

RISK ASSESSMENT FOR CHLORINATED PARAFFINS:

EFFECTS ON FISH AND WILDLIFE

Health and Environmental Review Division

Environmental Effects Branch

Toxicology Section

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PRELIMINARY RISK ASSESSMENT ON CHLORINATED n-PARAFFINS

EXECUTIVE SUMMARY

The following risk assessment is limited to 58 percent chlorinated, short chain-length (C₁₀₋₁₃) n-paraffins. The chemical/physical, exposure, and toxicological data were obtained mostly from open literature and reports submitted by the Chlorinated Paraffins Consortium. Predicted residue levels for the three scenarios are from a contract report by Versar Inc. which used releases estimated by PEI Associates, Inc.. Summary of the important information in this risk assessment are as follows:

- o Production levels for 1983 was 67 million pounds to be used in a wide variety of products. Releases from manufacture, reformulation, use, and disposal are estimated to be 50 million pounds per year.
- o Chloroparaffins are highly persistent, have low water solubility, sorb readily to sediments and organic matter, have a high bioconcentration potential and some accumulation between trophic levels in the food web.
- o Monitoring data indicate that chloroparaffins are present at sampling sites near two manufacturing plants in the U.S. and are wide-spread contaminants in the United Kingdom. Monitoring data also support the predicted environmental exposure levels made by Versar Inc. In some cases, residue levels in sediments have even been underestimated.
- o Chloroparaffins have little acute toxicity to fish, birds, and mammals, but they are highly toxic (less than 1 mg/l) to crustacea and algae. Chronic toxicity in most test species occurred at levels less than 20 ug/l for a wide array of reproductive parameters. Statistically significant (P=0.05) chronic effects were reported at levels as low as 2.4 to 3.1 ug/l for four test species. All four studies failed to identify a no-observed-effect level (NOEL).
- o Three scenarios were developed which are representative of many sites:

large and small rivers; low, high and tidal flows; fresh and estuarine areas; and north/south gradients. Similar effects at other sites may be expected.

- o Environmental exposures predicted in water in the three scenarios either approach or exceed the lowest chronic effect level (0.5 ug/l) leaving little or no margin for safety. The lowest effect level cannot be identified due to an absence of NOEL's in those four test species.
- o Population reductions can be anticipated in all three scenarios among aquatic species, including fish, zooplankton, crustacea, molluscs, and insect larvae. Benthic species may be expected to be directly affected most by the higher chloroparaffin residues present in the sediments.
- o Population reductions and loss of some benthic species can be expected to adversely affect the availability of food to species higher on the food web. Oyster reductions can also affect water quality, reduce primary productivity, and cause losses in the two aquatic habitats. Oyster reefs and seagrass beds are important habitats to commercially-important shrimp, blue crabs, and sport fishes in the Galveston Bay area. Population reductions will also affect food availability for the numerous aquatic birds which feed on fish and benthic organisms.
- o Reproduction in aquatic birds in Sugar Creek area may also be adversely affected by chloroparaffins in their food, which exceed the NOEL. Residue levels in biota approach the NOEL for birds in the Galveston Bay area, which is an important nesting and/or feeding area for many aquatic birds, including at least four endangered avian species.
- o Under the scenarios presented, chloroparaffin releases do not pose a toxicological barrier to migratory species moving through the area.
- o The extent of the toxic effects on benthic species from residues in sediments and residues bioconcentrated in biota can not be evaluated

without additional testing. Additional tests are also necessary to determine the no-effect level for fish reproduction and chronic effects on mysid shrimp and daphnids.

II. INTRODUCTION

A. Manufacture, Use, and Disposal

Chlorinated n-paraffins are a class of chlorinated hydrocarbons having the general formula $C_xH_{(2x-y+2)}Cl_y$. They are obtained by chlorination of normal paraffins (at least 98 percent linear) and wax fractions. The bulk of the manufactured products are based on C_{12} , C_{15} , and C_{24} feedstocks and are 40 to 70 percent chlorine. While a chlorinated n-paraffin product may be classified as C_{12} , the actual composition is a range of chain lengths that average C_{12} . Chlorinated n-paraffins may be liquids or solids with a wide range in viscosity.

The capacity of U.S. manufacturers to produce chlorinated paraffins far surpasses the past, present, or expected future demands for the compounds. During 1983, with two of the eight potential producing plants closed, active U.S. capacity was 217 million pounds, while demand was only 67 million pounds (Long, 1984).

There are over 200 commercial products that consist of pure chlorinated n-paraffins. They are used as extreme-pressure additives in lubrication oils and metal cutting oils, secondary plasticizers and flame retardants in plastics, softeners and flame retardants in rubber, plasticizers in paint, adhesives, sealants, and chinks (Long, 1984). Some uses are as fire and water retardants in fabric finishing and a constituent in printing inks. The National Institute for Occupational Safety and Health (NIOSH) has identified over 500 commercial products that contain chlorinated n-paraffins as a constituent (PEI Associates, Inc., 1984).

B. Regulatory Status

Chlorinated n-paraffins (35-64 % chlorine) were recommended for testing by the Interagency Testing Committee (Federal Register, 1977) based on the following information:

- 1) 1972 production levels of 80 million pounds;
- 2) use of these materials in a wide variety of household and paint products, as well as adhesives and flame retardants;
- 3) estimated release rates of 50 million pounds per year;
- 4) degenerative changes in the liver and spleen of mice exposed to chloro-paraffins in a chronic study;
- 5) concerns for human health effects on carcinogenicity, mutagenicity, teratogenicity and other chronic effects in the absence of data; and
- 5) the need for a critical assessment of the biological significance of the occurrence of chlorinated n-paraffin residues in fish and the aquatic environment.

The Environmental Protection Agency announced in the Federal Register (1982) that the EPA would not at that time propose a section 4(a) rule to require health or environmental effects testing of the chlorinated n-paraffins. That decision was based on the acceptance of a voluntary testing proposal made by a consortium of international manufacturers of chloroparaffins. Environmental fate needs included studies on solubility of four categories and an aerobic and anaerobic biodegradation tests. Environmental toxicity tests proposed by the Consortium are tiered tests (Federal Register, 1982). Phase 1 tests are 30-60 day lethal and sublethal studies on mussels and rainbow trout for each of four specified test compounds (see Appendix A). Phase 2 tests on the most toxic compound identified in Phase 1 tests include chronic and bioconcentration tests on aquatic invertebrates and fish. The American members of the Consortium also agreed to conduct a avian reproduction study on mallard ducks. EPA received the environmental toxicity studies from the Consortium in 1984 and the avian reproduction study in 1985. All of the studies have been reviewed and evaluated for scientific soundness and effect levels. The conclusions from that data validation process have been integrated into an environmental hazard assessment

(Rabert, 1985).

Information on releases and predicted environmental concentrations for an environmental exposure assessment were prepared by contractors. PEI Associates, Inc. (1985) estimated the release levels from manufacture, reformulation, use, and disposal. Versar Inc. (1985) then used those release estimates to prepare a preliminary exposure assessment for three manufacturing and/or use sites selected by EPA. Those three sites are the Schuylkill River in Pennsylvania, Sugar Creek in Ohio, and the Houston Ship Channel/Galveston Bay, Texas.

III. ENVIRONMENTAL EXPOSURE ASSESSMENT

A. Environmental Fate

Little environmental fate data are available on chlorinated n-paraffins. The complex nature of the mixtures and the difficult analytical methods needed to separate and quantify residues have limited the development of information. Even much of the data that has been developed is of questionable quality. Chlorinated n-paraffins are generally considered to be persistent. Chemical degradation is generally considered insignificant. Chloroparaffins do not hydrolyze, oxidize, or otherwise react at significant rates under ambient temperatures and relatively neutral conditions.

Data on biodegradation reported by Hildebrecht (1972), Zitko and Arsenault (1974 and 1975), and the Consortium are all inconclusive. Some biodegradation of 58% chlorinated, short chain-length n-paraffins by microorganisms in a 5-day biochemical oxygen demand (BOD) test was reported by Hildebrecht, but how much has been strongly debated. Zitko and Arsenault (1974 and 1975) demonstrated that microbial degradation in estuarine sediments is faster under anaerobic conditions than aerobic, but poor recovery of sorbed residues (about 20%) demonstrated by Ramm (1978) and erratic data make quantification of degradation rates difficult. Aerobic and anaerobic studies submitted by the Consortium also indicate little evolution of gases (a measurement of biodegradation)

for the four tested mixtures. In general, it is thought that dechlorination preceeds degradation of the paraffin moiety, but no information has been reported on the identity, persistence, or toxicity of degradates or metabolites.

Water solubility data submitted by the Consortium indicate that the chloro-paraffin products have low solubility. Solubility ranges from 3.6 - 6.6 ug/l (ppb) for the long chain-length mixtures (C₂₀₋₃₀) to 95 - 470 ug/l for the short chain-length mixtures (C₁₀₋₁₃). Insolubility in water also appears to increase with increased chlorine content. The hydrophobic nature of the chloroparaffins increases the likelihood that residues would readily adsorb to organic matter and suspended particles in both the water column and the sediments at the water-sediment interface.

Campbell and McConnell (1980) found that sediments typically contained 1000- to 2000-fold higher residue levels than measured in the overlying water column. Ramm (1978) found that spiked residues were tightly bound to sediments, such that only about 10-20 percent were recovered by use of solvents. Ramm (1978) concluded from residue data on benthic biota (chironomid larvae and worms) that chloroparaffins residues are accumulated by some benthic organisms.

Chloroparaffins are generally considered to have a low vapor pressure (about $1-2 \times 10^{-6}$ mm Hg at 20°C). Low volatilization of chloroparaffins would indicate low dispersion capability, but residue concentrations in domestic fowl and sheep wool near manufacturing plants (Campbell and McConnell, 1980) suggest some airborne dispersion. The range of chloroparaffin vapor pressures are not too dissimilar from PCB values, which indicates some potential for atmospheric transport to distant environments.

Little data exist which demonstrate mobility and transport of chlorinated n-paraffin residues from sites of manufacturing, reprocessing, use, or disposal. Very low solubility in water and low vapor pressure would predict low mobility, but monitoring data in the United Kingdom indicate widespread levels of low

contamination in water, sediments, aquatic organisms, and even commercial fish foods. Analyses of test organisms and food items used in the chronic tests indicated low levels of short to intermediate chain length chloroparaffins in rainbow trout (1.3-2.0 ppm), mussels (1.2 ppm), algae (1.8-2.6 ppm), Artemia (0.51-0.57 ppm), and fish food pellets (0.78-2.14 ppm) (Harland et al., 1983). How residues have spread to contaminate so many of these areas is not yet understood.

B. Environmental Exposure Levels

The exposure estimates used in this risk assessment include: extensive monitoring data collected in the United Kingdom by Campbell and McConnell (1980); unpublished monitoring data submitted to EPA by Diamond Shamrock for two sites; and the environmental concentrations estimated by Versar Inc. at the three U.S. sites.

Campbell and McConnell (1980) reported chloroparaffin residue levels found in water and sediments from numerous sites throughout the United Kingdom. In general, residue levels show an increase in chlorinated n-paraffins as river in water as it passes from the uplands into industrialized areas, and a decrease when the river joins the sea. In the industrial areas, residue levels in the sediments were 0.1-15.0 ppm, while concentrations in overlying waters ranged from 0.5 to 6.0 ppb. Residues in marine and non-marine waters remote from industrialized areas were frequently found in either the sediments, water, or both. The highest residue levels found in a non-industrial area was in the Sound of Taransay on the remote isle of Harris in the northwestern part of Scotland. Residues in water were 2.0 to 4.0 ppb in water and less than the limit of detection in the sediment (< 0.05 ppm). Slightly lower concentrations were found at many remote areas throughout the country and Irish Sea. About half of the sediment samples from the North Sea contained residues ranging from 0.05 to 0.3 ppm. Residue levels in sediment were about 103- to 104-fold

higher than residues in the overlying waters. Short to intermediate chain-length chloroparaffins were usually found in sediments at higher concentrations than the longer chain-length mixtures.

Biological samples from 5 aquatic species (plaice and pouting - two benthic fish species, pike - a predatory fish, mussels, and grey seal) collected in the rivers and sea in the United Kingdom, indicated chloroparaffin residues in all species. Campbell and McConnell also reported residues in seabirds (0.5 to 1.2 ppm) and seabird eggs (< 0.05 to 2 ppm). Liver samples in all three avian species and over 66 percent of the eggs contained chloroparaffins. Analysis of human foodstuffs in the United Kingdom indicated chloroparaffin residues in dairy products (0.3 ppm), vegetable oils and derivatives (0.15 ppm), and fruits and vegetables (0.025 ppm). While no residues were found in tissues of Welsh sheep grazed remote from chloroparaffin production, sheep grazed in Weston Point near a manufacturing plant contained 0.2 ppm in liver, 0.05 ppm in mesenteric fat and kidney, and no residues found in the heart, lung, or perinephritic fat.

Monitoring data from the lower Grand River at a Diamond Shamrock manufacturing plant near Plainsville, Ohio indicated significant levels of chloroparaffin residues in water, sediments, benthic biota, and plant roots (Ramm, 1977). Residues found in water were about 2 (0.5-3) ppb with the highest concentrations located at the two sampling sites located just above and below the discharge point. Residues in the sediments were considerably higher at the two sampling sites downstream from the discharge point (both 3.1 to 12.6 ppm) than the site just above (0.8 ppm). No residues were detected in several species of fish, crayfish, clams, and tadpoles collected at one or more of the sites. Chironomids and/or worms contained residues at all four sites with the highest residues occurring at the site just downstream from the discharge point. Residues were also found in the roots of potamogeton at all four sites, but the residue levels did not correlate to sediment levels. The author

concluded that there was no evidence of residue uptake by many of these species, but that the strong evidence of accumulation existed in insect larvae and worm samples. The observation was made by the author that "The abundance of insect larvae, especially in the lower river, was relatively low compared to that of other similar rivers we have investigated."

A plausible interpretation of the irregular pattern of residues in water and sediments would be that the manufacturing plant is a major source of residues in the river. The high residue levels in the sediment indicate adsorption from discharges over a prolonged period, while the similarity in residue levels in the water above and below the discharge point was caused by either an occasional reverse flow up the river the short distance to the nearby upstream sampling site possibly due to low flow in the river and high discharge rates or storm surges from Lake Erie.

Samples taken at the Diamond Shamrock manufacturing site in Houston, Texas on the Patrick Bayou also indicated widespread chloroparaffin contamination of sediments and biota (Ramm, 1978). Only one out of five water samples contained residues (1.5 ppm) above the level of detection at 1 ppb. All 26 sediment samples contained residues which ranged from 0.15 to 10.0 ppm. Residues found in biota were 0.10 to 0.52 ppm in whole crabs, 0.2 to 0.42 ppm in whole killifish, and 0.15 ppm in vegetation. While recovery levels for spiked samples were moderate for biota samples (70 to 85 percent), recovery in sediments was quite low (10 to 20 percent). "While measured sediment levels ranged from 0.2 - 10.0 ppm, the low recoveries for spiked sediments would suggest that the actual sediment concentrations are more probably in the range 1 - 50 ppm."

Versar Inc. (1985) predicted environmental concentrations in water, sediments, and biota for various segments of three aquatic areas near select manufacturing, reformulating, and/or use sites identified by EPA. The three sites were the Schuylkill River near Conchohocken, Pennsylvania; Sugar Creek

near Dover, Ohio; and the Houston Ship Channel/Upper Galveston Bay, Texas. The release estimates used in the modelling effort by Versar Inc. were obtained from the report from PEI Associates, Inc. (1984). In the absence of release data on chloroparaffins, PEI Associates made simple assumptions and used flat percentage estimates based on production volumes and use estimates in manufacturing, reformulating, packaging, cleaning, and spills. No release estimates were made for disposal. Releases from cleaning were 10 percent, 1.0 percent from packaging, and 0.01 percent from spills (0.1 percent spilled and 90 percent pick up with absorbents).

The residue concentrations of Chlorowax 500-C and Chlorowax 70 predicted in water, sediment, and biota by Versar Inc. are summarized in Appendix A. Given the difference in physical/chemical properties of these two chlorinated n-paraffins, they assumed that these residue estimates would bracket environmental concentrations for all other chloroparaffin products. Residue estimates were made for both controlled and uncontrolled releases. Controlled releases assume removal of some residues during wastewater treatment. Residues in water and sediments were each computed as dissolved, sorbed, and total residues. The assumption that residue concentrations in interstitial water would be the same as residues in the water column provides a minimal value. One might expect residue levels in interstitial water to be higher than these estimated levels based on equilibrium kinetics with sediment concentrations. How much higher is not known.

C. Summary of Environmental Exposure

Chloroparaffins are relatively insoluble in water. Residues in water readily sorb to suspended solids and tightly bind to sediments. Although chloroparaffins appear to be relatively non-volatile, residues have been found at sites that indicate atmospheric transport. Environmental monitoring in the United Kingdom, Ohio, and Texas indicate widespread, low-level contamination

in water, sediments, aquatic plants and animals, human foodstuffs, and human tissues. Residues in the low parts per million were found to contaminate the test organisms and their food sources. While environmental residue levels were generally found highest near industrialized areas and diminish when the rivers reach the sea, monitoring samples indicate high residue levels in water and sediments in some remote areas. Residue levels in sediment are about 1000-fold higher than concentrations in overlying water. Recovery of residues from spiked samples indicate poor recovery (10 to 20 percent). Residues in benthic organisms and benthic fish were higher than residue levels in organisms found in the upper water column.

Modelling of residue releases, transport, and environmental distribution at three manufacturing/use sites indicate widespread, low-level contamination of large areas. Comparison of the predicted chloroparaffin residue levels at three sites (a river, creek, and estuary) indicated the highest environmental concentrations of chloroparaffin would occur in Sugar Creek, followed by the the Houston Ship Channel/Galveston Bay area, Texas. The lowest chloroparaffin residue levels occurred in the Schuylkill River, Pennsylvania are probably due to continuous flushing and a comparatively high mean stream flow rate in the river (2,940 cfs). Estimated residue levels in the sediments followed the same site order.

IV. ENVIRONMENTAL HAZARD ASSESSMENT

A. Phase I and II -- Consortium Testing

Information on environmental effects of chlorinated n-paraffins from both Consortium sponsored studies and available literature were reviewed in depth by EEB (Rabert, 1985). The results of the Consortium's Phase I and II testing are summarized in Appendix B. Phase I testing consisted of 60-day toxicity tests conducted on rainbow trout and bay mussels to identify the most toxic mixture of four selected chloroparaffin groupings. The groupings included the following

combinations of chlorination and chain length: intermediate chlorination (58%) and short chain-length (C_{10-13}); intermediate chlorination (52%) and intermediate chain-length (C_{14-19}); and one low (42%) and one high (70%) chlorinated, long chain-length (C_{20-30}) mixture. The results of the Phase I tests indicated that the 58% chlorinated short (C_{10-13}) chain-length n-paraffins were more toxic than the other three tested chloroparaffin formulations. However, the testing matrix fails, to indicate if it is the most toxic of all chlorinated paraffin combinations. The other mixtures are not without observed chronic effects. Unquantified abnormal behavior were reported for all formulations, especially upon mussel filtration (feeding) activity. The effects indicate that chronic effects are likely to exist for all formulations. Bioconcentration factors reported in the studies indicate that residues of all four formulations will accumulate in biological tissues. The extent of bioconcentration in Phase I tests could not be ascertained due to the insufficient sampling. Consequently, the BCF values reported for the tested formulations in Phase I tests must be considered both preliminary and minimal values.

Phase II chronic tests on 58% chlorinated, short chain-length n-paraffins indicate significant ($P = 0.05$) chronic adverse effects in the range of 2.4 to 20 ug/l for rainbow trout, sheepshead minnow embryo-larvae, mussels, daphnids, mysid shrimp, and the marine alga. These effects generally include chronic lethality, altered growth, and reduced reproduction. Shortcomings identified in most of the studies precluded identification of the lowest effect level concentration as well as the percent of the adverse effect. Analysis of the aquatic data indicate that adverse effects occurred at the lowest concentration tested (0.5 ug/l) and that testing at lower levels may produce additional significant adverse effects below 1 ug/l.

B. Toxicological Effects of 58% Chlorinated (C_{10-13}) n-Paraffins

In the absence of sufficient toxicological data on other chloroparaffin

formulations, all further discussion of the toxicological effects shall be limited to the 58% chlorinated, short chain-length (C₁₀₋₁₃) n-paraffins tested in Phase II and whatever other environmental data are available on that formulation.

1. Acute Toxicity

Acute effect levels of chloroparaffins on some aquatic species must be interpreted with caution for some test species. The water solubility of C₁₁ is only about 0.095 to 0.47 ppm, therefore all toxicity values greater than that concentration are suspect. For example, all 96-hour fish LC50 values are greater than 100 ppm (Table 1). Thus, the absence of acute toxicity in some species is simply a function of too short a time period for the small amount of chloroparaffin available in the water to penetrate the organism. Further evidence that uptake rates are slow in some species is indicated by mortality and toxicological effects reported in both the Phase I and Phase II tests on rainbow trout and mussels. Consequently, the greatest concerns for this kind of chemical are usually chronic effects.

Table 1 contains what limited data are available on the acute effects for short chain-length (C₁₀₋₁₃) chloroparaffin formulations. Of these test species, the most acutely sensitive species to chloroparaffins are daphnids and mysid shrimp which were both affected by the 58% chlorinated, short chain-length n-paraffins at similar concentrations (the 96-hour LC50 values are 18 ug/l and less than 14 ug/l, respectively). Other acutely sensitive aquatic invertebrate species included the copepod Nitocra spinipes with a LC50 value of 100 ug/l, followed by the relatively insensitive chironomid midge, greater than 162 ug/l.

The two species of algae tested reacted very differently from each other when acutely exposed to 58% chlorinated short chain-length n-paraffins. The marine algae Skeletonema costatum was the more sensitive species with a 96-hour EC50 of 42.3 (27.3 - 93.1) ug/l for growth (cell count). The effect of the test

material on growth rate of the marine algae was transient and by Day 10 no difference in growth rates were apparent when compared to controls. The highest reduction in growth rate occurred during the first two days and produced a 48 hr EC50 of 31.6 (20.7 - 57.6) ug/l. Toxicant effects on the freshwater green algae, Selenastrum capricornutum, differed from the marine algae in that its growth reduction was produced by higher test concentrations and the greatest effect occurred at the end of the 10-day study. The lowest reported EC50 for the green algae was 1,310 (880 - 4,060) ug/l at 10 days, which was derived by extrapolation from the 45 percent reduction found at the highest test level, 1,200 ug/l. Increasing differences in growth rates compared to controls in the latter days of the study indicate that longer exposure would probably produce lower effect levels for green algae. How much lower is unknown. Still another factor affecting the interpretation of these static test results is the loss of 50 to 80 percent of the residues from the water column. Analyses of water and algae samples on Day 10 indicated that the balance of the residues had sorbed to the algal cells. Increase in the number of algal cells during the growth phase of this test has had the effect of distributing some residues to the new cells and thereby reducing the concentration per cell. While the longer-term toxicity in these tests might indicate toxic effects in algal populations in flowing water, these toxicity values would underestimate toxicity for algal populations in standing waters which would accumulate additional discharges, such as lakes, ponds, and estuaries.

The rat LD50 value of greater than 21.5 g/kg indicates minimal acute toxicity to mammals. No acute oral LD50 or LC50 data were available on birds.

2. Chronic Toxicity

Chronic effects were reported in all Phase I and Phase II test species for most chlorinated paraffin formulations tested (Appendix B). Chronic effects on sheepshead minnow larvae, rainbow trout, mussels, daphnids, mysid shrimp, and

marine algae indicated high sensitivity to chloroparaffins. All of these species indicated effects at measured concentrations below 20 ug/l. Due to various testing inadequacies found in each study, it is impossible to determine the actual MATC level in most studies. Statistically significant ($P=0.05$) effects probably occur at concentrations even lower than those reported. No observable effect levels (NOEL) were not identified in the following studies: mysid shrimp (0.6 ug/l - adult mortality), sheepshead minnow (2.4 ug/l - body length), daphnids (2.7 ug/l - number of young and offspring/female), and rainbow trout (3.1 ug/l - mortality). Data indicate that chronic effects are more dependent on the duration of exposure than the test concentration for chloroparaffins. It would appear that simply prolonging the exposure will elicit toxic effects, irrespective of the test concentration. For example, 50 percent of the rainbow trout exposed to 3.1 ug/l for 168 days in a bioconcentration test began dying 64 days into the depuration period, while the same species exposed to a slightly higher test level (3.4 ug/l) for the same time period in a growth study displayed no significant growth effects. The absence of growth effects is unusual, since it is considered one of the most sensitive, toxicological endpoints.

Adverse effects reported for chloroparaffins include chronic mortality, significantly ($P = 0.05$) increased and/or reduced growth, abnormal behavior, reduced filtration (feeding) activity, reduced offspring per female, offspring survival, reduced insect hatchability, reduced insect emergence, and reduced cell growth in algae. The maximum acceptable toxicant concentration (MATC) levels for these effects were identified as < 2.4 ug/l for the sheepshead minnow, < 2.7 ug/l for daphnids, and < 3.2 ug/l for rainbow trout. At the lowest concentration tested (0.5 ug/l), mysid shrimp mortality was 30 and 40 percent compared to 10 to 30 percent in controls and 25 and 30 percent in the acetone controls. Whether and how much of the mysid mortality at the level of

0.5 ug/l was induced by the toxicant is difficult to tell. The erratic mortality data may have resulted from toxicity of other contaminants in the food source. The food source, Artemia, contained 0.6 ug/g chloroparaffins and 1.4 ug/g PCBs and organochlorine pesticides, mostly DDT.

Chronic effects reported in chloroparaffin studies submitted by the Consortium are listed in Table 2 in order of increasing measured test concentrations. Reproductive effects, other than growth, were not found in either of the two sheepshead minnow studies (2.4 to 54.8 ug/l and 36.2 to 620.5 ug/l). The two studies indicated a statistically significant ($P = 0.05$) increased growth at low test concentrations (2.4 - 71.0 ug/l) and significant decreased growth at the highest test level (620.5 ug/l). The pattern of growth enhancement and growth reduction were repeated at similar test levels in rainbow trout studies. The similarity between the growth curves for the two species drawn from data in two separate tests on each of these species adds confidence to the validity of this unusual dose-response curve. No significant differences in susceptibility were found between the various early life stages in rainbow trout or sheepshead minnow. Some differences in fish species sensitivity to chloroparaffins were indicated by the absence of or only slight sublethal effects reported in bluegill and channel catfish studies.

The absence of reproductive effects found in the sheepshead minnow study should be interpreted with caution. First, the exposure period for these two studies were only 28 and 32 days long and adverse effects, especially in fish, are slow to manifest themselves, probably due to slow residue uptake. Second, these abbreviated reproduction studies began by introducing embryos to the test concentrations, rather than exposing adults to the chemical for weeks prior to spawning. It is generally understood that embryos will not sorb residues from water readily, therefore, the developing embryos were not metabolically-exposed to toxicant concentrations to the same degree that it would if the female had

deposited residues in the yolk. Given the significant male mortality reported in the mysid chronic study, it would appear that the differential mortality between the sexes resulted when females deposited some of their body burden of chloroparaffin residues into their eggs, a situation known to occur in birds, fish, and other organisms with DDT.

Growth studies on common mussels exposed to the same short chain-length chloroparaffin indicated reduced growth rates at concentrations greater than 2.3 ug/l and less than 9.8 ug/l (53 percent reduction in both tissue and shell length). Toxicant levels reducing mussel growth are less than the concentrations reported to reduce growth in sheepshead minnow (greater than 280 ug/l and less than 620 ug/l) and in rainbow trout (greater than 350 ug/l and less than 1,070 ug/l).

Chronic effects on both crustaceans were found at similar concentrations. The number of daphnid offspring per female was reduced by 44 percent at 2.7 ug/l, the lowest test concentration. In mysid shrimp, a 33 percent reduction in offspring/female occurred at 7.3 ug/l. Chironomid midges, another aquatic invertebrate, was not as sensitive as the above two crustaceans, but adverse reproductive effects on midge larvae were reported for hatching, emergence, and eggs per mass at concentrations of either 78 or 121 ug/l.

Reproductive effects of 58% chlorinated, short chain-length n-paraffins on mallard ducks included statistically significant effects on eggshell thickness and percent viable embryos per egg set at 1000 ppm. The no observed effect level found in the avian reproductive test was 166 ppm.

3. Bioconcentration

Long-term bioconcentration studies on mussels and rainbow trout exposed to 58% chlorinated, short chain-length n-paraffins demonstrated high BCF levels in whole organisms ranging from 24,800 to 40,900 and 3,550 to 5,260, respectively. While the data for some organs were erratic and never stabilized, equilibrium

between water concentrations and whole organism residue levels were reached in about 45 to 80 days in mussels and about Day 90 in rainbow trout. Depuration half-life rates for the whole organisms were reported as 9.2 to 19.8 days in the mussel and 18.7 to 19.8 days in the rainbow trout. Of the tissues measured the highest residues occurred in the digestive organs of both species. BCF levels in the mussel's digestive gland/stomach ranged from 104,000 to 226,000. In rainbow trout, initial residue levels were highest in the liver and viscera with BCF values of 11,430 to 15,970, but the levels in the liver declined in the latter half of the study to 2,770 to 3,930. BCF values found in flesh or carcass were considerably lower (1,330 to 5,040). Declining residues in trout liver give the impression that the active elimination of the Cl^{14} residues may occur via metabolic breakdown of the chloroparaffins.

The bioconcentration study on mussels exposed to nominal concentrations of 2.35 and 10.1 $\mu\text{g/l}$ of 58% chlorinated short chain-length paraffins indicate BCF values of 40,900 and 24,800, respectively for the whole animal. Compared to the gonad and residual tissues, the digestive gland had the highest residue levels with BCF values of 104,000 and 226,400 at levels of 2.35 and 10.1 $\mu\text{g/l}$, respectively. Whole animal residues attained equilibrium at the highest exposure level at about Day 42, which also corresponded to the onset of low level mortality that persisted throughout the 91-day exposure and through Day 125 (34 days into the depuration period). As discussed earlier, mortality also occurred in the rainbow trout bioconcentration study during the depuration phase. However the trout deaths began after 64 days of elimination and ceased on Day 69, leaving only two surviving fish at the lowest test level. Based on a comparison of chloroparaffin uptake from water and food in the literature, the contamination of the fish food source at 0.85 to 2.2 ppm could not be considered responsible for the late mortality during the depuration phase. The BCF values reported in the two bioconcentration studies agree well with results

reported on the same test material in the 60-day toxicity tests submitted on the mussel and rainbow trout (Table 3). These levels, however, are considerably higher than chloroparaffin values previously reported in the literature. The BCF values are in close agreement with BCF levels reported for the same mussel species exposed to DDT (4,550-49,600) and PCB (7,200-26,600) by Geyer et al. (1982).

Data in the two 10-day algal studies indicate low level accumulation of chloroparaffin residues directly from the water (Table 4). The algal residue data in Table 4 indicate a general increase in the BCF value as the test concentration increases. The low BCF estimates (< 1 to 7.6) compared to BCF values for the same exposure period in mussels (10,099 - 11,915) and rainbow trout (1,500 - 1,654), indicate that the uptake is probably passive sorbtion of the hydrophobic residues to the cell wall rather than active transport.

Depuration rates for chloroparaffins in whole mussels and fish are slow. The half-life for depuration in the whole organisms were reported to be 9.2 to 19.8 days in the mussel and 18.7 to 19.8 days in the rainbow trout.

4. Biomagnification

Estimation of BCF values resulting from dietary uptake of chloroparaffins was made from residues analyses results reported for Phase II studies. The dietary BCF estimates for mussels and rainbow trout are 0.46 and 1.5, respectively. Algae fed to the mussels in the bioconcentration study contained 2.6 ug/g wet weight. The food pellets used during the latter part of the rainbow trout study contained 0.85 ug/g short-intermediate chloroparaffins. Residue contributions from these contaminated food to the whole body residues would account for 11.8 to 13 percent in rainbow trout and 0.5 to 1.2 percent in whole mussels.

While one might expect residues in food to compliment residue uptake from water or sediments, their overall contribution to whole body residues is rela-

tively small. Test data reported in the literature by other researchers also indicate that chloroparaffin uptake from water are greater than from food sources. The real significance of dietary uptake of chloroparaffin is a transport mechanism for exposure of organisms that would not bioconcentrate residues directly from water.

C. Summary of Environmental Effects

Acutely, the 58% chlorinated short chain-length (C_{10-12}) n-paraffins are very toxic (less than 1 ppm) to most aquatic invertebrates and algal species tested. Due to insolubility levels in water chloroparaffins have not been found to be acutely toxic to fish. Adverse chronic effects due to 58% chlorinated short chain-length (C_{10-12}) n-paraffins are evident, however, over the wide array of taxonomic groups tested. Chloroparaffins had a wide range of effects on test organisms including: behavior modification, mortality, growth, insect hatching and emergence, aquatic invertebrate reproduction, and eggshell thinning and embryo viability in birds.

The most sensitive test species had statistically significant ($P \leq 0.05$) effects occurring in a range of about 2.4 to 20 ug/l. These species include both species of fish (rainbow trout and sheepshead minnow), mussels, daphnids, mysid shrimp, and one of the two algal species tested. No observed effect levels (NOEL) were below test levels in at least four of those test species (mysid shrimp, daphnids, sheepshead minnow, and rainbow trout). Adverse effects are indicated below 2.4 ug/l for some of these test species, but neither the level of effect nor no effect level can be assessed due to inadequacies in each study. Subsequently, adverse effects for chloroparaffin are indicated below these test levels into the parts per hundred trillion range. In most cases, similar toxicity patterns and effects were found between similar species tested in both marine and freshwater.

The two major factors affecting the toxicity of chloroparaffins appear to

be exposure time and concentration. While the effect of test concentration is an obvious factor, the effect of exposure duration, to the extent necessary to show toxicity in the chlorinated paraffins, is highly unusual. As seen in the rainbow trout bioconcentration study, 168 days exposure and an additional 64 days of post-exposure depuration passed before significant mortality occurred. Very few chemicals demonstrate such prolonged development of chronic effects, and even fewer chemicals produce delayed mortality so late into the depuration phase. This delayed mortality is reminiscent of toxic effects caused by the mobilization of stored DDT/DDF residues during periods of stress, such as starvation, migration, reproduction, and residue concentration in developing embryos.

The two sheepshead minnow studies are not adequate to test the effects of chloroparaffins on fish reproduction. First, the 28- and 32-day studies were not of sufficient duration for chloroparaffin toxicity to manifest itself. Second, the exposure in the fish reproduction studies began with embryos, thereby, failing to measure the effect of residues stored in egg yolk.

In the rainbow trout and mussel bioconcentration studies, the BCF values were reported as 3,550 - 5,250 and 24,800 - 40,900, respectively. These levels of bioconcentration are of considerable concern, especially when combined with persistence, such as has been indicated for chloroparaffins. Distribution of chloroparaffin residues in tissues appear to be similar for species as diverse as mussels, fish, quail, and mice. Residue levels tend to be highest in those tissues with high cell turnover rates and/or a high metabolic capacity. BCF values in mussels are similar to levels reported for DDT and PCB. Depuration half-life rates for chloroparaffins in whole mussels and fish are slow (9.2 to 19.8 days and 18.7 to 19.8 days, respectively).

Biomagnification of chloroparaffin from food sources appears to contribute considerably less chloroparaffin to tissues than bioconcentration from water.

Biomagnification is of special concern because it provides a residue transport mechanism to organisms that would not otherwise bioconcentrate residues directly from water. Biomagnification is also significant, because residues usually accumulate in those species at the top of the food web, which have low reproductive capability.

In general, one might expect biomagnification effects to be greatest in species feeding on benthic organisms which are exposed to higher chloroparaffin concentrations in the sediments than are found in water column. Consequently, chloroparaffin residues entering the aquatic environment, might be expected to be found in most, if not all organisms, especially those species at the top of the food web.

Insufficient data are available, however, to correlate body residue levels with toxicological effects. While no data is currently available to correlate hazard from tissue residue levels, concern for biomagnification remains because residues may accumulate in species at higher trophic levels in the food web. Mortality data reported in mussel and rainbow trout bioconcentration studies indicate that adverse effects do not necessarily cease when exposure ends. Both species experienced mortality during the depuration phase. All, but two, rainbow trout died at the lowest concentration within one week, 64 days into the depuration period. Total rainbow trout mortality occurred during the same time period at the highest level.

Chloroparaffin data indicate little toxicity to terrestrial species. Acute oral LD50 data to rats of greater than 21.5 g/kg indicate low acute concerns for mammals. Chronic effects on mammals is currently under review and can not be addressed at this time. Chronic effects on avian reproduction included statistically significant ($P = 0.05$) effects on mallard eggshell thickness and percent viable embryos per egg set at 1000 ppm (NOEL 166 ppm).

The breadth of toxic effects in a wide variety of species from various

environments in combination of high BCF values, slow depuration, high toxicity, persistence, and the widespread distribution of these chloroparaffin residues in the environment indicate that chlorinated paraffins pose a potential threat to a wide variety of organisms, especially aquatic species. Because this wide array of adverse effects occur in aquatic species at such low concentrations, at or below analytical detection limits, all chloroparaffin releases to the environment are of considerable concern with respect to fish and wildlife safety.

V. ENVIRONMENTAL RISK ASSESSMENT

A. Scenarios

The three environmental risk scenarios discussed below are based on the toxicological effects data identified in laboratory studies, some limited field monitoring data at chloroparaffin manufacturing sites, and environmental residue concentrations predicted by Versar Inc. for three manufacturing/use sites selected by EPA to represent a variety of exposure parameters. The three sites include a large river, a small river/creek, and an estuary. A summary of the predicted environmental concentrations (PEC) in water, sediments, and biota at one or more locations at each of these sites are listed in Appendix A.

Versar Inc. predicted environmental concentrations for both Chlorowax 500-C (C₁₀₋₁₂) and Chlorowax 70 (C₂₀₋₃₀) for both controlled and uncontrolled releases. No assessment of Chlorowax 70 can be made at this time, because the environmental effects data needed to make a risk assessment are only available for the shorter chain length compounds. Therefore, the evaluation of adverse environmental effects on fish and wildlife will be limited to anticipated effects from the 58% chlorinated short chain-length (C₁₀₋₁₂) n-paraffins.

This risk assessment is largely a comparison of predicted environmental concentrations in Appendix A and the toxicological effects listed in Table 2.

Chronic exposures are assumed at the predicted concentrations from frequent or

continuous releases. It also assumed that interstitial water concentrations are higher than water column concentrations, that residues sorbed to sediments are bioavailable, and that dissolved and total residues in water are at least partially, if not, completely available as exposure levels to organisms. Toxicological effects on the surrogate test species are extrapolated to local flora and fauna species and limited conclusions are made on the effect of species interactions. Residue levels in various organisms are estimated from data in Tables 3 and 4, using BCF values for the closest test concentration. Interpretation of residue levels in whole animals is limited considerably, because data correlating body residue levels to mortality and other effects are missing.

1. Schuylkill River, Pennsylvania

The predicted chloroparaffin residue levels in the Schuylkill River are presented in Table 5 for water, sediment and various trophic levels of biota. While the predicted water concentrations of 0.26 and 0.5 ug/l are too low to produce any acute toxicity according to available data, these water concentrations may be expected to cause significant adverse chronic effects in some of the more sensitive aquatic invertebrates and fish. The lowest chloroparaffin test concentration (0.6 ug/l) produced 30 and 40 percent mortality in mysid shrimp. How much of that mortality is due to chloroparaffin toxicity is hard to distinguish from the 10 to 30 percent mortality seen in controls and the 25 to 30 percent mortality in the acetone controls. The test results from other species (rainbow trout, sheepshead minnow, and daphnids) do not preclude adverse effects at 0.5 ug/l, and possibly 0.26 ug/l. No observable effect levels were below the lowest test levels for each of these four species. Larval growth (length) in sheepshead minnow was significantly affected at 2.4 ug/l. The number of daphnid young were reduced 43.6 percent at 2.7 ug/l. And at 3.1 ppb rainbow trout mortality was 50 percent.

Adverse effects on mussels at 2.3 ug/l included a 7.7 percent reduction the tissue growth rate which was not considered statistically significant ($P = 0.05$) and mortality slightly higher than controls (7% versus 5%). The effects of chloroparaffin residues in sediments at 440 ppb on the sensitive life stages such as reproduction and larval survival when setting on contaminated sediments have not been studied and are unknown for mussels, clams, and other benthic organisms. This residue level is considerably higher than the 10 ug/l concentration causing 33 percent mortality in the mussel BCF study and the 9.3 ug/l causing more than 50 percent growth reduction in the shell and tissue weight. A complete life-cycle test on fish with longer exposures, so that residues are present in the egg yolk, is also likely to cause significant adverse effects at lower test concentrations in water. However, additional testing to identify no effect levels or MATCs may present a problem in measuring exposure concentrations, because the limit of detection for chloroparaffins is about 1 ug/l.

Table 5 lists the predicted chloroparaffin residue levels in aquatic organisms from the Schuylkill River. Bioconcentration and biomagnification of chloroparaffin residues from water-only exposure would range from 0.03 ug/g in water column species to 30.7 ug/g in predators upon benthic species. Maximum residue levels in biota predicted by Versar Inc. was similar (33 ug/g). These residue levels are considerably less than the 166 ppm no effect level seen in the mallard reproduction study. Consequently, no direct effects on avian reproduction are anticipated from chloroparaffin residues released at this site. Population reductions may affect the availability of food for aquatic birds, especially wading birds which feed on benthic species.

Based upon the BCF value of 36,000X for rainbow trout, the chloroparaffin levels that bioconcentrated directly from the water in planktonic and nektonic species, would range from 0.94 - 1.8 ug/g. These species would include mostly planktonic unicellular and small colonial algae and other non-swimming organ-

isms, and nektonic species like daphnids and rotifers and filter-feeding fishes such as shiners, alewife, shad, and herring. Biomagnification of residues in nektonic primary carnivores, such as bass and possibly brown trout, would contain residues ranging from 1.4 to 2.7 ug/g (based on a 1.5-fold-accumulation factor derived from residues found in the rainbow trout controls in the BCF study). These residue levels of 1.8 ug/g are, in fact, similar to the chloroparaffin contamination levels present in the food fed rainbow trout in the BCF study.

Bioconcentration of chloroparaffin in benthic organisms, such as aquatic insect larvae of chironomid midges, mayflies, and stoneflies, clams, worms, and other benthic invertebrate filter feeders and detritus feeders, are estimated to be between 10.6 and 20.5 ug/g (based on a BCF value of 40,900X for mussels). Benthic carnivores, such as sunfishes, catfish, bullheads, goldfish, carp, minnows, and suckers, feeding on these benthic species would be expected to accumulate residue levels of 16.0 to 30.7 ug/g.

Monitoring data from a manufacturing site on the Grand River in Ohio, indicated some possibly adverse effects on aquatic insect larvae at similar chloroparaffin concentrations measured in the water at Site I downstream from the release point (Ramm, 1977). Possible adverse effects were indicated by the authors in their observation that, "The abundance of insect larvae, especially in the lower river, was relatively low compared to that in other similar rivers we have investigated." Verification of this reduction due to chloroparaffin levels is not possible since no sediment toxicity data are available from which chronic toxicity to benthic organisms can be correlated to chloroparaffin residue levels in the sediments. Measured residue levels in sediments (3.1 - 12.6 ppm) and benthic chironomid larvae and worms (7.29 ppm) were about 10-fold higher than predicted for that water concentration in Table 5. Barely detectable levels of chloroparaffins found in some fish tissues may simply indicate

that the sampled fish are recent immigrants and not long-term residents. The absence of measurable residues in fish samples may have been due to either chronic toxicity and/or reduction in food availability reported as reduced larval insect populations.

Results from the available chronic studies are too erratic to make any predictions on the interactions between species and between trophic levels. New chronic tests would be needed for daphnia, mysids, and a complete life cycle study on fish, in order to quantify the adverse effects of chloroparaffin residues at the exposure levels predicted for these uncontrolled releases. No adverse effects are anticipated on birds or avian reproduction from predicted residues in biota at 33 ug/g.

Predicted residue levels from controlled releases (bottom of Table 5) in the Schuylkill River are lower than any levels which might be expected to cause adverse chronic effects.

Predicted chloroparaffin residue levels in the Schuylkill River from uncontrolled releases are sufficiently low that no acute toxicity effects are anticipated on any aquatic species and these concentrations would not form a toxic barrier to migration of species through the area. Predicted residue levels in the water approach the lower end of test levels producing adverse chronic effects in several test species, therefore adverse effects might be expected in sensitive aquatic species. Monitoring data from the Grand River with chloroparaffin concentrations in sediments similar to predicted levels in the Schuylkill River indicated reduced larval insect populations. Since laboratory tests indicate that the insect larvae are not the most sensitive species to chloroparaffins, population reductions may be anticipated on other benthic organisms. Population reductions in these insect larvae and other important benthic organisms might be expected to affect the availability of food for many aquatic species occupying higher trophic levels, including important sport

fish species, ducks, and wading birds such as herons.

2. Sugar Creek, Ohio

Chloroparaffin residue levels in Sugar Creek, Ohio exceeded adverse effect levels in the aquatic segments of the creek both above and below the confluence with the Tuscarawas River. The mean stream flow rates in the two segments of the creek were 330 cfs in the first segment and 1740 cfs in the second segment below the confluence. The predicted water concentrations of 0.4 to 4.1 ug/l are too low to produce any acute toxicity according to available data and as such would not be expected to act as a toxic barrier to movement of aquatic organisms through the contaminated segments.

Chronic effects, however, would be expected in some of the more sensitive aquatic invertebrates and fish from these residue concentrations in water in both segments of the river. Below the confluence with the Tuscarawas River the residue levels are similar to estimated concentrations in the Schuylkill River in Pennsylvania. Since the fauna would be similar in the two areas, chronic effects similar to those predicted for the Schuylkill River would be expected.

Since estimated chloroparaffin residues in water (4.1 ug/l) in the segment above the confluence are clearly greater than measured test concentrations causing chronic effects in several test species, adverse chronic effects would be expected on aquatic organisms. The reported adverse effects below 4.1 ug/l include mysid shrimp mortality and a 20.8 percent reduction in the number of mysid young, 43.6 percent reduction in young daphnids and young daphnids per female, 50 percent mortality in rainbow trout, and increased growth in both rainbow trout and sheepshead minnow. The 4.1 ug/l estimate also correlates well with the 3 ppm measured concentration at Site II, the discharge point from a manufacturing site on the Grand River in Ohio. Adverse effects noted during the sampling period included reduced larval insect populations, in fact, the

only aquatic invertebrates sampled were a crayfish (normally a relatively insensitive species) and chironomids. Organisms in the other sampling sites variously also included clams, snails, tadpoles, and worms.

Table 6 lists the estimated chloroparaffin residue levels in aquatic organisms from Sugar Creek. Bioconcentration and biomagnification of chloroparaffin residues in the upper segment from water-only exposure would range from 7.56 - 14.8 ug/g in water column species to 128.8 - 251.5 ug/g in carnivores upon benthic species. Maximum residue level in biota predicted by Versar Inc. was similar (274 ug/g). These residue levels are slightly higher than the 166 ppm no effect level seen in the mallard reproduction study, but considerably less than the chronic level of 1000 ppm causing eggshell thinning and embryo viability in mallard ducks. Consequently, adverse chronic effects on avian reproduction might be possible from chloroparaffin residues released at this site for birds feeding on predators upon benthic organisms and, possibly but not likely, for birds feeding directly on benthic species.

Based upon the BCF for rainbow trout (36,000X), the chloroparaffin residue levels that bioconcentrated directly from the water in planktonic and nektonic species, would range from 7.6 to 14.8 ug/g. These species would include mostly planktonic unicellular and small colonial algae and other non-swimming organisms, and nektonic species such as small mobile crustaceans like daphnids and rotifers and filter-feeding fishes such as shiners, alewife, shad, and herring.

Biomagnification of residues in nektonic primary carnivores, such as bass and possibly brown trout, would contain residues ranging from 11.3 to 22.1 ug/g. These residue levels are equal to or greater than residues levels measured in rainbow trout BCF study when 50 to 100 percent mortality occurred during depuration.

Bioconcentration of chloroparaffin in benthic organisms, such as aquatic insect larvae of chironomid midges, mayflies, and stoneflies, clams, worms, and

other benthic invertebrate filter feeders and detritus feeders, are estimated to be between 85.9 and 167.7 ug/g. In fact, the residue levels measured in chironomid larvae at the discharge point were 93.4 ppm. Benthic carnivores, such as sunfishes, catfish, bullheads, goldfish, carp, rockbass, white bass, minnows, and suckers, feeding on these benthic species would be expected to accumulate residue levels of 130 to 250 ug/g. The hardly detectable residues in some fish species of this trophic level cause one to question whether the sampled fish were residents or whether any resident fish could survive chronic exposure. All of the bioconcentration tests conducted on fish indicate accumulation of chloroparaffins from either water or dietary exposures.

Predicted chloroparaffin residue levels in Sugar Creek from uncontrolled releases are sufficiently low that no acute toxicity effects are anticipated on any aquatic species and these concentrations would not form a toxic barrier to migration of species through the area. Predicted residue levels in the water exceed the lower end of test levels producing adverse chronic effects in several test species, therefore adverse effects might also be expected in sensitive aquatic species such as fish, daphnids, and small crustaceans. Monitoring data from a manufacturing site on the Grand River in Ohio, indicated adverse effects on some aquatic insect larvae at similar chloroparaffin concentrations measured in the water at Site II adjacent to the release point (Ramm, 1977). Population losses in sensitive species will reduce the availability of food to aquatic species in higher trophic levels, including aquatic birds such as ducks and wading birds. In addition, avian reproduction might be affected by feeding on aquatic organisms, since the chloroparaffin residues in the food web are predicted to be higher than the chronic no effect level.

While insufficient data are available to evaluate the chronic effects of chloroparaffin levels predicted in the food web on fish reproduction, the residue levels predicted in rainbow trout would suggest adverse effects.

Results from sediment toxicity tests would most likely also indicate adverse effects on reproduction and settling capability in freshwater clams and other benthic species. Sediment toxicity results might also explain the absence of clams in the sampling at Site II in the Grand River.

Controlled releases into Sugar Creek might be expected to cause chronic adverse effects on aquatic species. While chloroparaffin levels in the water column are not likely to impact organisms, sediment levels of 130 ppb may reduce populations of benthic species and affect the availability of food for all other aquatic species.

3. Houston Ship Channel/Galveston Bay, Texas

The Houston Ship Channel enters the northwestern part of Galveston Bay near the mouth of the San Jacinto River (Figure 2). The shipping channel then turns south along some islands that partially separate it from a series of interconnecting embayments to the east. These bays from north to south are Burnet, Scott, Tabbs, and the upper San Jacinto Bays. Tidal flow and water circulation in these estuarine areas are such that while chloroparaffin residues are greatest in the channel itself, the residues are also spread into these highly productive, estuarine embayments.

The U.S. Department of the Interior, Fish and Wildlife Service (1982) on their Gulf Coast ecological inventory maps indicate that the Galveston Bay area is a breeding and nursery area for many species of birds, fish, and aquatic invertebrates. Many of these species are important either as a commercial fishery or as a sport fishery. The Houston Ship Channel is a nursery area for such sport and commercially-important fish and crustacea, as sheepshead, drum, southern flounder, white shrimp, brown shrimp, and blue crabs. The adjacent San Jacinto Battleground Historic Park is inhabited by dabbling ducks, red-shouldered hawks, gulls, terns, herons, and egrets.

Scott Bay east of the Houston Ship Channel is indicated as habitat for

herons, egrets, roseate spoonbills, and olivaceous cormorants. Tabbs Bay to the south is a nursery area for white and brown shrimp, blue crabs, and commercial and/or sport fish species including drum, sheepshead, and southern flounder.

The shallow shore areas in the upper Galveston Bay are a vast nursery for commercially-important white and brown shrimp, blue crabs, and commercial and/or sport fish species: drum, sheepshead, and southern flounder. The upper Galveston Bay area is also a breeding area for olivaceous cormorants, the white-faced ibis (an state endangered species), gulls, terns, herons, egrets, and a breeding and nursery area for eastern oysters. Other aquatic birds, like great blue herons, Louisiana herons, snowy egrets, roseate spoonbills, and black skimmers, live and breed on the small islands and along the edge of the upper bay.

Predicted chloroparaffin residue levels in the Houston Ship Channel and the adjacent estuarine areas approach or exceed the lower limits of anticipated effect levels in at least ten out of the eleven segments modeled by Versar Inc. (Table 7). The possible lone exception is Burnet Bay located across the mouth of the San Jacinto River opposite the Houston Ship Channel. The predicted water concentrations range from 0.56 - 1.4 ug/l in the Houston Ship Channel to 0.08 - 1.0 ug/l in the embayments. These concentrations in water are too low to produce any acute toxicity according to the available studies. Therefore, chloroparaffin releases would not be expected to act as a toxic barrier to migratory movement of aquatic organisms up the San Jacinto River.

Chronic effects would be expected, however, in the more sensitive resident species of aquatic invertebrates and fish from these chloroparaffin residue levels in water, as well as sediments. Since the predicted chloroparaffin residues in water are similar to the levels predicted in the Schuylkill River scenario, a similar concern for adverse affects exists in the absence of firm

no effect levels in the chronic tests.

Table 7 lists predicted chloroparaffin residue levels in aquatic organisms in the Houston Ship Channel (the first four segments), adjacent embayments, and Galveston Bay. Bioconcentration and biomagnification of chloroparaffin from a water-only exposure are estimated to range from 0.29 - 5 ug/g in plankton/nekton species to 4.9 - 85.9 ug/g in first-level carnivores upon benthic species. Higher residue levels might be found in second-level carnivores and in other species near the top of the estuarine food web. The maximum residue level in biota predicted by Versar Inc. was similar (100 ug/g).

Based upon the bioconcentration factor (BCF) for rainbow trout (36,000X), the chloroparaffin residue levels that bioconcentrate directly from the water to planktonic and nektonic species, would range from 0.29 to 5.0 ug/g. These species would include mostly planktonic unicellular and small colonial algae, diatoms, copepods, small shrimp, a multitude of larval stages of crustaceans, molluscs, polychaetes, fish, etc. that utilize water currents to distribute their young, and filter feeding fish such as shad, silversides, menhaden, sardines, and anchovies present in Galveston Bay system. Biomagnification of these residues in first-level nektonic carnivores, such as jacks, would contain residues ranging from 0.4 to 7.6 ug/g.

Bioconcentration of chloroparaffin in benthic filter feeders, such as oysters, mussels, clams, and some polychaete worms, are estimated to be 3.3 to 57.3 ug/g. Biomagnification of residues from these benthic organisms in predatory molluscs, sheepshead, drums, and stingrays, would range from 4.9 to 85.9 ug/g.

Biomagnification of sediment residues in benthic fish such as mullet, pinfish, and catfish, and benthic invertebrates such as detritus feeders, crabs, shrimp, mysids, amphipods, polychaete worms, whelks, and other benthic invertebrates, are estimated as 0.2 to 2.0 ug/g. Predators upon these benthic

organisms, such as seatrout, spot, croakers, killifish, and flounder, might be expected to contain 0.3 to 3.0 ug/g.

Monitoring data collected at a manufacturing site on the edge of the Houston Ship Channel (Figure 2) reported chloroparaffin residues in sediments somewhat higher than the 1.3 ug/g predicted levels in the upper segment of the Houston Ship Channel (Ramm, 1978). The residues at Stations H and I in the channel ranged from 1.5 to 6.0 ppm, when corrected for poor analytical recovery. The highest residue level (50 ppm) occurred at Station D where the discharge from Patrick Bayou enters the shipping channel. Out of five water samples, the only sample found to contain chloroparaffins was from Station F.

A possible explanation for the lack of correlation between residue levels in the water and sediment samples and the location of the various sampling sites might be due to increased insolubility of chloroparaffin in saline water. Solubility levels of organic chemicals are typically lower in saltwater than freshwater. Station F, source of the single positive water sample, was located in a small ditch near two outfalls from the manufacturing site and as such probably discharges freshwater, thereby, being less saline compared to the other stations located in Patrick Bayou and the shipping channel. The measured level at Station F was 1.5 ppb, reported to be at the edge of the detection limit (1.0 ppb). At the other sampling sites, residue levels in water below the detection limit could have been due to reduced solubility due the higher salinity. No data are available that indicate the difference in solubility between fresh and saltwater.

Three out of the four stations having the highest chloroparaffin residues in sediments were located where water salinity were highest. Station D which had the highest residue level, was located at the point where salinity would increase dramatically as the Bayou discharged into the shipping channel. Stations H and I were located at the higher saline sites in the shipping channel.

High residue levels at Station A, the fourth site, could be attributed to poor flushing. Station A was located upstream from two outfall points at the manufacturing site. Transport of chloroparaffin residues to this site would be dependent on incoming tidal currents in the bayou to the sampling site further up the bayou. The residues would readily sorb to the organics, settle into the sediments, and persist, because flushing at that station would be less than flushing at any sampling site.

Chloroparaffin residues were also measured in a few biological samples from five stations. The samples included whole crabs, killifish, and vegetation. The residue levels in the killifish and crabs ranged from 0.20-- 0.42 ppm to 0.10 to 0.52 ppm, respectively. The highest residue levels were found in the crabs collected at Station C, the station nearest Station D, which had the highest residue levels in sediments. Residue levels in crabs decreased as the distance of Stations B and J increased from Station C. Of Stations B and C, the only sites at which fish were sampled, the highest chloroparaffin residue levels were found at Station B, the station nearest the two outfall points in Patrick Bayou. No biological samples were reported from the four sampling stations with the highest sediment residue levels. Although no prediction was made for residue levels in the Patrick Bayou from which to estimate residues in biota, these residue levels are about 10-fold below residue levels estimated for the shipping channel (2.0 ug/g). As in the case of the Grand River, low residue levels in highly mobile species such as these crabs and killifish, probably indicate that these individuals were not long-term residents in the area.

The highest estimated chloroparaffin residue levels, i.e., those in carnivores upon benthic species are slightly less than the 166 ppm no effect level seen in the mallard reproduction study. Consequently, adverse chronic effects are unlikely on avian reproduction, based on these residue estimates. However,

given the fact that predicted sediment values have been consistently lower than levels monitored at similar sites by Ramm (1977 and 1978), the model used by Versar Inc. may be consistently underestimating releases and/or partition into sediments. These sediment predictions would also affect estimates of residues in biota.

In the absence of toxicity data correlating residue levels in sediments to toxic effects in benthic organisms, it is impossible to assess probable adverse effects on the nearly 200 benthic macroinvertebrate species listed in Galveston Bay by Shidler (1960). Holland et al. (1973) listed 32 benthic species at Station 22 alone in the upper Galveston Bay. Gillard (1974) delineated four characteristic benthic assemblages in the area of Tabbs Bay and upper Galveston Bay.

Residue levels predicted in the Houston Ship Channel range from 1,300 ug/kg (ppb) in the upper channel to 950 ug/kg in the lower channel. These levels were less than the 1,500 to 6,000 ppb residues measured in the upper ship channel. Residue levels in the upper embayments and Galveston Bay ranged from 140 to 940 ug/kg (ppb). If exposure to these residues were directly equivalent to concentrations tested in the toxicity studies, all test species and their surrogates might be expected to be affected. Exposure to chloroparaffins would include dermal, respiratory, and dietary exposures for organisms like shrimp, crabs, and polychaetes that burrow in the sediments. Clams and other burrowing molluscs would receive some protection from their shells and from respiration from overlying water pumped into the animal. Oysters and mussels prefer solid substrates and would be in even less contact with residues in sediment, except under two circumstances. First, planktonic larvae of most benthic species must find a suitable, non-toxic substrate upon which to settle. Chloroparaffin residues in sediments might prevent such larvae from successfully finding a suitable substrate. Second, chloroparaffin residues in the sediments may be

resuspended into the water column on particles by less sensitive, benthic organisms like polychaetes turning over sediments as they feed.

The oyster is the most commercially, and perhaps, ecologically-important benthic organisms to be found in the Galveston Bay system. Commercially, the bay provides 50 to 90 percent of the entire Texas oyster fishery. Besides the areas open to the public, 658 acres are privately leased as of 1972, the last year for which data was found. Ecologically, the oyster is important in the sedimentation of inorganic particulate matter from the water column and the reduction of water turbidity below the critical levels. Water clarity affects the depth of light penetration into the water and consequently, the amount of primary productivity (the base of the food web) by phytoplankton, benthic algae, and seagrasses. Turbidity also determines how deep vegetation such as seagrasses can grow. Oyster reefs and seagrass beds, which are both dependent on healthy oyster populations, provide the two most important aquatic habitats in the bay. The seagrass beds are nursery areas for many fish species like young sheepshead, seatrout, southern flounder, red drum, croaker, and kingfish, shrimp, and many other invertebrates. Galveston Bay has the highest commercial yields of any Texas bay and often leads in production of brown and white shrimp and blue crabs. Galveston Bay has the most heavy fishing pressure of any Texas bay system and the oyster reefs are prime habitat for many sport fish such as adult sheepshead, black and red drums, and Atlantic croaker. Oysters are also important for production of pseudofeces which provide the basis for additional food chains. Sediment toxicity tests are needed before the predicted residue levels in sediments can be evaluated for adverse effects on benthic species, including oyster spat setting and survival.

Of the 349 avian species reported from the Galveston Bay area, about 120 plus aquatic avian species might be expected to be directly exposed to chloroparaffin residues in their food. If chloroparaffins are to affect any avian

species in the Galveston Bay area, those species most likely to be affected would be benthic feeders such as the roseate spoonbill, ibises (including the state-endangered white-faced ibis), herons, egrets, the federally-endangered wood stork, bitterns, rails, least curlew, loons sandpipers, plovers, oystercatcher, ducks, grebes, and mergansers. Upper trophic-level, fish-eating bird species, like the federally-endangered brown pelican and bald eagle, the white pelican, and osprey, might also be at risk. Additional reproduction tests on other avian test species may indicate if any of these avian species might be adversely affected by chloroparaffin releases into the Galveston Bay system. Current avian reproduction studies do not indicate a margin of safety for the upper-trophic level birds in the Galveston Bay area based on the predicted chloroparaffin levels in aquatic biota.

Residue levels from controlled releases into the Galveston Bay system have been predicted to range from 0.004 to 0.12 ug/l in water, from 10 to 100 ug/kg in sediments, and from 0.02 to 4.91 ug/g in biota. These residues in water are sufficiently low that even at the highest level 0.12 ug/l, chronic effects are unknown at this time. The effect of the residue levels in sediments and biota are less certain. Chloroparaffin residues in rainbow trout measured during the depuration period were only 0.9 to 3.0 ug/g wet weight, when 50 percent mortality occurred in the 3 ug/l test level. While it is possible that residue levels in biota may reach lethal levels in some species and reduce some populations under controlled releases, it is doubtful that chloroparaffin residues would bioaccumulate sufficiently to directly affect avian reproduction.

The potential for adverse effects in the Houston Ship Channel/Galveston Bay area from uncontrolled releases is great. The bay is the most productive bay system in Texas for commercial oysters, shrimp, and blue crabs. The oyster reefs and seagrass beds are the two most important aquatic habitats for young and adult fish, and both habitats are dependent on healthy oyster populations.

Galveston Bay has the heaviest fishing pressure of any Texas bay system. The important sport fish include seatrout, sheepshead, drum, and southern flounder. Predicted chloroparaffin concentrations in water are sufficiently high that chronic adverse effects may be anticipated in species such as fish, zooplankton, shrimp, mussels and oysters. Population reductions in these species will alter availability of food for many higher trophic-level species, including numerous aquatic avian species nesting and feeding in the Galveston Bay system.

Population reductions in oysters would not only affect the commercial value of the crop, but oyster losses over some critical limit could alter water quality in the bay. Increased turbidity in the water due to oyster losses will reduce primary productivity, the base of the food web, and reduce the amount of areas in the bay where seagrass beds can grow. Reduction in oyster reefs and seagrass beds would affect the two most important habitat areas in the bay for young and adult sport fish, commercially-important shrimp and blue crab.

Predicted chloroparaffin residues in the sediments are sufficiently high to anticipate population reductions in sensitive benthic organisms. Population losses would affect availability of food to some species higher in the food web, including numerous aquatic bird species nesting and feeding in the bay. Unknown are the adverse effect levels of chloroparaffins in sediments on recruitment and larval settling of benthic species. Predicted residue levels bioconcentrated and/or biomagnified in biota exceed levels measured in rainbow trout at a time when 50 percent of the remaining fish died. The effect of these residue levels on survival or reproduction are unknown for many aquatic species including fish. Predicted residues from uncontrolled releases approach the no effect level for avian species and leave no margin of safety.

B. Direct Effects

1. Acute Toxicity

Under the conditions described in the three scenarios, chloroparaffin

releases are not likely to acutely affect any aquatic mammals, birds, fish, or other aquatic species. Absence of acute toxicity in fish and mammals appears to be largely related to relatively low water solubility and low uptake rates. Consequently, chloroparaffin releases predicted by Versar Inc., are not likely to form a toxic barrier for migratory species through the contaminated area. Based on the mammalian acute oral toxicity data and avian dietary levels in the reproduction test, bioconcentration of chloroparaffin in biota will not contain an acutely lethal dose. While chloroparaffins are highly acutely toxic to crustacea, algae, and zooplankton species, it is doubtful they would pose an acute hazard to fish or wildlife.

2. Chronic Toxicity

Chloroparaffin testing has indicated high chronic toxicity to several test species. Six out of the eight test species showed chronic effects below 20 ug/l. No observed effect levels (NOEL's) were below test concentrations in four of these test species, including the rainbow trout, sheepshead minnow, mysid shrimp, and daphnids. Higher mortality in males than females in the mysid shrimp test suggested that males are more sensitive to chronic exposures than females. The cessation of mortality in the daphnid test after Day 6 suggests that the difference in mortality between sexes may be due to reduction in body burdens via deposition of chloroparaffins into the yolk of their eggs. Since male mysids have no such pathway to dispose of chloroparaffin, residues continued to increase until lethal levels were reached. Transfer of residues to egg yolks has been confirmed by published data showing chloroparaffin residues in seabird eggs.

The reproductive effect of chloroparaffins residues deposited in eggs was tested in chronic tests on daphnids, mysid shrimp, chironomids, and mallard ducks. Omission of stored residues in eggs in the sheepshead study started with embryos raises concerns about adverse effects in early fish developmental

stages. Also given the slow uptake rate of chloroparaffins, the 28- to 32-day exposures were not of sufficient duration to measure the full extent of chronic toxicity.

Chronic exposure to the chloroparaffin levels predicted in the water and sediments at the three scenarios is expected to reduce the species diversity in the receiving waters of all three sites. Predicted concentrations in water either exceeded or approached the test concentrations that affected both fish species, mysid shrimp, and daphnids. Additional tests at lower concentrations are necessary to evaluate the level of effect for all four species. Sorption of chloroparaffins to sediments at 1,000 to 10,000 times the water level, suggest that sensitive benthic organisms are also likely to be effected. However, sediment toxicity data are not available to correlate residue levels in sediments with toxic effects.

Evidence of population reductions in aquatic organisms was reported in a monitoring study of the Grand River that indicated insect larval populations lower than seen in similar Ohio rivers. It is unclear whether the paucity of biological samples and species at sampling sites were coincidental with high residue levels measured in the sediments in the Grand River and Houston Ship Channel or indicative of areas depopulated by chloroparaffins. Toxic effects from sediment residues could be even greater than indicated. Based on measured residues that were higher than predicted in both the Grand River and Houston Ship Channel, it may be necessary to modify the model used by Versar Inc. to predict higher chloroparaffin residues in sediments.

3. Bioconcentration

Data indicate that chloroparaffins are bioconcentrated from water and are biomagnified from one trophic level to another in the food web. Residue levels in biota exceed the no effect level in the avian study and may pose a risk to avian reproduction in Sugar Creek area, and possibly the Houston Ship Channel/

Galveston Bay area. While predicted residue levels in the upper segment of Sugar Creek exceeded the mallard reproduction NOEL of 166 ppm, the residues are not close to the 1000 ppm effect level. The importance of the Houston Ship Channel and Galveston Bay to a wide range of aquatic birds and four endangered species might require additional evaluation of data and reconsideration of all assumptions.

Except for evaluation of risk to avian reproduction, insufficient toxicity data are available to correlate toxic effects from either tissue residues or dietary levels. Fifty and one hundred percent mortality in the remaining rainbow trout between Day 64 and 69 of the depuration period at two test concentrations, indicates that death may occur long after exposure from water has ceased and even after a considerable loss of residues. Residue levels in rainbow trout sampled during that period of mortality were lower than residue levels predicted in fish in all three scenarios. Therefore, predicted residue levels in fish and other might be expected to have adverse effects, including death.

C. Indirect Effects

1. Short-term Effects

Chloroparaffin releases predicted by Versar Inc. are not expected to cause any short-term indirect effects.

2. Long-term Effects

Indirect adverse effects from chloroparaffins may be from two general sources, reduction in the availability of food to higher organisms and loss of productive habitats. The effect of reduced food availability are obvious (reduced growth, lower reproductive potential, and possibly malnutrition and death), but the effects from habitat loss are generally even more devastating.

The most devastating indirect effect that chloroparaffins could have is probably the loss of oysters in Galveston Bay. Oyster losses could result in

increased turbidity in water, reduced primary productivity in phytoplankton, benthic algae, and seagrasses (basis of an extensive food chain in estuaries), and losses in productive habitats including the oyster reefs and seagrasses beds which are nursery areas for many juvenile and adult fish, shrimp, and blue crabs. Without oysters filtering particulate matter out of the water column below some critical level, light penetration in the water would be highly restricted and subsequently, the productive volume of bay would be reduced by the turbidity. Population reduction in filter feeding species may also affect water quality such that other species cannot survive.

A second major indirect effect from chloroparaffins would be reduction in benthic faunal diversity as anaerobic conditions in the sediments increase. The loss of sensitive burrowing benthic organisms from toxic sediments reduces the amount of sediment turnover and subsequent oxygenation of the sediments. When oxygen can no longer diffuse readily into the pore water, the sediments become anaerobic as organisms consume the limited amount of oxygen, die and decompose, the anaerobic level slowly rises toward the surface of the sediments driving out even the chemically non-sensitive species for lack of oxygen. In freshwater and estuaries, clams are important both as filter feeders and as burrowers. Predicted chloroparaffin levels in sediments may be toxic to clams. The absence of sampled clams at the Grand River site which had the highest chloroparaffin residue levels in sediments may be indicative of toxic effects. While the effects of these two examples may be the most far-reaching, losses of other populations can have unpredicted effects other than simply the loss of that species from the ecosystem and/or food chain.

Disruption of the food web from the loss of chemically-sensitive species and other species displaced by anaerobic sediments will affect many species in both freshwater and estuaries. Benthic organisms in the Galveston Bay area form a large portion of the diet of many species of commercially-important

fish, as well as benthic-feeding birds such as roseate spoonbills, and the endangered white-faced ibis and wood stork. Reduction in fish populations from either loss of food or chemical-sensitivity will affect other species of fish and fish-eating birds such as the osprey, herons, egrets, and the endangered bald eagle and brown pelican.

VI. CONCLUSIONS

About 67 million pounds of chloroparaffins are manufactured per year for a wide array of uses. Releases from manufacture and uses are estimated to be 50 million pounds per year. Chloroparaffins are persistent in the environment and widespread contamination is indicated by monitoring in the United Kingdom and around two manufacturing sites in the U.S.. Chloroparaffins are relatively insoluble in water and sorb readily to sediment at levels 1,000 to 10,000 times higher than overlying water. Residues bioconcentrate at levels from 10,000 to 40,000 in aquatic species and can also further biomagnify in the food web (1.5-fold). Chloroparaffins have been measured in many benthic organisms and benthic fish species contain higher residue levels than the fish higher in the water column. Residues have been found in seabirds and their eggs; in terrestrial crops, and in human foodstuffs.

Analysis of uncontrolled chloroparaffin releases from manufacturing and use sites in three distinct aquatic areas, the Schuylkill River in Pennsylvania, Sugar Creek in Ohio, and the Houston Ship Channel/Galveston Bay area in Texas, indicate that chronic toxicity levels are approached or exceeded for several test species in all three environments. Monitoring studies adjacent to the Houston Ship Channel and in the Grand River in Ohio indicate that predicted residue levels in water, sediments, and benthic biota from releases are realistic, if not too low for sediments.

Predicted chloroparaffin levels in all three scenarios are sufficient in water and sediments that chloroparaffins are expected to have adverse chronic

effects on a wide range of sensitive, local aquatic species. Biological data reported in the monitoring studies at two manufacturing sites suggested that population reductions occurred in some benthic species. Chironomid larvae were reported to be less numerous than seen in other comparable rivers in the state. And the absence of biological samples at the four sampling stations in Patrick Bayou and the Houston Ship Channel where the highest residue levels were found in sediments could be either a coincidence or indicative that benthic species were not present. The monitoring study reported only residue levels and gave no details about biological sampling. Measured residues in the highly motile species at levels lower than predicted compared to chironomid data, suggest that the motile species were not permanent residents.

Absence of chronic no observed effect levels (NOEL) in four test species (rainbow trout, sheepshead minnow, daphnia, and mysid shrimp) at concentrations close to predicted environmental levels suggest that chronic effects will occur in each scenario. Much higher residue levels in the sediments suggest that chronic effects will also occur in benthic species. The level of these adverse effects are unknown due to poor test results in the studies and the absence of sediment toxicity tests. Comparison of chronic toxicity levels of chironomid larvae with other test species, suggest that, if the less sensitive, chironomid population was reduced by these residue levels in sediment, than all other more sensitive benthic populations would also be affected. Oysters and clams are two sensitive benthic organisms which can affect the aquatic environment well beyond simple reduction in food availability like many species. Populations reductions in oysters could reduce water quality, inhibit primary production by phytoplankton (the base of food web), and destroy the two most productive habitats in Galveston Bay estuary. Population reductions in sediment-burrowing species like clams affect sediment porosity and dissolved oxygen penetration into sediments, which causes sediments to become anaerobic and uninhabitable

for most benthic infauna. Benthic population reductions would affect food availability for a wide array of aquatic species including wading birds like the roseate spoonbill, and the endangered white-faced ibis and wood stork, and fish-eating birds like the herons, egrets, osprey, and endangered bald eagle and brown pelican in the Galveston Bay area. Predicted residues in Sugar Creek were sufficiently high to exceed the NOEL for avian reproduction. Widespread utilization of the Galveston Bay area by aquatic birds also warrants close scrutiny for possible toxic effects. Predicted chloroparaffin levels in the biota of Galveston Bay indicate no margin of safety for aquatic birds. No adverse effects are anticipated in migratory species (fish, birds, or invertebrates) which traverse any of the three release sites.

While insufficient data are available from existing tests to quantify chloroparaffin effects on fish reproduction, sediment toxicity to benthic species or toxic effects on settling of planktonic larvae of benthic species, monitoring data indicate that predicted residue levels will adversely affect aquatic species in all three scenarios. Although predicted chloroparaffin levels may be highest in Sugar Creek, the complexity, sensitivity, and productivity of the Galveston Bay area make it the most ecologically and economically important of the three scenarios. Chloroparaffin levels measured in rainbow trout when 50 percent mortality occurred during the depuration period, indicate that adverse effects can be anticipated from predicted residue levels in biota at three sites. Any correlation between internal residue levels and their effects are uncertain, because the mechanism(s) of chloroparaffin toxicity and metabolically-active site of concern is unknown.

In the absence of predicted environmental releases and residue levels, no effort has been made here to evaluate the risk posed by the disposal of chloroparaffins. Monitoring data in United Kingdom indicate that while chlorinated n-paraffin residues are usually highest near manufacturing sites, residues

were found at remote sampling sites. The source of these remote residues are thought to have occurred from disposal. Chronic exposure to these levels would be expected to adversely affect sensitive species. However, the absence of measurable residues in the study does not mean adverse chronic effects will not occur, because the limit of detection in water is too high to adequately monitor either test concentrations or environmental samples.

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Table 1. Acute environmental LC50 values for short (C10-13) chain-length chloroparaffins (58% chlorination unless indicated otherwise)

| Test Species | Duration (hours) | Test Concentration (mg/l) | Reference ** |
|--|---------------------|------------------------------|---------------------------|
| <u>Fish:</u> | | | |
| Bluegill Sunfish (<u>Lepomis macrochirus</u>) | 96 | > 300 | Johnson and Finley (1980) |
| Channel Catfish (<u>Ictalurus punctatus</u>) | 96 | > 300 | Johnson and Finley (1980) |
| Fathead Minnow (<u>Pimephales promelas</u>) | 96 | > 100 | Johnson and Finley (1980) |
| Rainbow trout (<u>Salmo gairdneri</u>) | 96 | > 300 | Johnson and Finley (1980) |
| <u>Bleaks</u> (<u>Alburnus alburnus</u>) | | | |
| Witacior 49 49% Cl | 96 | > 5,000 | Linden et al. (1979) |
| Witacior 55EN 56% Cl | 96 | > 10,000 | Linden et al. (1979) |
| Witacior 63 63% Cl | 96 | > 5,000 | Linden et al. (1979) |
| Chlorparaffin Huls 70C 70% Cl | 96 | > 10,000 | Linden et al. (1979) |
| Witacior 71P 71% Cl | 96 | > 5,000 | Linden et al. (1979) |
| <u>Aquatic Invertebrates:</u> | | | |
| Waterflea | 48 | 0.046 * | Chloroparaffin Consortium |
| (<u>Daphnia magna</u>) | 96 | 0.018 | Chloroparaffin Consortium |
| Mysid Shrimp (<u>Mysidopsis bahia</u>) | 96 | < 0.0141 * | Chloroparaffin Consortium |
| <u>Copepod</u> (<u>Nitocra spinipes</u>) | | | |
| Witacior 49 49% Cl | 96 | 0.06 | Tarkpea et al. (1981) |
| Cereclor 50LV 49% Cl | 96 | 0.10 | Tarkpea et al. (1981) |
| Cereclor 70L 70% Cl | 96 | < 0.3 | Tarkpea et al. (1981) |
| Chlorparaffin huls 70C 70% Cl | 96 | < 5 | Tarkpea et al. (1981) |
| Midge larvae (<u>Chironomus tentans</u>) | 48 | > 0.162 | Chloroparaffin Consortium |
| <u>Algae:</u> | | | |
| Marine Diatom | 48 | 0.0316 | Chloroparaffin Consortium |
| (<u>Skeletonema costatum</u>) | 96 | 0.0423 | Chloroparaffin Consortium |
| Freshwater Green Alga | 96 | 3.69 | Chloroparaffin Consortium |
| (<u>Selenastrum</u> | 168 | 1.55 | Chloroparaffin Consortium |
| <u>capricornutum</u>) | 240 | 1.310 | Chloroparaffin Consortium |

* Revised value based on best estimate from raw data.

** Citations may be found in the Hazard Assessment Document

Table 2. Chronic environmental toxicological effects in order of increasing test concentrations.

| Test Level (ug/l) | Test Species | | | Toxicological Effect |
|----------------------|--|--------|---|--|
| 0.6 | Mysid Shrimp (Chronic - 28 days) | 35 | % | adult mortality (controls 20-27.5%) |
| 1.2 | Mysid Shrimp (Chronic - 28 days) | † 45 | % | adult mortality (controls 20-27.5%) |
| | | 14.7 | % | reduction in number of young |
| 2.1 | <u>Daphnia magna</u> (Semi-static - 14 days) | | | no effect |
| 2.3 | Common Mussels (Growth - 84 days) | 2.6 | % | increase in growth rate of shell |
| | | 7.7 | % | reduction in growth rate of tissue (dry weight) |
| 2.35 | Common Mussel (BCF - 147 + 98 days) | 7 | % | mortality (5 % control mortality) |
| 2.4 | Mysid Shrimp (Chronic - 28 days) | * 42.5 | % | adult mortality (controls 20-27.5%) |
| | | 2.0 | % | reduction in number of young |
| 2.4 | Sheepshead Minnow Study 1 - 28 days) | * 3.8 | % | increase in body weight |
| | | * 4.0 | % | increase in body length |
| 2.7 | <u>Daphnia magna</u> (Chronic - 21 days) | * 43.6 | % | reduction in number of offspring |
| | | † 43.9 | % | reduction in offspring/female |
| 3.1 | Rainbow Trout (BCF - 168 + 64-69 days) | * 50.0 | % | mortality |
| 3.4 | Rainbow Trout (Growth - 168 days) | 0.02% | | increase in body weight |
| | | 0.7 | % | increase in body length |
| 3.5 | <u>Daphnia magna</u> (Semi-static - 14 days) | | | NOEL |
| 3.8 | Mysid Shrimp (Chronic - 28 days) | 32.5 | % | adult mortality (controls 20-27.5%) |
| | | 20.8 | % | reduction in number of young |
| 4.1 | Sheepshead Minnow (Study 1 - 28 days) | * 14.9 | % | increase in body weight |
| | | * 3.7 | % | increase in body length |
| 4.5 | Marine Diatom <u>Skeletonema costatum</u> (Acute - 2 days) | 0.9 | % | increase in cell density |
| | | 0.8 | % | increase in growth rate |
| 5.0 | <u>Daphnia magna</u> (Chronic - 21 days) | 16.4 | % | reduction in number of offspring |
| | | 13.0 | % | reduction in offspring/female |
| | | 9.9 | % | mortality in offspring |

Table 2. (cont.).

| Test Level (ug/l) | Test Species (Study - Exposure) | Toxicological Effect | |
|----------------------|--|------------------------------------|--|
| 5.0 | Mysid Shrimp (Acute - 4 days) | 20 % | mortality |
| 6.2 | <u>Daphnia magna</u> (Semi-static - 14 days) | 6.9 % | reduction in young/female |
| 6.4 | Sheepshead Minnow * (Study 1 - 28 days)* | 31.3 % 5.5 % | increase in body weight increase in body length |
| 6.7 | <u>Skeletonema costatum</u> (Acute - 2 days) | 5 % 2.4 % | reduction in growth rate increase in cell density |
| 7.1 | Mysid Shrimp (Acute - 4 days) | | no mortality |
| 7.3 | Mysid Shrimp (Chronic - 28 days) | 30 % 27.4 % 32.6 % | adult mortality (controls 20-27.5%) reduction in number of young reduction in offspring/female |
| 8.9 | <u>Daphnia magna</u> (Chronic - 21 days) | * 36.6 % 66.1 % * 49.9 % | mortality reduction in number of offspring reduction in offspring/female |
| 9.3 | Common Mussel * (Growth - 84 days) * | 52.6 % 53.8 % | reduction in growth rate of shell reduction in growth rate of tissue (dry weight) |
| 10.0 | <u>Daphnia magna</u> * (Semi-static - 14 days) † 29 - 57 | 50.0 % 78.9 % 59.8 % 57 % | adult mortality reduction in number of offspring reduction in offspring/female increase in the number of days to first release of young from brood |
| 10.1 | Common Mussel * (BCF - 91 + 84 days) | 33 % | mortality (5 % control mortality) |
| 12 | <u>Daphnia magna</u> * (Chronic - 21 days) | 50.0 % | mortality |
| 12.1 | <u>Skeletonema costatum</u> (Acute - 2 days) † | 12 % 14.3 % | reduction in growth rate reduction in cell density |
| 13 | Common Mussel † (Phase I - 60 days) | | occasional reduction in filtration activity |
| 13.7 | Mysid shrimp * (Acute - 4 days) | 50 % | mortality |

Table 2. (cont.).

| Measured Test Level (ug/l) | Test Species (Study - Exposure) | | | Toxicological Effect |
|----------------------------------|--|----------------------------|-------------|---|
| 14.3 | Rainbow Trout (BCF - 168 + 64-69 days) | * 100 | % | mortality in remaining population |
| 14.9 | Mysid Shrimp (Acute - 4 days) | * 40 | % | mortality |
| 16.3 | <u>Daphnia magna</u> (Chronic - 21 days) | * 100 | % | mortality |
| 17.2 | Rainbow trout (Growth - 168 days) | * 25.4 6.2 | % % | increase in body weight increase in body length |
| 19.6 | <u>Skeletonema costatum</u> (2 days) | * 30.0 * 44 | % % | reduction in cell density reduction in growth rate |
| 22.1 | Sheepshead Minnow (Study 1 - 28 days) | * 27.5 * 7.2 | % % | increase in body weight increase in body length |
| 23.8 | Mysid Shrimp (Acute - 4 days) | * 95 | % | mortality |
| 24.0 | Mysid Shrimp (Acute - 4 days) | * 100 | % | mortality |
| 31.6 | Marine Diatom <u>Skeletonema costatum</u> (2 days) | * 50 | % | reduction in growth (cell count) |
| 33 | Rainbow Trout (Phase I - 60 days) | † 33.3 † 37.9 † 34.2 | % % % | mortality increase in body weight increase in body length |
| 36.2 | Sheepshead Minnow (Study 2 - 32 days) | * 21.3 * 7.4 | % % | increase in body weight increase in body length |
| 43.1 | Marine Diatom <u>Skeletonema costatum</u> (2 days) | * 47 * 34.2 | % % | reduction in rate growth reduction in cell density |
| 44 | Common Mussel (Phase I - 60 days) | † | | occasional reduction in filtration activity |
| 54.8 | Sheepshead Minnow (Study 1 - 28 days) | * 31.7 * 6.4 | % % | increase in body weight increase in body length |
| 61 | Midge - larvae (<u>Chironomus tentans</u>) (Chronic - 49 days) | 19.3 - 21.7 6.1 - 9.4 | % % | reduction in emergence reduction in filial eggs/ egg mass |

Table 2. (cont.).

| Test Level (ug/l) | Test Species (Study - Exposure) | Toxicological Effect | |
|----------------------|---|----------------------------|--|
| 71.0 | Sheepshead Minnow * (Study 2 - 32 days)* | 15.1 % 5.6 % | increase in body weight increase in body length |
| 71 | Common Mussel † (Phase I - 60 days) | 50.0 % | mortality |
| 78 | Midge - larvae * (<u>Chironomus tentans</u>) (Chronic - 49 days) | 60.0 % 16.9 % 10.5 % | reduction in parent egg hatch reduction in emergence reduction in filial eggs/egg mass |
| 100 | Rainbow Trout † (Phase I - 60 days)† | 13.3 % 13.5 % 6.7 % | mortality increase in body weight increase in body length |
| 100 | Copepod <u>Nitocra spinipes</u> (4 days) | 50 % | mortality |
| 110 | Green Algae (<u>Selenastrum</u> <u>capricornatum</u>) (Acute - 3 days) | 16 % | reduction in cell density |
| 121 | Midge - larvae * (<u>Chironomus tentans</u>) (Chronic - 49 days) | 100 % | reduction in emergence |
| 130 | Common Mussel † (Phase I - 60 days) | 96 % | mortality |
| 161.8 | Sheepshead Minnow (Study 2 - 32 days)* | 13.0 % 3.4 % | increase in body weight increase in body length |
| 162 | Midge - larvae * (<u>Chironomus tentans</u>) (Acute - 2 days) | 100 % | reduction in emergence |
| 220 | Green Algae * (Acute - 3 days) | 23 % | reduction in cell density |
| 279.7 | Sheepshead Minnow (Study 2 - 32 days) | 1.9 % 1.9 % | increase in body weight increase in body length |
| 350 | Rainbow Trout † (Phase I - 60 days) | 58.6 % 3.1 % 1.9 % | mortality decrease in body weight decrease in body length |
| 390 | Green Algae * (Acute - 4 days) | 18 % | reduction in cell density |

Table 2. (cont.).

| Measured Test Level (ug/l) | Test Species (Study - Exposure) | Toxicological Effect | |
|----------------------------------|------------------------------------|----------------------|------------------------------------|
| 570 | Green Algae | * 35 | % reduction in cell density |
| | (Acute - 10 days) | * 14 | % reduction in growth rate |
| 620.5 | Sheepshead Minnow | * 30.9 | % decrease in body weight |
| | (Study 2 - 32 days)* | 9.2 | % decrease in body length |
| 900 | Green Algae | * 31 | % reduction in cell density |
| | (Acute - 10 days) | | |
| 930 | Common Mussel | † 100 | % mortality |
| | (Phase I - 60 days) | | |
| 1,070 | Rainbow Trout | † 80.0 | % mortality |
| | (Phase I - 60 days)† | 57.6 | % decrease in body weight |
| | | † 28.7 | % decrease in body length |
| 1,200 | Green Algae | * 45 | % reduction in cell density |
| | (Acute - 10 days) | | |
| 1,310 | Green Algae | * 50 | % reduction in growth (cell count) |
| | <u>Selenastrum</u> | | |
| | <u>capricornutum</u> | | |
| | (10 days) | | |
| 3,050 | Rainbow Trout | † 90.0 | % mortality |
| | (Phase I - 60 days)† | 74.7 | % decrease in body weight |
| | | † 32.6 | % decrease in body length |

* Statistically significant ($P \geq 0.05$) difference compared to the acetone control

† Insufficient data available to make a statistical analyses, but the values would appear to be significantly different than acetone controls

Table 3. Bioconcentration data in order of increasing exposure concentrations by species

| Test Level (ppb) | Test Species (Study - Exposure) | BCF Value | Residue Levels (range) (ppm) |
|---------------------|--------------------------------------|-----------|---------------------------------|
| <u>Mussel</u> | | | |
| 2.35 | Common Mussel (BCF - 147 days) | 40,900 | 122 (76-187) |
| 10.1 | Common Mussel (BCF - 91 days) | 24,800 | 249 (144-365) |
| 13 | Common Mussel (Phase I - 60 days) | 25,292 | 329 |
| 44 | Common Mussel (Phase I - 60 days) | 16,427 | 723 |
| 71 | Common Mussel (Phase I - 60 days) | 5,785 | 411 |
| 130 | Common Mussel (Phase I - 60 days) | 12,177 | 1,583 |
| <u>Fish</u> | | | |
| 3.1 | Rainbow Trout (BCF - 168 days) | 3,600 | 11.0 (8.3-15.6) |
| 14.3 | Rainbow Trout (BCF - 168 days) | 3,300 | 75.2 (62.6-87.3) |
| 33 | Rainbow trout (Phase I - 60 days) | 7,155 | 236 |
| 100 | Rainbow trout (Phase I - 60 days) | 7,816 | 782 |
| 350 | Rainbow trout (Phase I - 60 days) | 3,723 | 1,303 |
| 1,070 | Rainbow trout (Phase I - 60 days) | 2,642 | 2,827 |
| 3,050 | Rainbow trout (Phase I - 60 days) | 1,173 | 3,577 |

Table 4. Comparison of 10-day bioconcentration estimates for four aquatic species

| Test Species (Study - Exposure) | Test Level* (ppb) | BCF Value | Residue Level (ppm) |
|--|----------------------|-----------|------------------------|
| Marine Diatom <u>Skeletonema costatum</u> (Acute - 10 days) | 1.4 | < 1.1 | < 0.0016 |
| | 2.5 | < 1 | < 0.0025 |
| | 6.6 | 2.4 | 0.0224 |
| | 6.8 | 5.5 | 0.0372 |
| | 12.1 | 4.0 | 0.0479 |
| | 17.8 | 3.5 | 0.0622 |
| Freshwater Green Alga <u>Selenastrum capricornutum</u> (Acute - 10 days) | 35 | 1.5 | 0.051 |
| | 62 | 1.9 | 0.118 |
| | 79 | 3.2 | 0.251 |
| | 100 | 4.1 | 0.410 |
| | 150 | 4.7 | 0.710 |
| | 140 | 7.6 | 1.060 |
| Common Mussel (<u>Mytilus edulis</u>) (BCF - 10 day est.) | 2.35 | 11,915 | 28 (24-32) |
| | 10.1 | 10,099 | 102 (87-117) |
| Rainbow Trout (<u>Salmo gairdneri</u>) (BCF - 7 and 10 days) | 3.1 | 1,500 | 4.65 (3.4-5.9) |
| | 14.3 | 1,654 | 23.65 (19.2-28.1) |

* - Water concentrations used to compute the BCF value in algae were measured concentrations on Day 10 (the same day residues in the algae were measured).

Table 5. Chloroparaffin residue levels (ug/g) in biota due to bioconcentration and biomagnification in the Schuylkill River near Conchohocken, Pa.

| Source of Exposure | Bioconcentration (BCF) | | Biomagnification (1.5X BCF or PEC) | | |
|-----------------------------------|----------------------------|--------------------------|------------------------------------|--------------------------|--------------------|
| | Plankton & Nekton (3,600X) | Filter Feeders (40,900X) | Detritus Feeders | First-level Planktivores | Benthic Carnivores |
| Water | | | | | |
| Dissolved (ug/l) | | | | | |
| 0.26 | 0.94 | 10.6 | | 1.4 | 16.0 |
| Total (ug/l) | | | | | |
| 0.50 | 1.8 | 20.5 | | 2.7 | 30.7 |
| Sediment (ug/kg) | | | | | |
| 440 | 1,600* | 18,000* | 0.66 | | |
| <u>Controlled Releases</u> | | | | | |
| Water | | | | | |
| Dissolved (ug/l) | | | | | |
| 0.009 | 0.003 | 0.04 | | 0.005 | 0.06 |
| Total (ug/l) | | | | | |
| 0.02 | 0.07 | 0.82 | | 0.11 | 1.2 |
| Sediment (ug/kg) | | | | | |
| 20 | 72* | 820* | 0.03 | | |

* No known biological component for residue level.

Table 6. Chloroparaffin residue levels (ug/g) in biota due to bioconcentration and biomagnification in Sugar Creek near Dover, Ohio

| Source of Exposure | Bioconcentration (BCF) | | Biomagnification (1.5X BCF or PEC) | | |
|------------------------------|----------------------------|--------------------------|------------------------------------|--------------------------|--------------------|
| | Plankton & Nekton (3,600X) | Filter Feeders (40,900X) | Detritus Feeders | First-level Planktivores | Benthic Carnivores |
| <u>Uncontrolled Releases</u> | | | | | |
| Water | | | | | |
| Dissolved (ug/l) | | | | | |
| 2.1 | 7.56 | 85.9 | | 11.3 | 128.8 |
| 0.4 | 1.44 | 16.4 | | 2.2 | 24.5 |
| Total (ug/g) | | | | | |
| 4.1 | 14.8 | 167.7 | | 22.1 | 251.5 |
| 0.7 | 2.5 | 28.6 | | 3.8 | 42.9 |
| Sediment (ug/kg) | | | | | |
| 3,600 | 13,000* | 147,200* | 5.4 | | |
| 600 | 2,200* | 24,500* | 0.9 | | |
| <u>Controlled Releases</u> | | | | | |
| Water | | | | | |
| Dissolved (ug/l) | | | | | |
| 0.07 | 0.25 | 2.9 | | 0.38 | 4.3 |
| 0.01 | 0.04 | 0.41 | | 0.05 | 0.6 |
| Total (ug/l) | | | | | |
| 0.14 | 0.52 | 3.7 | | 0.79 | 8.6 |
| 0.03 | 0.11 | 1.2 | | 0.16 | 1.8 |
| Sediment (ug/kg) | | | | | |
| 130 | 468* | 5,320* | 0.20 | | |
| 20 | 72* | 820* | 0.03 | | |

* No known biological component for residue level.

Table 7. Residue estimates (ug/g) in biota due to bioconcentration and biomagnification in the Houston Ship Channel/Galveston Bay area, Texas from uncontrolled chloroparaffin releases

| Source of Exposure | Bioconcentration (BCF) | | Biomagnification (1.5X BCF or PEC) | | |
|--------------------|-------------------------------|-----------------------------|---------------------------------------|--------------------------|--------------------|
| | Plankton & Nekton (3,600X) | Filter Feeders (40,900X) | Detritus Feeders | First-level Planktivores | Benthic Carnivores |
| Water | | | | | |
| Dissolved (ug/l) | | | | | |
| 0.76 | 2.7 | 31.1 | | 4.1 | 46.6 |
| 0.67 | 2.4 | 27.4 | | 3.6 | 41.1 |
| 0.60 | 2.2 | 24.5 | | 3.2 | 36.8 |
| 0.56 | 2.0 | 22.9 | | 3.0 | 34.4 |
| 0.55 | 2.0 | 22.5 | | 3.0 | 33.7 |
| 0.51 | 1.8 | 20.9 | | 2.8 | 31.3 |
| 0.39 | 1.4 | 16.0 | | 2.1 | 23.9 |
| 0.33 | 1.2 | 13.5 | | 1.8 | 20.2 |
| 0.26 | 0.9 | 10.4 | | 1.4 | 16.0 |
| 0.24 | 0.9 | 9.8 | | 1.3 | 14.7 |
| 0.08 | 0.3 | 3.3 | | 0.43 | 4.9 |
| Total (ug/l) | | | | | |
| 1.4 | 5.0 | 57.3 | | 7.6 | 85.9 |
| 1.3 | 4.7 | 53.2 | | 7.0 | 79.8 |
| 1.2 | 4.3 | 49.1 | | 6.5 | 73.6 |
| 1.1 | 4.0 | 45.0 | | 5.9 | 67.5 |
| 1.0 | 3.6 | 40.9 | | 5.4 | 61.4 |
| 1.0 | 3.6 | 40.9 | | 5.4 | 61.4 |
| 0.8 | 2.9 | 32.7 | | 4.3 | 49.1 |
| 0.6 | 2.2 | 24.5 | | 3.2 | 36.8 |
| 0.5 | 1.8 | 20.5 | | 2.7 | 30.7 |
| 0.4 | 1.4 | 16.4 | | 2.2 | 24.5 |
| 0.2 | 0.7 | 8.2 | | 1.1 | 12.3 |
| Sediment (ug/kg) | | | | | |
| 1,300 | 4,680* | 53,200* | 2.0 | | 3.0 |
| 1,200 | 4,320* | 49,100* | 1.8 | | 2.8 |
| 1,000 | 3,600* | 40,900* | 1.5 | | 2.3 |
| 950 | 3,420* | 38,900* | 1.4 | | 2.1 |
| 940 | 3,380* | 38,450* | 1.4 | | 2.1 |
| 870 | 3,130* | 35,600* | 1.3 | | 2.0 |
| 700 | 2,520* | 28,600* | 1.1 | | 1.7 |
| 570 | 2,050* | 23,300* | 0.9 | | 1.4 |
| 450 | 1,620* | 18,400* | 0.7 | | 1.1 |
| 420 | 1,510* | 17,200* | 0.6 | | 1.0 |
| 140 | 500* | 5,730* | 0.2 | | 0.3 |

* No known biological component for residue level.

Table 8. Residue estimates (ug/g) in biota due to bioconcentration and biomagnification in the Houston Ship Channel/Galveston Bay area, Texas from controlled chloroparaffin releases

| Source of Exposure | Bioconcentration (BCF) | | Biomagnification (1.5X BCF or PEC) | | |
|-------------------------|-------------------------------|-----------------------------|---------------------------------------|--------------------------|--------------------|
| | Plankton & Nekton (3,600X) | Filter Feeders (40,900X) | Detritus Feeders | First-level Planktivores | Benthic Carnivores |
| Water | | | | | |
| Dissolved (ug/l) | | | | | |
| 0.06 | 0.22 | 2.4 | | 0.32 | 3.7 |
| 0.03 | 0.11 | 1.2 | | 0.16 | 1.8 |
| 0.03 | 0.11 | 1.2 | | 0.16 | 1.8 |
| 0.02 | 0.07 | 0.82 | | 0.11 | 1.2 |
| 0.02 | 0.07 | 0.82 | | 0.11 | 1.2 |
| 0.02 | 0.07 | 0.82 | | 0.11 | 1.2 |
| 0.01 | 0.04 | 0.41 | | 0.05 | 0.6 |
| 0.01 | 0.04 | 0.41 | | 0.05 | 0.6 |
| 0.01 | 0.04 | 0.41 | | 0.05 | 0.6 |
| 0.004 | 0.01 | 0.16 | | 0.02 | 0.02 |
| Total (ug/l) | | | | | |
| 0.12 | 0.43 | 4.91 | | 0.77 | 7.4 |
| 0.06 | 0.22 | 2.45 | | 0.32 | 3.7 |
| 0.05 | 0.18 | 2.05 | | 0.27 | 3.1 |
| 0.05 | 0.18 | 2.05 | | 0.27 | 3.1 |
| 0.05 | 0.18 | 2.05 | | 0.27 | 3.1 |
| 0.04 | 0.14 | 1.64 | | 0.22 | 0.2 |
| 0.03 | 0.11 | 1.2 | | 0.16 | 1.8 |
| 0.03 | 0.11 | 1.2 | | 0.16 | 1.8 |
| 0.02 | 0.07 | 0.82 | | 0.11 | 1.2 |
| 0.02 | 0.07 | 0.82 | | 0.11 | 1.2 |
| 0.007 | 0.03 | 0.28 | | 0.04 | 0.4 |
| Sediment (ug/kg) | | | | | |
| 100 | 360* | 4,090* | 0.2 | | |
| 50 | 180* | 2,040* | 0.08 | | |
| 50 | 180* | 2,040* | 0.08 | | |
| 40 | 144* | 1,640* | 0.06 | | |
| 40 | 144* | 1,640* | 0.06 | | |
| 40 | 144* | 1,640* | 0.06 | | |
| 30 | 108* | 1,230* | 0.04 | | |
| 30 | 108* | 1,230* | 0.04 | | |
| 20 | 72* | 820* | 0.03 | | |
| 20 | 72* | 820* | 0.03 | | |
| 10 | 36* | 410* | 0.02 | | |

* No known biological component for residue level.

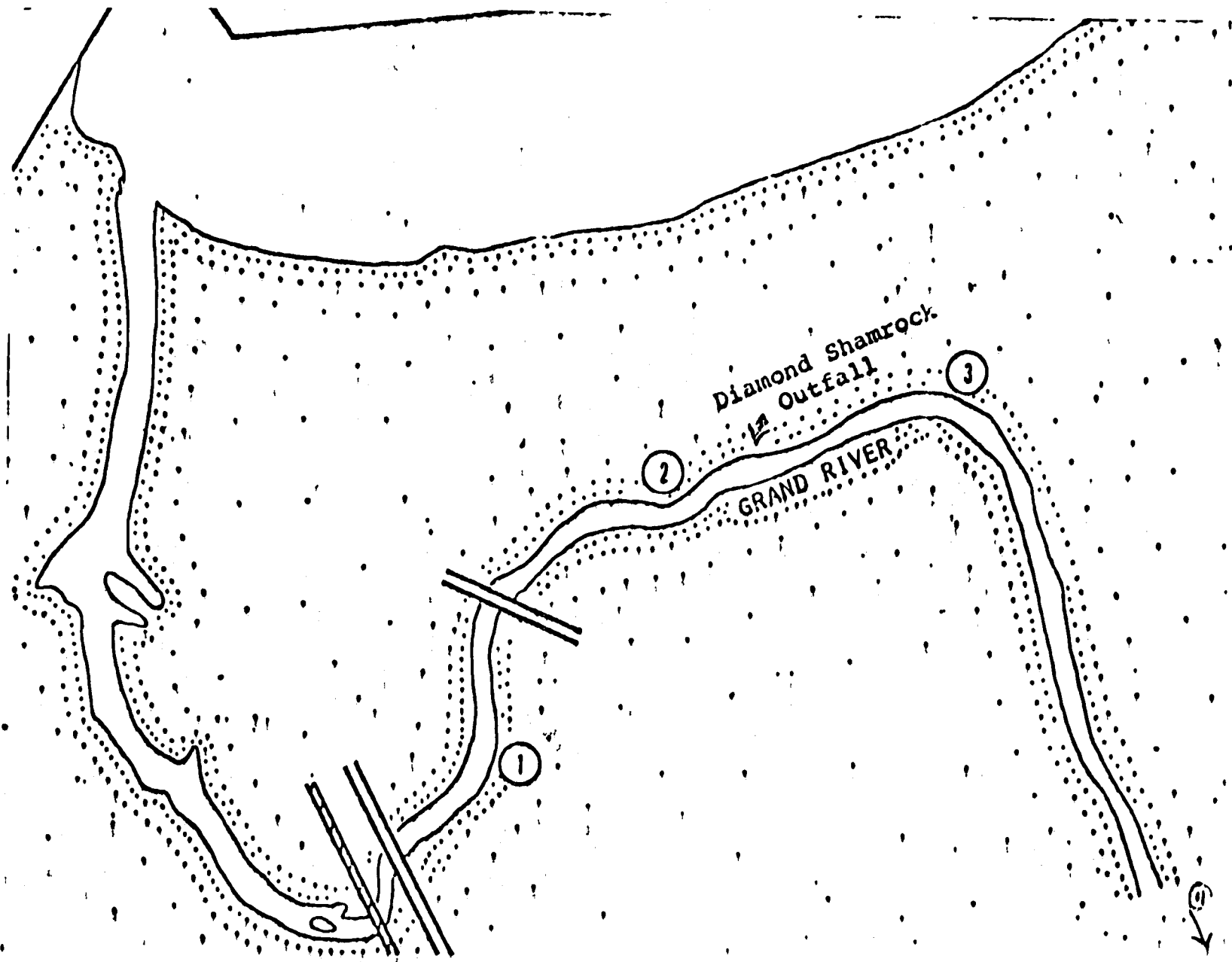


Figure 1. Map of the sampling stations at the Diamond Shamrock Manufacturing Plant on the Grand River near Painesville, Ohio.

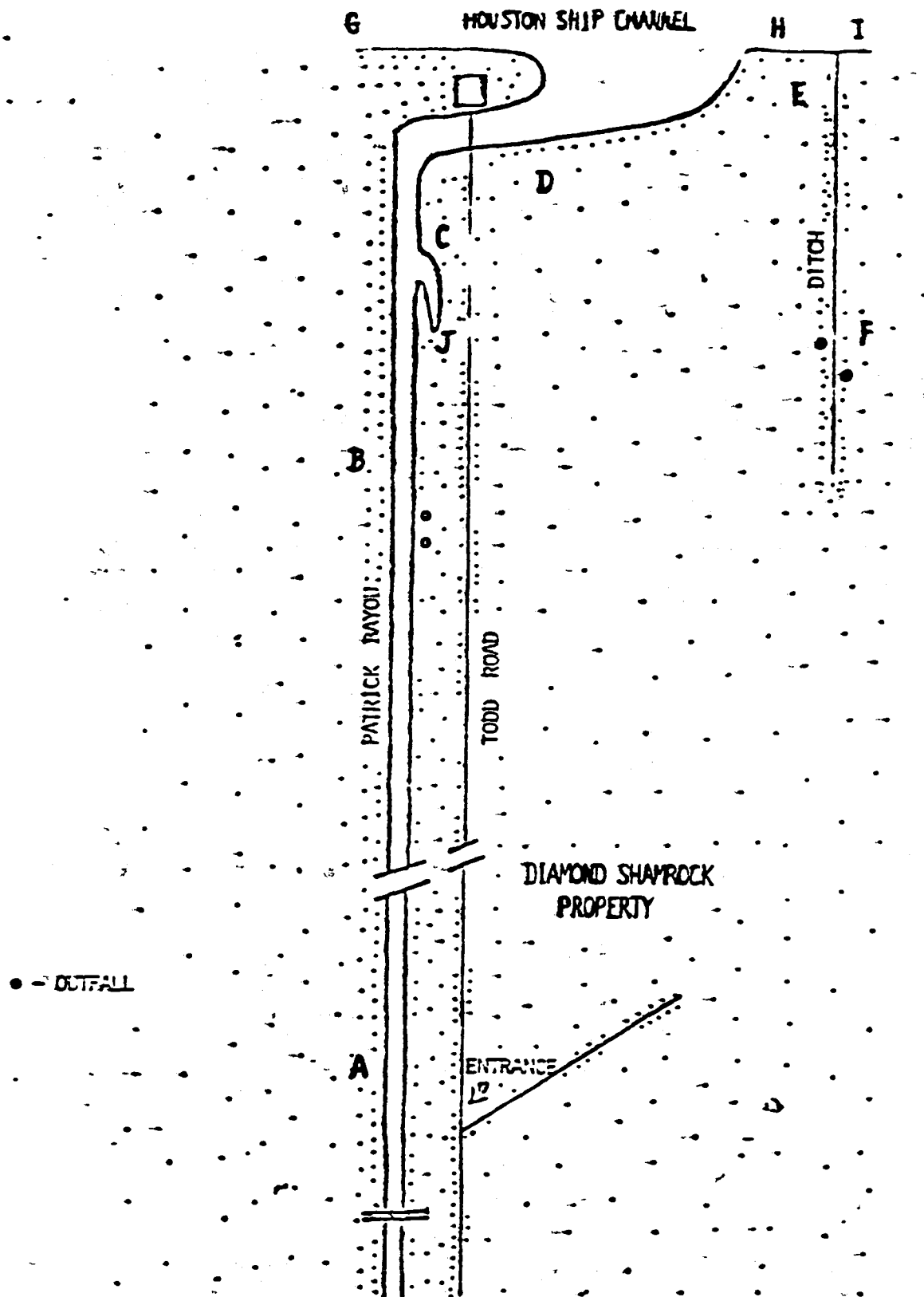


Figure 2. Map of sampling stations at Diamond Shamrock Manufacturing Plant on Patrick Bayou adjacent to the Houston Ship Channel in Texas.

Figure 3. (cont.) Key to those organisms identified in the Gulf Coast Inventory of the Galveston Bay area.

| | Code | Organism |
|---------------|------|---|
| Plants | | |
| | 2 | Widgeon grass (<u>Ruppia maritima</u>) |
| Invertebrates | | |
| Crustacea | | |
| | 51 | White shrimp (<u>Penaeus setiferus</u>) |
| | 52 | Brown shrimp (<u>Penaeus aztecus</u>) |
| | 54 | Blue crab (<u>Callinectes sapidus</u>) |
| Molluscs | | |
| | 57 | Eastern oyster (<u>Crassostrea virginica</u>) |
| | 59 | Brackish-water clam (<u>Rangia cuneata</u>) |
| Fish | | |
| | 107 | Drum (<u>Sciaenidae</u>) |
| | 119 | Sheepshead (<u>Argosargus probatocephalus</u>) |
| | 120 | Southern flounder (<u>Paralichthys lethostigma</u>) |
| Birds | | |
| Shore birds | | |
| | 551 | Gulls and terns (<u>Laridae</u>) |
| | 557 | Least tern (<u>Sterna albifrons</u>) |
| | 562 | American avocet (<u>Recurvirostra americana</u>) |
| | 563 | Forster's tern (<u>Sterna forsteri</u>) |
| | 567 | Black skimmer (<u>Rynchops nigra</u>) |
| Wading birds | | |
| | 601 | Herons (<u>Ardeinae</u>) |
| | 602 | Egrets (<u>Ardeinae</u>) |
| | 606 | White-faced ibis (<u>Plegadis chihi</u>) |
| | 607 | White ibis (<u>Eudocimus albus</u>) |
| | 608 | Roseate spoonbill (<u>Ajaia ajaia</u>) |
| | 609 | Great egret (<u>Casmeriodus albus</u>) |
| | 611 | Louisiana heron (<u>Hydranassa tricolor</u>) |
| | 614 | Cattle egret (<u>Bubulcus ibis</u>) |
| Waterfowl | | |
| | 651 | Dabbling ducks (<u>Anatinae</u>) |
| Raptors | | |
| | 711 | Red-shouldered hawk (<u>Buteo lineatus</u>) |
| | 753 | Olivaceous cormorant (<u>Phalacrocorax olivaceus</u>) |

--Habitat Use

| | | | |
|---|----------------------------|---|--------|
| a | Breeding area | w | Spring |
| b | Nursery area | x | Summer |
| g | Commercial harvesting area | y | Fall |
| h | Sport fishing/hunting area | z | Winter |

APPENDIX A. Chloroparaffin residue levels in the Schuylkill River near Conchohocken, Pennsylvania predicted by Versar Inc. (1985) based on uncontrolled and controlled release estimates.

Predicted Chlorowax 500-C Residue Levels

| Segment Location | Water (ug/l) | | Sediment (ppm) - Total | Biota (ppm) |
|------------------|--------------|-------|---------------------------|----------------|
| | Dissolved | Total | | |

Uncontrolled Releases

| | | | | |
|-----------------------|------|------|------|----|
| Below Discharge Point | 0.26 | 0.50 | 0.44 | 33 |
|-----------------------|------|------|------|----|

System self-purification time is roughly 5 months.

Controlled Releases

| | | | | |
|-----------------------|-------|------|------|-----|
| Below Discharge Point | 0.009 | 0.02 | 0.02 | 1.2 |
|-----------------------|-------|------|------|-----|

System self-purification time is roughly 5 months.

Predicted Chlorowax 70 Residue Levels

| Segment Location | Water (ug/l) | | Sediment (ppm) Total | Biota (ppm) |
|------------------|--------------|-------|-------------------------|----------------|
| | Dissolved | Total | | |

Uncontrolled Residues

| | | | | |
|-----------------------|-------|-----|-----|-------|
| Below Discharge Point | 0.007 | 9.7 | 2.6 | 1,344 |
|-----------------------|-------|-----|-----|-------|

System self-purification time is roughly 27 months.

Controlled Residues

| | | | | |
|-----------------------|----------|-------|--------|-----|
| Below Discharge Point | 0.000001 | 0.002 | 0.0005 | 0.3 |
|-----------------------|----------|-------|--------|-----|

System self-purification time is roughly 27 months.

APPENDIX A (cont.). Chloroparaffin residue levels in Sugar Creek near Dover, Ohio predicted by Versar Inc. (1985) based on uncontrolled and controlled release estimates.

Predicted Chlorowax 500-C Residue Levels

| Segment Location | Water (ug/l) | | Sediment (ppm) Total | Biota (ppm) |
|------------------|--------------|-------|-------------------------|-------------|
| | Dissolved | Total | | |

Uncontrolled Releases

| | | | | |
|------------------|-----|-----|-----|-----|
| Discharge Point | 2.1 | 4.1 | 3.6 | 274 |
| Below Confluence | 0.4 | 0.7 | 0.6 | 49 |

System self-purification time is roughly 4 months.

Controlled Releases

| | | | | |
|------------------|------|------|------|-----|
| Discharge Point | 0.07 | 0.14 | 0.13 | 10 |
| Below Confluence | 0.01 | 0.03 | 0.02 | 1.7 |

System self-purification time is roughly 4 months.

Predicted Chlorowax 70 Residue Levels

| Segment Location | Water (ug/l) | | Sediment (ppm) Total | Biota (ppm) |
|------------------|--------------|-------|-------------------------|-------------|
| | Dissolved | Total | | |

Uncontrolled Residues

| | | | | |
|------------------|------|----|------|--------|
| Discharge Point | 0.06 | 76 | 20.5 | 10,550 |
| Below Confluence | 0.01 | 14 | 3.9 | 2,003 |

System self-purification time is roughly 18 months.

Controlled Residues

| | | | | |
|-----------------------|----------|-------|--------|-----|
| Below Discharge Point | 0.00001 | 0.015 | 0.004 | 2.1 |
| Below Confluence | 0.000002 | 0.003 | 0.0008 | 0.4 |

System self-purification time is roughly 18 months.

APPENDIX A (cont.). Chloroparaffin residue levels in the Houston Ship Channel/
Galveston Bay area, Texas predicted by Versar Inc. (1985) based on
uncontrolled release estimates.

| Segment Location | Predicted Chlorowax 500-C Residue Levels | | | |
|---|--|-----------------------|-------------------------|----------------|
| | Dissolved | Water (ug/l) Total | Sediment (ppm) Total | Biota (ppm) |
| <u>Uncontrolled Releases</u> | | | | |
| Houston Ship Channel (west of mouth of San Jacinto River) | 0.76 | 1.4 | 1.3 | 100 |
| Houston Ship Channel (west of Scott Bay) | 0.67 | 1.3 | 1.2 | 87 |
| Houston Ship Channel (west between Scott Bay and Tabbs Bay) | 0.60 | 1.2 | 1.0 | 78 |
| Houston Ship Channel (between Tabbs Bay and Morgans Point) | 0.56 | 1.1 | 0.95 | 72 |
| Barbours Cut | 0.55 | 1.0 | 0.94 | 71 |
| San Jacinto River | 0.39 | 0.8 | 0.68 | 51 |
| Scott Bay | 0.51 | 1.0 | 0.87 | 66 |
| Tabbs Bay | 0.33 | 0.6 | 0.57 | 43 |
| Galveston Bay | 0.26 | 0.5 | 0.45 | 34 |
| Upper San Jacinto Bay | 0.24 | 0.4 | 0.42 | 32 |
| Burnet Bay | 0.08 | 0.2 | 0.14 | 10 |

System self-purification time is roughly 28 months

| Predicted Chlorowax 70 Residue Levels | | | | |
|--|-------|---------|-----|-------------|
| <u>Uncontrolled Releases</u> | | | | |
| Upper most part of the Houston Ship Channel | 0.006 | 8.7 | 2.4 | 1,233 |
| San Jacinto River and Galveston Bay | 0.003 | 3.8-4.0 | 1.1 | 545-571 |
| Lower Houston Ship Channel and other areas | 0.006 | 7.4-7.5 | 2.1 | 1,065-1,074 |

System self-purification time is roughly 74 months.

APPENDIX A (cont.). Chloroparaffin residue levels in the Houston Ship Channel/
Galveston Bay area, Texas predicted by Versar Inc. (1985) based on
controlled release estimates.

| Segment Location | Predicted Chlorowax 500-C Residue Levels | | | |
|--|--|-------|----------------|-------|
| | Water (ug/l) | | Sediment (ppm) | Biota |
| | Dissolved | Total | Total | (ppm) |
| <u>Controlled Releases</u> | | | | |
| Houston Ship Channel (west of mouth of San Jacinto River) | 0.06 | 0.12 | 0.10 | 8.0 |
| Houston Ship Channel (west of Scott Bay) | 0.03 | 0.06 | 0.05 | 3.9 |
| Houston Ship Channel (between Scott Bay and Tabbs Bay) | 0.03 | 0.05 | 0.05 | 3.5 |
| Houston Ship Channel (between Tabbs Bay and Morgans Point) | 0.02 | 0.05 | 0.04 | 3.2 |
| Barbours Cut | 0.02 | 0.05 | 0.04 | 3.2 |
| San Jacinto River | 0.02 | 0.03 | 0.03 | 2.0 |
| Scott Bay | 0.02 | 0.04 | 0.04 | 2.9 |
| Tabbs Bay | 0.01 | 0.03 | 0.03 | 1.9 |
| Galveston Bay | 0.01 | 0.02 | 0.02 | 1.5 |
| Upper San Jacinto Bay | 0.01 | 0.02 | 0.02 | 1.4 |
| Burnet Bay | 0.004 | 0.007 | 0.01 | 0.5 |

purification time is roughly 20 months.

| | | | | |
|--|-----------|----------|--------|-----|
| Upper most part of the Houston Ship Channel | 0.000002 | 0.003 | 0.0008 | 0.4 |
| San Jacinto River and Galveston Bay | 0.0000006 | 0.0007-8 | 0.0002 | 0.1 |
| Lower Houston Ship Channel and other areas | 0.000001 | 0.0001 | 0.0004 | 0.2 |

System self-purification time is roughly 53 months.

APPENDIX B. Results of Phase II testing of 58 % Chlorinated Short-Chain Length (C₁₀₋₁₂) n-Paraffins on additional species.

| Test Species | Test Type | LC50 | Overall MATC | MATC Hatchability (percent) | MATC Survival (percent) | MATC % Growth Rate Length | Weight |
|--|------------------------------|--|---|---|--|---|---|
| <u>Sheepshead Minnow</u> <u>Cyprinodon variegatus</u> | Embryo-larvae (Study # 1) | | > 2.4 < 4.1-55 ug/l (increased growth) | > 55 ug/l (77 - 95) | > 55 ug/l (68 - 90, 88 -100) | > 2.4 - 55 ug/l (4 - 7 % increase) | > 2.4 < 4.1-55 ug/l (14 - 31 % increase) |
| | (Study # 2) | | < 36-71 < 162 ug/l (increased growth) | > 620 ug/l (80 - 95) | > 620 ug/l (65.8- 90.7, 75.8-100) | < 36- 71 < 162 ug/l (5 - 7 % increase) | < 36- 71 < 162 ug/l (15 - 21 % increase) |
| | | | > 280 < 620 ug/l (reduced growth) | | | > 280 - < 620 ug/l (9 % red.) | > 280 - < 620 ug/l (31% red.) |
| <u>Waterflea</u> <u>Daphnia magna</u> | Life-cycle | 530 ug/l* | < 2.7 ug/l* | < 2.7 ug/l* | > 5.0 - | > 8.9 ug/l* | |
| | | 46 ppb (48-hr EC50) 12 ug/l* > 8.9 < 16.3 ug/l (6-21 day EC50) | (reduced young per female) < 8.9 ug/l* (66 % red. in total reprod.) | (44 % red. offspring /female) | < 8.9 ug/l* (37 % dead offspring not sign.) | (1 % red.) | |
| <u>Mysid Shrimp</u> <u>Mysidopsis bahia</u> | Life-cycle | 14.1 ug/l* | > 7.3 < 13.7 ug/l* | > 5.0 - | > 0.5 - | > 7.3 ug/l | > 7.3 ug/l |
| | | < 14.1 ug/l (96-hr LC50) | > 0.6 < 1.2 ug/l (sign. parental mortality) | < 7.3 ug/l (33 % red. offspring /female) | < 1.2 ug/l (40-50 % parental deaths) | (1 % increase) | (0.4 % reduction) |
| <u>Midge</u> <u>Chironomus tentans</u> | Life-cycle | > 162 ug/l | > 60 < 78 ug/l | > 60 - | > 78 - | < 78 ug/l | < 78 ug/l |
| | | (48-hr LC50 no deaths) | (red. hatching) | < 78 ug/l (60 % red. hatching) | < 121 ug/l (no emergence) | (10 % red. in eggs/mass) | (1 % red. in hatch) |

* Data value can not be used with confidence.

APPENDIX B (cont.)

| Test Species | Test Type | LC50 | MATC | Cell Growth (particle count) |
|--|-----------|--|--|--|
| Green Alga <u>Selenastrum</u> <u>capricornatum</u> | Acute | 3,690 ug/l* > 1,200 ug/l (96-hr EC50) | > 390 < 570 ug/l (35 % reduction in growth) | > 390 < 570 ug/l (35 % reduction in cell growth) |
| | | 1,310 ug/l* > 1,200 ug/l (10-day EC50) | | |
| Marine Alga <u>Skeletonema</u> <u>costatum</u> | Acute | 31.6 ug/l (48-hr EC50) | > 12.1 < 19.6 ug/l (44 % reduction in growth on Day 2) | > 12.1 < 19.6 ug/l (44 % reduction in growth on Day 2) |
| | | 42.3 ug/l (96-hr EC50) | > 19.6 < 43.1 ug/l (Day 4 - 34 % red.) | > 19.6 < 43.1 ug/l (Day 4 - 34 % red.) |
| | | > 69.8 ug/l (10-day EC50) | > 69.8 ug/l (Day 10 - no sign.) | > 69.8 ug/l (Day 10 - no sign.) |

* Data can not be used with confidence.