000 lb PAQ).

Release of PAEs from Production Activity

Domestic production of PAEs was 61.5 million pounds (23.8 million pounds PAQ) in 1973. A loss rate between 0.1 and 0.3% of total production has been accepted as reasonable for report purposes but should be made subject to verification through monitoring. This calculates to a loss of between 61.5 and 184.5 thousand pounds (23.8 thousand and 71.4 thousand pounds PAQ) for 1973. All of this activity occurred in the Southern Ontario and mid-St. Lawrence Basins.

Release of PAEs from Use as Plasticizers in PVC Products

Flooring

Industry estimates typical volatilization of phthalate plasticizer in the production of vinyl asbestos tile to be between 1% and 5%. Losses of PAEs in the production of homogeneous floor tile and roll goods result from volatilization during calendaring and are a function of the surface area of the goods being calendared. Based on reported loss factors, the processing of flooring vinyl goods contributed 130 to 650 thousand pounds (50 to 250 thousand pounds PAQ) of vapours to the plant atmosphere in 1973. Note that losses incurred through the use of plastisols (which have a high phthalate content) in the production of PVC foam for flooring underlay are quantified in the section entitled "Plastisols."

Releases of PAEs to the mid-St. Lawrence and Southern Ontario drainage basins are combined for confidentiality purposes.

PVC Sheeting and Film

Industry estimates indicate that 0.1-0.3% of the original phthalate plasticizer content of the PVC formulation is lost over the time required to extrude and calender the sheet. Scrap generated in the production of vinyl sheeting was once discarded but is now recycled, hence phthalate losses from scrap disposal are nil.

Based on a total consumption of 24.2 million pounds of phthalates in 1973, losses due to volatilization amounted to 24 to 72 thousand pounds (9.3 to 28 thousand pounds PAQ). Of this total, 26% and 74% were released in the mid-St. Lawrence and Southern Ontario drainage basins, respectively.

Wire and Cable Insulation

Plasticizer loss has apparently not been measured by Canadian processors. Estimates vary between 0.1% and 0.2% of total plasticizer present. In 1973, consumption of plasticizer amounted to between 10.0 and 10.5 million pounds, resulting in a loss of 10.5 to 21 thousand pounds (4 to 8.1 thousand pounds PAQ). Most of this was lost to the plant atmosphere, whereas some was undoubtedly released to water in the baths used to cool the insulated cable. Two thirds of the releases occurred in the Southern Ontario basin, with the remainder going to the mid-St. Lawrence basin.

Plastisols

In 1973, plastisol production consumed 55 million pounds of PVC and 24.5 million pounds of phthalate plasticizer. Using a loss factor of 0.1% by weight for compounding operations, releases totalled 24,500 pounds (9,300 pounds PAQ). Releases to the plant atmosphere from the processing of plastisols ranged between 1.2 and 2.5 million pounds of PAEs (484 to 959 thousand pounds PAQ), based on a loss factor of 5-10% by weight. Note that a large number of plants take measures to reduce the work place concentrations and protect workers. All scrap is recycled, so losses here are nil.

The Southern Ontario basin received 72% of PAE releases from plastisol production and use, with the rest going to the mid-St. Lawrence basin.

Other Vinyl Extrusions and Mouldings

In this category, a phthalate loss of 0.1% by weight is accepted as reasonable. Spillage is nil, since the phthalate used is received in pelleted compound form and all scrap is reworked. In 1973, 4.5 million pounds of PAEs were consumed, resulting in a calculated loss of 4,500 pounds (1,700 pounds PAQ) to the plant atmosphere. Of this total, 87% was released to the mid-St. Lawrence basin and the rest to the Southern Ontario basin.

Release of PAEs from Use as Plasticizers in Other Products

Adhesives

In the production of adhesives, the plasticizer and poly(vinyl acetate) resin are combined in kettles, which are open to the air. Losses of PAEs are therefore atmospheric. Based on a consumption of 500 thousand pounds of phthalate plasticizer in 1973, and an estimated loss rate of 2% by weight, losses of phthalates were approximately 10,000 pounds in 1973 (4,000 pounds PAQ). This amount has been arbitrarily allocated evenly between the mid-St. Lawrence and Southern Ontario drainage basins.

Nitrocellulose Lacquer Coating for Cellulose (Viscose) Film

The formulation of the coating and its application to the film constitute a continuous process. Atmospheric loss rates for the application of the lacquer to the film are estimated to be less than 0.1%. This calculates to a loss of 6,600 pounds (3,700 pounds PAQ), all of which is assigned to the Southern Ontario basin.

Miscellaneous

The phthalate content of the miscellaneous products mentioned in Chapter 3 was estimated at 700,000 pounds for 1973. An arbitrary loss rate of 1% has been used in the calculation of PAE releases during the manufacture of these products. This calculates to a loss of 7,000 pounds in 1973 (2,600 pounds PAQ) and is arbitrarily allocated evenly between the Southern Ontario and mid-St. Lawrence basins.

RELEASES TO THE ENVIRONMENT OF PAEs THROUGH USE AND DISPOSAL ACTIVITIES

Introduction

The technical quantitative data required to establish releases of PAEs to the environment from the use and disposal of articles containing them is in early stages of development. Very little information is available on the major aspects of the issue. These include the loss of plasticizer from articles during their useful lifetimes, the levels of PAEs and their combustion products in the stack gases of incinerators and the behaviour of PAEs in buried items, for example, the migration patterns of PAEs under varying conditions in landfill sites.

While information is available on the overall composition of refuse (e.g., wood, metal, plastics, putrescible matter, etc.), the PAE content can only be estimated. A study of solid waste in Canada is being carried out by the Solid Wastes Management Branch, Department of Fisheries and the Environment. Data from

that study pertaining to per capita quantities of refuse disposed of in Canada have been combined with demographic data to arrive at estimates of regional PAE release to the environment.

In the following sections, the routes by which PAEs gain access to the environment from use and disposal activities are described, in addition to estimates of the quantities reaching the environment from these sources.

Routes

The routes by which PAEs are released to the environment at the consumer level are described briefly in the following paragraphs. They include

- a) volatilization of PAEs from articles during their useful lifetimes;
- b) disposal of articles containing PAEs by sanitary landfill; and
- c) incineration of refuse, a percentage of which is articles containing PAEs.

Plasticizers may migrate from articles during the useful lifetime of those articles. Examples include the volatilization of PAEs in vinyls used in cars (mats, seat covers, door liners, etc.), garden hose, shower curtains and patio furniture, which become brittle and inflexible due to loss of plasticizer. It is also worth noting that such loss of plasticizer often renders the article useless and brings about its disposal. PAEs are known to migrate from buried items, such as cable insulation, during their useful lifetimes, however, it is uncertain whether this process is physical or biological. The contribution of these sources to the total releases of PAEs to the environment is unknown, but it may be considerable owing to the large quantity of these articles in use.

Solid refuse, a percentage of which will be items containing PAEs, is generally disposed of in landfill sites or by incineration, depending on local disposal practices. In the case of direct burial the PAEs become subject to migration from the articles. The migration pattern depends on factors such as temperature, pressure due to overburden, and the influence of impinging groundwater and other fluids from the refuse mass. There seems to be no quantitative information on such migration patterns, beyond some basic trends. In some instances the PAEs may remain in the articles. Once removed, however, they become available for accumulation in the surrounding soil, or they may be carried into rivers and streams via groundwater.

In either case, they may enter biological food chains or be degraded by certain microorganisms. The available information on the environmental fate of these compounds was reviewed in Chapter 2. The pathways, or routes of transport, in the environment are not as well understood.

Incineration gives rise to three possible routes of PAE entry to the environment. First, the stack gases may contain PAEs or their combustion products, which may be discharged to the atmosphere. Secondly, where scrubbers are used to remove particulates and other impurities in the stack gases, the collected PAEs and/or combustion products are discharged with the scrubber water to treatment facilities or untreated to a receiving water body. Thirdly, the residue of the incinerated waste, consisting primarily of ash and other non-combustible materials, is disposed of in landfill and may contain some PAEs or decomposition products. This last case is unlikely because of the volatile nature of PAEs in high temperature conditions.

The technical data required to confirm the presence of PAEs and their combustion products in incinerators are lacking. There are currently no programs in Canada under which PAE levels in incinerators are monitored. At some sites, the PAE level may be expected to be low owing to plastics removal from the refuse fuel.

For example, at the Lakeview Generating Station in Mississauga, a presort condition will dictate the removal of certain plastics, notably PVC, from the refuse to be burned in the "Watts from Waste" program. This is being done to prevent corrosion of boiler tubing by the hydrogen chloride produced during the combustion of PVC. Synthetic rubber may be left in the fuel mix, and this would result in the combustion of some PAEs. The exclusion of PVC, however, will mean the exclusion of the vast bulk of PAEs in the trash. As a result of presort, the plastics content of the "reject" feed will be significantly higher than in the unsorted refuse. If the plastics are subsequently removed from the reject feed mix and recycled, the problems of leachate in landfill and PAE emissions during incineration will be largely reduced. If, on the other hand, the reject feed is sent to landfill, this will result in PAEs entering the site in higher concentrations than in unsorted refuse.

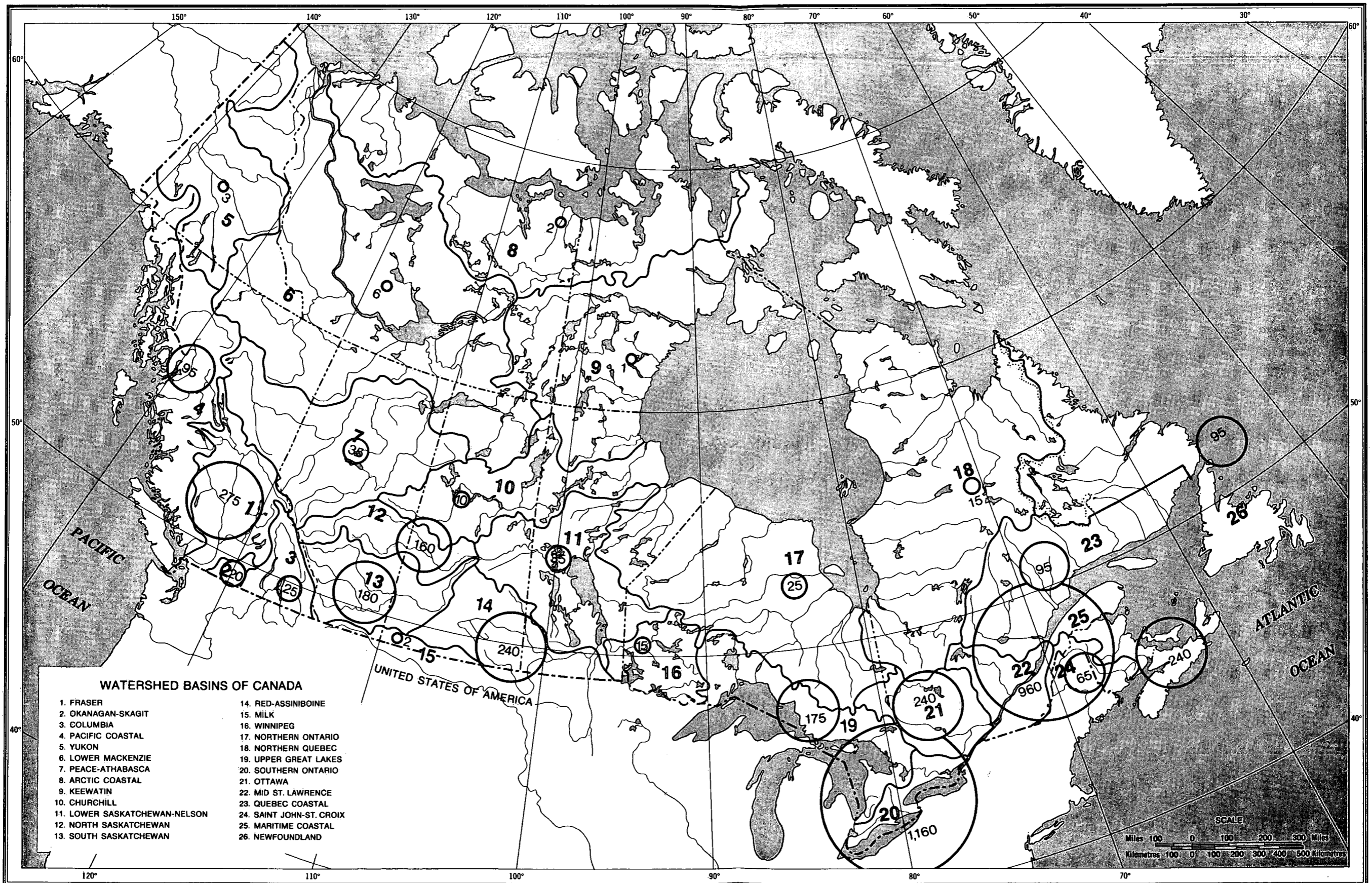
Quantities

Although there is little information on which to form accurate estimates, communications with the Solid Waste Management Branch, Department of the Environment (J. Payne, personal communication), have provided insight into the disposal habits of Canadians. In 1973, some 11.87 million tons of refuse were disposed of in Canada. This figure includes residential, commercial and non-specific industrial wastes. It does not include wastes from industrial processes, which were dealt with in the section entitled "Releases to the Environment of PAEs during Production and Processing Activities." Of the total material disposed of approximately 3.5% was plastics. Slightly less than 5% of that figure was PVC and PVC complexes, half of which fall into the flexible vinyls category. This material is assumed to contain an average of 40% by weight plasticizer, the bulk of which is phthalates. This calculates to a disposal of PAEs at the consumer level of approximately 4,175 tons (3.1 million pounds PAQ) in 1973. Note that no account has been made in this calculation of PAEs volatilized during the useful lifetime of products. It has been assumed that all the plasticizer has remained in the article and is released to the environment after disposal of the article. This assumption does not alter the estimates of PAEs released to the environment, since there has been no attempt to quantify releases on the basis of the various routes discussed above. Only the total released from all the sources has been estimated in terms of the watersheds illustrated in Map 1.

The generation of refuse by urban dwellers was just over 3 pounds per capita per day in 1973. The figure for rural dwellers has been arbitrarily set at two thirds that of urban dwellers (approximately 2 pounds per capita per day). This factor, although completely arbitrary, will take into account the fact that urban refuse also includes large amounts of waste from office buildings, factory cafeterias, hospitals and other sources of commercial and non-specific industrial refuse. For report purposes, the two-thirds factor is assumed to apply to the various components of the refuse, i.e., the plastics disposal rate of a rural dweller will be two-thirds that of an urban dweller.

Quantities of PAEs released to the environment at the consumer level within each of the drainage basins depicted in Map 1 have been calculated using the factors developed above in conjunction with 1971 demographic data. These figures are presented in Table 11 and illustrated in Map 3. It should be kept in mind that 1971 demographic data were used in this calculation. Although accurate data for 1973 will not become available until after the 1976 census, it has been assumed for report purposes that the ratio of urban to rural dwellers in Canada did not change appreciably from 1971 to 1973.

It is appropriate to emphasize here the fact that the numbers listed in Table 11 and illustrated in Map 2 represent the total quantities leaving the consumer inventory of PAEs as depicted in Figure 2, Chapter 4. They say nothing



Map 3. Releases to the environment of PAEs from use and disposal activities, 1973 (tons).

Table 11. Releases of PAEs from Use and Disposal Activities by Drainage Basin, 1973 (tons)

Basin	1971 Population ¹ (/000)	% of total population	Approximate PAE content of residential, commercial and non- specific industrial wastes (tons)		
			Urban	Rural	Total ²
1. Fraser	1,395	6.5	244.2	32.6	275
2. Okanagan-Skagit	101	0.5	10.9	6.9	20
3. Columbia	135	0.6	15.1	8.9	25
4. Pacific-Coastal	507	2.4	72.2	22.9	95
5. Yukon	17	<0.1	2.3	0.8	3
6. Mackenzie	31	0.1	3.2	2.3	6
7. Peace-Athabasca	209	1.0	20.4	15.8	35
8. Arctic-Coastal	11	<0.1	0.4	1.3	2
9. Keewatin	4	<0.1	-	0.6	1
10. Churchill	59	0.3	2.7	6.5	10
11. Nelson	219	1.0	12.2	22.7	35
12. North Saskatchewan	837	3.9	126.4	33.1	160
13. South Saskatchewan	948	4.4	151.0	32.2	180
14. Red-Assiniboine	1,282	5.9	190.9	52.5	240
15. Milk	15	<0.1	-	2.1	2
16. Winnipeg	87	0.4	9.7	5.8	15
17. Northern Ontario	144	0.7	19.7	7.0	25
18. Northern Quebec	83	0.4	10.9	4.4	15
19. Upper Great Lakes	946	4.4	129.4	46.4	175
20. Southern Ontario	5,774	26.7	1,053.2	106.8	1,160
21. Ottawa	1,250	5.8	186.1	51.2	240
22. Mid-St. Lawrence	4,800	22.2	863.1	97.1	960
23. Quebec-Coastal	513	2.4	71.6	24.2	95
24. Saint John-St. Croix	369	1.7	42.6	23.4	65
25. Maritime Coastal	1,346	6.2	145.7	91.7	240
26. Newfoundland	522	2.4	62.8	31.4	95
Total	21,604	100.0	3,446.7	730.6	4,175

¹ Source: National Water Needs Study, Phase 1. Unpublished Draft Report, July 1972.

² Totals rounded.

Table 12. Potential Annual Releases of Plasticizer and Dissociation Products from Incineration in Selected Canadian Cities (tons)¹

City	Tons	Drainage basin
Charlottetown	2.5	Maritime Coastal (25)
Dartmouth	2.5	Maritime Coastal (25)
Halifax	9	Maritime Coastal (25)
Alma, Quebec	1	Quebec Coastal (23)
Quebec City	20	Mid-St. Lawrence (22)
Montreal	50	Mid-St. Lawrence (22)
St. Eustache, Quebec	1.5	Lower St. Lawrence (22)
Algonquin Park	0.25	Ottawa (21)
Hamilton	5	Southern Ontario (20)
Toronto	40	Southern Ontario (20)
Simcoe, Ontario	1	Southern Ontario (20)
Dresden, Ontario	0.4	Southern Ontario (20)
Port Colborne	1	Southern Ontario (20)
Corunna	0.5	Southern Ontario (20)
Collingwood	0.5	Upper Great Lakes (19)
Regina	5	Milk River (15)
Winnipeg	10	Red-Assiniboine (14)
Powell River	0.6	Pacific Coastal (4)
North Cowichan	0.25	Pacific Coastal (4)
Total	151.00	

¹ Based on incineration tonnage and location data, Air Pollution Control Directorate, Ottawa, weighted by available demographic data.

about what quantities entered the environment by each of the routes described above (volatilization during use, landfill, incineration). Some information on quantities of PAEs released from incineration has been developed from data provided by the Air Pollution Control Directorate in Ottawa. Figures for selected cities are presented in Table 12. A few large cities, notably Toronto and Montreal, have a good idea of the percentages of their municipal refuse disposed of by city-operated landfill sites and incinerators but this does not necessarily include trash incinerated in apartment and hospital incinerators. Information on the daily tonnage of trash reaching over 1,000 landfill sites throughout Ontario has been assembled by the Land Drainage Reference Group, Task B2 (102). In the other provinces the analysis of solid waste disposal is somewhat less advanced. In light of other information gaps and assumptions, the quantification of consumer level PAE release on a national basis by route of entry would be somewhat arbitrary at this time, and has not been attempted in this report. It is not unreasonable to expect, however, that the bulk of such releases will be via landfill.

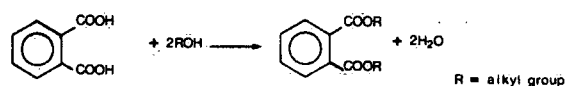
CONCLUSION

Any PAEs remaining in effluent streams (liquid or gaseous) after treatment are released directly to the environment. PAEs contained in aqueous effluents are discharged to receiving water bodies (rivers, lakes, etc.). Because of their generally low solubility in water, the PAEs may be expected to combine and perhaps form complexes with suspended organic matter or other materials. A percentage of the PAEs released directly to the atmosphere will undoubtedly be dispersed by wind over large areas. For purposes of the estimates developed throughout this chapter, it has been assumed that any airborne PAEs will precipitate out within the same drainage basin as their origin. Airborne PAEs precipitating directly onto soil, in addition to PAEs released in landfill sites, may form complexes with some component of the soil, e.g., fulvic acid, or they may be carried into adjacent water bodies by runoff or groundwater. Throughout these processes, the PAEs are subject to chemical and/or biological degradation, including possible entry into the food chain. More research into the environmental movement of PAEs is required before any idea of the ultimate fate, or "resting place," of these chemicals can be firmly established.

Background Information

CHEMISTRY AND PROPERTIES OF PAES

The term "phthalic acid ester" is restricted to the ortho form of benzene dicarboxylic acid prepared by reacting phthalic acid with a specific alcohol to form the desired ester:



Industrially, the esters are prepared from phthalic anhydride rather than from the acid. Commercial phthalate esters are not pure compounds, but reasonably pure ones can be prepared for specific applications. Most are colourless liquids, have low volatility and have poor solubility in water, but are soluble in organic solvents and oils (Table 13).

Table 13. Physical and Chemical Properties of Phthalate Esters

Compound	Molecular weight	Specific gravity	Bp, °C	Solubility in H ₂ O, g/100 ml
Dimethyl phthalate	194.18	1.189 (25/25)	282	0.5
Diethyl phthalate	222.23	1.123 (25/4)	296.1	Insoluble
Diallyl phthalate	246.27	1.120 (20/20)	290	0.01
Diisobutyl phthalate	278.3	1.040	327	Insoluble
Dibutyl phthalate	278.34	1.0465 (21)	340	0.45 (25°C)
Dimethoxyethyl phthalate	282.0	1.171 (20)	190-210	0.85
Dicyclohexyl phthalate	330.0	1.20 (25/25)	220-228	Insoluble
Butyl octyl phthalate	334.0	—	340	—
Diethyl phthalate	334.0	0.990	—	Insoluble
Butylphthalyl butyl glycolate	336.37	1.097 (25/25)	219/5 mm	0.012%
Dibutoxyethyl ethyl phthalate	366.0	1.063	210	0.03
Di-2-ethylhexyl phthalate	391.0	0.985 (20/20)	386.9/5 mm	Insoluble
Diisooctyl phthalate	391.0	0.981	239/5 mm	Insoluble
Di-n-octyl phthalate	391.0	0.978	220/5 mm	Insoluble
Dinonyl phthalate	419.0	0.965	413	Insoluble

SOURCE: Patty (76).

Two other isomeric forms of benzene dicarboxylic acid esters having important industrial applications are also available. These are the meta form (or isophthalate esters) and the para form (or terephthalate esters):



Terephthalic acid and its esters (terephthalates) are important starting chemicals for certain types of polymers (e.g., Dacron). They are used occasionally in animal feed to enhance the physical properties of the feed and the bioavailability of added components such as antibiotics. Isophthalates are also used in the production of certain types of polymers and resins, but not to the same extent as the phthalates and terephthalates.

PAES AS PLASTICIZERS

A plasticizer has been defined (103) as a material incorporated in a plastic to increase its workability and its flexibility or distensibility. In external plasticization, chemicals are compounded with the host resin to improve its processability. In this case, the plasticizer is bound by physical, rather than chemical, forces. Compounds used in external plasticization may be further subdivided into primary and secondary plasticizers. Both can be described as relatively non-volatile solvents for resinous (or polymer) substances, which, when compounded with the resin, improve its physical properties and processability. Secondary plasticizers are, by definition, less expensive and may be used to displace a portion of the primary plasticizer without adversely affecting the end use properties of the plastic.

In internal plasticization, the reaction of a co-polymer with a portion of the reactive sites present within the host (virgin) resin renders both more easily processible than the original virgin resin. The plasticizing co-polymer is in this case chemically bound to the host resin, thus eliminating plasticizer migration, exudation and other problems associated with external plasticization. Intensive effort has been expended by vinyl resin producers to develop co-polymer based systems competitive on the basis of price performance with externally plasticized products. So far, attempts in this area have met with only limited success.

Although some polymers such as polyethylene, polypropylene and polystyrene can be processed into useful products without the use of plasticizers, others such as cellulose nitrate, cellulose acetyl butyrate, and poly(vinyl chloride) require plasticizers in many of their end uses.

The classification of plasticizers is shown in Appendix B.

Plasticizer formulations are subjected to a number of tests designed to measure certain physical characteristics of the material to determine their suitability for a particular end use. Some of these characteristics are described in the following paragraphs.

Volatility

This is normally expressed in terms of percentage weight loss from a compound at elevated temperatures. Volatility is particularly important in products such as coatings for electrical wiring (which gets hot) and automobile upholstery, where fogging of automobile interiors and windows has been known to occur. The volatility of phthalates generally increases with decreasing molecular weight.

Resistance to Extraction by Liquids

This is expressed in terms of percentage weight loss under standard conditions relating to the intended end use of the PVC. The ease of extraction is greater for organic solvents than water-based solvents. It increases with increasing molecular weight in the case of organic solvents, and with decreasing molecular weight in the case of water-based solvents. The extraction of plasticizer from PVC in landfill may also be enhanced by impinging oils and organic solvents, although this has never been measured. The extraction rates of some plasticizers are presented in Table 14.

Table 14. Extraction ^{1, 2} of Phthalate Plasticizers from PVC by Selected Solvents (%)

Phthalate	Distilled water ³	1% Soap solution ³	1% Detergent solution ³	Mineral Oil ³	Isooctane ⁴	Diisobutylene ⁴	Isooctane + toluene ⁴
Di- <i>n</i> -butyl	0.50	1.00	0.90	1.05	1.85	2.10	14.5
Diisobutyl	0.50	1.30	1.80	1.50	3.50	6.30	14.0
Di-2-ethylhexyl	0.10	0.30	0.55	1.50	20.3	23.0	16.3
Diisooctyl	0.05	0.40	0.50	1.30	20.2	23.4	16.4
Dinonyl	0.05	0.10	0.15	1.90	28.9	29.2	21.0
Diisodecyl	0.15	0.15	0.40	7.05	28.5	29.3	20.8
Ditridecyl	0.20	0.05	0.60	20.0	33.0	33.8	32.6

¹ SOURCE: Penn (104).

² The results are expressed as a percentage loss in weight of a test piece of dimensions 3 in. x 2 in. x 0.05 in. The solvents were neither stirred nor renewed during the test.

³ 240 hr @ 23°C.

⁴ 24 hr @ 23°C.

Resistance to Exudation

Industry tests for exudation (migration from PVC) of phthalates under hot humid conditions, such as those encountered by flooring, wall coverings, shower curtains and upholstery. Monomeric phthalates exude in high weight percentages if used alone. The addition of high molecular weight polymeric plasticizers, however, tends to lock them into the polymeric mass. If the PAEs tend to migrate under normal end use conditions, they may be expected to exude in landfill sites owing to tons of overburden in addition to the rise in temperature due to composting.

Resistance to Migration into Other Materials

This characteristic is assessed in industry by tests designed to suit particular circumstances. Examples of "trouble areas" include PVC refrigerator gaskets (used in contact with polystyrene parts) and PVC sheeting coated with lacquers (e.g., food wraps) and adhesives. The permanence of monomeric phthalates is observed to be poor.

Resistance to Attack by Microorganisms (Bacteria and Fungi)

Plasticized PVC products used outdoors, especially in contact with soil and/or moisture, are susceptible to attack from microorganisms. Such products include garden hose, foul-weather clothing and cable coating. Actually, it is the plasticizer which is attacked, apparently as food for the microbe. Soil burial tests show that high plasticizer content promotes propensity to microbial attack. Epoxidized oil plasticizers are particularly susceptible. Some phthalates are reasonably resistant, but as a class are more susceptible than phosphates.

Resistance to Insect and Animal Attack

Building and outdoor uses of PVC (e.g., cable coverings, wall cladding, piping and roofing) are susceptible to insect and animal attack, which hastens the disposal rate to incineration, landfill or reclamation. Insect or animal attack does not represent significant dissemination of phthalates to the environment per se.

PVC FORMULATIONS, COMPOUNDING, PROCESSING AND FABRICATION

Formulations (Flexible PVC)

Products made of flexible PVC contain varying quantities of PAEs as plasticizers. Flexibilized PVC normally contains formulations of di-(2-ethylhexyl) phthalate (DEHP), formerly known as dioctyl phthalate (DOP), diisooctyl phthalate (DIOP), and to a lesser extent, diisodecyl phthalate (DIDP). Some PVC compounders favour either DIOP or DEHP in their formulations, although they are considered interchangeable.

Production rates and costs depend on the speed of solvation, which is the speed at which the fillers (plasticizers, stabilizers, etc.) have their surfaces "wetted" by the vinyl chloride resin. Efficient "wetting" is necessary to produce homogeneity throughout the mass of the product. Plasticizers that possess higher solvating power are used mainly in flooring and other highly loaded (extended or filled) products. These contain plasticizers such as butylbenzyl phthalate (BBP), butyldecyl phthalate (BDP) and butyloctyl phthalate (BOP).

The plasticizer content varies from zero in rigid vinyl products such as sheet and pipe to over 100 parts of plasticizer per 100 parts of resin (parts per hundred resin, phr). Plasticizers may account for up to 40% by weight of the material. Plasticsols, which are paste-like suspensions of PVC polymer particles in plasticizers, show the highest plasticizer content for any one type of vinyl chloride use area, an average of some 70 phr.

Compounding, Processing and Fabrication

The purpose of this section is to provide an overview of the processes used in the production of items dealt with in Chapter 4.

Extrusion

The PVC material (the result of PVC compounding techniques where plasticizer loss to the plant atmosphere is known to occur) is charged into the hopper in granular or powder form and gravity-fed into the feed zone of the screw. Material is conveyed forward and at some stage fuses to a continuous melt. The molten material is forced into a die to form the required shape. The actual extrusion barrel is sometimes a closed system, but more often the barrel of the extruder is vented. In the closed systems, the only possibility for loss of plasticizer would be at the point of discharge.

The molten plastics material leaving the screw of the extruder is fed through what is termed the die-head and die. This is a potential loss point of plasticizer.

Dies vary enormously, both in size and in complexity, from the very large pipe dies, which tend to dwarf the extruder, down to the very small cross-sectional

profile dies. Commercial units have vacuum venting equipment in the barrel of the extruder and this must be considered a loss point for plasticizer.

Examples of items produced by extrusion techniques are wire coating, hoses, flexible and rigid pipe, blown and cast flexible film, rigid sheets and rigid and flexible mouldings.

Injection Moulding

In the injection moulding process, plastic moulding compounds are converted into a melt, injected into a mould and allowed to cool to form a solid moulding, which is subsequently ejected.

Types of injection moulding machines include ram (plunger) and screw types. In the preferred screw type machines, the melting and injection functions are combined within what is essentially a heated extrusion unit. The screw is also capable of a reciprocating action to carry out the injection step.

Decomposition of PVC is possible at the high temperatures used in modern processing. Prolonged exposure to these high temperatures is also not uncommon. It is for this reason that heat stabilizers and use of modifiers are required. Plasticizers also provide a processing-aid in rolling flexible compounds. Even well-stabilized PVC compounds, however, can evolve small amounts of decomposition products (primarily hydrogen chloride, HCl). It is for this reason that venting of moulds is particularly important, not only to allow escape of entrapped air (under extreme pressure) but also extraneous gaseous decomposition products in addition to volatilized plasticizers. This is a definite loss point for plasticizer.

Blow Moulding

In this process, a gas under pressure is introduced at one point into a space surrounded by molten PVC, and the material is thereby blown outwards into conformity with the cavity of a mould and cooled. This forms a hollow article. Blow moulding of rigid bottles from PVC emerged early in the 1960's. Note that plasticized compounds are not generally suitable for bottles. For this reason rigid PVC bottles are the most important of blow-moulded PVC products. Since there is seldom a plasticizer in rigid PVC formulations, blow moulding is not a source of volatilized plasticizer.

Calendering and Moulding

Very large quantities of calendered sheet are made today. Calendering is used for manufacture of a considerable amount of unsupported film made for inflatable goods, clothing, upholstery, industrial linings, household goods such as curtains, tablecloths and so on. Modern high-quality machines now give closely controlled finishes at high speeds.

Compression and transfer moulding of PVC is now virtually extinct. The advent and practice of extrusion, injection moulding, blow moulding, calendering and vacuum forming, as well as fabrication techniques and the development of paste methods have made the process obsolete.

The type of plasticizer has an important bearing on processing characteristics. Consistency of temperature is important. The equipment temperature should be high and closely controlled. The calendering of rigid PVC is much the same as for flexible PVC. In calendering rigid products, temperatures may be a little higher, with calender rolls at 155-170°C. Calendering rigid plastic packaging involves calender temperatures of about 175°C.

Economic production requires working on a large scale in calendering. This requires continuous methods of production, and for this purpose a calender "train" is used. This "train" of equipment will generally consist of an internal mixer, two mills, a four-bowl calender, embossing rolls and cooling rolls. The plastic compound is dumped directly from the mixing operation onto one mill where it is sheeted and taken off as an unsupported strip onto the nip roll of the second mill or the hopper of the extruder. From there it goes by heated conveyor to the calender. High temperatures prevail up to and including the embossing roll. From here the sheets are taken to cooling rolls. Therefore, all plasticizer volatilization experienced in calendering takes place before or during embossing. Production rates of some 2,000 pounds per hour can be achieved. Venting is common in such a piece of equipment and this constitutes a loss point for plasticizer.

Low-Pressure Moulding Methods

The two principal methods by which plastic articles can be made by low-pressure processing are:

- a) vacuum forming; and
- b) true low-pressure methods (often using both a male and female die).

The term "thermoforming" is also used for both, although thermoforming usually means vacuum forming.

Principles involved are the same in both cases. A sheet of thermoplastic is heated to the best forming temperature and, in this softened state, forced into the desired shape by the application of a low pressure. Low pressure is effected by use of the positive pressure from an air-hydraulic press or indirectly by application of vacuum to one side. Vacuum forming is by far the most commonly used. In these methods the die, as well as the sheet of plastic compound, is brought up to temperature, and with variations in technique, vacuum is quickly applied. Rigid PVC compounds, however, are mostly used in thermo-forming techniques. Large volumes of PVC are processed this way. To the extent that rigid PVC and not flexible PVC is utilized, it does not represent a source of lost plasticizer. All moulds must be vented to apply vacuum at various points.

PVC Sheet and Its Fabrication

Sheet PVC is considered the intermediate product upon which the greatest variety of fabrication operations are carried out. Fabrication methods include hot gas welding, cementing, high frequency welding, machining and operations of various kinds. Loss of plasticizer at these points is considered miniscule by industry. Time at high temperature is short, most heating is internal and surface area involved relative to the volume fabricated is small.

The PVC materials involved include rigid as well as flexible unsupported sheeting, flooring, fabric-supported sheeting, foil and film. Most sheets and foils are supplied in pigmented or clear grade, and plasticized sheeting is available in various embossed grades. Several companies in Canada manufacture a range of PVC sheets and foils.

Types of unsupported PVC sheets include the following:

1. Rigid (unplasticized) PVC homopolymer sheeting, foil and film.
2. Rigid copolymer sheeting, foil and film.
3. Plasticized sheeting foil and film.
4. Plasticized/unplasticized laminated sheeting.

PVC Pastes (Plastisols)

Poly(vinyl chloride) pastes (plastisols) have been in common use for some time. Those containing stabilizers and other additives such as colorants and viscosity modifiers are used in considerable volume. Because of plastisol development, the processes of coating and rotational casting have evolved on a large scale.

During the preparation of the pastes the temperature is kept at 30°C or lower. Loss of plasticizer during preparation is therefore probably low. All dry components (pigments, fillers, solids, stabilizers, etc.) are first predispersed in a small quantity, e.g., one to three parts by weight of plasticizer to one part by weight of the dry materials. This is done on ordinary mill type equipment or by ball milling. The polymer is then placed in the mixer with plasticizer in quantity just sufficient to form a paste. Into this predispersed system the dry components are added. Mixing is carried on for 10 to 30 minutes depending on conditions, and at the end of this period the plasticizer and diluents are gradually added. Blending the plasticizer at this point takes about one hour. Air removal is highly desirable, and mixing under vacuum avoids air entrapment.

Heating must be applied to gel or to solidify PVC paste. Initially this heating results in a drop in viscosity, probably because the viscosity of the plasticizer itself is reduced by the heat before the polymer particles are sufficiently dissolved to counteract the effect on the viscosity of the paste as a whole. At a given point in the heating cycle, there is a sharp viscosity rise, which is sometimes referred to as the "set temperature." Final conversion to a uniform "gel" is achieved usually at a considerably higher temperature than the set temperature. This is known as the "temperature of gelation." The set temperature is influenced dramatically by the composition of the paste and in particular by the plasticizer system in use. The complete gelation will not normally take place unless the paste is heated to at least about 160°C. If the temperature becomes too high, some plasticizer loss will result and decomposition may also occur. However, even before the 160°C temperature is reached, plasticizer loss is experienced during the gelation cycle.

Some variant forms of PVC pastes show unique suitability in many applications. "Plastigels" are plastisols to which a thickening agent has been added. This results in a considerable increase in the viscosity of the paste. "Rigisols" are specially formulated plastisols which result in much harder products.

Plasticizer content in paste technology is high, averaging in the order of 70 phr. Volatilization of plasticizer takes place during the heating and gelation processes, but loss is minimized in that the system is closed. Processing and curing of these systems in open air and convection ovens, however, results in major losses.

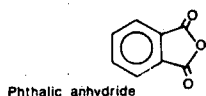
THE USE AND RELEASE TO THE ENVIRONMENT OF PHTHALIC ANHYDRIDE, TEREPHTHALIC ACID AND DIMETHYL TEREPHTHALATE

This section has been included to provide an overview of the uses of phthalic anhydride (PA) other than in the production of PAEs. In addition, the production of polyester fibre from dimethyl terephthalate (DMT) and terephthalic acid (TPA) is outlined.

Phthalic Anhydride

Phthalic anhydride (PA) is one of the starting materials, along with various alcohols, in the production of all ortho-phthalates (PAEs). The particular

phthalate produced depends upon the alcohol used. In addition, PA is used to a great extent in the production of other chemicals and products.



In the base year 1973, domestic production of PA was 45 million pounds (50 million pounds PAQ). Imports and exports totalled some 20 million and 5.8 million pounds respectively (22 million and 6.5 million pounds PAQ). Of the remainder, 37 million pounds (41.5 million pounds PAQ) were used in the production of polymers, such as alkyd and polyester resins. The rest was assigned to miscellaneous uses and losses. These figures are depicted in Figure 2, Chapter 4.

In 1973, releases to the environment of phthalic anhydride totalled between 417 thousand and 1.39 million pounds (466 thousand and 1.43 million pounds PAQ). Sources included the production of phthalic anhydride and the manufacture of alkyd resins and polyester resins. These figures are listed in Table 15.

Table 15. Releases of Phthalic Anhydride, Dimethyl Terephthalate (DMT) and Terephthalic Acid (TPA), 1973 ('000 lb PAQ)

Activity	Releases
Phthalic anhydride production*	50
Alkyd resin production*	264-925
Polyester resin production*	152-457
Polyester fibre production†	103
TOTAL	569-1535

* Releases in form of phthalic anhydride.

† Releases in form of DMT, TPA.

Alkyd Resin Manufacture

Alkyd resins are polymers used in retail paints, and industrial and baked coatings applications. In Canada in 1973, 23.6 million pounds of phthalic anhydride (26.5 million pounds PAQ) were consumed in the manufacture of 46.5 million pounds of alkyd resin. This in turn was converted to between 183 and 193 million pounds of formulated paint ready for application. Of the total consumption of phthalic anhydride, 4.9 million pounds (20.7%) were consumed in Quebec, 17.7 million pounds (75%) in Ontario and one million pounds (4.3%) in British Columbia.

Losses of phthalic anhydride in the manufacture of alkyd resins have been estimated by manufacturers to be between 1% and 3.5% of the total consumption. This calculates to a release of between 236 and 826 thousand pounds (264 and 925 thousand pounds PAQ) in 1973. Of this total, 75% was released in the Southern Ontario drainage basin, 21% in the mid-St. Lawrence drainage basin, and 4% in the Fraser drainage basin.

It is estimated that sewered plant effluent accounted for between 20% and 70% of all phthalic anhydride released during alkyd resin manufacture. The balance was released to the atmosphere through volatilization during reaction of raw materials, as well as during the transport and storage of molten phthalic anhydride.

Polyester Resin Manufacture

Polyester resin manufacture is similar to alkyd resin manufacture. In fact, many producers utilize dual-purpose kettles that allow both types of resin to be

produced. Polyester resins, otherwise known as non-oil alkyds, are reaction products of an unsaturated organic acid (e.g., phthalic anhydride or maleic anhydride) with a polyol.

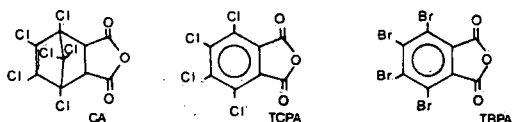
The bulk of polyester resins are considered general purpose materials and are used in fiberglass reinforced plastics (FRP). As such they go into a wide range of retail and industrial uses.

In 1973, Canadian producers of polyester resins consumed 13.6 million pounds of phthalic anhydride (15 million pounds PAQ) in the manufacture of 48 million pounds of polyester resin. This material was sold primarily to fabricators throughout Canada, where the resin was converted into fiberglass-reinforced products and paint or dip coatings. Of the total phthalic anhydride consumed, about 10.3 million pounds (75.7%) were converted to resin in Ontario, one million pounds (7.4%) in Quebec, and 2.3 million pounds (16.9%) in British Columbia.

The reaction by which the polyester resin is manufactured produces large amounts of water which, when driven off as steam, carry off some remaining phthalic anhydride starting material directly to the atmosphere, in the order of 1-3% of the total starting material. This calculates to a loss of between 136 and 408 thousand pounds (152 and 457 thousand pounds PAQ) in 1973. In installations where scrubbing towers are used, most of this will be collected and deposited in chemical sumps or settling ponds. Sump material is removed and disposed of in chemical disposal areas. Of the total, 75.7% was released in the Southern Ontario drainage basin, 7.4% in the mid-St. Lawrence drainage basin and the remainder in the Fraser drainage basin. These releases were assumed proportional to consumption of phthalic anhydride.

Flame Retardants

The three major monomeric phthalic anhydride-type compounds that are used to impart flame retardancy to polymerized resin are chlorendic anhydride (CA), tetrachlorophthalic anhydride (TCPA) and tetrabromophthalic anhydride (TBPA).



All are used as reactives for polyester resins. TBPA has also been used as a reactive intermediate for rigid urethane foams in the United States. CA is probably the most widely used polyester intermediate, primarily for the manufacture of corrosion-resistant resins used in tanks, pipes and ducts for pulp, mining and chemical process industries. It is also used as a curing (hardening) agent for epoxy resins, which is its second largest end-use, and as a chemical intermediate in the production of dyes and pesticides.

Imports of CA are not listed separately by Statistics Canada. It has been estimated, however, that between one and two million pounds of halogenated derivatives of phthalic anhydride were imported from the U.S. in 1973. This was based on chemical import trends from the Department of Industry, Trade, and Commerce.

In the U.S., the growth in demand for the halogenated fire retardants has decreased owing to the development of cheaper substitutes and processes. This trend is expected to develop in Canada as well.

Losses of these phthalic anhydride derivatives to the environment are considered minimal during production, none of which is done in Canada. Release

from disposed items, e.g., in landfill, may prove to be considerable, but was considered beyond the scope of this study.

Terephthalic Acid and Dimethyl Terephthalate

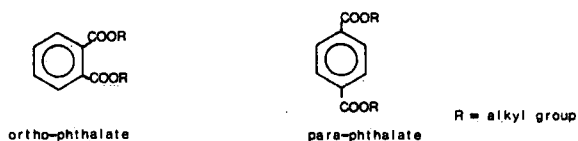
Polyester Fibre Manufacture

The raw materials of concern under this heading are terephthalic acid (TPA) and its ester, dimethyl terephthalate (DMT). Polyester fibres manufactured in Canada are made from polymers (chains) of these materials. All TPA and DMT is imported. Consumption of both DMT and fibre-grade TPA is increasing in Canada. Each material has characteristic advantages which are primarily a function of the cost of production and type of filament desired.

Polyester fibres, used in tire cord and textured knitting yarns for apparel, are all increasing in demand. The demand for polyester staple in apparel is not increasing as rapidly, primarily because it already has a large share of the market. Polyester is not an ideal textile fibre, but is blended with other materials to produce a widely accepted product.

Imports of TPA and DMT, based on field reports, were 38 million and 39 million pounds respectively (38 million and 34 million pounds PAQ) in 1973. All polyester fibres were produced in the Southern Ontario drainage basin.

DMT is a para-phthalate, different in chemical structure from the ortho-phthalates (PAEs) of primary concern in this study. The end use (polyester fibre)



requires that it be converted to a polymeric form (chains of molecular units), whereas phthalate plasticizers are generally monomeric ortho-phthalates. Releases of the monomeric form of DMT during the production of polyester fibre are summarized below. It is assumed that, once the monomer has been incorporated into the chain, it is no longer free to reach the environment as a monomer. This may prove otherwise, however, as was the case with PVC and vinyl chloride monomer.

Industry estimates that spillages of TPA and DMT (in pellet form) during polyester fibre manufacture amount to no more than 0.1%. Minor amounts of TPA might be released while the material is being blown into silo storage. Cleanout of reaction vessels would result in the loss to sewer systems of some low polymers (dimers, trimers, etc.) of polyethylene terephthalates. This amount is estimated by industry to be very low. Using a total loss factor of 0.15% for these loss points, 1973 releases of DMT and TPA were 51,000 and 58,500 pounds respectively (44,000 and 58,500 pounds PAQ). All releases occurred in the Southern Ontario drainage basin, and are itemized in Table 15.

Conclusions and Recommendations

Based on the material presented in this study, several conclusions may be drawn. The most important of these are the following:

1. Phthalic acid esters are a widely used group of chemicals. They are employed in a variety of products, including flexible PVC, which constitutes their largest current end-use. Amounts of PAEs released to the environment from the production, use and disposal of PAEs and the products containing them appear to be considerable (between 9.9 and 11.9 million pounds in 1973). All of the above activities are confined to a relatively small, populated portion of the country.
2. Residues of PAEs have been detected in all sectors of the environment, i.e., air, water, soil and living things, including man.
3. The acute toxicities of PAEs appear to be relatively low compared to pesticides. High LD₅₀'s are observed for fish and laboratory animals. The most sensitive species presently known is the water flea (Daphnia magna), whose reproduction is significantly inhibited by even very low concentrations of DEHP. The resulting long-term effects on the environment as a whole are as yet unknown.
4. The acceptable daily intake (ADI) for humans is several orders of magnitude above the normal daily exposure estimated in this study. There are two cases where this normal daily exposure may be exceeded. First, individuals who work in areas where PAEs are manufactured or processed are likely to undergo above-normal exposure, regardless of the level of industrial hygiene practiced. Secondly, patients receiving blood transfusions or hemodialysis therapy may undergo relatively high exposure to PAEs from certain plastic medical devices, particularly PVC blood storage bags. The toxic effects of such exposure remain unconfirmed, but are being investigated by the Department of National Health and Welfare.

The following information gaps became apparent during the assembly of information for this study:

1. Quantitative data on the sources and levels of PAEs in the environment are far from complete. Very little is known concerning the physical or biological pathways of transport or the ultimate environmental sinks of PAEs.
2. Virtually nothing is known about the teratogenic (direct effects on the developing fetus) or mutagenic (changes to the nature of cells in culture, i.e., in vitro) effects on humans brought about by long-term exposure to PAEs from various sources.

A firm and/or continued commitment in a number of research areas would serve to better determine the significance of PAEs in terms of environment and human health.

1. A data base on environmental levels of PAEs should be developed which includes not only the monitoring of PAE discharges and residues in soil, water and biota in the immediate vicinity of industrialized and populated areas, but also in remote regions. This is vital in determining the pathways and extent of PAE dispersal throughout the environment, the rates and locations of environmental accumulation and the stability of PAEs in

the environment. Combined with the use of a suitable indicator species, such information would serve to flag any potential environmental problems that may result from the use of these chemicals. These concepts are, of course, standard in establishing the impact of any environmental contaminant.

2. Investigations into the toxicity to humans (especially teratogenic and mutagenic effects) of long-term exposure to realistic levels of PAEs in air, food and water should be investigated. (The toxic effects of PAEs in medical devices are presently being examined by the Department of National Health and Welfare.)

Poly(vinyl chloride) and other products containing phthalate plasticizers are important items of commerce, for which there are currently no economically feasible substitutes. Any restrictions on the use of PAEs could not be justified on the basis of present knowledge of their impact on the environment and human health. (PVC medical devices are an exception, for which alternative materials are currently being sought.) However, data generated by the research efforts described above could conceivably demand a critical reassessment of the hazard potential of this group of organic compounds.

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Canadian Manufacturers of Phthalic Acid Esters and Products Containing Phthalic Acid Esters

Canadian Producers of Phthalic Acid Esters (PAEs), 1973

Quebec Carlew Chemicals, Montréal
 Monsanto, Montreal

Ontario BASF, Cornwall
 Canadian General Electric, Toronto

Canadian Manufacturers of Vinyl Flooring, 1973

Quebec American Biltrite Rubber Company (Canada) Ltd.,
 Sherbrooke
 Armstrong Cork (Canada) Limited, Montreal
 Domco Industries Limited, Farnham

Ontario Flintkote Co. of Canada Limited, Toronto

Canadian Manufacturers of Calendered and Extruded Film and Sheet, 1973

Quebec B.F. Goodrich (Canada) Limited, Shawinigan
 Plastishaw, Shawinigan

Ontario Monsanto, Oakville
 Canadian General Tower Limited, Cambridge
 Uniroyal Limited, Kitchener
 Stauffer Chemical Co. of Canada Limited, Toronto
 Borden Chemical Co. (Canada) Limited, West Hill
 Goodyear Tire and Rubber Co. of Canada Limited, Toronto
 TCF of Canada Limited, Cornwall
 Rubbermaid (Canada) Limited, Toronto

Canadian Manufacturers of Wire and Cable Insulation, 1973

Quebec Northern Electric, Montreal
 Pirelli Cables Limited, St. Jean
 ITT Wire and Cable, St. Jerome
 Rochevert Inc., Valleyfield

Ontario Canada Wire and Cable Limited, Toronto
Philips Electronics Industries Limited, Brockville
General Wire and Cable Co. Limited, Cobourg
Alcan Wire and Cable, Bracebridge
Fabricon Manufacturing Limited, Trenton
Canadian General Electric, Peterborough
Industrial Wire and Cable (1970) Limited, Toronto
Cable-Tech Wire Co. Limited, Stouffville

Canadian Formulators and Consumers of Vinyl Plastics, 1973

Quebec Beckwith-Bemis Limited, Sherbrooke
Edmont (Canada) Limited, Cowansville
National Vintex Corp., Candiak
Stedfast Rubber Co. (Canada) Limited, Granby
British Rubber, Montreal
Crown Cork and Seal Co. Limited, Montreal
Daly and Morin Limited, Montreal
Dewey and Almy Chemical, Montreal
Pervel Limited, Montreal

Ontario Allen Industries (Canada) Limited, Hamilton
Barry Manufacturing Co. Ltd., Mississauga
Bata Industries Limited, Trenton
Bilrite Rubber (1969) Limited, Toronto
Carlaw Footwear, Toronto
Continental Can Co. of Canada Ltd., Toronto
Fortune Footwear, Hamilton
B.F. Goodrich (Canada) Limited, Kitchener
Kaufman Footwear Limited, Kitchener
M & T Products, Hamilton
Mobern, Cornwall
Rehau, Prescott
W.R. Grace and Co. Limited, Mississauga

Canadian Manufacturers of Other Vinyl Extrusions and Mouldings, 1973

Quebec Rochevert Inc., Valleyfield
General Plastics Co. Limited, Cookshire

Ontario Rehau, Prescott

Canadian Manufacturers of Adhesives, 1973

Quebec Dural Products Limited, Dorval

Ontario Polyresins Limited, Don Mills
Borden Chemical Co. Canada Limited, West Hill
Industrial Adhesives Limited, Toronto
Swift Chemical Company, Bramalea
Morgan Adhesives of Canada Limited, Brampton
3M Canada Limited, London

Canadian Manufacturers of Nitrocellulose Film, 1973

Quebec Du Pont of Canada Limited, Montreal
Ontario TCF of Canada Limited, Cornwall

Canadian Manufacturers of Alkyd Resins, 1973

Quebec Agrabec, Montreal
Dural Products Limited, Dorval
Reichhold Chemicals Limited, Ste-Thérèse-de-Blainville
Sherwin-Williams, Montreal

Ontario Alma Paint and Varnish, London
Ashland Oil, Toronto
Canada Varnish, Toronto
Canadian General Electric, Toronto
Canadian Industries Limited, Toronto
Canadian Pittsburgh, Toronto
De Soto Chemical, Toronto
SCM Canada, Glidden Division, Toronto
Lawter Chemicals, Toronto
Mobil Paint, West Hill
Benjamin Moore, Toronto
Polyresins Limited, Toronto
Pratt and Lambert, Fort Erie
Reichhold Chemicals Limited, Toronto
Rohm and Haas, West Hill
Schenectady Chemicals, Toronto
Inmont, Scarfe Division, Brantford

British Bapco Paint, Victoria
Columbia Reichhold Chemicals Limited, Port Moody

Canadian Manufacturers of Polyester Resins, 1973

Quebec Reichhold Chemicals Limited, Ste-Thérèse-de-Blainville

Ontario Alma Paint and Varnish, London
Canadian General Electric, Toronto
Canadian Pittsburgh, Toronto
Hooker Chemical, Durez Division, Fort Erie
Fiberglass Canada, Elmira
SCM Canada, Glidden Division, Toronto
BASF, Cornwall
Reichhold Chemicals Limited, Toronto

British Fibreplast, New Westminster
Columbia Reichhold Chemicals Limited, Port Moody

Canadian Manufacturers of Polyester Fibres, 1973

Ontario Celanese Canada Limited, Millhaven
Du Pont of Canada Limited, Kingston

Classification of Plasticizers

Abietates

Methyl abietate
Hydrogenated methyl abietate

Adipates

di-(n-hexyl) adipate
dicapryl adipate
diisooctyl adipate
dinonyl adipate
di-(butoxyethyl) adipate
dicyclohexyl adipate

Azelates

di(2-ethylhexyl) 4-thioazelate
diisobutyl azelate

Citrates

tributyl citrate

Glycol and polyol esters

diethylene glycol dibenzoate
Dipropylene glycol dibenzoate
Glycerol triacetate
glycerol tripropionate
triethylene glycol diacetate
triethylene glycol dipropionate
triethylene glycol di-2-ethylbutyrate
triethylene glycol di-2-ethylhexoate
polyethylene glycol di-2-ethylhexoate

Glycolates

methyl phthalyl ethyl glycolate
ethyl phthalyl ethyl glycolate
butyl phthalyl butyl glycolate

Phosphates

triethyl phosphate
tributyl phosphate
tri-(butoxyethyl) phosphate
triphenyl phosphate
tricresyl phosphate
monophenyl di-xenyl phosphate
diphenyl mono-xenyl phosphate
di-(t-butylphenyl)mono-(t-butylcresyl)
phosphate

Phthalates

dimethyl phthalate (DMP)
diethyl phthalate (DEP)

dibutyl phthalate (DBP)
diamyl phthalate
dihexyl phthalate (DHP)
di-(methylisobutylcarbinyl) phthalate
butyl octyl phthalate (BOP)
butyl isohexyl phthalate (BIHP)
di-(n-octyl) phthalate (DOP)
diisooctyl phthalate (DIOP)
di-(2-ethylhexyl) phthalate (DEHP)
n-octyl-n-decyl phthalate
dicyclohexyl phthalate (DCHP)
butyl cyclohexyl phthalate (BCHP)
di-(methoxyethyl) phthalate
di-(ethoxyethyl) phthalate
di-(butoxyethyl) phthalate
methylcyclohexyl isobutyl phthalate
dibenzyl phthalate
diphenyl phthalate
butyl benzyl phthalate (BBP)
2-ethylhexyl benzyl phthalate
hexamethylene bis(2-ethylhexyl
phthalate)
diisodecyl-4,5-epoxytetrahydro-
phthalate

Sebacates

dimethyl sebacate
dibutyl sebacate
dioctyl sebacate
diisooctyl sebacate
di(2-ethylhexyl) isosebacate
dibutyl isosebacate
butyl benzyl sebacate
dibenzyl sebacate

Sulfonates and Sulfonamides

ethyl p-toluenesulfonate
o-cresyl p-toluenesulfonate
cyclohexyl p-toluenesulfonamide

Miscellaneous

tetrahydrofurfuryl oleate
chlorinated paraffin
benzyl benzoate
ethylacetanilide
triphenylguanidine
diphenyl ether
methyl pentachlorostearate
camphor
dibutyl tartrate



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REMINDER**

16 APR 2003

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