Chlorinated Paraffins: Properties, Uses, and Pollution Potential

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ABSTRACT

The chemistry and applications of high molecular weight chlorinated paraffins (C_{10}-C_{30}, 20-70% chlorine) are reviewed and data on solvent partitioning, thin layer chromatography and biodegradation of chlorinated paraffins are presented. Chlorinated paraffins are not as stable as polychlorinated biphenyls and are not likely to contaminate the environment to the degree encountered with polychlorinated biphenyls. Improved analytical techniques for chlorinated paraffins and their degradation products are needed.

RÉSUMÉ

La chimie et les applications des paraffines chlorinées à poid moleculaire élevé (C_{10}-C_{30}, 20-70% chlorure) sont revueés et les doneés sur la partition des solvents, chromatographie à plaque mince et la biodégradation des paraffines chlorinées sont présenteés. Les paraffines chlorinées sont moins stables que les biphényls polychlorinés et tout probablement contamineront l'environment à un degré moin intense qu'on rencontre pour les biphényls polychlorinés. On a besoin des techniques analytiques améliorées pour les paraffines chlorinées et leurs produits de dégradation.

INTRODUCTION

The term chlorinated paraffins is in this report used for technical preparations based primarily on C_{10}-C_{30} paraffins and containing 20-70% chlorine. Some other aliphatic hydrocarbons may also be present since chlorinated paraffins are industrially prepared by chlorination of paraffinic fractions obtained during the refining of crude oil. The majority of chlorinated paraffin preparations contains C_{20}-C_{28} paraffins and is chlorinated to either 40 or 70% chlorine.

The production of chlorinated paraffins on an industrial scale started in the Thirties and in 1969 the annual production in the U.S.A. reached 28 x 10^6kg. This placed chlorinated paraffins on the third place after low molecular weight chlorinated hydrocarbons (carbon tetrachloride, chloroform, tetrachloroethylene, etc.) and PCB (polychlorinated biphenyls). Due to the recent restrictions on the use of PCB, the production of chlorinated paraffins may now exceed that of PCB. In addition to U.S.A., the other major producers of chlorinated paraffins are located in Great Britain and Germany. Chlorinated paraffins are used as plasticizers, fire retardants, fillers and antistatic agents in plastics, fire retardants and plasticizers in paints, antiwear additives in cutting oils, etc. Little is known about the environmental behaviour and fate of chlorinated paraffins. This report reviews literature dealing with the preparation, properties, analytical chemistry, toxicity and applications of chlorinated paraffins. Additional experimental data are presented in the Appendix.

On the basis of literature and experimental data conclusions are made about the possible environmental impact of chlorinated paraffins.

PREPARATION

Chlorinated paraffins are manufactured by liquid phase chlorination at 60-100°. The reaction may be carried out with or without a solvent. Carbon tetrachloride is the most frequently used solvent, but other low molecular weight chlorinated paraffins may also be used. The chlorination is a radical reaction and is catalyzed by UV light, but the use of radical initiators, such as azodiisobutyronitrile, was also reported. The reaction is exothermic and the reactor must be cooled. Both batch and continuous processes are used and in the latter the chlorination unit may consist of 3-4 cylindrical reactors, connected in series.

The rate of mass transfer between the gaseous chlorine phase and the liquid paraffin phase is important for the chlorination efficiency and several engineering studies of this

aspect of the chlorination are available (Ramage and Eckert 1973; Ding et al. 1974; Lechev 1971).

Different paraffin feedstocks, ranging from the kerosine-gas oil fraction of petroleum to n-paraffins are used, and the number of carbon atoms per molecule may vary from 10 to 30. The content of chlorine in the final product is usually 40, 50 or 70% on weight basis, but preparations with a different chlorine content are also available. As will be discussed later, the choice of feedstock affects the properties of chlorinated paraffins, particularly their thermal stability. Aromatic hydrocarbons in the feedstock would of course be converted into chlorinated aromatic hydrocarbons which may be quite toxic and persistent in the environment.

Chlorinated paraffins have been produced on an industrial scale since about 1930, numerous patents describing the processes are available in the literature, and only a few recent ones will be briefly mentioned. Henderson and Krol (1974) describe a liquid phase chlorination of C_8-C_{16} paraffins in the presence of 2-20% of a solvent, such as carbon tetrachloride, chloroform, ethylene chloride, methyl chloroform, trichloro or perchloro ethylene, yielding chlorinated paraffins with 10-75% chlorine. Khachaturova et al. (1971) chlorinated a low melting mixture of petroleum hydrocarbons, containing naphthenic and aromatic hydrocarbons with branched chains, to a chlorine content of 40%. Koelbel et al. (1972) used a C_{14}-C_{30} petroleum paraffin stock with a residual oil content below 0.1-0.5% and obtained a thermally stable chloroparaffin preparation. Krol and Henderson (1971) improved the properties of C_{20}-C_{25} chlorinated paraffins by adding a small amount of ferrocyanides during the chlorination. Losonczy et al. (1972) patented a unit for continuous chlorination of C_{12}-C_{35} paraffins. McConnel and Goodwin (1972) described a process for the preparation of chlorinated paraffins with 70% chlorine. The feedstock was a solution of C_{20}-C_{30} chlorinated paraffins (40% chlorine) in carbon tetrachloride, containing 0.5% of azodiisobutyronitrile. The chlorination was carried out by a mixture of chlorine and hydrogen chloride. Zagorova (1972) chlorinated a kerosine-gas oil fraction of petroleum in the presence of solid magnesium or cupric chloride and obtained a product containing 50-54% chlorine.

The process of preparation of chlorinated paraffins may affect their properties. According to Shumyagskaya and Kuleshova (1972) chlorinated paraffins prepared by a continuous process had a lower compatibility with polyvinyl chloride and a lower thermal stability than those prepared by a batch type process.

CHEMISTRY

During the radical chlorination of paraffins, less acidic hydrogen atoms are easier replaceable with chlorine and, consequently, tertiary carbon atoms are chlorinated faster than secondary, and these in turn are more reactive than primary carbons. At 300° in the gas phase the relative chlorination rates are 4.43:2.25:1, respectively (Bratolyubov 1961). For the same reason, electronegative chlorine atoms, present already in the molecule, deactivate hydrogens on neighboring carbon atoms by increasing their acidity. Some solvents may change these relations, but those used commonly in the manufacture of chlorinated paraffins have little effect. The excellent review by Bratolyubov (1961) should be consulted for further details.

The distribution of chlorines along the paraffinic chain is based on the above described reactivities, but is otherwise statistical and was calculated by Frensdorff and Ekiner (1967) and by Saito and Matsumura (1973). In the former paper a simplifying assumption was made that the chlorination does not affect the reactivities beyond the nearest neighbors. The model predicts the absence of CCl_2 groups which was confirmed experimentally from NMR spectra of chlorinated paraffins with less than 60% chlorine (Gusev et al. 1968) and of chlorinated polyethylene (Heintke and Keller 1971). It is very difficult, because of the complexity of chlorinated paraffin preparations, to elucidate experimentally other details of the distribution of chlorine atoms.

The distribution of paraffins according to the degree of chlorination was determined by Teubel et al. (1962) and by Koennecke and Hahn (1962). The separation of chlorinated paraffins according to the degree of chlorination was achieved in both cases by chromatography on silica, activated at 450-500°. Mixtures of petroleum ether and benzene were used for elution. Koennecke and Hahn separated mixtures of chloroparaffins resulting from the chlorination of hexakontane (C_{26}) into fractions containing the residual paraffin, mono-, di-, and polychlorohexakontane. The first three fractions were eluted with petroleum ether, the last fraction was eluted with benzene. Some of the results are presented in Table 1.

Table 1. Distribution of chlorinated hexakontanes at different degrees of chlorination (Koennecke and Hahn 1962).

Degree of chlorination (wt.% chlorine)	Hexakontane (%)	Chlorohexakontanes,%		
		mono-	di-	poly-
17.2	10.6	27.3	20.1	40.6
24.0	2.7	12.6	16.9	65.7
32.9	0.3	1.8	4.0	93.1
42.8	0.0	0.1	0.4	98.9
46.8	-	-	-	99.1

It can be seen from Table 1 that up to an overall chlorine content of 33% the product still contains some hexakontane and its mono- and dichloro derivatives, whereas at a chlorine content over 46% the product consists exclusively of polychlorohexakontanes. Teubel et al. (1962) carried out a more detailed separation and isolated also the tri-, tetra-, penta-, and hexachloro compounds. A C_{19} fraction, purified via urea adducts and thus containing practically pure straight chain paraffins was chlorinated in the laboratory to a chlorine content of 26.0% (2.64 chlorine atoms/mole). In addition, a commercial chlorinated paraffin preparation, based on a C_{20}-C_{30} fraction and containing 26.1% chlorine (4.3 chlorine atoms/mole) was fractionated and the results are summarized in Table 2.

Table 2. Distribution of chlorinated paraffins (Teubel et al. 1962).

Atoms of chlorine/mole	Preparation	
	C_{19} 26.0% chlorine (2.64 atoms/mole)	C_{20}-C_{30} 26.1% chlorine (4.3 atoms/mole)
	Content of fractions, vol. %	
0	4.4	1.1
1	17.8	3.7
2	27.8	11.0
3	28.9	14.2
4	11.2	24.1
5	7.7	25.2
6	-	12.2
More than 6	-	8.2

Roesner and Berthold (1965) fractionated a laboratory prepared C_{20}-C_{33} chlorinated paraffin with 15.85% chlorine on silica, activated at 325°, and noticed that some fractions undergo a partial dehydrochlorination, detectable by the appearance of a maximum at 970 cm^{-1} in the IR spectrum. The dehydrochlorination could be eliminated by deactivation of silica by the addition of 0.05% of diphenylamine, or by treating silica with 5% sodium hydroxide, washing and drying at 130° to a moisture content of 10%. Products with a chlorine content of up to 30% could be fractionated on the sodium hydroxide-treated silica. Paraffins containing up to 4 chlorine atoms were eluted with hexane and carbon tetrachloride was used to elute the higher chlorinated fractions. In addition, small amounts of colored, oily material were eluted with benzene and acetone. Fractionation of chlorinated paraffins obtained by chlorination of material containing 10% oil, yielded colored fractions, with color intensity increasing with the degree of chlorination. Oil-containing paraffins showed a tendency to form relatively higher proportions of higher chlorinated products at the same overall degree of chlorination than pure paraffins.

Washall (1969) described an analytical method for the determination of paraffins (C_{10}-C_{13}) and their mono-, di-, and trichloro derivatives by chromatography on silica. Fluorescent dyes were used as indicators of separation. Washall et al. (1970) patented a separation of monochloroparaffins according to the position of substitution and molecular weight by chromatography on silica. The adsorption decreased with increasing molecular weight and, at the same molecular weight, with substitution approaching the center of the molecule. Bauso (1971) separated paraffins and naphthenes from chloroparaffins by chromatography on alumina, using petroleum ether as the solvent. The alumina was activated at 100-110° for 1 h, and the method was suitable for chlorinated paraffins with more than 40% chlorine.

An industrial method for the separation of paraffins from chlorinated paraffins was patented by Fuhrmann et al. (1973). Paraffins were precipitated at low temperature from an acetone solution of the mixture.

The great variety of products with different degrees of chlorination is obvious from the above data. Each class of compounds with a given number of chlorine atoms in the molecule is likely to consist of a number of isomers with different location of chlorine atoms in the paraffin molecule. Little is known about these detailed structural features. Weintraub and Mottern (1965) described methods for the determination of labile and vicinal chlorine atoms. Labile chlorine atoms were determined by refluxing chlorinated paraffins with silver nitrate in an aqueous acetone solution. Vicinal chlorine atoms were determined by refluxing chlorinated paraffins with zinc dust in n-butanol. Results obtained on two chlorinated paraffin preparations are given in Table 3.

Table 3. Labile and vicinal chlorine atoms in chlorinated paraffin preparations (Weintraub and Mottern 1965).

Mol. weight	% chlorine	Fraction of chlorine atoms, %	
		vicinal	labile
851	57.9	57	15.8
1090	67.0	70	3.7

The stability of chlorine in chlorinated paraffins is inversely related to the ease of chlorination, mentioned earlier. Thus the stability decreases in the order primary Cl>secondary Cl>alicyclic Cl>benzylic Cl>allylic Cl>tertiary Cl. The majority of chlorine atoms in chlorinated paraffins is present as secondary chlorines, but tertiary chlorines may be present in isoparaffins, dehydrochlorination may lead to the formation of allylic chlorines, and benzylic chlorines may be present in naphthenes. Consequently, the proportion of labile chlorines in chlorinated paraffin preparations increases with the amount of hydrocarbons other than n-paraffins, present in the feedstock.

The loss of chlorine from chlorinated paraffins occurs in most cases by dehydrochlorination. Thermal decomposition of chlorinated paraffins via this process is an undesirable property in their applications. Appreciable dehydrochlorination starts above 200°C and the thermal stability of chlorinated paraffin preparations may somewhat vary depending on the amount of labile chlorines present. Isolated double bonds (IR absorption maximum at 970 cm^{-1}) are formed initially, followed later by the formation of conjugated double bonds (2-3 absorption maxima in the IR spectrum between 1600 and 1700 cm^{-1}, Rubin and Drabkin 1966). The dehydrochlorination is more pronounced in the presence of oxygen than under nitrogen (Kennedy 1970), and is also accelerated by hydrogen chloride, zinc, tin, and antimony chlorides (Mayer and Obereigner 1973), which indicates that it proceeds by an ionic mechanism.

Binding of the hydrochloric acid formed retards dehydrochlorination, and various stabilizers, based on this principle, are usually added to chlorinated paraffin preparations. Epoxides, such as alkanediol diglycidyl ethers (Krockenberger 1972) or organotin compounds (Viska et al. 1972), may be used, and the use of thymol (Hirashima and Miyazaki 1972a) and acetonitrile (Hirashima and Miyazaki 1972b) were also patented. The removal of labile chlorine atoms by treatment with an alkaline earth hydroxide also results in thermal stabilization of chlorinated paraffin preparations (Nishimura et al. 1972). Traces of iron may promote the decomposition, and complexing agents such as EDTA or NTA were patented as stabilizers (Compagnie Francaise de Raffinage 1972).

In comparison to dehydrochlorination, dechlorination of chlorinated paraffins was given little attention. Carrega et al. (1970) studied the nature of end groups in PVC by reduction with lithium aluminum hydride and linear C_{11}-C_{14}, chlorinated paraffins with 56% chlorine were some of the model compounds used to study the scope of this reaction. Secondary chlorines were quantitatively reduced after 6 days at 100° in tetrahydrofuran, but vinyl chlorines were not reducible. Another reducing agent, sodium bis(2-methoxyethoxy) aluminum hydride, suitable for reduction of halogen compounds was described by Capka and Chvalovsky (1969). Zitko (1974a) used this reagent in a confirmatory test for chlorinated paraffins. Preparations with up to 50% chlorine were dechlorinated and yielded the parent hydrocarbons and some byproducts containing double bonds and hydroxy groups. Chlorinated paraffins with 70% chlorine yielded only the unsaturated hydroxy compounds.

The behaviour of chlorinated propanes on silica-supported metals was studied by Anju et al. (1972). Both dechlorination and dehydrochlorination took place, the proportion of these two processes depending on the catalyst. The reaction was not studied with chlorinated paraffins.

Chlorinated paraffins are sometimes considered as intermediates for the introduction of other functional groups or for polymerization. Berlin and Bass (1965) studied the reaction of a chlorinated paraffin preparation, containing 45% chlorine, with quinoline and with sodium butoxide. The reaction with quinoline at 200° resulted in a partial dehydrochlorination and incorporation of some quinolinyl moieties into the molecule, the resulting product contained 8.4% chlorine, 2.6% nitrogen and had an iodine number of 238. The reaction with sodium butoxide yielded a product with 9.6% chlorine and an iodine number of 178, containing some butoxy groups, as evidenced by an IR maximum at 1085 cm^{-1}. Both products were epoxidized by perbenzoic acid (IR maxima at 885 and 1250 cm^{-1}) and could be hardened by crosslinking with maleic anhydride or polyethylenepolyamine. Cobalt oleate catalyzed hardening of the primary products. Kuliev et al. (1967) described the preparation of alcohols from chlorinated paraffins. Vasil'eva et al. (1973a) studied the reaction of chlorinated paraffins with somewhat different chlorine substitution pattern with sulfuric and nitric acids. Unsaturated ketones were the main reaction products. On the other hand, diethyl amine yielded N-diethyl compounds by replacing allylic chlorine atoms (Vasil'eva et al. 1973b). Wetroff et al. (1968) patented the preparation of chlorinated paraffins containing hydroxy, nitrile, or dialkylphosphoryl groups and claimed improved thermal and photochemical stability of the products.

DETERMINATION

Chlorinated paraffins do not have convenient physicochemical properties which could be used for their determination, and a determination of chlorine is the only method available for their quantitation. A number of methods for the determination of chlorine is available in the literature. All the methods measure chlorine in the form of hydrochloric acid, or chloride liberated from the sample either by combustion or by reduction with metallic sodium. The determination is usually carried out titrimetrically with silver nitrate, by halogen-selective electrodes, or micro-coulometrically.

The sodium reduction technique combined with the microcoulometric determination of chloride was originally developed as a screening method for chlorinated hydrocarbon pesticides (Phillips and DeBenedictis 1954; Koblitsky et al. 1962). The sensitivity of the method is approximately 5 µg/g lipid and could be further improved, but the method was never widely used for pesticides, mainly because the lack of specificity in comparison with gas chromatographic methods. Krijgsman et al. (1970) determined 0.1-10 µeq of chlorine by titration with silver nitrate using a silver-selective ion electrode. The sample was combusted in oxygen at 900-1000°C over palladium and the liberated hydro-halogenides were absorbed in 80% acetic acid containing 1% of each hydrogen peroxide and hydrazine. Problems of recovery of hydrogen chloride on combustion were discussed by Corliss et al. (1972).

Chloride-selective electrode was used by Hassan (1973). Samples were combusted in the usual manner and the method was tested on a number of organochlorine compounds. Volodina et al. (1973) used a glow discharge in an ammonia atmosphere to decompose the samples. Chloride was then determined argentometrically.

Chumachenko and Alekseeva (1971) determined chlorine in organic compounds by high temperature (1100-1150°) pyrolysis in the presence of saturated hydrocarbons. The generated hydrochloric acid was separated from dicyan (resulting from the pyrolysis of nitrogen compounds) by chromatography on an surfactant-coated sodium chloride column at 85°, and from hydrogen sulfide on either a tricresyl phosphate- or dioctyl phthalate-coated Chromosorb W, or surfactant-coated sodium chloride column. Hydrochloric acid was absorbed in a mercuric nitrate solution and quantitated conducto-metrically.

A commercial system, consisting of a combustion furnace and a microcoulometer is available commercially (Dohrmann microcoulo-metric system MCTS-20). Samples are combusted in oxygen-nitrogen mixtures and the products are swept into the microcoulometric cell, containing a solution of silver acetate in 70% acetic acid. The sensitivity of this system is 2 ng of chloride and the recoveries of chloride from chlorinated paraffins were 78% or better, provided the samples were injected into the furnace in solvent mixtures containing a non-volatile component such as diethylhexyl phthalate or Nujol (Zitko 1973a).

Koppe and Rautenberg (1970a,b) detected organochlorine compounds on thin layers of silica by the reaction with silver nitrate under a UV light. This is a well known reaction for the detection of chlorinated hydrocarbon pesticides and can also be used for chlorinated paraffins.

The determination of chlorine is obviously not a specific method for the quantitation of chlorinated paraffins. In addition, in some of the above methods, other halogens, sulfur and nitrogen compounds would interfere with the determination of chlorine. The samples may also contain other organochlorine compounds, either man-made or natural. More than 150 naturally occurring chlorine and 50 bromine compounds are known (Siuda and DeBernardis 1973). A separation of chlorinated paraffins from interfering and other organochlorine compounds is therefore required.

While the fractionation of chlorinated paraffins was studied in detail, their separation from compounds other than hydrocarbons received very little attention. Cachia et al. (1958) developed a procedure for the determination of plasticizers including chlorinated paraffins in mixed plasticizer formulations. The plasticizers were separated by column chromatography on silica. Chlorinated paraffins (degree of chlorination not stated) were eluted with carbon tetrachloride. Phthalates, other ester plasticizers, and phosphates were then eluted by 1.5-5% diisopropyl ether in carbon tetrachloride. Separated plasticizers were identified by infrared spectra and quantitated by weighing. The described method did not separate chlorinated paraffins from PCB (Aroclor 1242).

Zitko (1973a) investigated the behaviour of chlorinated paraffins in a cleanup procedure used for the preparation of extracts of biological samples for the determination of PCB and chlorinated hydrocarbon pesticides. The cleanup consisted of column chromatography on alumina and silica columns (Holden and Marsden 1969). On alumina columns a fraction of chlorinated paraffins (42 and 70% chlorine) was eluted with hexane and the remainder with 10% ethyl ether in hexane. However, when the extract applied to the column contained more than 40 mg lipid, which is often the case with biological samples, chlorinated paraffins were completely eluted with hexane. The elution of chlorinated paraffins from silica columns was achieved by 10% ethyl ether in hexane. This fraction normally contains chlorinated hydrocarbon pesticides such as p,p'-DDD, p,p'-DDT, dieldrin, and lindane. It should be noted that on silica columns chlorinated paraffins could be separated from chlorinated aromatics such as hexachlorobenzene, PCB, chlorinated naphthalenes, and from p,p'-DDE, which are eluted with hexane.

In contrast to other chlorinated hydrocarbons, the analysis of chlorinated paraffins by gas chromatography has not been described in the literature. Published data are limited to low molecular weight mono- and dichloroparaffins. Roganov et al. (1969) separated secondary C_5-C_9 chloroparaffins, and Jaworski (1971) used

gas chromatography for C_{10}-C_{13} monochloroparaffins. Dichloro butanes, pentanes, and hexanes were analyzed by Bayer et al. (1972), and Castello and D'Amato (1973a,b) correlated physical properties and gas chromatographic behaviour of C_3-C_8 monohalogenoparaffins, substituted in the position 1,2 or 3. In terms of the retention time, one chlorine atom was equivalent to 2.5 carbon atoms and the effect of increasing carbon chain length was most pronounced for compounds substituted in the 1 position.

Chlorinated paraffins would, under conventional gas chromatographic conditions, require very high column temperatures for elution, and decompose on the column. Extrapolating from the data of Castello and D'Amato, the equivalent carbon chain length of chlorinated paraffins with 40% chlorine would be 30-40, and 70-80 for preparations with 70% chlorine.

High pressure liquid chromatography may be a useful technique for the separation of chlorinated paraffins from other compounds and for the determination of chlorinated paraffins by a microcoulometric or electrolytic conductivity detector, but the technique has not been used as yet.

Roesner and Berthold (1965) described infrared spectra of C_{20}-C_{33} chlorinated paraffins and assigned the maxima at 615 and 665 cm^{-1} to C-Cl stretching, and those at 1270 and 1310 cm^{-1} to the first overtone of the former frequency. The maximum at 615 cm^{-1} was used for quantitation.

Mass spectra of chlorinated paraffins were studied by Valovoi and Polyakova (1970), and by Hutzinger and Safe (private communication 1973). Except for a few peaks at low masses, the spectra are of little diagnostic value.

TOXICITY

Only a few data are available on the toxicity of chlorinated paraffins. In view of the long history of their use, this may indicate a low toxicity, since no episodes of poisoning in workers involved in the production or application of chlorinated paraffins have been reported. In comparison, poisonings in workers handling polychlorinated biphenyls or chlorinated naphthalenes were reported relatively early in the industrial history of these compounds.

In toxicity tests reported by Dover Chemical Corporation, PAROIL 1042 (40-41% chlorine) and Chlorez 700 (70% chlorine) were not irritant to human skin on a 5-day contact and caused no irritation after a 2-day reapplication 3 weeks later. Rats given orally 10-50 g/kg Chlorex 700 survived a 2-week observation period. A mortality of 20% occurred on administration of 60 g/kg. Guniea pigs survived under similar conditions doses of up to 25 g/kg, and a 40% mortality was encountered at 30 g/kg (Dover Chemical Corporation 1972). Abasov (1970) studied the acute oral toxicity of a chlorinated paraffin preparation KhP-470 in mice and

rats. The original paper could not be obtained so that the chlorine content of this preparation and other experimental details are not available. According to the abstract, the minimum lethal dose in mice was 19 g/kg, LD50 and LD100 were 21.85 and 24.0 g/kg, respectively. In rats these values were 24.5, 26.1 and 28.0 g/kg. The chlorinated paraffin did not affect the skin, but caused conjunctivitis on contact with the mucous membrane of the eye. Resorptive effects were not observed and the chloroparaffin did not accumulate.

Fish did not accumulate chlorinated paraffins Cereclor 42 (42% chlorine) and Chlorez 700, when exposed to these compounds adsorbed on silica. For comparison, significant amounts of PCB (Aroclor 1254) were taken up under similar conditions. An uptake of these chlorinated paraffin preparations from food at levels of 10 and 100 µg/g was not detectable in a 181-day feeding experiment with juvenile Atlantic salmon (Zitko 1974b). However, mortality occurred among the dosed fish.

The few toxicity data, available in the literature, indicate that chlorinated paraffins have a very low acute toxicity and this is also reflected in the regulations, permitting the use of C_{10}-C_{17} preparations with 40-70% chlorine in food-packaging adhesives (Anon. 1969). The high molecular weight of chlorinated paraffins may make them more or less biologically unavailable. Even the gastrointestinal absorption of normal paraffins decreases considerably with increasing molecular weight. For example, the absorption of octadecane, eicosane, docosane, hexacosane, and octacosane in rats is 97, 91, 85, and 57%, respectively (Popovic et al. 1973). However, some breakdown products or chlorinated impurities present in chlorinated paraffin preparations may be more toxic. It is difficult to give chlorinated paraffins a clean bill of health on the basis of the available information and some additional research, particularly on chronic toxicity, is required.

Nothing is known about the behaviour of chlorinated paraffins in the environment. It may be expected that due to their low solubility in water, chlorinated paraffins will be adsorbed readily on suspended solids in the aquatic environment. The aliphatic carbon-chlorine bond is easier biodegradable than the aromatic one and it is likely that chlorinated paraffins are less persistent in the environment than, for example, polychlorinated biphenyls. However, this assumption has to be proven experimentally.

USES

The history of the early uses of chlorinated paraffins was summarized by Scheer (1944). A small amount of chlorinated paraffins was used during the World War I as a solvent for nasal and throat sprays. Large scale industrial production of chlorinated paraffins started in 1932, and in World War II these compounds were widely used for impregnation of textile materials.

More exotic uses, mentioned in this review include the application of chlorinated paraffins as chewing gum additives and components of terpene insecticides. A recent review of industrial applications of chlorinated paraffins was published by Shumyanskaya et al. (1972), but was not available when this report was in preparation.

Chlorinated paraffins are currently used mainly as plasticizers and fire retardants. Minor applications include the use of chlorinated paraffins as additives in lubricants and cutting oils, tanning compositions, abrasive products, adhesives, etc.

Chlorinated paraffins with 40-50% chlorine are used as plasticizers in polyvinyl chloride plastics where they partly replace the more expensive phthalates (Ball and Kolker 1969; Potnis 1969). Chlorinated paraffin – plasticized products have a good high temperature stability, which is usually important during the manufacture of the products, but may perform poorly at low temperature (Brighton 1971).

Polyvinyl chloride resin compositions may contain from 15 to 50% of chlorinated paraffin plasticizer (Izumi and Sakan 1972; Sakan and Izumi 1972a,b). Polyvinyl chloride pastes and fibers may also be plasticized by chlorinated paraffins (Iida et al. 1971; Fujii et al. 1972).

Chlorinated paraffins may also be added to polyvinyl chloride compositions to improve their fire resistance.

Burning of plastics is a complicated process, but there is a general agreement that radical reactions take place in the flame zone while heat feedback generates combustible volatile products by pyrolysis. Fire retardants may act either by inhibiting the radical reactions in the flame, by retarding the condensed phase pyrolysis reactions, or by slowing down the heat and mass transfer between the flame and the condensed phase (Warren 1971). Chlorine radicals are good inhibitors of radical reactions and there is little doubt that this is the reason for fire-retarding properties of organochlorine compounds including chlorinated paraffins. The fire retarding efficiency of organochlorine compounds is usually further improved by the addition of antimony trioxide. The mechanism of this interaction is less well understood but it is likely that the volatile antimony trichloride is involved.

The use of chlorinated paraffins together with antimony trioxide in polyvinyl chloride compositions was described (Bell et al. 1969). Antimony trioxide may in certain compositions be replaced by ammonium chloride (Tsukamoto and Masuda 1969) or by potassium polymetaphosphate (Koizumi et al. 1973).

In contrast to the type of chlorinated paraffins, used as plasticizers, chlorinated paraffins with 70% chlorine are mostly

used in the fire retardant applications.

Polyolefins (polyethylene, polypropylene) are frequently flameproofed by chlorinated paraffins (Hofmann 1971). Chlorinated paraffins with 70% chlorine are used, usually together with antimony trioxide, but other fire-retarding additives may also be present. The amount of chlorinated paraffins added is 2.6-7%. A few patented formulations are presented in Table 4.

Table 4. Composition of flameproofed polyolefins.

Reference	Polymer	Additive	%
Raley 1973	Polyethylene	Carbon black	3.3
		Chlorinated paraffin	8.0
		Red phosphorus	4.94
Raley 1972	Ethylene-vinyl acetate copolymer	Chlorinated paraffin	7.5
		Antimony trioxide	7.5
Rensmann et al. 1972	Polypropylene	Tin oxide	4
		Chlorinated paraffin	4
		Brominated diphenyl ether (70% bromine)	6
Gray and Brady 1973	Ethylene-propylene block copolymer	Antimony trioxide	6
		Chlorinated paraffin	3
		1,2-bis(3,4-dibromocyclohexyl)-1,2-dibromoethane	3

Organophosphorus compounds such as cresyl-2-bromoethyl methyl phosphonate may be used together with chlorinated paraffins instead of antimony trioxide in fire-retardant polyolefins (Hindersinn and Porter 1971).

A number of additional patents dealing with the fireproofing of polyolefins may be found in the literature (see for example Hartlein 1972; Kobayashi et al. 1973; Parausanu and Andrei 1973; Savel'ev et al. 1973; Shiozawa 1973).

Chlorinated paraffins with 50-80% chlorine are suitable fire retardants for plastic products based on polystyrene. The level added is usually 4-35%, antimony trioxide or organophosphorus compounds such as tritolyl phosphate are also added (Lindemann 1973).

Chlorinated paraffins are used as fire retardants in natural and synthetic rubbers (Fabris and Sommer 1973). Typical products requiring flameproofing are for example rug underlays,

foam backings for carpets, and conveyor belts. The concentration of chlorinated paraffins may be 1-4%. Other additives include antimony trioxide and tris-2,3-dibromopropylphosphate. A self-extinguishing acrylonitrile-styrene-butadiene copolymer, containing 1.5% of chlorinated paraffins, 9.4% of octabromobiphenyl, and 3.3% of antimony trioxide, was patented (Praetzel and Jenkner 1972). Carbon black-filled rubbers which are normally combustible, may be reformulated to yield non-burning products by adding mixtures of chlorinated paraffins and antimony trioxide (Trexler 1973).

Both 30-50% and 70% chlorine-containing chlorinated paraffins are used in flameproofing of acrylics and modacrylics. Chlorinated paraffins may be incorporated into the product during compounding, or the finished product may be impregnated by a solution containing emulsified chlorinated paraffins. In the latter case sorbitol monostearate or Tween are used as emulsifiers (Torrance and Shaw 1971). For examples of patented acrylic or modacrylic compositions containing chlorinated paraffins, see Schmidt et al. 1972, Takeya et al. 1973, and Yamauchi and Efuji 1972.

Somewhat less frequently, chlorinated paraffins were used to formulate fire retardant polyurethane products. Self-extinguishing polyurethane resins were prepared by adding a mixture of chlorinated paraffins and antimony trioxide to the polyol before polymerization (Suzuki et al. 1971), or in the case of elastomers, after the polymerization (Stephens et al. 1973). A mixture of chlorinated paraffins, silica sand, and ammonium phosphate was used to prepare a rigid polyurethane foam (Treadwell 1972).

A mixture of chlorinated paraffins with 70% chlorine and chlorobrominated paraffins containing 4% of chlorine and 59% of bromine was used to prepare flame-resistant polyesters based on phthalic acid (McAdam 1971). This is one of the few reports of the application of a chlorobrominated paraffin preparation.

According to a review by Sunshine (1973) on flame retardancy of phenolic and urea-formaldehyde resins, chlorinated paraffins are occasionally used in flame-retardant phenolic resins.

Fireproofing of cellulosic textiles was one of the major applications of chlorinated paraffins in the past, but the patent literature in this field is still active. Chlorinated paraffins may be added to viscose before spinning or may be used to treat the fiber or fabric. In the first case from 25 to 80%, based on cellulose, of chlorinated or chlorobrominated paraffins, sometimes in conjunction with an organophosphorus compound may be added (Isono et al. 1972; Mahomed 1973). The preparation of fire-resistant cellulose acetate fibers, containing up to 20% of chlorinated paraffins and up to 20% of tris(chlorobromopropyl) phosphate, both added before spinning, was patented (Hayashi and

Kitamura 1972). A process was patented by Ueno (1973) for the treatment of the finished fabric. A decorative rayon fabric was dipped into an 80% solution of phosphoric acid, containing 1% of copper chloride, and then treated with a 5% solution of a chlorinated paraffin with 60% chlorine, dissolved in xylene.

Fire-resistant acrylic textiles were prepared by spraying with an emulsion of chlorinated paraffins (50% chlorine) and zinc fluoroborate (Fidell 1971).

In paints, chlorinated paraffins are used as plasticizers, binders, and fire retardants. Several reviews on this subject are available in the literature (Allsebrook 1972; Eckhardt and Grimm 1971; Murray et al. 1954). The levels of chlorinated paraffins in paints are usually 5-15%, and other additives such as brominated organophosphates may be present to improve the fire retardancy.

Chlorinated paraffins are also used in marine paints, mainly to improve water resistance, and as binders. Marine paints are usually based on chlorinated rubber and, in the past, contained a chlorinated paraffin with 70% chlorine as a binder and a PCB preparation to improve water resistance. After the withdrawal of PCB from paint applications these were replaced by chlorinated paraffins with 40% chlorine, and marine paints may now contain approximately 7% of chlorinated paraffins with 70% chlorine and 4% of chlorinated paraffins with 40% chlorine (Bowerman 1971; Ford 1972). The detection of chlorinated paraffins in an antifouling paint was recently described (Zitko 1974a).

Clear lacquers for wood, hardboard and similar substrates may be based on polyurethanes and contain 10% or more chlorinated paraffins (Bhatnagar 1972). Additional examples of paint or coating formulations are presented in Table 5.

According to Zubchuk et al. (1971) chlorinated paraffins with 47% chlorine may be used as plasticizers in coatings based on chlorinated polyvinyl chloride or vinyl acetate-vinyl chloride copolymers and have better compatibility with the polymers than dibutyl phthalate, tricresyl phosphate, or PCB.

Chlorinated paraffins may also be present in some highway marking paints (Jnojewyj and Rheineck 1971).

Impregnation of wood by a solution of chlorinated paraffins in trichloroethylene was patented as a process for fireproofing of wood materials (Takiuchi and Date 1973). Vulpe et al. (1972) produced fire retardant wood panels from wood waste, impregnated with hexachlorobutadiene, compressed and treated with polyethylene, chlorinated paraffin (70% chlorine), antimony trioxide, and magnesium silicate. The content of chlorinated paraffin was 12%.

Fireproofed bituminous compositions, usable as antihumidity

Table 5. The compositions of paints and coatings.

Reference	Binder	Additive	%
Houghton et al. 1971	Ethylene-vinyl acetate copolymer		32
		Paraffin	33
		Chlorinated paraffin 50% chlorine	33
		Corrosion inhibitor	2
Peterson 1973	Polyvinyl acetate 50% emulsion		26
		Chlorinated paraffin	5
		Tris(2-chloroethyl) phosphate	2.5
		Calcium carbonate	7
		Titanium dioxide	3.5
		Antimony trioxide	6
		Asbestos	27
		Water	22
Hamada 1973	Acrylic emulsion		17.6
		Sodium silicate	70.6
		Chlorinated paraffin	5.9
		Cement	5.9
Bhatnagar and Preik 1973	Polyisocyanate		57.3
		Chlorinated paraffin 70% chlorine	42.7
Kehr et al. 1972	Polypropylene		24.0
		Barite	72.0
		Chlorinated paraffin 70% chlorine	2.9
		Antimony trioxide	0.5
		Antioxidant	0.2
		Dilauroylthiodipropionate	0.2
		Calcium stearate	0.2

barriers in wooden construction materials or roofing felt, may contain 5-35% of chlorinated paraffins, together with chlorinated aromatics or antimony trioxide (Regeaud and Trebillon 1972; Moore and Druce 1971). Chlorinated paraffins may be used as paper-sizing agents. A preparation containing 70% chlorine could completely replace the normally used rosin (Vizante et al. 1972), and a formulation containing chlorinated paraffins was patented as a paper-sizing agent (Chiba and Adachi 1970).

Chlorinated paraffins are present in some adhesives. For

example, an aluminum foil-kraft adhesive, containing 34% of chlorinated paraffins with 70% chlorine, was patented (Munawwar 1972). Patents describing adhesives for metal to rubber and rubber to rubber, and containing chlorinated paraffins have been recently obtained (Inoue 1971; Kimura and Mitsuo 1973a,b,c).

Miscellaneous applications of chlorinated paraffins include their use as antistatic agents on nylon (Ban et al. 1972), as components of tanning compositions (Komarek and Spahrkaes 1973), heat-protecting coatings (Prosser 1972), polysulfide compositions (Nakanishi and Kobayashi 1973), and abrasive coated products (Buell 1972). Chlorinated paraffins were also patented as soot inhibitors for fuel oil (Morita and Sugiyama 1973) and coating for tableted calcium hypochlorite, used in the treatment of sewage and swimming pool waters (Horvath and Parsons 1972). Chlorinated paraffin sulfonic acids may be used as emulsifiers for biocidal concentrates (Diery et al. 1972).

The majority of applications described thus far involved chlorinated paraffins as plasticizers, fire retardants, extenders, binders, etc. Chlorinated paraffins play a different role in lubricants and cutting oils. Here chlorinated paraffins form wear-resistant boundary films on metal surfaces (Sakurai et al. 1967; Kichkin et al. 1971), and chlorinated paraffins, usually with 35-40% chlorine, but at times also with 60% chlorine, in levels of 1-5%, were patented as lubricating oil additives (Vesely et al. 1971; Goettner 1973; Kuehl and Schwarz 1974; Amaroso and Griffith 1972; Okabe et al. 1973).

The levels of chlorinated paraffins in cutting oils are higher, and the concentration of chlorinated paraffins in a machine tool oil, patented by Sano and Yamaura (1972), was 20%. In general, the activity of organochlorine compounds as cutting oil additives is inversely related to the C-Cl bond strength (Mould et al. 1972).

CONCLUSIONS: POSSIBLE ENVIRONMENTAL EFFECTS OF CHLORINATED PARAFFINS.

Little experimental evidence is available to make conclusions about the environmental effects of chlorinated paraffins and the following discussion is based mostly on extrapolations, derived from the preceding review of the literature and from some additional experimental data presented in the Appendix.

Chlorinated paraffins may reach the environment mainly as components of plastics, discarded as solid waste, in waste oils, and by leaching from antifouling and marine paints. These routes are similar to some of the routes by which PCB enter the environment and it may be useful to compare the behaviour and properties of these two classes of compounds.

Chlorinated paraffins have in general higher molecular weight than PCB and, consequently, are less volatile. Data on the solubility of chlorinated paraffins in water are not available, but, considering the solubilities of the parent hydrocarbons (biphenyl

and C_{20}-C_{30} normal paraffins) and the solubility-decreasing effects of chlorine substitution, it is very likely that chlorinated paraffins are less soluble in water than PCB. Both higher molecular weight and lower solubility mean that chlorinated paraffins would be much less leachable from solid refuse than PCB and also much less taken up by living matter, which hasbeen demonstrated experimentally.

Chlorinated paraffins are much less thermally stable than PCB, and decompose to a large extent at relatively low temperatures (300-400°C), whereas a temperature of at least 800°C is required for the decomposition of PCB. As a result of the high decomposition temperature of PCB, these are volatilized well before the decomposition temperature is reached and the PCB emissions from incinerators may be quite significant unless special precautions (afterburners) are taken. On the other hand, chlorinated paraffins would be decomposed before significant volatilization could occur.

The main thermal decomposition product of chlorinated paraffins is hydrochloric acid. Little is known about the possible formation of low molecular weight chlorinated hydrocarbons and this should be investigated in view of the recently discovered carcinogenicity of vinyl chloride.

Chlorinated paraffins are also chemically less stable than PCB and as the data in the Appendix indicate, most of the chlorinated paraffins is decomposed in both aerobic and anaerobic sediments after a relatively short period of time. The decomposition products have not been identified, but it it likely that the main route is dehydrochlorination and possibly dechlorination. However, some chlorinated hydrocarbons such as chlorinated alicyclic hydrocarbons may be more persistent than chlorinated straight-chain paraffins. Chlorinated aromatic hydrocarbons, particularly those with attached paraffinic side chains, may be present as impurities in chlorinated paraffin preparations and these also may be more persistent.

A more detailed study of the environmental behaviour of chlorinated paraffins is hampered by the lack of sensitive analytical techniques. In general, the qualitative and quantitative characterization of chlorinated paraffins is much more difficult and less developed than that of PCB. For example, gas chromatography with electron capture detector or gas chromatography-mass spectrometry which are extremely sensitive tools for the investigation of PCB, are not applicable to chlorinated paraffins. Chlorinated paraffins are not stable enough for gas chromatography at temperatures above 200°C and little work has been carried out with the potentially applicable high pressure liquid chromatography.

In conclusion, there are more gaps than solid data in the knowledge of the environmental properties of chlorinated paraffins, but it is likely that at comparable production volumes the degree of environmental contamination by chlorinated paraffins will be less than that by PCB.

A P P E N D I X

This section contains results of recent studies on chlorinated paraffins in this laboratory. The studies were aimed primarily at improved or supplementary methods of clean-up of lipid-rich biological samples for the determination of chlorinated paraffins, but additional data on the complex chemical composition of chlorinated paraffin preparations, and preliminary data on their biodegradation were also obtained.

Solvent partitioning

Solvent partitioning is a well known technique for the confirmation of pesticide residues, and is also employed in some cleanup procedures (see for example McMahon and Sawyer 1973). Chlorinated paraffins with medium (Cereclor 42, 42% chlorine) and high (Chlorez 700, 70% chlorine) chlorine content were used, and the partitioning between hexane and acetonitrile, dimethyl formamide, and dimethyl sulfoxide was determined.

A solution of chlorinated paraffins in hexane (3 mℓ, concentration of chlorinated paraffins approximately 60 µg/mℓ) was agitated for 30 sec with 3 mℓ of the other solvent on a minishaker. After the separation of the phases, any volume changes were noted and the concentration of chlorinated paraffins was determined microcoulometrically as described previously (Zitko 1973a) in both phases. The dimethyl sulfoxide (DMSO) phase could not be analyzed directly due to the interference by sulfur, was diluted to 50v% with water, extracted with hexane, and the hexane phase was analyzed. It was noticed later that this extraction recovers only approximately 50% of chlorinated paraffins from the DMSO phase and the distribution coefficients were corrected accordingly. The data are summarized in Table 6. Asterisked values were obtained in preparative-scale partitionings, described later.

Table 6. Distribution coefficients ($C_{hex}/C_{solvent}$) of chlorinated paraffins.

Other solvent	Cereclor 42	Chlorez 700
Acetonitrile (MeCN)	0.35 0.62*	0.70 0.75*
Dimethyl formamide (DMF)	0.12	0.12
Dimethyl sulfoxide (DMSO)	0.81 0.82*	0.11 0.06*

*Preparative-scale partitioning

It can be seen from Table 6 that Chlorez 700 is extracted into DMSO to a larger extent than Cereclor 42. The order of extractability of these two chlorinated paraffin preparations into acetonitrile is reversed, and the extractability into DMF is the

same for both preparations. Consequently, DMF is the best solvent for the extraction of chlorinated paraffins from hexane when both types of chlorinated paraffins have to be recovered. Since at the same time only a small portion of lipids is extracted by DMF under these conditions (Zitko 1973b), the hexane-DMF partitioning could be used as a cleanup procedure in the determination of chlorinated paraffins in biological samples containing large amounts of lipids.

The recovery of Cereclor 42 and Chlorez 700 from hexane solutions (concentration of chlorinated paraffins approximately 60 µg/mℓ) by all the three above-mentioned solvents was determined and the data are presented in Table 7. Hexane solutions of chlorinated paraffins (initial volume 3 mℓ) were extracted by 3 mℓ portions of the solvents, and the amount of chlorinated paraffins, remaining in the hexane phase after each extraction, was determined.

Table 7. Recovery of chlorinated paraffins from hexane.

	Cumulative Recovery, %					
	Cereclor 42			Chlorez 700		
Solvent Extraction	MeCN	DMF	DMSO	MeCN	DMF	DMSO
1	46.9	70.7	33.3	31.6	69.9	88.0
2	66.2	86.3	43.3	59.3	93.1	93.3
3	85.3		59.1	71.4		95.1

The data in Table 7 confirm the conclusions made on the basis of the distribution coefficients (Table 6) and illustrate that chlorinated paraffins can be recovered from hexane by two extractions with DMF in a yield better than 85%. To achieve comparable recoveries, three extractions with acetonitrile and DMSO are required. Acetonitrile is a better solvent for Cereclor 42, and DMSO for Chlorez 700.

Chlorinated paraffins are mixtures of compounds and the distribution coefficients in Table 6 are not true physico-chemically defined distribution coefficients of pure compounds. In addition, as demonstrated below, solvent partitioning of chlorinated paraffins is not only a function of the degree of chlorination, but depends also on the hydrocarbon composition of the preparation. Not enough data are yet available to use solvent partitioning of chlorinated paraffins as a diagnostic tool and its main application is at the moment only in the sample cleanup.

Preparative fractionation by solvent partitioning

Cereclor 42, Chlorez 700, and Clorafin 40 were fractionated by solvent partitioning on a preparative scale. The last preparation was studied to compare its properties with those of Cereclor 42. Both are chlorinated to approximately equal chlorine content (42 and 40-43.5%, respectively), but Clorafin 40 yielded much less of straight chain paraffins on dechlorination than Cereclor 42 (Zitko 1974a).

For the preparative fractionation, chlorinated paraffins were dissolved in hexane (500-1000 mg of chlorinated paraffins in 50 mℓ hexane) and the solution was equilibrated with 50 mℓ of either acetonitrile or DMSO. The hexane phase was extracted with 2 x 50 mℓ of distilled water to remove any residual acetonitrile or DMSO, and hexane was evaporated in vacuum on a rotatory evaporator. The other solvent phase was diluted with 50 mℓ of distilled water and extracted with 50 mℓ of hexane. The hexane solution was worked up as above, and the aqueous phase was further extracted with 50 mℓ of diethyl ether. The ether phase was washed with water, dried over anhydrous sodium sulfate, and ether was evaporated in vacuum on a rotatory evaporator. The aqueous DMSO phase was further extracted with 2 x 50 mℓ chloroform, followed by an extraction with 2 x 50 mℓ ethyl acetate. The extracts were worked up as described for the ether extract.

The fractions were weighed and characterized by determining their chlorine content (microcoulometry), IR and in some cases UV spectra, and by dechlorination. Chlorine content of the fractions was also calculated from the IR spectra. The absorption at 1270 cm^{-1} (b) and at 2925 cm^{-1} (a) were used, and a correction for the baseline absorption was made at 1500 and 3100 cm^{-1}, respectively. The ratio a:b was a linear function of the degree of chlorination, as established on several chlorinated paraffin preparations. This method is not as accurate as the microcoulometric determination of chlorine, but is much faster and may serve as a quick check for the absence of interferences in the microcoulometric determination, providing simultaneously data on other functional groups.

The yield of fractions obtained from the three chlorinated paraffin preparations by the outlined procedure is given in Table 8. It can be seen that from two to five fractions were obtained, and DMSO may be a better fractionating solvent than acetonitrile. Clorafin 40 shows the most complex composition yielding significant amounts of material extractable from aqueous DMSO with chloroform and ethyl acetate. Differences between the two preparations, Cereclor 42 and Clorafin 40, occur in the DMSO fraction. Only 1.9% of Clorafin 40 is recovered from aqueous DMSO by hexane, as compared to 35.1% in the case of Cereclor 42, and almost twice as much Clorafin 40 than Cereclor 42 is recovered by ether. As already mentioned, Clorafin 40 contains two additional fractions.

Table 8. Yield of chlorinated paraffin fractions on partitioning, %.

Other solvent	Cereclor 42 MeCN	Cereclor 42 DMSO	Clorafin 40 DMSO	Chlorez 700 MeCN	Chlorez 700 DMSO
Hexane	36.6	43.3	40.7	38.6	5.8
Recovered from 50% aqueous other solvent with					
Hexane	58.7	35.1	1.9	48.7	47.8
Ether		20.1	36.3	30.1	50.2
Chloroform			16.6		
Ethyl acetate			0.7		
Total Recovery	95.3	98.5	96.2	90.3	103.8

The differences in chemical composition of the fractions must be largely due to the structure of the parent hydrocarbons. The chlorine content of the fractions generally increases with their polarity, i.e., the DMSO fractions contain more chlorine than the hexane fractions, and among the DMSO fractions the chlorine content increases from hexane to chloroform, but the differences are quite small (Table 9). On the other hand, as

Table 9. Chlorine content of chlorinated paraffin fractions.

Other solvent	Chlorine %									
	Cereclor 42				Clorafin 40		Chlorez 700			
	MeCN		DMSO		DMSO		MeCN		DMSO	
	Coul.	IR	Coul.	IR	Coul.	IR	Coul.	IR	Coul.	IR
Hexane	40.9	43.5	39.3	36.8	34.8	27.0	65.4	67.0	44.5	54.5
Recovered from 50% aqueous other solvent with										
Hexane	40.7	48.5	40.7	42.0			68.8	66.0	52.4	51.0
Ether	Fraction absent		44.6	46.0	41.6	49.5		64.0	65.9	66.0
Chloroform	Fractions absent				45.0	47.5	Fractions absent			

data in Table 10 indicate, the yield of straight chain paraffins, obtained by dechlorination from Cereclor 42 and Clorafin 40 is higher for the original hexane fractions than for the fractions recovered from the DMSO phase. The chlorine content affects somewhat the yield of straight chain paraffins since vicinally substituted hydrocarbons yield olefins and alcohols on dechlorination

Table 10. Yield of straight chain paraffins on dechlorination, %.

Other solvent	Cereclor 42 MeCN	Cereclor 42 DMSO	Clorafin 40 DMSO
Hexane	44.0	49.4	49.5
Recovered from 50% aqueous other solvent with			
Hexane	31.6	25.7	27.3
Ether	Fraction absent	28.8	19.8
Chloroform	Fractions absent		22.2
Ethyl acetate	"	"	

(Zitko 1974a), but the differences in chlorine content between the fractions are probably too small to have a significant effect on the yield of straight chain paraffins. It is likely that the differences in yield of straight chain paraffins are due to differences in the parent hydrocarbon structure, and the DMSO and acetonitrile fractions may contain a higher proportion of various chlorinated cycloparaffins as compared to primarily chlorinated paraffins in the original hexane fractions.

The composition of straight chain paraffins in fractions of Cereclor 42 and Clorafin 40, obtained by the DMSO fractionation, is summarized in Table 11.

Table 11. Composition of straight chain paraffins obtained on dechlorination of Cereclor 42 and Clorafin 40 fractions from DMSO fractionation, %.

Fraction		C_{21}	C_{22}	C_{23}	C_{24}	C_{25}	C_{26}	C_{27}	C_{28}
Hexane	Cereclor 42	4.0	12.7	20.4	23.0	18.9	12.6	5.3	3.3
	Clorafin 40	4.1	9.0	15.3	17.8	24.5	15.2	9.9	4.3
Recovered from 50% aqueous DMSO with									
Hexane	Cereclor 42	3.9	11.5	18.8	22.3	21.3	12.1	6.7	3.6
	Clorafin 40	4.5	10.3	17.1	19.4	18.9	14.8	9.9	5.1
Ether	Cereclor 42	3.6	10.6	18.1	21.8	20.1	13.3	8.3	4.6
	Clorafin 40	4.2	9.7	16.8	19.4	19.6	15.3	9.7	5.4
Chloroform	Clorafin 40	3.7	9.7	16.6	19.4	19.5	15.3	9.6	6.1
Ethyl acetate	Clorafin 40	2.1	5.5	12.5	17.7	21.0	19.4	12.8	9.0

In comparison to Cereclor 42, the original hexane fraction of Clorafin 40 yields on dechlorination somewhat higher proportions of the longer chain paraffins C_{25}-C_{28}, and a trend towards enrichment in the longer chain paraffins with increasing polarity of the fractions is noticeable for both preparations, but the changes are much less pronounced than those in the overall yield (Table 10).

The more polar fractions recovered from DMSO may also contain some chlorinated aromatic hydrocarbons. UV spectra of these fractions usually have a small shoulder at approximately 275 nm. These aromatic hydrocarbons may be of the alkylbenzene type with long chain alkyl groups. Absorbances of the DMSO fractions are summarized in Table 12. The values are quite low and indicate that the concentration of chlorinated aromatic hydrocarbons in the studied chlorinated paraffin preparations may not be very high.

Table 12. Absorbance/mg/mℓ in 1 cm cell at 275 nm.

	Cereclor 42	Clorafin 40	Chlorez 700
Recovered from 50% aqueous DMSO with			
Ether	0.021	0.050	0.072
Chloroform	Fraction absent	0.037	Fraction absent
Ethyl acetate	" "	0.076	" "

Thin layer chromatography

Alumina and silica layers were initially used to investigate TLC properties of Cereclor 42 and Chlorez 700. Less diffuse spots were consistently observed on silica than on alumina and the study was continued using only layers of silica. Of the solvents tested, 25% diethyl ether in hexane gave the best results, and the R_f values were 0.48 and 0.61 for Cereclor 42 and Chlorez 700, respectively. The results obtained with other solvents are qualitatively indicated in Table 13.

To visualize the spots cf chlorinated paraffins, the plates were sprayed by the conventional silver nitrate, 2-phenoxyethanol, acetone mixture (0.1 g silver nitrate in 1 mℓ water, diluted with 10 mℓ 2-phenoxyethanol and made to 200 mℓ with acetone), and exposed to UV light for approximately 30 min. Under these conditions the detection limit was 130 and 2 µg for Cereclor 42 and Chlorez 700, respectively. The sensitivity for Cereclor 42 was substantially improved (detection limit 8-10 µg) when the plate, following exposure to UV light, was sprayed with 1N sulfuric acid and heated at 100°C for approximately 30 min. A similar sensitive, but faster procedure consisted of spraying the plate with 1N silver nitrate and 0.1% fluoresceine in 50% aqueous ethanol and heating at 100°C for 10 min.

Table 13. Thin layer chromatography of chlorinated paraffins in different solvents.

Solvent	Result
Hexane	Low R_f
Hexane-ether-acetic acid (90:10:1)	Tailing
10% ether in hexane	Low R_f
50% ether in hexane	High R_f

In mixtures of chlorinated paraffins with cod liver oil or juvenile Atlantic salmon crude lipid extract, the former were clearly separated from the main lipid spot (triglycerides), but both chlorinated paraffin preparations had approximately the same R_f value. The detectable concentration of chlorinated paraffins in lipids was approximately 10 and 1% for Cereclor 42 and Chlorez 700, respectively. This is a very low sensitivity and lipids would have to be removed for example by solvent partitioning for the detection of lower concentrations of chlorinated paraffins.

Determination of chlorinated paraffins in spiked sediments

Samples of estuarine sediments were spiked with Cereclor 42 and Chlorez 700 to contain 463 and 277 µg/g on wet weight basis (moisture content of sediment 22.35%), respectively.

Chlorinated paraffins could not be extracted from the wet spiked sediment by either acetone or dimethyl formamide, but could be recovered by extracting air-dried sediment with hexane. The sediment (1 g) was placed in a 45 x 0.7 cm glass column and the sediment layer was percolated with hexane. A total effluent volume of 24 mℓ was required to elute 89.7% of the chlorinated paraffins, and a recovery of 99.2% was achieved by a total volume of 36 mℓ. To reduce the required solvent volume, 50% ether in hexane was used and 90% of chlorinated paraffins was extracted with 10 mℓ of this solvent. These experiments were carried out with sediment spiked only in the chromatographic column to contain 400 µg/g dry weight of Chlorez 700. Under similar conditions the average recovery of Cereclor 42 and Chlorez 700 from the preparatively spiked sediments was 75.6 and 63.2%, respectively. The sediment itself contained a background level of 5.65 µg/g on dry weight basis of microcoulometrically detectable material, and the recoveries of chlorinated paraffins were corrected accordingly. It is not known whether this background is due to some organochlorine compounds or to interference by sulfur or nitrogen compounds.

Biodegradation of chlorinated paraffins in spiked sediments

Sediment was charged to 500 mℓ Erlenmeyer flasks (25 g per flask), 300 mℓ of sea water, and 10 mℓ of a suspension of decomposing organic matter in sea water, collected near the Biological Station, were added and the flasks were kept at room temperature (19-22°C). A set of three flasks (control sediment, sediment containing 463 µg/g of Cereclor 42, and sediment containing 277 µg/g of Chlorez 700) was aerated, and the volume of sea water was kept constant by adding distilled water as required. Another set of three flasks was kept stoppered. Samples of sediment were taken periodically and analyzed as described above. Volatile microcoulometrically active interferences were encountered in the control, and particularly in the sediment spiked with Cereclor 42, and were largely removed by drying the sediment at 46°C in vacuum (27 psi) overnight. The results are presented in Table 14.

Table 14. Biodegradation of chlorinated paraffins in spiked sediments.

	Concentration in sediment, µg/g dry weight			
	Conditions			
	Aerobic		Anaerobic	
Time, (days)	Cereclor 42	Chlorez 700	Cereclor 42	Chlorez 700
0	596	357	596	357
10	257	76	80	41
21	147	128	194	33
28	377	72	98	50

After 30 days all of the remaining sediments were dried in vacuum, extracted as described and the extracts were examined by thin layer chromatography and IR spectrophotometry. Only traces of chlorinated paraffins were detectable. The extracts of both control and spiked sediments contained a number of spots visible on the plates under the UV light. A blue fluorescent spot, just below that of chlorinated paraffins was present only in the extracts of spiked sediments.

The data indicate that chlorinated paraffins are biodegraded in the sediments. The rate of biodegradation is higher under anaerobic than under aerobic conditions and Chlorez 700 may be degraded more than Cereclor 42. The analytical techniques must be further improved to eliminate interfering compounds and to measure also the more polar, chlorine containing transformation products. Under the present conditions, transformation products containing a few polar groups such as hydroxyl or carboxyl would not be extracted and the actual degradation (conversion of organically bound chlorine to chloride) may be much less than data in Table 14 indicate.

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