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DIGEST ON CHLORINATED PARAFFINS AND THE ENVIRONMENT

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ABSTRACT

This document is an overview of the current state of knowledge concerning chlorinated paraffins. Properties, use-patterns, environmental levels, and fate and effects are covered.

TABLE OF CONTENTS

LIST OF TABLES

CONCLUSIONS AND RECOMMENDATIONS

The main conclusions to be drawn from this review document on chlorinated paraffins can be summarized as follows:

- chlorinated paraffins are persistent chemicals and are thus capable of accumulating in the environment;
- in Canada, about one million kilograms of chlorinated paraffins are used per year;
- it is likely that chlorinated paraffins lost to the environment during their manufacture or use account for only a small fraction of the total consumption; a much larger fraction will enter into the environment as a constituent of plastics disposed of after service: mobilization of chlorinated paraffins from these plastics matrices into the open environment is likely to be a very slow process;
- chlorinated paraffins that become dispersed in the environment will tend to adsorb to soils and sediments, and this will result in reduced availability for uptake by biota;
- in toxicological studies, none of the results obtained suggest that significant biological effects would occur in organisms exposed to doses of chlorinated paraffins that are comparable to levels that have been detected in environmental samples.

On the basis of this review of the available information on chlorinated paraffins, there is yet no evidence that these substances should be of great concern in terms of adverse effects on the environment or on its biota (human health effects are not addressed in this document). Given that chlorinated paraffins are the object of an extensive testing program in the United States, it is suggested that any further assessment activities, as part of the Environmental Contaminants Program, be limited to the gathering of data on environmental levels in heavily industrialized areas and on trends in the amounts used domestically.

1 INTRODUCTION

The first official reference made to chlorinated paraffins under the Environmental Contaminants Act was in August 1980 with the publication of a Canada Gazette notice concerning a Canadian use-pattern survey of selected candidate chemicals (The Canada Gazette, 1980). On the basis of the information gathered through the survey and of published data about persistence, chlorinated paraffins were given the status of Category III chemicals in the 1982 List of Priority Chemicals (The Canada Gazette, 1982). This category includes those chemicals that are recognized as a potential threat to human health or the environment and those about which additional information is actively sought.

The present document provides an overview of the current state of knowledge drawn from the published literature concerning chlorinated paraffins. The following aspects, with particular reference to the Canadian situation, are addressed in this review: properties, use-patterns, environmental levels, and fate and effects. Human health effects of chlorinated paraffins are not addressed in this document. The main purpose of the review is to establish whether or not chlorinated paraffins should be considered an environmental concern at this point in time, and to make pertinent recommendations. More detailed information on chlorinated paraffins can be found in the various review articles that have been published (Zitko and Arsenault, 1974; Howard et al., 1975; Lindén and Svanberg, 1978; Svanberg and Lindén, 1979; Campbell and McConnell, 1980; Madeley and Birtley, 1980; Birtley et al., 1980).

2 IDENTIFICATION AND PHYSICOCHEMICAL PROPERTIES

In North America the appellation "chlorinated paraffins" designates mixtures of saturated chlorinated hydrocarbons obtained from the chlorination of petroleum wax fractions (Hardie, 1964). Chlorinated paraffins are identified collectively under the CAS number 63449-39-8; they consist of molecules that possess a linear skeleton of 10 to 30 carbon atoms and have chlorine contents that account for 40-70% of their weight. As illustrated by Table 1, commercial chlorinated paraffins are usually identified by a trade name followed by a number reflecting the chlorine percentage composition. There is quite an array of chlorinated paraffins offered in commerce, for each individual chlorinated paraffin usually corresponds to a mixture of isomers and congeners whose carbon skeletons belong to one of three main groups (in terms of chain length): C_{10-13}, C_{14-17} and C_{18-26}. The degree of chlorination is another factor that can be varied. In this context, it is more appropriate to refer to average molecular formula and molecular weight for most chlorinated paraffins. The general average formula is $C_xH_{2x-y+2}Cl_y$ and the average molecular weights range between 300 and 1100. Analyses of chlorinated paraffins have shown that, in the case of molecules with a high chlorine percentage, the chlorine atoms are bound predominantly to vicinal carbon atoms of the alkyl chain (Weintraub and Mottern, 1965). The maximum chlorine content of roughly 70%, achieved under the conditions used for the production of commercial chlorinated paraffins, corresponds to alkanes bearing one chlorine atom bound to each carbon atom within the chain.

Although the length of the carbon chain and the degree of chlorination of chlorinated paraffins affect their physical properties, these substances are generally either viscous liquids or waxy solids and are coloured, mostly in the yellow range. Chlorinated paraffins are denser than water, they are lipophilic and they have a very low vapour pressure and a low water solubility. Values of octanol/water partition coefficients (P_{oct}) have been calculated for a few chlorinated paraffins from reverse phase chromatography data. Ranges of values of log P_{oct} were reported and they cover the interval of 4.4 to 12.8 (Renberg et al., 1980).

Chlorinated paraffins are stable mixtures, but in aqueous conditions they can undergo slow hydrolysis or dehydrochlorination. When subjected to high temperatures they release HCl. This property is the basis of some of their main uses. Commercial chlorinated paraffins are often stabilized against decomposition by the addition of small quantities of substances that can act as acid acceptors.

TABLE 1 REPRESENTATIVE EXAMPLES OF CHLORINATED PARAFFINS(1)

Name of Product(2)		Chlorine Content (% by weight)	Carbon Skeleton	Average Molecular Formula	Specific Gravity(3)
Cereclor	42	42	C_{22-26}		1.16
	S45	45	C_{14-17}		1.16
	50LV	49	C_{10-13}		1.19
	70	70	C_{23}	$C_{23}H_{26}Cl_{22}$	1.63
	70L	70	C_{10-13}		1.55
Chlorowax	40	43	-	$C_{24}H_{43}Cl_{7}$	1.17
	50	48	-		1.23
	500C	59	-	$C_{12}H_{20}Cl_{6}$	1.35
	70	70	-	$C_{24}H_{28}Cl_{22}$	1.66
Witaclor	163	62-64	C_{10-13}		1.43 @ 20°C
	340	40-41	C_{14-17}		1.11-1.12 @ 20°C
	544	43-45	C_{18-26}		1.17-1.19 @ 20°C

(1) Information reproduced from Lindén and Svanberg (1978).

(2) Cereclor, Chlorowax and Witaclor are registered trademarks of Imperial Chemical Industries (ICI), Diamond Shamrock and Dynamit Nobel, respectively.

(3) Values given are for a temperature of 25°C, unless otherwise stated.

3 PRODUCTION AND USE-PATTERNS

Chlorinated paraffins are prepared industrially by the liquid phase chlorination of paraffinic feedstocks made up essentially of straight chain alkanes containing from 10 to 30 carbon atoms. The various feedstocks used differ only in that the carbon skeletons of their constituent alkanes fall in one of three ranges: C_{10-13}, C_{14-20} and C_{20-30}. The chlorination process is an exothermic radical reaction that is usually carried out in the presence of no catalyst other than ultraviolet light and at a temperature of 100°C, producing hydrogen chloride and the chlorinated paraffins. The reaction conditions are adjusted to achieve a given level of chlorination of the starting material; the usual limits being around 40% and 70%. Normally the chlorination does not require the use of a solvent except for the preparation of chlorinated paraffins that have a high chlorine content, as they tend to be very viscous.

The results of Zitko's (1974) reductive dechlorination experiments on preparations of various chlorinated paraffins demonstrate clearly the complexity of these products as well as the variability in composition in the case of comparable products (see Table 2).

In Canada, Canadian Industries Ltd. (CIL) Cornwall, Ontario, is the sole producer of chlorinated paraffins. The production there is limited to a few members of the Cereclor™ family of products. Based on data gathered through a Canadian use-patterns survey conducted in 1980, it seems that the consumption of chlorinated paraffins in Canada has been fairly stable at about one million kg/yr over the past few years. This level of consumption will at least be maintained in the future, if not slightly increased.

On a volume basis, most chlorinated paraffins are used as: secondary plasticizers in PVC and other materials; flame retardants in numerous products, such as rubbers, plastics and paints; or extreme pressure additives in lubricating and metal cutting oils. There is a multitude of applications of chlorinated paraffins which accounts for the remaining volume.

Uses of chlorinated paraffins as flame retardants and high pressure additives are derived from their ability to release HCl upon heating. The HCl released in one case interferes with the radical process occurring in a flame, while in the other, the HCL reacts with metal surfaces to produce metal chlorides which have good lubricant properties. Although the information is limited, it appears that short chain (C_{10-13}) chlorinated paraffins are used in Canada on a much smaller scale in comparison to the medium and long chain analogs.

TABLE 2 COMPOSITION OF PARAFFINS OBTAINED BY DECHLORINATION OF DIFFERENT CHLORINATED PARAFFINS(1)

Chlorinated Paraffins	C_{21}	C_{22}	C_{23}	C_{24}	C_{25}	C_{26}	C_{27}	C_{28}
			Percent Composition					
Chloroparaffin, 40%	4.5	10.0	15.7	19.3	18.5	15.3	9.8	6.7
Chlorafin 40	3.7	8.2	14.0	17.5	19.2	17.4	12.4	7.6
CP 40	3.9	9.1	14.9	19.2	19.8	18.0	15.1	-
Cereclor 42	3.6	8.8	14.7	18.6	19.5	17.1	11.5	6.0
Chloroparaffin, 50%	7.4	14.9	20.7	23.1	19.9	14.0	-	-

(1) Information reproduced from Zitko (1974).

4 ENVIRONMENTAL LEVELS

Considering the principal applications of chlorinated paraffins, unless they are destroyed by incineration, it is likely that these substances will enter the environment either at the time of manufacture or use, or as a result of the disposal of products containing them. Since chlorinated paraffins have a very low volatility and are not involved in dispersive uses, they are not expected to be present at any significant level in the atmosphere. Entry into the environment is more likely to come from direct emissions into the aquatic medium via industrial and sewage treatment plant effluents in areas where chlorinated paraffins are used. The aquatic medium should also play an important role for the movement and dispersion of chlorinated paraffins that are mobilized in the environment. It has been predicted that a major portion of the environmental input of chlorinated paraffins is likely to remain in the aquatic environment adsorbed to various surfaces (Madeley and Birtley, 1980).

Most attempts to determine environmental levels of chlorinated paraffins have been hampered by the lack of an adequate analytical method. In general, although the results published so far indicate that chlorinated paraffins can be extracted with good recovery from various matrices, the analytical methods employed have been found to be of limited application, lacking in sensitivity and selectivity, and often being lengthy and tedious. One approach for the analysis of chlorinated paraffins has centered on the determination of the total chlorine content by microcoulometric (Zitko, 1974; Lombardo, 1975) or neutron activation analysis (Svanberg et al., 1978; Bengtsson et al., 1979). These methods have not been found to be applicable to the analysis of chlorinated paraffins in most environmental samples because of a lack of sensitivity as well as possible interference by other chlorinated substances such as PCBs and chlorinated pesticides. Gas-liquid chromatography has never been used extensively for the determination of chlorinated paraffins because these substances tend to decompose when heated at temperatures which would be required to overcome their very low volatility. A thin layer chromatography method has been developed and used with some success for the analysis of chlorinated paraffins in environmental samples; however, the method can only differentiate C_{13-17} products from C_{20-30} and is limited to products with certain chlorine contents (Hollies et al., 1979). Preliminary reports of analyses based on negative ion chemical ionization mass spectrometry have been published recently and they show good promise (Gjøs and Gustavsen, 1982).

To this date, there has been no report concerning levels of chlorinated paraffins in the Canadian environment. The only published information in regard to environmental levels pertains to the situation in the U.K. and Japan. Campbell and McConnell (1980) have reported levels of chlorinated paraffins in various components of the aquatic environment - water, sediments and biota. The samples analysed were collected in areas remote from or close to industry. In general, the C_{20-30} products were detected less often and at lower levels than the C_{10-20} analogs. Many samples of marine water and underlying sediments did not reveal any detectable level of chlorinated paraffins. When detected, however, levels ranged between 0.5 and 4 ppb in water and up to 0.5 ppm in the sediments. In fresh or non-marine waters and associated sediments taken from water bodies receiving industrial effluents, chlorinated paraffins were detected at levels of 1-6 ppb and 1-10 ppm, respectively. The higher levels detected in sediments have been attributed to the rapid adsorption of chlorinated paraffins on solids, once they reached the aquatic environment. Chlorinated paraffins were detected in some samples of aquatic organisms and eggs of aquatic birds; however, the levels did not exceed 1 ppm in most cases, except for those samples obtained close to industrial effluents in which case the levels reached 6-12 ppm. Fragmentary information has been published on levels of chlorinated paraffins in the Japanese environment (Department of Environmental Health, 1981). These substances were not detected in any of the 51 water samples analysed while about half of the samples of associated sediments showed levels of 0.6 to 10 ppm.

5 ENVIRONMENTAL FATE AND EFFECTS

Based on the properties of chlorinated paraffins, it has been predicted that upon entering into the environment they will tend to become adsorbed to surfaces, making them less available for uptake by biota. Considering their chemical properties, chlorinated paraffins are expected to be fairly resistant to chemical degradation, but there is evidence that they can undergo at least partial degradation through photochemical and/or biological processes. Zitko (1977) has reported the disappearance of chlorinated paraffins added to sediments, this occurring more rapidly under anaerobic than under aerobic conditions. Studies carried out by Madeley (1980) on the microbial degradation of various chlorinated paraffins have established that degradation proceeds faster and to a larger extent if acclimatized microorganisms are used and when the chlorinated paraffins have a short carbon chain and a chlorination level not exceeding 50%.

The uptake of chlorinated paraffins by aquatic biota was reported initially by Zitko (1974) and Lombardo (1975), and later confirmed through more elaborate studies. Bengtsson's (1979, 1982) experiments showed that the uptake of chlorinated paraffins by bleaks (fish) (*Alburnus alburnus*) exposed to contaminated water or food occurs more readily in the case of products possessing a short carbon chain and a low level of chlorination. Upon termination of the exposure, depuration was observed. In feeding studies (Madeley and Birtley, 1980), where common mussels and rainbow trout were exposed to Cereclor 42 (a long chain chlorinated paraffin with 42% chlorination), the uptake of the product by both organisms was observed, although at a much lower level in the case of mussels. In both cases, a termination of exposure was accompanied by elimination of the contaminant, while evidence of some metabolism of the substance in trout was also observed. More evidence of the metabolism of chlorinated paraffins is provided by the results of Biessman's (1982) experiments on the distribution and metabolism of two synthetic polychlorinated alkanes fed to Japanese quail; the length of the carbon chain and/or the degree of chlorination of the test substances were found to affect the rate of their metabolism. In most of the uptake studies carried out with fish, behavioural changes in the exposed fish were reported and found to last as long as the exposure was maintained. Although the uptake of chlorinated paraffins has been observed in aquatic, avian and terrestrial (mammalian) organisms, there has been no report of bioaccumulation or biomagnification in any food chain.

To this date, there has been no data published linking environmental levels of chlorinated paraffins with biological effects. However, the results of a significant number of toxicological studies involving these substances have appeared in the literature, and most of this work has been carried out by groups in the U.K., Sweden and Norway. The various lethality data that have been reported indicate a low acute and subacute toxicity for various chlorinated paraffins. For instance, oral LD_{50} values exceeding 4 g/kg and in some cases 10 g/kg were reported for rats (Birtley et al., 1980) and values exceeding 1 g/kg and 24 g/kg for ducks and pheasants (Madeley and Birtley, 1980), respectively. Generally, whenever biological effects were observed in conjunction with exposure studies on mice (Lundberg, 1979) or rats (Nilsen and Toftgård, 1981; Nilsen, 1981; Ahotupa, 1982), the liver was found to be the prime target organ and high doses (g/kg) of chlorinated paraffins had been used. As well, in most studies, the short carbon chain chlorinated paraffins consistently elicited a stronger response than the long carbon chain analogs and the degree of chlorination of the paraffins was also suspected of affecting the response. Some chlorinated paraffins were tested for their mutagenic potential and they were found to be non-mutagenic (Birtley et al., 1980; Meijer et al., 1982). In exposure studies of bleaks to various chlorinated paraffins (Lindén, 1979), 96-h LC_{50} values exceeding 5 g/L and in some cases 10 g/L were established.

Additional data about effects of chlorinated paraffins will become available in future months as a result of a two level testing program currently underway in the United States under the sponsorship of "The Chlorinated Paraffins Consortium" (Federal Register, 1982).

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