United States
Environmental Protection
Agency

Office of Toxic Substances
Exposure Evaluation Division
Washington, DC 20460

EPA 560/5-87-012
February 1988

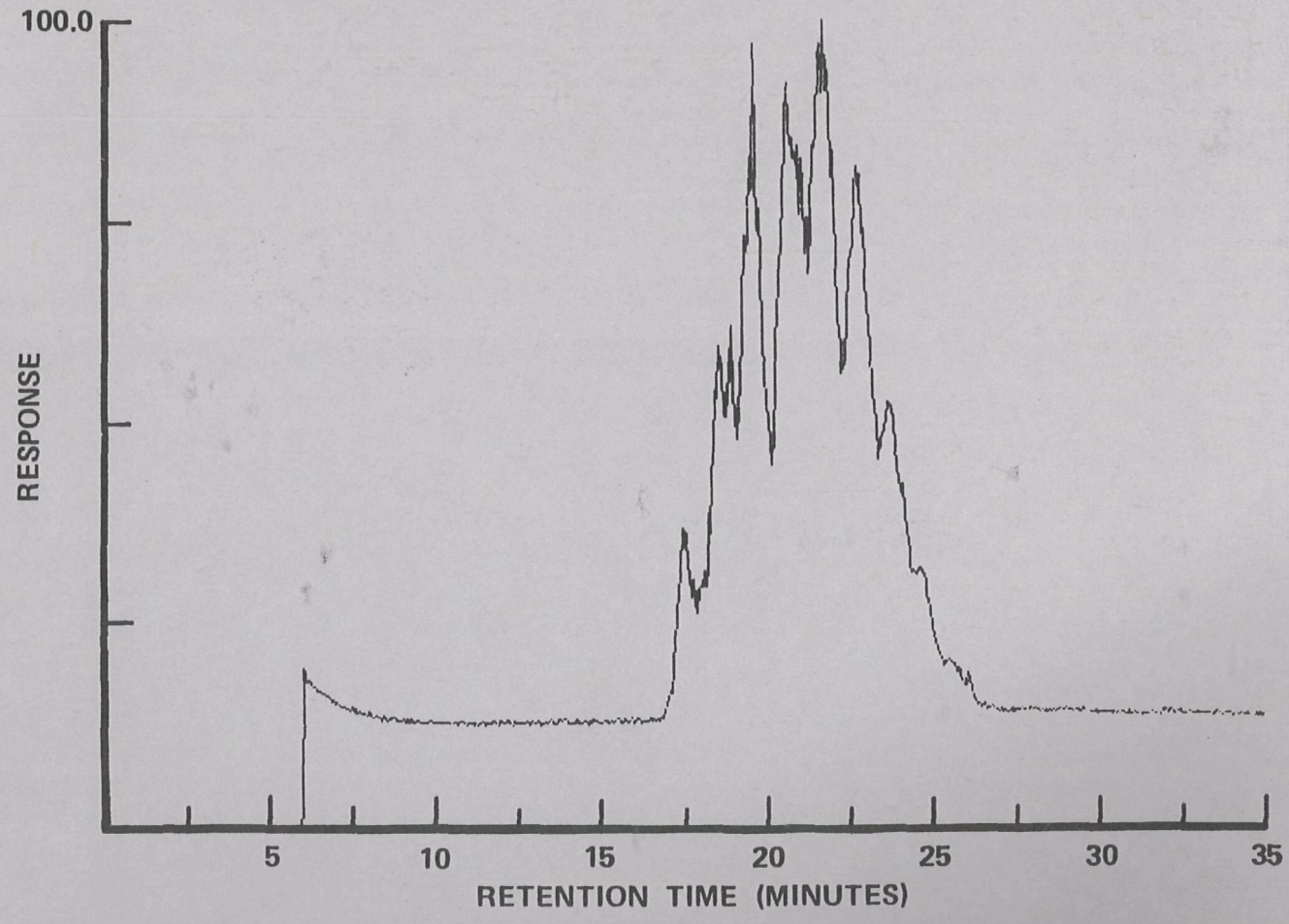
Toxic Substances

EPA

Chlorinated Paraffins

A Report on the Findings from Two Field Studies Sugar Creek, Ohio Tinkers Creek, Ohio

Volume I – Technical Report



CHLORINATED PARAFFINS

A REPORT ON THE FINDINGS FROM TWO FIELD STUDIES

SUGAR CREEK, OHIO AND TINKERS CREEK, OHIO

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JANUARY 22, 1988

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AUTHORS AND CONTRIBUTORS

The information contained in this report represents the joint efforts of several organizations and many individuals. Names of the principal authors and the contributions of the various organizations are summarized below.

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ACKNOWLEDGMENTS

The Environmental Protection Agency (EPA) expresses its appreciation to the managements and staffs of those industrial facilities involved in these studies for their cooperation and valuable assistance. EPA also acknowledges the cooperation and valuable assistance of EPA Region V, especially Ms. Francine Norling, and the State of Ohio EPA, especially Mr. John Estenik and Mr. Eric Nygard.

Valuable advice was provided by Dr. Peter Schmid of the Institute of Technology, Swiss Federal Institute of Technology and University of Zurich and Dr. Ian Campbell of the Imperial Chemical Industries Ltd., United Kingdom.

PREFACE

This report details the results of two field studies whose objective was to collect environmental information that would help EPA determine, preliminarily, if chlorinated paraffins (CPs) exist in selected water environments and at what concentrations. The first waterbody selected for this study is a stream receiving waste discharged from a CP manufacturer; the second waterbody is a stream receiving discharge from a plant known to use lubricating oils likely to contain CPs. The information gained from these field studies will be coupled with that from other environmental and health studies to collectively contribute to a risk assessment for chlorinated paraffins.

These field studies were completed cooperatively by an EPA Office of Toxic Substances Exposure Technical Team and under two EPA contracts. The first is Midwest Research Institute, No. 68-02-4252, Work Assignment 53, "Chloroparaffins Environmental Field Study." Mr. Tom Murray is the EPA Work Assignment Manager and Dr. Joseph Breen, the EPA Project Officer. Mr. David Steele is Midwest Research Institute's Work Assignment Leader.

The second contract is Battelle Columbus Division, No. 68-02-4243, WA# 2-33. Ms. Mary Frankenberry is the EPA Work Assignment Manager and Ms. Cindy Stroup, the EPA Project Officer. Dr. J. Chesson, Dr. Michael Samuhel, and Ms. Barbara Leczynski were the Battelle Columbus Division Project Managers; they were assisted by Mr. Robert Heath, consultant to Battelle Columbus Division.

EXECUTIVE SUMMARY

This report presents the results of two field studies conducted in 1986 by the Environmental Protection Agency to measure chlorinated paraffins (CPs) in segments of two watersheds: Sugar Creek, Ohio and Tinkers Creek, Ohio. The objective of these field studies was to collect environmental information that would help EPA determine, preliminarily, if chlorinated paraffins exist in these watersheds and at what concentrations. These watersheds were selected for study because of their association with a known CP manufacturer (Sugar Creek) and a user of lubricating oils which commonly contain CPs (Tinkers Creek).

The results from these field studies will be combined with other environmental and health data and collectively contribute to an EPA risk assessment for CPs. The field study results are summarized below:

Sugar Creek, Ohio

Analysis of the first of three sets of environmental samples collected from this study site shows that chlorinated paraffins, represented in this study by three technical mixtures (short-chain C_{10-12} (50-60% Cl), medium-chain C_{14-17} (50-60% Cl), and long-chain C_{20-30} (40-50% Cl) CPs), are generally present at quantifiable concentrations in the parts-per-billion to parts-per-million range in both the discharge from the CP manufacturing plant and in Sugar Creek downstream from the discharge. These CPs are most prevalent in the sediment, suspended particulates, and biological matrices. The findings that chlorinated paraffins are adsorbed very strongly to sediments and suspended solids in water confirm those of Campbell and McConnell (Campbell and McConnell 1980). Where detected in the filtered water, these CPs were generally present in trace (low parts-per-billion) amounts. Of the three CPs addressed by this study, the long-chain C_{20-30} (40-50% Cl) CP was found at the highest levels.

The highest CP concentrations were found in the surface impoundment lagoon which sequesters the manufacturing plant effluent before allowing it to discharge to Sugar Creek. Here, quantifiable concentrations as high as 170,000 µg/kg were found in the lagoon sediments. Measurements made in the ditch which carries the lagoon drainage to Sugar Creek showed concentrations as high as 3,600 µg/kg in the sediments. Concentrations were also recorded in Sugar Creek downstream from the drainage ditch confluence ranging from trace levels to 21 µg/kg. Generally, concentrations measured in the particulates were less than those

in the sediments and those measured in the filtered water fraction less still. However, concentrations measured in the biological matrices (mussels) ranged as high as 280 µg/kg in Sugar Creek downstream from the drainage ditch. Few quantifiable concentrations of CPs were found in Sugar Creek upstream of the influence of the drainage ditch.

Because only one set of samples was analyzed, the statistical significance of differences between the concentrations found upstream of the drainage ditch and those found downstream from the ditch cannot be properly tested. However, the relative differences in CP levels, coupled with the consistency of the chemistry, strongly suggest that the manufacturing plant and its surface impoundment lagoon is a major contributor of CPs to Sugar Creek.

Modeling estimates of in-stream concentrations of CPs for Sugar Creek, calculated using actual environmental releases measured during this field study, compare well with the actual environmental levels measured in the stream. While too few field data were collected during this study to fully validate the model, the correspondence between model predictions and field measurements adds credibility to the further use of these modeling techniques in predicting pollutant loadings in other areas to which chlorinated paraffins of the types considered by this report may be discharged.

Tinkers Creek, Ohio

Analysis of the first of three sets of environmental samples collected from this study site failed to detect CPs in any of the samples collected near the outfall of the lubricating oil user or in the drainage network carrying its discharge to Tinkers Creek. Most of the samples analyzed from this site, especially the sediment samples, contained a variety of organic constituents which would have masked the presence of any CPs. Chlorinated paraffins, however, were measured in the low parts-per-billion range in one sample collected from the process wastestream of the lubricating oil user located at this site.

CONTENTS

APPENDICES

FIGURES

TABLES

TABLES (Continued)

CHAPTER I. INTRODUCTION

This report presents the initial results of two field studies conducted in 1986 by the Environmental Protection Agency's Office of Toxic Substances (EPA/OTS) under the Existing Chemicals Program to screen selected waterbodies for the presence of chlorinated paraffins (CPs). The information gained from these field studies will be coupled with that from other environmental hazard and environmental exposure studies and collectively contribute to an EPA risk assessment for this class of chemical.

PROJECT BACKGROUND

Chlorinated paraffins are saturated straight-chain hydrocarbons ranging from 10 to 30 carbons in length and containing 20 to 70 percent chlorine by weight ($C_xH_{(2x-y+2)}Cl_y$). Commercially available CPs are complex mixtures of varied chain lengths and chlorinated isomers which are distinguished by the average carbon chain length and the degree of chlorination. These mixtures, often described as a 9-cell matrix (Fig. 1), are marketed mainly as high pressure lubricants, flame retardants, and secondary plasticizers.

In 1977, in anticipation that the Interagency Testing Committee (ITC) would recommend chlorinated paraffins for environmental and health effects testing, a group of CP producers formed the Chlorinated Paraffins Consortium. This Consortium, in consultation with EPA, developed a phased testing scheme for CPs. Independently, the National Toxicology Program (NTP) tested two CPs for carcinogenicity. The ITC did recommend CPs for testing, but the Agency published a decision in 1982 not to require testing beyond those already undertaken by the industry and the NTP. In 1983, the results of the environmental testing prompted the Consortium to submit a Notice of Substantial Risk under section 8(e) of the Toxic Substances Control Act (TSCA). After the test results were validated by EPA, it was decided that hazard and exposure assessments and, subsequently, an environmental risk assessment should be prepared.

In 1984, EPA completed a draft hazard assessment for CPs (USEPA 1984) based in large part on the consortium data. This assessment reported acute toxicity (Phase I) information which showed chlorinated paraffins to be toxic to mussels and rainbow trout at concentrations as low as a few parts per billion. It also reported that the 58% chlorinated short-chain (C_{10-12}) paraffin was the most toxic of the four formulations tested. The assessment also reported the results of chronic toxicity (Phase II, life cycle) studies on a variety of test species which showed statistically significant ($P \leq 0.05$) toxic effects at measured concentrations of the 58% chlorinated short-chain

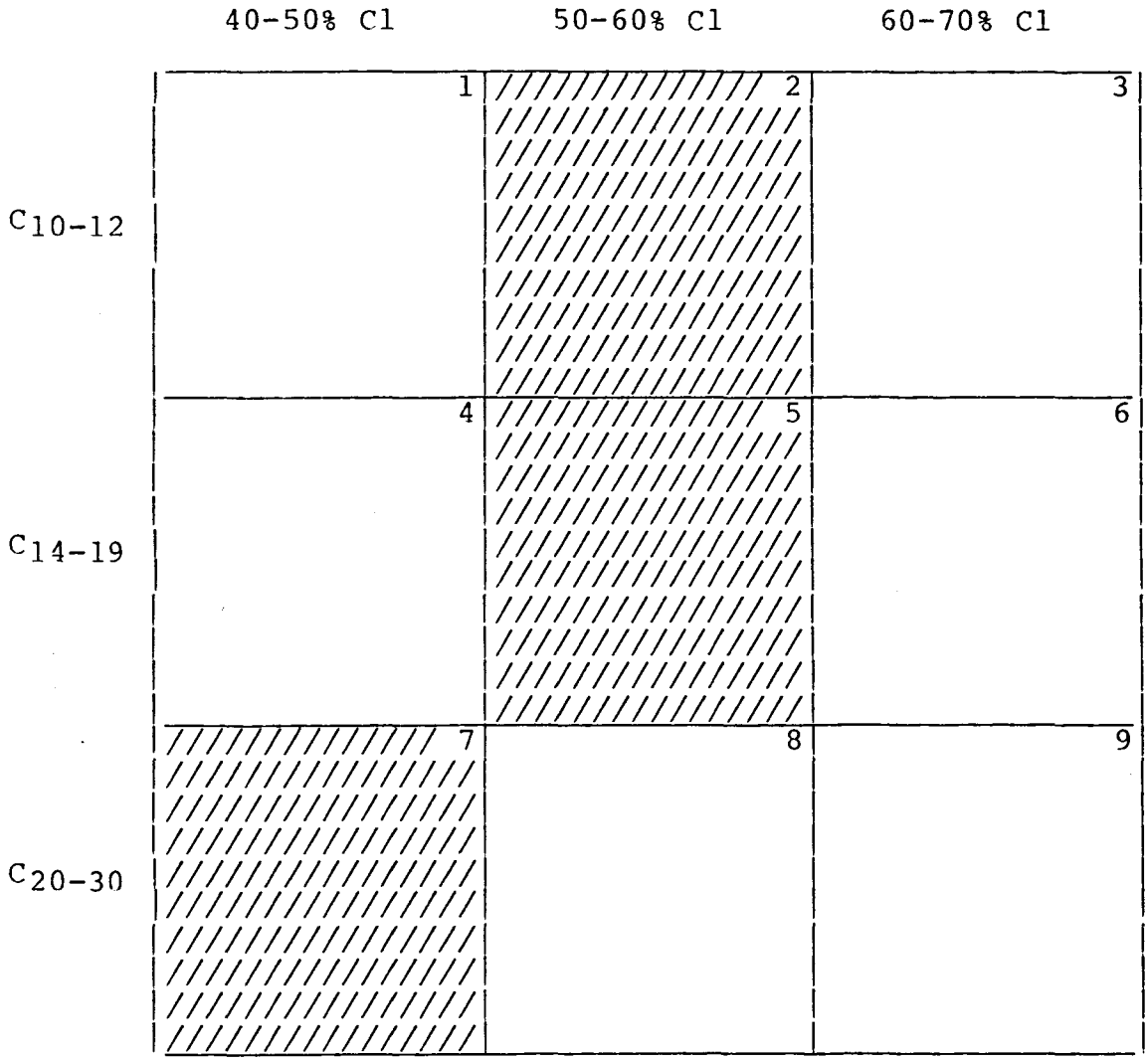

FIG. 1. - Commercially Available Chlorinated Paraffins

The rows represent the different paraffin carbon chain-lengths commonly manufactured. The columns represent the range of percent chlorination commonly applied to the paraffins. The resulting nine cells represent the full array of chlorinated paraffin mixtures commercially available.

Analytical measurements for this study are based on standards obtained for the CPs which are shaded.

(C_{10-12}) paraffin of less than 10 µg/L for sheepshead minnow, daphnids, and mussels and at less than 20 µg/L for rainbow trout, mysid shrimp, and marine algae. The chronic effects of the short-chain 58% chlorinated paraffin included abnormal behavior, growth effects, reduced reproduction and lethality.

The NTP test data showed clear evidence of carcinogenicity in rats and mice, both sexes, for a C_{12} (58% Cl) CP. It also showed mixed results, ranging from no evidence to clear evidence of carcinogenicity, for a C_{23} (43% Cl) CP.

While sufficient information was available to perform an environmental hazard assessment, there was a paucity of information with which to prepare an environmental exposure assessment. Only three previous studies were available: two performed for the Diamond Shamrock Corporation at its Houston, Texas, and Grand River, Ohio, locations (Ramm 1978, Ramm 1977) and a third by ICI Limited at selected sites in Great Britain (Campbell, 1980). EPA also conducted a modeling analysis which predicted environmental levels based on available release estimates and professional judgement. These studies, while providing useful insight into CP levels in environmental samples, fell short of providing the specific data necessary to prepare an exposure assessment, i.e. measurements of specific CPs quantitated in the low parts-per-billion range. This paucity of information prompted several actions. First, an analytical method was sought that could discriminate the various CPs shown in the 9-cell matrix (See Fig. 1) with priority given to those for which specific toxicity information was available. Further, it must be able to measure these CPs in different environmental matrices, and surmount any potential analytical interferences of other organochlorine compounds. Second, the method of choice must be carefully evaluated and validated using reliable standards. Third, the method must be applied to field samples collected according to a sound sample design.

STUDY OBJECTIVE

The objective of these field studies was to collect information that will help EPA determine, preliminarily, if chlorinated paraffins exist in select water environments--i.e. in the water column (including suspended material), sediment and/or biological tissue--and, if so, at what concentrations. Because chlorinated paraffins in the United States are used predominantly in lubricating oils (50% of total U.S. consumption), site selections for this study were based on the assumption that if CPs exist in the aquatic environment, they will most likely be found in waters receiving discharge from CP manufacturers, processors of CP-containing lubricating oils, and users of these oils.

Two areas were selected for study based on this premise: Sugar Creek in Dover, Ohio, the site of a CP manufacturing plant; and Tinkers Creek near Bedford, Ohio, the site of a lubricating oil user.

A critical first step to the development of these field studies was to develop and validate an analytical method capable of measuring specific chlorinated paraffins in different environmental matrices. Therefore, the following five additional objectives were established, specific to this activity. The analytical procedure must be able to:

- o discriminate specific CPs (see Fig. 1), with priority given to those CPs for which toxicity information was available.
- o reach a limit of detection in the low ppb range.
- o obtain CP concentrations for replicate spiked samples with a range percent (precision) of less than 30% of the mean of these values.
- o obtain CP concentrations with a percent difference (accuracy) of less than 30% of the actual CP concentration.
- o establish a recovery efficiency in the range of 70-130%.

The study, therefore, consisted of the following tasks:

1. Develop, and validate with field samples, an analytical method for measuring specific CPs in water, suspended solids, sediment, and biota.

2. Develop a Quality Assurance/Quality Control (QA/QC) Project Plan (QAPP) and a field study and sampling design for the study. (These were combined to form one document.)

3. Conduct a reconnaissance survey of each study site.

4. Finalize the study and sampling designs with information obtained from the reconnaissance surveys.

5. Collect field samples from the study sites following the protocol described in the QAPP.

6. Perform the necessary laboratory analyses of the samples collected from the field.

7. Analyze data; prepare results and conclusions.

8. Write draft and final reports.

The remainder of this report describes the development of the analytical protocol, the field study selection process, field sampling and the analytical results and conclusions of the study. The Quality Assurance Project Plan for this study is found in Appendix D and is available under separate cover (USEPA, 1986).

CHAPTER II. SITE SELECTION PROCESS

The objective of these field studies was to collect information that will help EPA determine, preliminarily, if CPs exist in selected water environments and at what concentrations.

Field study sites were selected on the premise that if CPs exist in the aquatic environment, they would most likely be found in waters receiving discharge from CP manufacturers, processors of CP-containing lubricating oils, and users of these oils. Therefore, the prime criterion for selecting sites was the presence of a discharger which fell into one of these three categories. Beyond this, candidate sites were evaluated using the following selection criteria.

1. A simple hydrology was preferred: one with few confounding hydrologic influences and the appropriate environmental media characteristics and conditions for collecting water, sediment, and biological samples.

2. A single discharge scenario was preferred not only to facilitate a classic upstream vs. downstream evaluation but also to reduce the likelihood of matrix interferences caused by other point source discharges.

3. Inclusion of an upstream site, remote from the influence of any point source discharge, was preferred. This upstream site would serve as a control site.

4. Good cooperation was needed at the EPA Region, State, and facility level to promote effective planning and field sampling.

All sites receiving discharge from known CP manufacturing plants and lubricating oil processors were identified. After careful consideration, the site that best met the selection criteria was Sugar Creek, Dover, Ohio, which is the receiving water for a CP manufacturer. No sites were selected to represent lubricatinng oil processors because of hydrological complexity.

Considerable effort was then made to locate a potential lubricating oil user site. Only one user site could be identified and this site did not meet all of the selection criteria defined for the study. However, as the only user site candidate, the decision was made to sample this area with the understanding that while it may not provide the depth of information expected from the Sugar Creek site, any information collected there would

advance EPA's current understanding of CP levels in the aquatic environment. The lubricating oil user site is Tinkers Creek, Bedford, Ohio.

These sites are described in detail in the following sections.

CHAPTER III. FIELD STUDY SITE 1--SUGAR CREEK, OHIO

DESCRIPTION OF THE STUDY AREA

Sugar Creek is located in east central Ohio. From its source in Wayne County near Wooster, Ohio, it flows south-southeast toward its confluence with the Tuscarawas River. Near Beach City, Ohio, Sugar Creek is impounded. Here it recharges the aquifer supplying the city of Canton's well field.

The drainage basin of Sugar Creek is largely rural. It is classified by the Ohio EPA as a warm water habitat. The focus of this field study was on the lower four miles of Sugar Creek from below Strasburg to its mouth with the Tuscarawas River. A map of the Sugar Creek study area is given in Figure 2.

Waste Inputs

The only point source discharges to this segment of Sugar Creek are from the Dover Chemical Corporation facility (River Mile(RM) 1.8) and the city of Strasburg wastewater treatment plant (RM 7.3). Acid mine drainage from Goettge Run (RM 1.8) is a principal nonpoint source of pollution.

Dover Chemical Corporation was the outfall of interest to this study. Dover Chemical Corporation is a major manufacturer of chlorinated paraffins, with an annual production capacity of 45 million pounds. As such, Dover Chemical produces about 21% of the total U.S. production (SRI 1986). Dover Chemical is located at 15th and Davis Streets in Dover, Ohio. At present, Dover Chemical continuously pumps approximately 2.2 mgd of water from two of their four wells and discharges 1.6-1.8 mgd of water. The Dover Chemical facility employs about 90 people and at the time of the study was operating 24 hours a day, 10 days on and 4 days off.

Chlorinated Paraffins Process Description

At a typical CP manufacturing plant, such as Dover Chemical, chlorine gas and paraffin are continuously reacted to form the chlorinated paraffins. Generally, excess chlorine (5-15%) must be used because the chlorination reaction is not 100%. Manufacture of resinous chlorinated paraffins requires the use of a solvent (usually carbon tetrachloride) during the chlorination process.

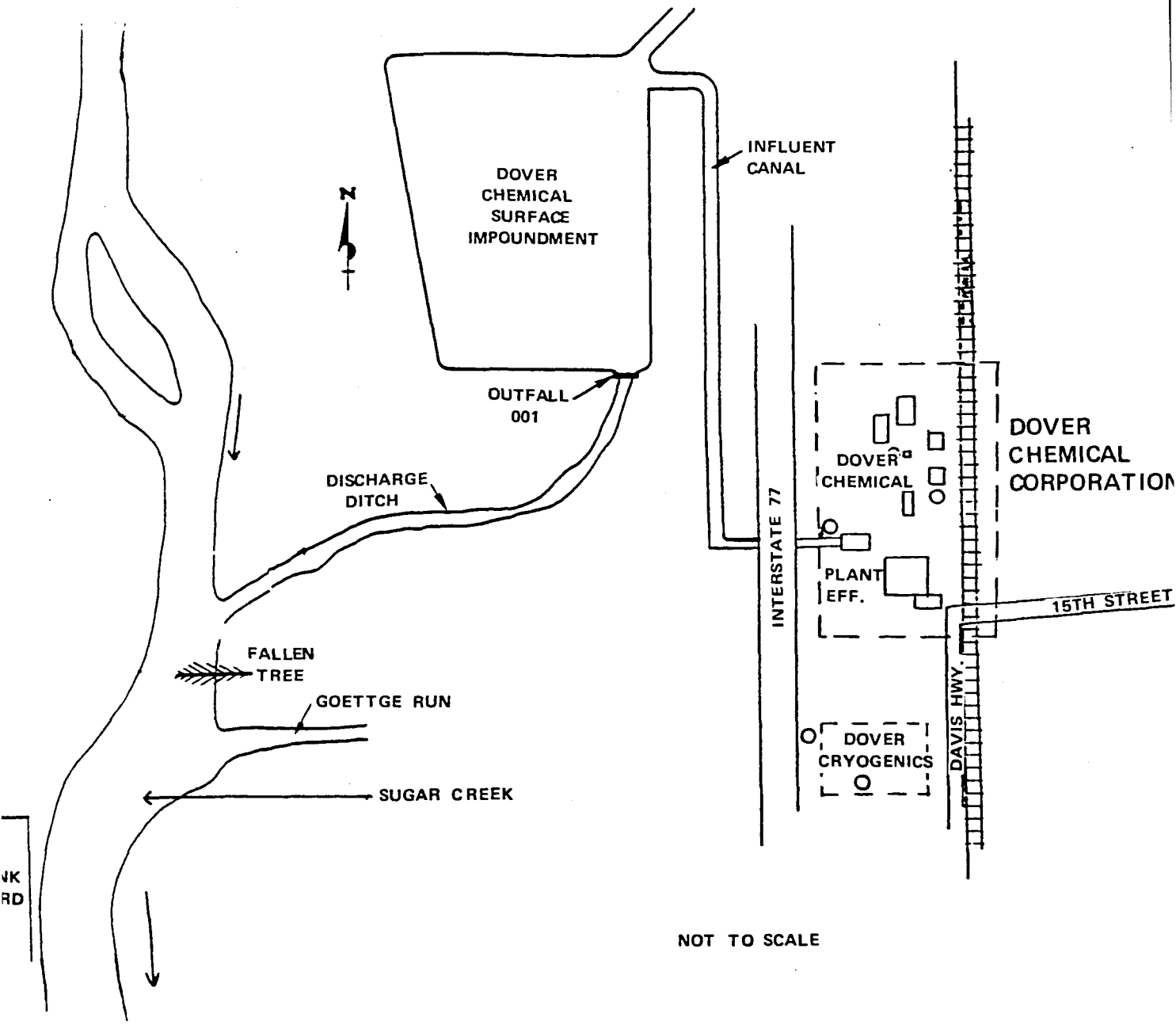

FIG. 2 -- Sugar Creek Study Site

Conventional soluble stabilizers may be blended with the chlorinated paraffin product to protect it from undue dehydrochlorination if elevated temperatures are encountered for extended periods of time during storage and subsequent use. Generally, up to 5%, by weight, of stabilizer is added.

Resinous products are piped from the reactor to a solvent stripping unit. Here, the product is passed through a degasser to vaporize the carbon tetrachloride. The carbon tetrachloride is then condensed and reused while the freed chlorine is used to produce sodium hypochlorite (bleach). After the chlorinated paraffin has passed through the degasser, it is deposited on a conveyor belt for water cooling with well water until hardened.

The resin dust from the grinding operation is collected by two dry dust collectors and then sold for use in making resin. The water used for cooling is sent to the treatment system.

Liquid chlorinated paraffins are manufactured in a batch reaction kettle. After reaction, the chlorinated paraffins are sent through a degasser for removal of hydrogen chloride gas which is used to make hydrochloric acid (HCl). The other product of this reaction is free chlorine gas which is used to make sodium hypochlorite. When the concentrations of gases in both by-products are too low to form their end products, they are water scrubbed. This scrubbing water is then sent to the water treatment system.

Chlorinated paraffins are packaged and shipped by a variety of methods. Liquid products are piped from the reactor to a holding tank from which they are packaged in steel drums or shipped, in bulk, by tank truck or rail car.

Chlorinated paraffin resin is ground, screened, and stored in fiber drums and multiwall Kraft bags prior to sale.

A schematic of a typical process for the manufacture of chlorinated paraffins is shown in Fig. 3.

Dover Chemical Corporation's Wastewater Treatment Process

Wastewater consists of noncontact cooling water, boiler blowdown ion exchange regenerant, scrubber water, and floor drainage. All wastewaters with the exception of noncontact

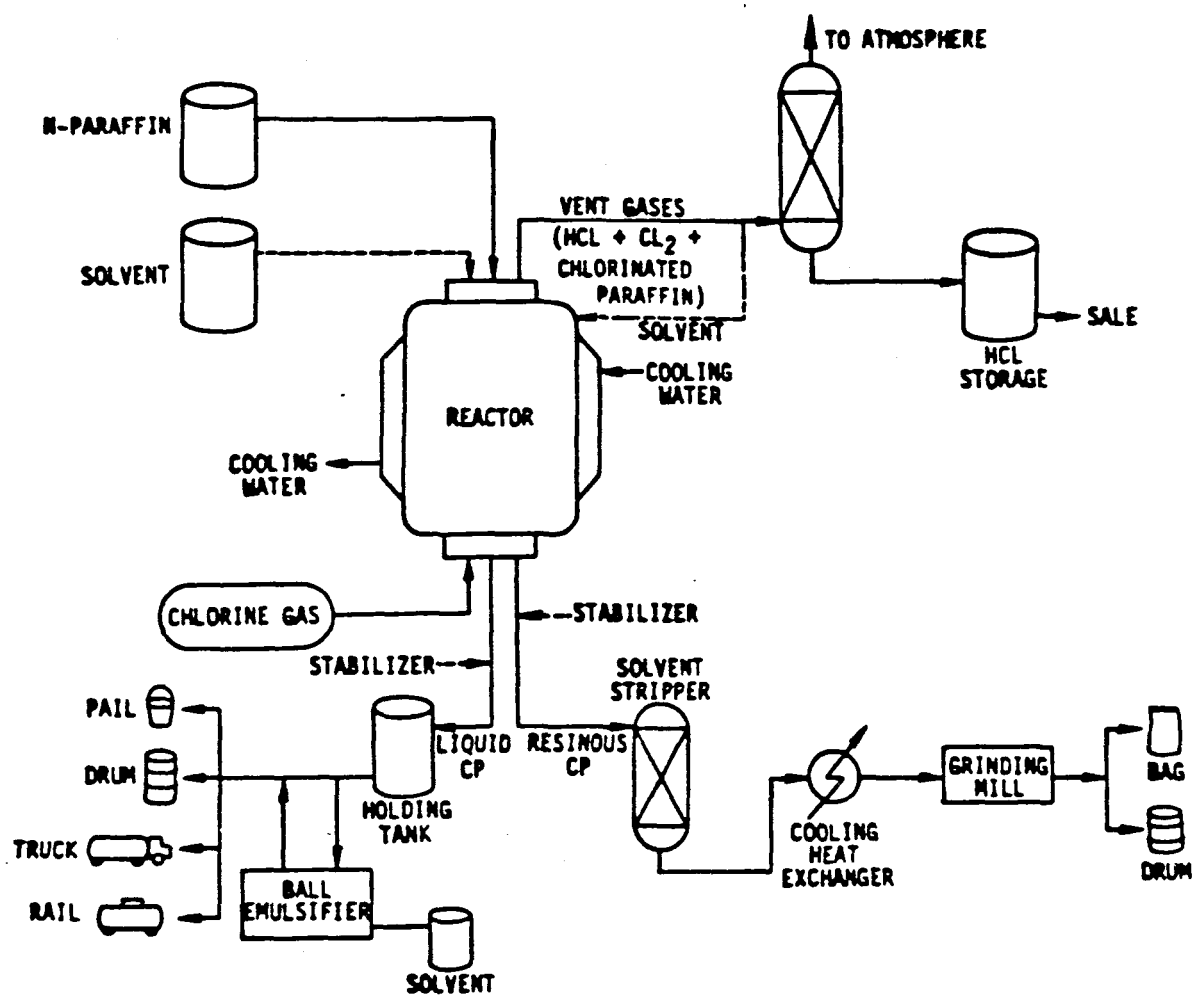

FIG. 3 Schematic of Process Followed in the Manufacture of Chlorinated Paraffins (Source: PEI 1984)

cooling water enter a 10,000 gallon settling tank which overflows into a limestone neutralizing bed. This first settling tank is equipped with both a rotating oil skimmer and a continuous belt skimmer. Oil and grease accumulated by the skimmers are transferred to a separation tank. The aqueous portion is returned to the first settling tank. Solids from the first tank are pumped to a 20,000 gallon tank for further separation. This tank is occasionally drained of the aqueous layer which is subsequently passed through an activated carbon bed prior to pumping to the first settling tank. Water passing through the limestone bed flows to the second settling tank which is equipped with an oil boom and underflow weir prior to discharging over a 4-ft rectangular weir with end contractions. Noncontact cooling water enters the second settling tank. The discharge flows several yards through a pipe and then enters a narrow canal. This canal carries the discharge to a surface impoundment lagoon. Discharge from the lagoon flows through a small ditch to Sugar Creek.

The surface impoundment lagoon is owned by the Dover Chemical Corporation. The impoundment is 8.6 acres in area and is approximately 23 ft deep in most places. It contains a captive population of fish, frogs, and turtles. The impoundment has flooded in the past, overflowing into Sugar Creek; however, no such incidents have occurred in the last 2 to 3 years.

A simple schematic diagram of the Dover Chemical Corporation's Wastewater Treatment Process is given in Fig. 4.

RECONNAISSANCE SURVEY

On August 12 and 13, 1986, a field team of Midwest Research Institute (MRI) and PEI Associates personnel and Robert Heath, consultant to Battelle Columbus Division, conducted a reconnaissance survey of the Sugar Creek field study site. The objectives of this reconnaissance visit were twofold: (1) to collect field samples for use in estimating the recovery efficiency and precision of the analytical method for CPs which was being validated at the time by MRI, and (2) to obtain the areal information necessary to prepare an efficient study design for the area.

In support of the first objective, water and sediment samples were collected from three sites (stations) in Sugar Creek.

- Site A - At Tuscarawas Road, downstream from the Dover Chemical facility discharge.

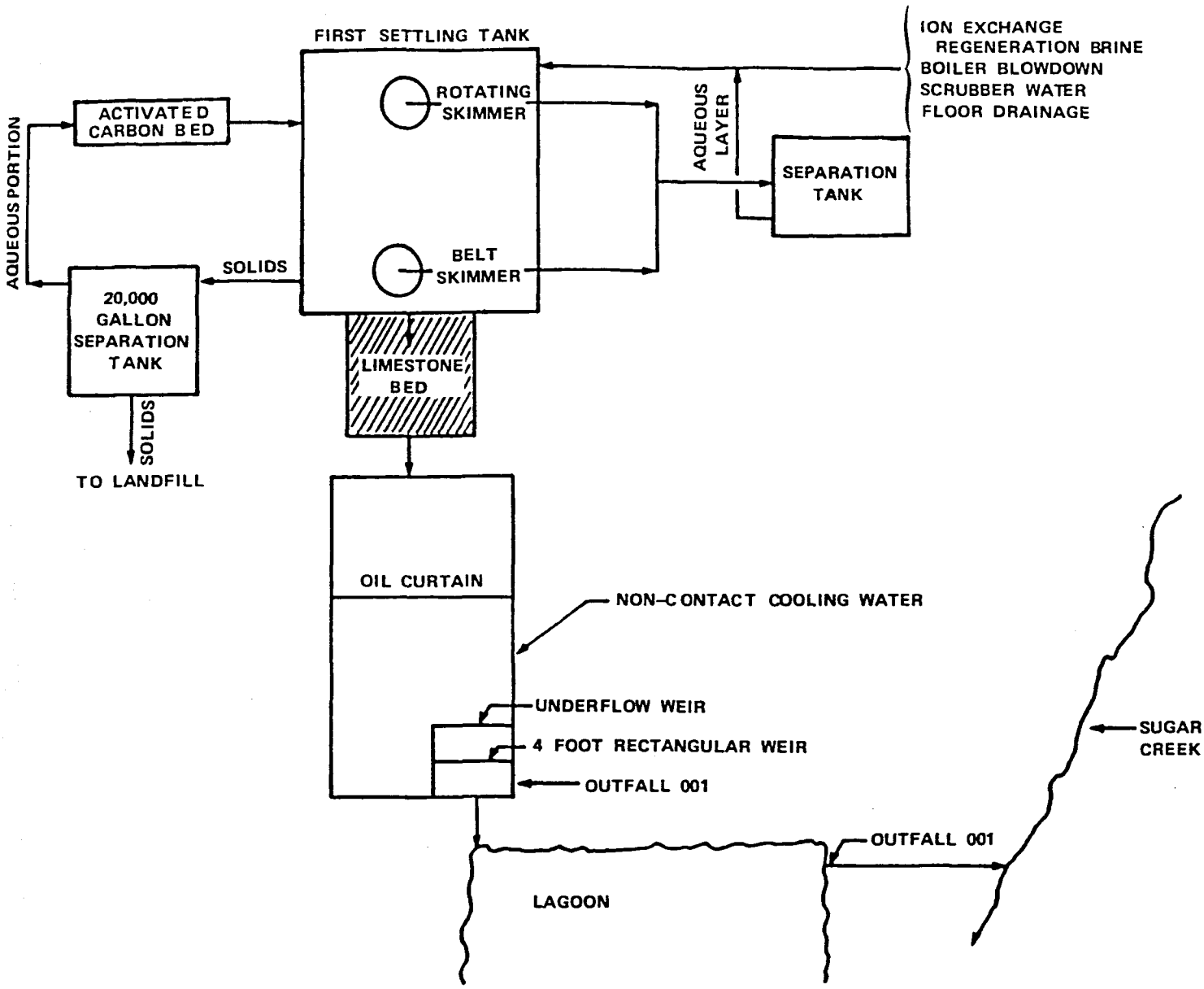

FIG. 4 -- Dover Chemical Corporation's Wastewater Treatment Process

- Site B - Upstream of Dover Chemical facility discharge under the bridge which carries the road to Winfield.

- Site K - Route 39 downstream from Site A and just above the confluence with the Tuscarawas River.

Sufficient water and sediment samples were collected to allow for a series of analyses aimed at validating the analytical method. Mussels were not collected at this time pending the issuance of a collection permit. Instead, mussels purchased from a Kansas City, Missouri, market were used for method validation. (It is recognized that the extraction efficiency obtained by analyzing mussel tissue spiked with CPs cannot be demonstrated to exactly reproduce the recovery from mussels which have ingested CPs while alive. This is an inherent limitation when dealing with biota, which may metabolize or assimilate an analyte. However, the analytical method incorporates a sulfuric acid digestion step, which destroys the biological matrix and can be expected to release CPs for extraction and analysis in a manner similar to spiked samples.)

In support of the second objective, the team was able to meet and review information about the area with the State of Ohio EPA personnel. They also walked the Sugar Creek watershed and visited the Dover Chemical facility. Permission was granted by facility managers to collect, from their property, whatever samples were necessary for the study. They requested only that samples collected during the study be split and shared with the Dover Chemical Corporation and that any photographs taken be made available to Dover Chemical management.

FIELD STUDY DESIGN

The design for this study established eight sampling stations: four stations in Sugar Creek and four stations in the lagoon and its effluent ditch. The station locations are listed in Table 1 and shown in Figures 5 and 6.

The design called for the collection of a minimum of three samples of water and three samples of sediment at each of the eight stations (Table 2). It also called for the collection of biological samples at each sampling station, where available.

For each stream station, each sample was composed of three subsamples collected along a stream transect to account for any incomplete lateral mixing. Because the stream was shallow, vertical mixing was assumed to be complete. Samples collected in the lagoon were depth-integrated to account for incomplete vertical

TABLE 1 - Stations Locations for the Sugar Creek Study Site

Station ID	Location
L1	In the Dover Chemical Plant surface impoundment lagoon near its effluent to the drainage ditch.
L2	In the Dover Chemical Plant surface impoundment lagoon near the influent from the plant.
L3	In the Dover Chemical Plant surface impoundment lagoon in the approximate middle of the lagoon.
D	In the lagoon discharge ditch immediately above the point of discharge to Sugar Creek.
B	Sugar Creek upstream of Dover Chemical and under the road to Winfield.
B'	Sugar Creek just upstream of Dover Chemical discharge ditch.
A'	Sugar Creek just downstream from the Dover Chemical Plant discharge ditch and above the confluence with Goettge Run.
K	Downstream from the Dover Chemical Plant discharge and Goettge Run; just upstream of the confluence of Sugar Creek and the Tuscarawas River.

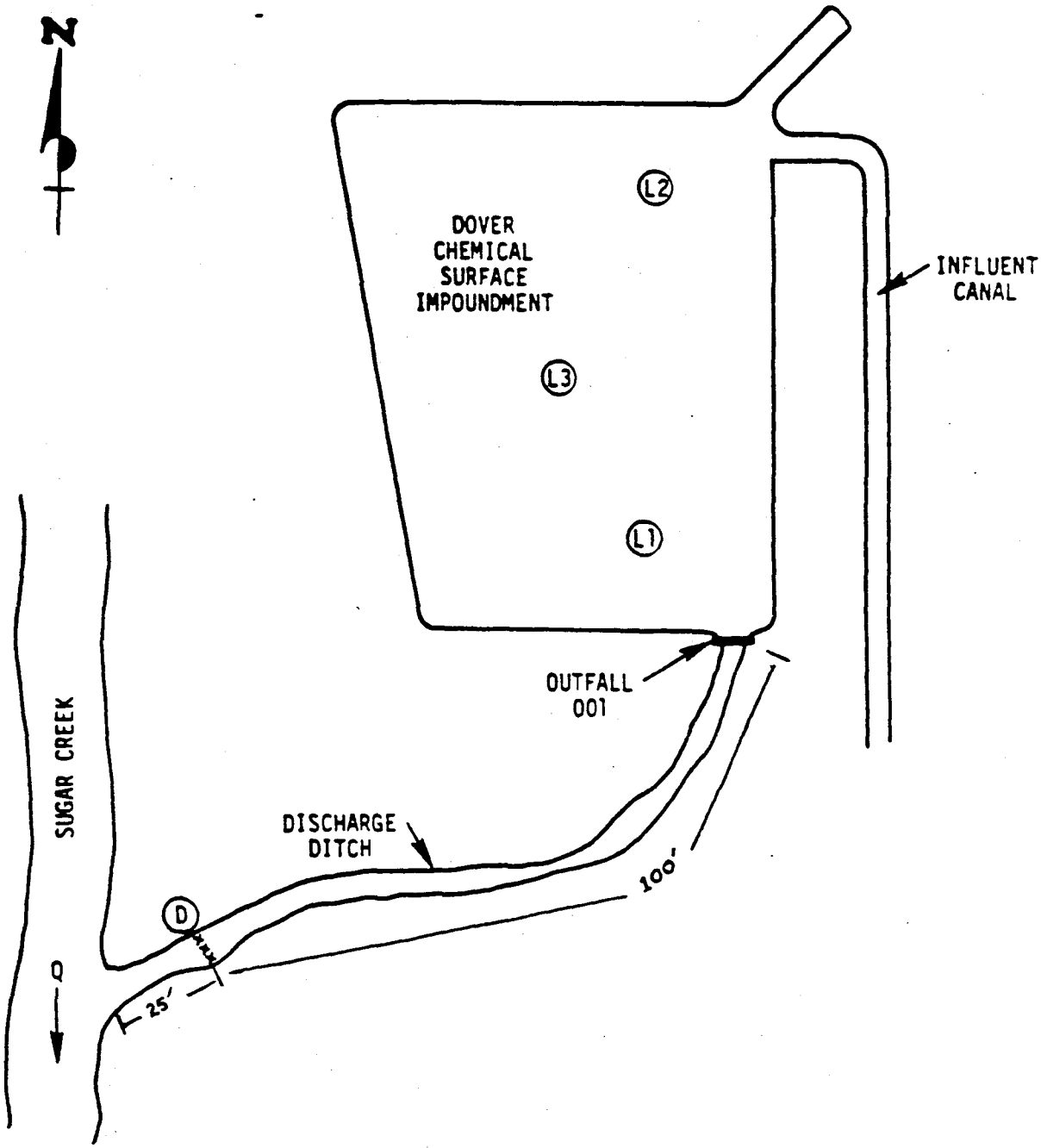

FIG. 5 - Location of Sampling Points in the Dover Chemical Impoundment and Drainage Ditch

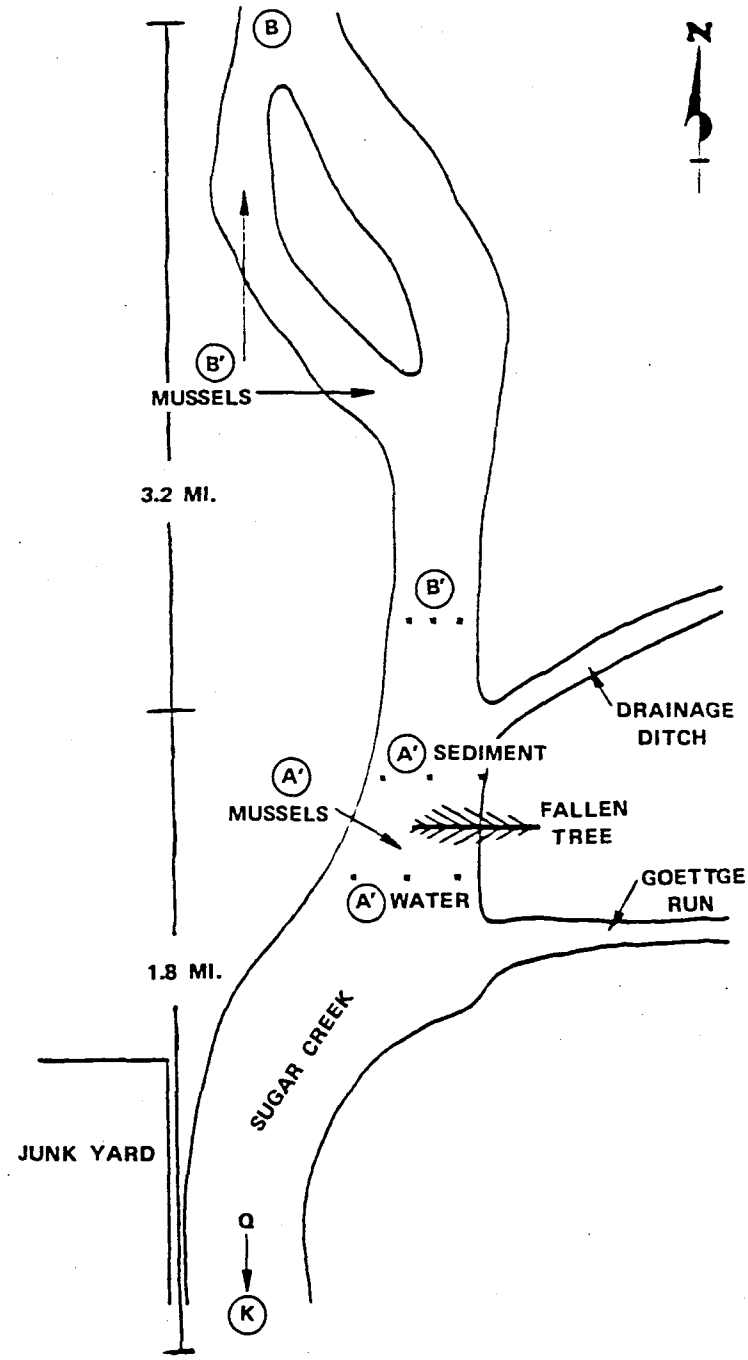

FIG. 6 -- Location of Sampling Points in Sugar Creek

TABLE 2 - Samples Collected from the Sugar Creek Study Site

PLANT DISCHARGE

	SAMPLE SET I				SAMPLE SET II				SAMPLE SET III			
STATION	L_1	L_2	L_3	D	L_1	L_2	L_3	D	L_1	L_2	L_3	D
MEDIUM:												
Water	1	1	1	1	1	1	1	1	1	1	1	1
Sediment	1	1	1	1	1	1	1	1	1	1	1	1
Mussel	-	-	-	-	-	-	-	-	-	-	-	-
QC Water	1*	-	-	-	-	-	-	-	-	-	-	-

SUGAR CREEK

	SAMPLE SET I				SAMPLE SET II				SAMPLE SET III			
STATION	B	B'	A'	K	B	B'	A'	K	B	B'	A'	K
MEDIUM:												
Water	1	1	1	1	1	1	1	1	1	1	1	1
Sediment	1	1	1	1	1	1	1	1	1	1	1	1
Mussel	1	1	1	-	-	-	-	-	-	-	-	-
QC Water	1*	-	-	-	-	-	-	-	-	-	-	-

* Equivalent in volume to 4 field samples

mixing. This sample type (hereafter referred to as composite sample) provided the most cost-efficient way of producing an average concentration of CPs for a given volume of water at a given time.

Mussels were selected over fish to represent the biological community of Sugar Creek because past studies (Madeley and Birtley, 1980) have shown that mussels do not metabolize long-chain CPs, at least to any great extent, while these same studies indicate that fish will metabolize CPs to varying degrees. The estimated bioconcentration factor (BCF) for CPs in mussels ranges in the order of 24,000 to 41,000. The BCF for CPs in trout has been reported to be between 3,500 and 5,200.

In the study design a mussel sample was defined as a composite of the flesh of 8 to 10 individual specimens. This was an estimate based on the size of the mussels purchased for the methods development and validation work. (The mussels collected from Sugar Creek during the actual field study were significantly larger than those on which this design estimate was based. Consequently, only one or two individual specimens were required to constitute a sample.)

FIELD SAMPLE COLLECTION

The Sugar Creek field study was conducted from September 22 through 25, 1986. All sample collection activities were conducted by PEI Associates under contract to the Midwest Research Institute (MRI). The sampling was supervised by MRI and compliance with the study design was monitored by a representative of Battelle Columbus Division. A representative of Dover Chemical Corporation observed portions of the sampling effort and received splits of all but mussel samples collected from the field. Dover Chemical was actively producing CPs at the time of the study.[1]

The flow and suspended solids loading in Sugar Creek during the study period were higher than those observed during the reconnaissance survey. This was due primarily to intermittent precipitation in the drainage area before and during the sampling period. However, although flows were elevated, they were still far below the mean flow which has been reported for the drainage basin (330 cfs).

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[1] Because the lagoon retains the Dover Chemical discharge, no direct temporal relationship can be drawn between the CP levels found in Sugar Creek and the CPs produced by Dover Chemical during the time of the field study.

Sampling proceeded according to the Quality Assurance Project Plan and followed the sample collection protocol described in Appendix C.

A daily account of the field sampling effort follows:

September 23, 1986--Surface Impoundment Lagoon.

A QC sample equivalent in volume to four field samples was collected at station L_1 from a depth of 11 ft and used to prepare field spikes and field blanks.

Three discrete depth-integrated water samples, plus a split sample for Dover Chemical, and a composite sample of three individual sediment grab samples, plus a split sample for Dover Chemical, were collected from each of the three lagoon stations in the following order, L_1, L_3 and L_2. This sampling order, i.e from lagoon effluent to near the lagoon influent was chosen to minimize possible cross-contamination of the samples.

Water depths at stations L_1, L_2 and L_3 were 19 to 23 ft. A depth-integrated sample was achieved by taking subsamples from 2, 10 and 17-20 ft depths at each location. Temperatures at these depths were all between 21.5° and 22°C. The water was clear to slightly cloudy at all locations.

Sediment was a mostly black to dark gray fine silt with some, but not strong odor. Two of the samples taken at station L_3 were fine silt, light brown in color with no odor.

After collecting the water and sediment samples, the perimeter of the lagoon was searched for mussels, but no evidence of mussels was found.

All samples were then placed on ice in coolers; each cooler contained samples from a single station plus the corresponding sample data sheet. The coolers were then shipped by overnight delivery to the MRI laboratory in Kansas City, Missouri.

Station D

Three discrete mid-depth water samples (plus a split sample for Dover Chemical), each a composite of single grab samples from three equidistant points across the small ditch, were then collected. Then, three discrete sediment samples (plus a split sample for Dover Chemical), each a composite of single grab samples of sediment collected from the same three points across the ditch, were obtained.

The total width of the ditch at station D was 12 ft. The water temperature at this site was 23.5 °C. It was not possible to measure the velocity of the water in the ditch at this site because the water was too shallow and there were many obstructions. However, representatives from Dover Chemical reported that they routinely measure the flow rate at the outfall from the impoundment to be about 1.2 cubic feet per second (cfs). This area was also searched for mussels; none were found.

September 24, 1986 - Station K

To minimize possible cross-contamination of the Sugar Creek samples, sampling began with the farthest downstream station (K) and proceeded upstream. At station K, the field crew collected three discrete mid-depth water samples (plus a split sample for Dover Chemical), each a composite of single grab samples taken from three equidistant points across the stream. They then collected three discrete sediment samples (plus a split sample for Dover Chemical), each a composite of single grab samples of sediment collected from the same three equidistant points across the stream. Sediment consisted of gravel to fine brown silt with no odor. The water temperature was 25 °C.

The cross-sectional area of the stream was determined by measuring the water depth at 2-ft intervals along a transect of the stream and measuring the stream width. The cross-sectional area was estimated to be 96 ft^2. The flow velocity was estimated by measuring the time required for 12 floats (oranges) to travel a distance of 100 ft. The estimated velocity ranged from 0.4 to 0.6 ft/s. The estimated flow was then calculated and fell within the range of 38 to 58 cfs.

Considerable time was spent searching the streambed for mussels. None were found, nor was there evidence (shells on shore or in the water) of mussels. According to local residents, mussels were generally absent from this stretch of the stream because of the acid mine drainage from Goettge Run. They also believed that a junkyard located just below station A' had recently contributed a spill of unknown magnitude to Sugar Creek which may have affected the mussel populations in the area.

Station A'

The field crew collected three discrete mid-depth water samples (plus a split sample for Dover Chemical), each a composite of single grab samples collected from three equidistant points across the stream. They then collected three discrete sediment samples (plus a split sample for Dover Chemical). The sediment samples were collected

approximately 15 ft upstream of the water samples because only coarse gravel and cobble were present at the designated location. The water temperature was 20.5°C. The stream width was 46 ft. The depth and velocity of the water was not measured at this station because of interferences caused by a fallen tree across the stream, sharp bends in the stream and deep water pools. Because this station is immediately downstream from them, an estimated stream flow can be made by adding the flows reported for station B' and the ditch carrying the impoundment discharge, Using this approach, the flow rate for Station A' was estimated to be 40 to 68 cfs.

Station A' was searched for mussels for several hours, but only two mussels (family Unionidae) were found. These were collected and immediately placed in coolers.

Station B'

The field crew collected three discrete mid-depth water samples (plus a split sample for Dover Chemical) and three discrete sediment samples (plus a split sample for Dover Chemical), each a composite of single grab samples from three equidistant points across the stream. The water temperature was 20.5°C. The cross-sectional area of the stream was estimated by measuring the water depth at 2-ft intervals along a transect of the stream. The flow velocity was estimated by measuring elapsed time for 12 floats to travel a distance of 100 feet. With an estimated cross-sectional area of 55 ft^2 and a flow velocity ranging from 0.7 to 1.2 ft/s, the flow was estimated to range from 38 to 66 cfs.

The field crew searched the stream bed for mussels and collected eight specimens (family Unionidae). Most of the mussels were collected in a small portion of the stream situated on the west side of a small island located about 150 ft upstream of the designated station B' location.

September 25, 1986 - Station B

Station B was designated as a Quality Control station. Therefore, one QC sample, equivalent in volume to four field samples, was collected. This sample was a composite of single grab samples collected at mid-depth from three equidistant points across the stream. From this QC sample, spiked and field blank QC samples were prepared and set aside for transport to the laboratory.

In addition to the QC sample, the field crew collected three discrete mid-depth water samples (plus a split sample for Dover Chemical) and three discrete sediment samples (plus a split for Dover Chemical), each a composite of single grab samples from three equidistant points across the

stream. Water temperature was 20.5°C. The cross-sectional area of the stream was again estimated by measuring the water depth at 2-ft intervals along a transect of the stream. The flow velocity was estimated using the same procedure that was employed at the other stream stations. The total width of the stream at this station was 96 ft. The cross-sectional area was estimated to be 116 ft^2. The flow velocity was estimated to be between 1.1 and 1.3 ft/s. The calculated flow ranged from 127 to 150 cfs. The flow measured at this station was greater than the flow measured at the downstream stations the day before. This was most probably due to the contribution of precipitation which had occurred in the upstream drainage basin.

Ten mussel specimens (family Unionidae) were collected from this station. Most of these were collected along the west bank.

CHAPTER IV. FIELD STUDY SITE 2--TINKERS CREEK, OHIO

DESCRIPTION OF THE STUDY AREA

Tinkers Creek is located in Northeast Ohio. From its source, it flows south and then to the northwest toward its confluence with the Cuyahoga River.

The drainage area of Tinkers Creek is largely industrial and urban. The focus of this field study was on the upper reaches of Tinkers Creek and tributaries in the Walton Hills area. This area is called the Deerlick Run Drainage Network. A map of the study area is given in Figure 7.

The tributaries to Tinkers Creek in the study area--Hukill and Ferro tributaries and Deerlick Run and its South Branch--are small surface streams 3 to 5 ft wide and several inches deep at the points where they flow under Egbert Road. These streams have gravel and silt substrates and are easily accessible. Deerlick Run, at the point of its confluence with Tinkers Creek is 8 to 10 ft wide, 6 in deep and has a shale bedrock and coarse gravel substrate. Tinkers Creek, at its confluence with the tributary Deerlick Run, is about 50 ft wide, 1 to 3 ft deep and has a coarse gravel and shale bedrock bottom. Deerlick Run and Tinkers Creek have relatively steep gradients with several waterfalls and rapids. Flow is estimated at 100-150 cfs. During the Spring, Tinkers Creek is a Class V whitewater stream. During summer low-flow conditions, about 80% of the volume of Tinkers Creek is contributed by upstream sewage effluents. Several oil spills and industrial releases have impacted these tributaries in recent years. The Ohio EPA (OEPA) has conducted monitoring and toxicity studies on these streams. These studies indicate the presence of stream pollution from many diverse sources in this area.

Waste Inputs

The S.K. Wellman Company, a metalworking facility located in the study area, was the focus for this field study. This company is a user of lubricating oils thought likely to contain chlorinated paraffins as an additive. This company operates a plant that manufactures clutch and brake friction materials for trucks and heavy equipment. While Ohio EPA officials could not confirm that CPs were used in the process, other sources of information indicated that CP-containing oils were used. Process wastewaters from S.K. Wellman, up until about 1984, were discharged directly to Hukill Tributary and ultimately to Tinkers Creek. The plant now discharges to the city of Bedford's Publicly-Owned Treatment Works (POTW). Pollutants including heavy metals (mainly copper), ammonia, oil, grease,

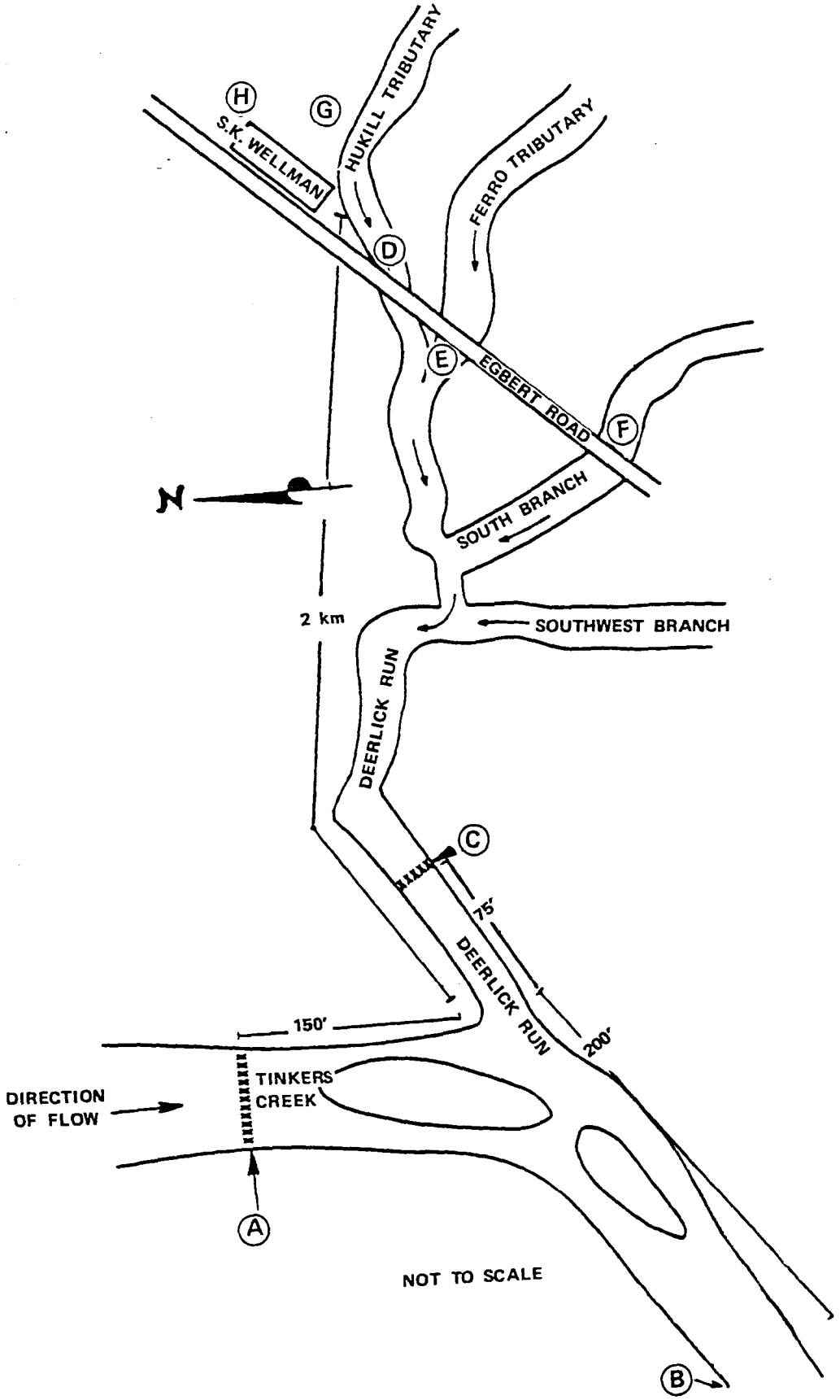

FIG. 7 -- Tinkers Creek Study Site -- Deerlick Run Drainage

acids, and bases are present in the process wastewater. Noncontact cooling water and stormwater are still discharged from the plant property through National Pollutant Discharge Elimination System (NPDES) outfalls to Hukill Tributary that then flows a distance of about 2 km before it enters Tinkers Creek. It is likely that ground water carrying contaminants from past waste management practices (e.g., surface impoundments) located on site also enters this tributary to Tinkers Creek. This company employs about 250 people.

In the study area, there are also at least 17 industrial facilities including chemical manufacturers, metal fabricators, concrete plants, drum recyclers, three facilities with hazardous waste units regulated under the Resources, Conservation, and Recovery Act (RCRA) and one facility at which EPA performed an emergency response cleanup of hazardous waste. The hazardous waste facilities are located in the close proximity to each other. Many of these facilities also have nonpoint source discharges to this network of tributaries to Tinkers Creek.

The tributaries of this network originate immediately upgradient of these industrial facilities. Storm sewer outfalls, runoff, ground-water inflow, and nonpoint source discharges are the sources of flow. There are no non-impacted upstream control sites. Tinkers Creek is impacted by POTW and industrial outfalls upstream of its confluence with this network of small tributaries.

RECONNAISSANCE SURVEY

On October 1 and 2, 1986, a reconnaissance survey was conducted in the study area by Mr. Tom Janszen and Mr. Bob Hoye of PEI Associates. Additionally, a meeting was held with Ohio EPA representatives on October 2, 1986, to discuss their knowledge of the operations conducted at the S.K. Wellman facility, the physical setting of this and other plants in the area and their discharges to surface waters. The purpose of the visit was to gather the information necessary to design a field study for the area, including the sampling of surface waters, sediments, and mussels for CP analysis.

In their meeting with the Ohio EPA, the representatives of PEI Associates were able to obtain only limited information about the proposed sampling area. However, they were able to visit the proposed site, photograph prospective sampling sites, and evaluate the hydrology of the area. Their efforts produced the following information about the area:

- There was no evidence of mussels or any other macro-invertebrates or fish in the proposed study area. In the best judgement of the reconnaissance team, it was unlikely that mussels would be found in the area.

- Because Tinkers Creek flows through the Cleveland Metroparks Bedford Reservation in the proposed study area, permission to take samples from Tinkers Creek and Deerlick Run could only be obtained from the Metroparks Administration.

- No special sampling gear would be required in implementing the field study.

- Streams in the study area were generally accessible.

- Stream samples collected in the study area would likely contain a variety of organic and metal constituents from past and current operations in the area.

- Sediment samples would be limited due to predominantly gravel and rock substrate. Some silt is obtainable from upstream areas within the tributary network.

FIELD STUDY DESIGN

The field study design for the Tinkers Creek area was developed without the knowledge of the frequency of occurrence of discharged constituents in the study area or the statistical parameters associated with these constituents. Further, although the S.K. Wellman Company's process wastewater was now discharged to a POTW, the design was developed based on the expectation that because this change was within the last 2 years, some residual CPs could, in fact, still reside in the sediments of the Hukill Tributary. Therefore, the design included six sampling stations; two stations in Tinkers Creek, one on Deerlick Run at its confluence with Tinkers Creek, and one each on Hukill Tributary, Ferro Tributary, and South Branch Tributary where they flow under Egbert Road. A seventh sampling station was established to capture a sample of the wastewater discharged from the facility's NPDES outfalls which are discharged directly to Hukill Tributary. Finally, arrangements were made with the facility manager to collect samples from the process wastestream inside the plant before it is discharged to the POTW. The station locations are listed in Table 3 and shown in Figures 8 and 9.

With the exception of stations G and H, the design called for the collection of a minimum of three individual grab or composite water and sediment samples (Table 4).

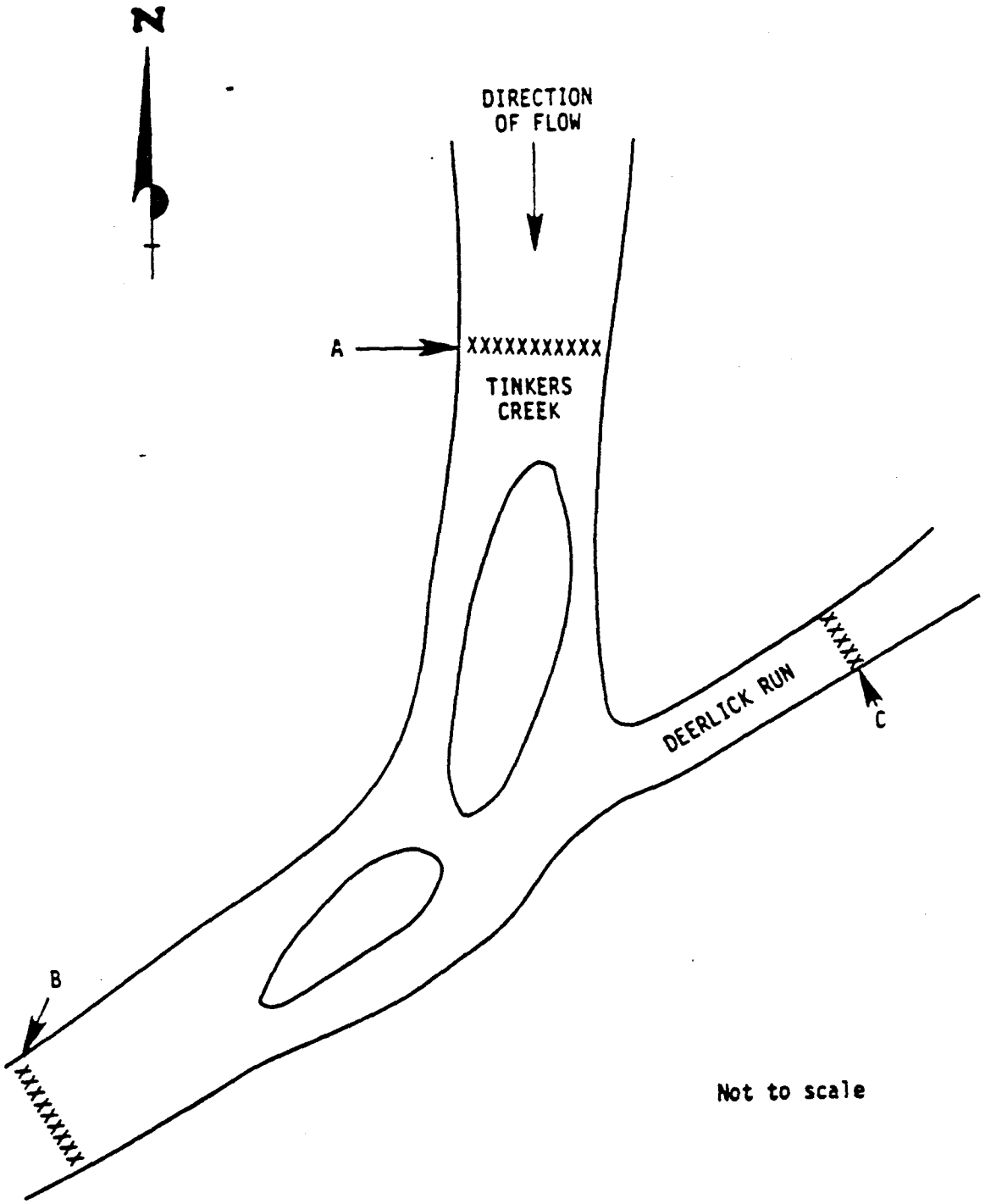

FIG. 8 - Location of Sampling Stations A through C at the Confluence of Tinkers Creek and Deerlick Run

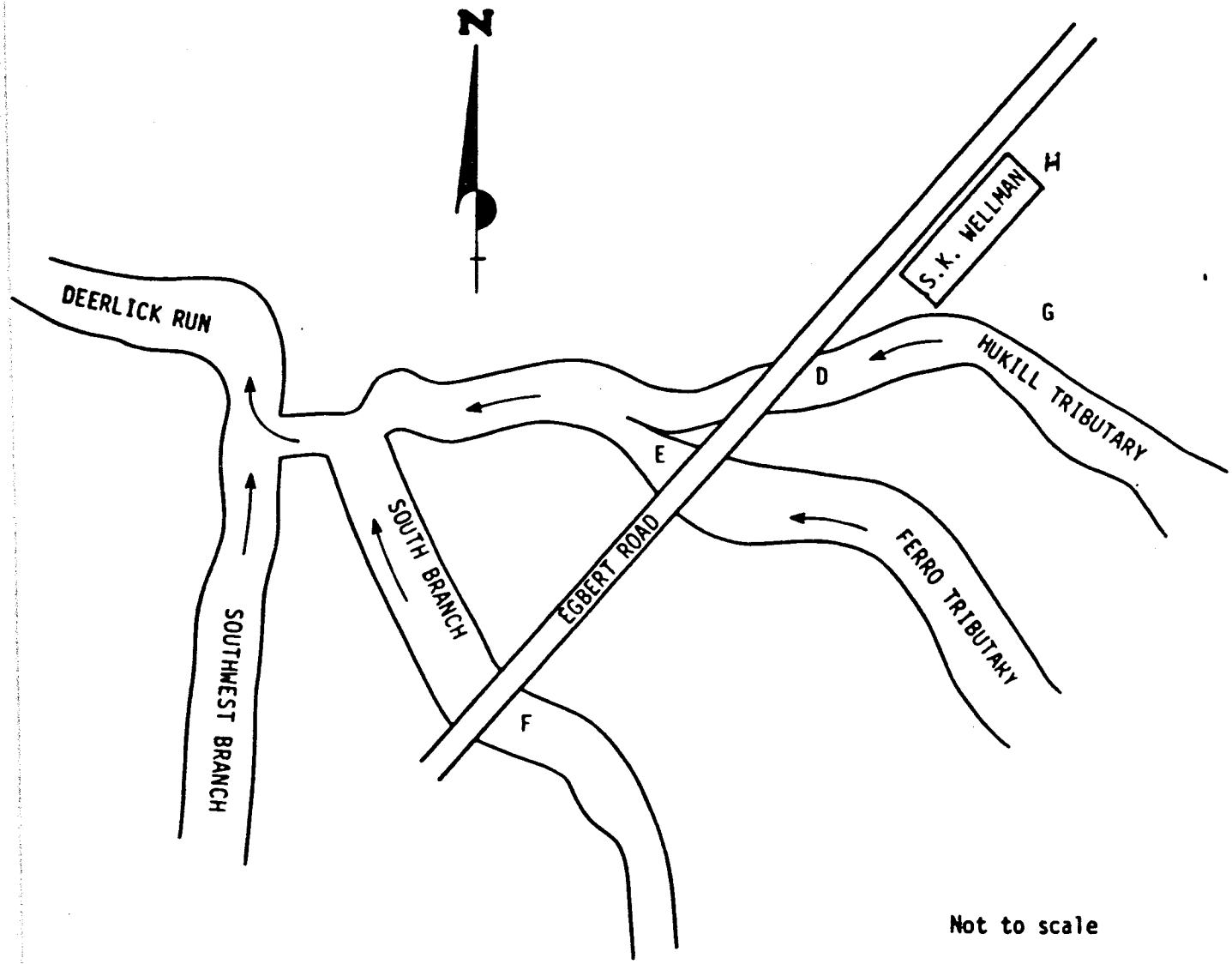

FIG. 9 - Location of Sampling Stations D through G

TABLE 3 - Station Locations for the Tinkers Creek Study Site

Station ID	Location
A	Tinkers Creek immediately upstream of the Deerlick Run confluence.
B	Tinkers Creek immediately downstream from the Deerlick Run confluence.
C	Deerlick Run at its confluence with Tinkers Creek.
D	Hukill Tributary downstream from the S.K. Wellman discharge and at Egbert Road.
E	Ferro Tributary at Egbert Road.
F	South Branch Tributary at Egbert Road.
G	S.K. Wellman's NPDES outfalls.
H	Process wastestream inside the S.K. Wellman facility.

TABLE 4 - Samples Collected from the Tinkers Creek Study Site

	SAMPLE SET I								SAMPLE SET II								SAMPLE SET III							
STATION	A	B	C	D	E	F	G	H	A	B	C	D	E	F	G	H	A	B	C	D	E	F	G	H
MEDIUM:																								
Water	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	-	1	1	1	1	1	1	1	-
Sediment	1	1	1	1	1	1	-	-	1	1	1	1	1	1	-	-	1	1	1	1	1	1	-	-
Biota*	1	-	-	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
QC Water**	1	-	-	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

* In lieu of mussels, fish samples were collected

** Equivalent in volume to 4 field samples

FIELD SAMPLE COLLECTION

The Tinkers Creek field study was conducted from October 14-16, 1986. All sample collection activities were performed by PEI Associates under contract to MRI.

The observed flow and suspended solids loading in Tinkers Creek during the study period was lower than observed during the earlier reconnaissance survey. The flow in Tinkers Creek, a perennial stream, has wide seasonal variations and short-term fluctuations reflecting the effects of precipitation events in the drainage area.

Sampling of Tinkers Creek, its tributaries, and the outfalls at S.K. Wellman proceeded according the QAPP and followed the sample collection protocol described in Appendix C.

A daily account of the field sampling effort follows.

Tuesday, October 14, 1986 - Stations A and B

The PEI Associates field team arrived at the study site and met with MRI personnel to review the QAPP. The field study team then proceeded to Cleveland's Metroparks Bedford Reservation, where stations A, B, and C were located. First, a visit was made to the Ranger's Office to confirm permission (obtained earlier) to take samples from Tinkers Creek within the Reservation. Then, the team proceeded to the confluence of Tinkers Creek and Deerlick Run.

Three discrete mid-depth water samples, each a composite of single grab samples from three equidistant points across the stream, were collected at stations A and B. Three discrete sediment samples, each a composite of single grab samples from three equidistant points along a transect of the stream, were taken at station A. The substrate at station B consisted of large boulders; little silt or gravel sediment was present in mid-stream because of the high velocity of the water flowing in this area. Therefore, the grab samples for each integrated sediment sample were taken on or near the stream banks from areas that are periodically submerged. Generally, sediment collected from stations A and B consisted of gravel, shale, and fine sand/silt with no odor.

The field team also collected a QC sample at Station A. This QC sample, equivalent in volume to four field samples, was a composite of single grab samples collected at mid-depth from three equidistant points across the stream transect. From this QC sample, MRI prepared the field spike and field blank QC samples for transport back to the laboratory.

Tinkers Creek is about 70 ft wide at station A and 25 ft wide at station B. A thorough search for benthic organisms, such as mussels and the larval and pupal forms of the order Diptera (e.g., Chironomidae), was made along the stream and in the stream substrate in the area of Stations A and B. No larval or pupal insect forms of any type were found; no mussels or any other benthos were observed.

The swift current prevented the safe access to points across the stream necessary to measure flow. Water temperature at both stations was 14°C. The sampling team completed the field activities at dusk, approximately 7:00 p.m. The samples collected from stations A and B were prepared for shipment by packaging them in coolers with sufficient cushioning material and ice.

Wednesday, October 15, 1986 - Stations C, D, E, and F

The field study team proceeded to the confluence of Tinkers Creek and Deerlick Run to collect samples at station C. Three discrete mid-depth water samples and three discrete sediment samples, each a composite of single grab samples from three equidistant points across the stream were collected. Deerlick run at this location was 8 to 15 ft wide and 6 to 8 in deep with pools 1 to 1.5 ft deep. The substrate was mostly bedrock shale. Loose sediment consisted of gravel, shale, and fine sandy material with no odor. The station was then thoroughly searched for larval insect forms; none were found. The nature of the run (pools, riffles, falls, and shallow water) was not amenable to flow measurement. This effort was, therefore, aborted. Water temperature at station C was 9.2°C. Some minnows (family Cyprinidae) were observed in the pools at this station.

The team returned to stations A and B to observe stream conditions. While station B was still considered unsafe because of the fast current, station A had improved sufficiently to measure flow. The cross-sectional area of the stream was determined by measuring the water depth at 2-ft intervals along a transect of the stream. Stream width at this point was 69 ft. The cross-sectional area was estimated to be 101 ft^2. The flow velocity was estimated by measuring the time required for 12 floats (oranges) to travel a distance of 100 ft. The estimated velocity ranged from 1.4 to 0.9 ft/s. The estimated flow at station A was calculated to range from 90 to 140 cfs.

The field team proceeded to stations F, E, and D, respectively. Three discrete water samples and three discrete sediment samples were collected at each station. Because the tributaries were so small, compositing samples was determined to be unnecessary. Therefore, each sample was a single grab sample. The creek beds at each station were thoroughly searched for larval insect forms;

none were found. No mussels or other benthos were observed. These tributaries were very small streams 4 to 8 ft wide and only a few inches deep. Water temperatures at stations D, E and F were 8.9°, 9.4° and 11.3°C respectively.

At station D, the field team collected a QC sample, equivalent in volume to four field samples, and used this sample to prepare field spikes and field blanks.

The field team completed the necessary sample forms, packaged the samples and shipped them by overnight delivery to MRI's laboratory in Kansas City, Missouri.

In lieu of any other biological specimens, the field team decided to collect two fish samples. Minnows (family Cyprinidae) had been observed in several pools of Deerlick Run. Seining of two Deerlick Run pools just upstream of station C yielded enough biomass for a sample. The field team also conducted extensive seining from station A to a point approximately 0.3 mi upstream of station A. By dark, the team had collected enough biota for a sample. The fish samples were packed in a cooler with ice and the sample forms were completed.

Thursday, October 16, 1986 - Stations G and H

The field team met with the management of the S.K. Wellman Company. After a brief discussion, the field team was allowed to collect one grab sample of the process water which is discharged to the City of Bedford's POTW. A split sample was given to the management of S.K. Wellman.

S.K. Wellman also has three NPDES discharges, one which carries parking lot and roof drain runoff and two which carry noncontact cooling water. These outfalls occasionally contain traces of oil. The field team collected two discrete water samples (plus a split sample for S. K. Wellman). Each sample was a composite of single grab samples collected from each of the three NPDES discharge pipes.

CHAPTER V. EXPERIMENTAL SECTION

A total of 52 field samples plus 12 QC samples from Sugar Creek were received by the MRI laboratory. An additional 41 field samples and 12 QC samples were received from Tinkers Creek. Each sample, identified by the barcode labeling system, was inventoried as it arrived in the laboratory (See Tables C-1 and C-2, Appendix C). An inspection of the samples showed that all were intact; all mussels survived.

As was shown in Tables 2 and 4, three sets of samples were constructed such that the first set (Set I) consisted of the first samples of each type of medium collected at each of the field stations. The second set (Set II) consisted of the second samples of each medium, etc. Subsets comprise all samples of a given medium within a set. To enhance study efficiency and minimize analytical costs, analyses were to be conducted in a logical sequence of sets and subsets.

The results presented in this report reflect the analysis of Set I from Sugar Creek (See Table 5) and Set I from Tinkers Creek (See Table 6). Because biological samples were so limited at both field study sites, their analyses were done independently. For example, all mussel samples collected from Sugar Creek were analyzed as a part of Set I as proposed in the study design. The fish samples collected from Tinkers Creek are being held in reserve, since their collection was not directly called for in the QAPP.

Within sets, the extracted field samples and the QC samples were quantified in random order, "blind" to the GC/MS analyst.

EQUIPMENT

GC/MS analyses were performed using a Finnigan MAT 4000 Gas Chromatograph/ Mass Spectrometer system. This system was equipped with a 30-M x 0.25 mm i.d. fused silica capillary column, a negative chemical ionization source and a J & W on-column injector. The system was interfaced with an Incos 2400 data handling system. Operating conditions and parameters are listed in Appendix A, Table A-1.

TABLE 5 - Sequence of Analytical Runs for Samples Collected From the Sugar Creek Study Site

(Analyses within each run were made in random sequence and unknown (blind) to the operator; method blanks were analyzed with each run)

	RUN NO.	SUBSET	NO. OF SAMPLES
SET I	1	Filtered water	8 field samples + 4 QC field samples
	2	Suspended Solids	8 field samples + 4 QC field samples
	3	Sediment	8 field samples
	4	Mussels	3 field samples
	5	Mussels	2 field samples
SET II	5	Filtered Water	8 field samples + 4 QC field samples
	6	Suspended Solids	8 field samples + 4 QC field samples
	7	Sediment	8 field samples
	8	Mussels	not available
SET III	9	Filtered Water	8 field samples
	10	Suspended Solids	8 field samples
	11	Sediment	8 field samples
	12	Mussels	not available

TABLE 6 - Sequence of Analytical Runs for Samples Collected from the Tinkers Creek Study Site

(Analyses within each run were made in random sequence and unknown (blind) to the operator; method blanks were analyzed with each run)

	RUN NO.	SUBSET	NO. OF SAMPLES
SET I	1	Filtered Water	7 field samples + 4 QC field samples
	2	Unfiltered Water	1 in-plant sample
	3	Suspended Solids	7 field samples + 4 QC field samples
	4	Sediment	6 field samples
	5	Biota	1 field sample
SET II	6	Filtered Water	7 field samples + 4 QC field samples
	7	Suspended Solids	7 field samples + 4 QC field samples
	8	Sediment	6 field samples
	9	Biota	not available
SET III	10	Filtered Water	7 field samples
	11	Suspended Solids	7 field samples
	12	Sediment	6 field samples
	13	Biota	not available

This GC/MS system was calibrated prior to sample analysis over a range which covered the expected sample concentrations. The initial calibration was then checked, at a minimum daily, with a midpoint calibration standard at the beginning of the sample run. Additional calibration standards were analyzed if instrument instability was noted.

SAMPLE PREPARATION

The first set of environmental samples collected from Sugar Creek and Tinkers Creek were extracted and analyzed following the protocol described in Appendix A. Sample preparation was performed in MRI lab 315W. With the exception of the mussel samples from Sugar Creek, samples were extracted within 1 week of receipt. The mussel samples were stored at -20°C. This holding time was appropriate since chlorinated paraffins are very stable at moderate temperatures. A check on the integrity of the samples was provided by analytical comparison of the trip-spiked samples with the lab-spiked samples. The trip-spiked samples were deionized water spiked in the field, transported and stored with the environmental samples; the lab-spiked samples were deionized water spiked just prior to extraction. Results showed that little or no sample degradation had occurred (see Figures 10 and 11). Analysis of the trip blanks--deionized water taken from the lab to the field and maintained, shipped, stored, and analyzed with the environmental samples--demonstrated that contamination of the samples had not occurred.

With each sample batch a method blank was analyzed. (A method blank is a procedural blank, which is carried through the entire procedure to check for contamination.) These consisted of distilled water for the water samples, sodium sulfate for sediment, and mussels and blank filters for suspended solids. The following control checks were used during the analysis: a performance sample was run prior to sample analysis; and if instrument instability was noted, standards were run between every two samples. Chlorinated paraffins were quantitated using the average of the two response factors bracketing the samples.

Experience gained during sample analysis indicates that Negative Chemical Ionization Mass Spectrometry (NCIMS) is rather unstable when environmental extracts are analyzed. Upon installation of a new filament, a period of slow but steady decline in sensitivity was noted. This was followed by a rapid deterioration and burn out of the filament. Several filaments were burned out during the course of analysis of the environmental samples. This instrument behavior can be attributed to the complex nature

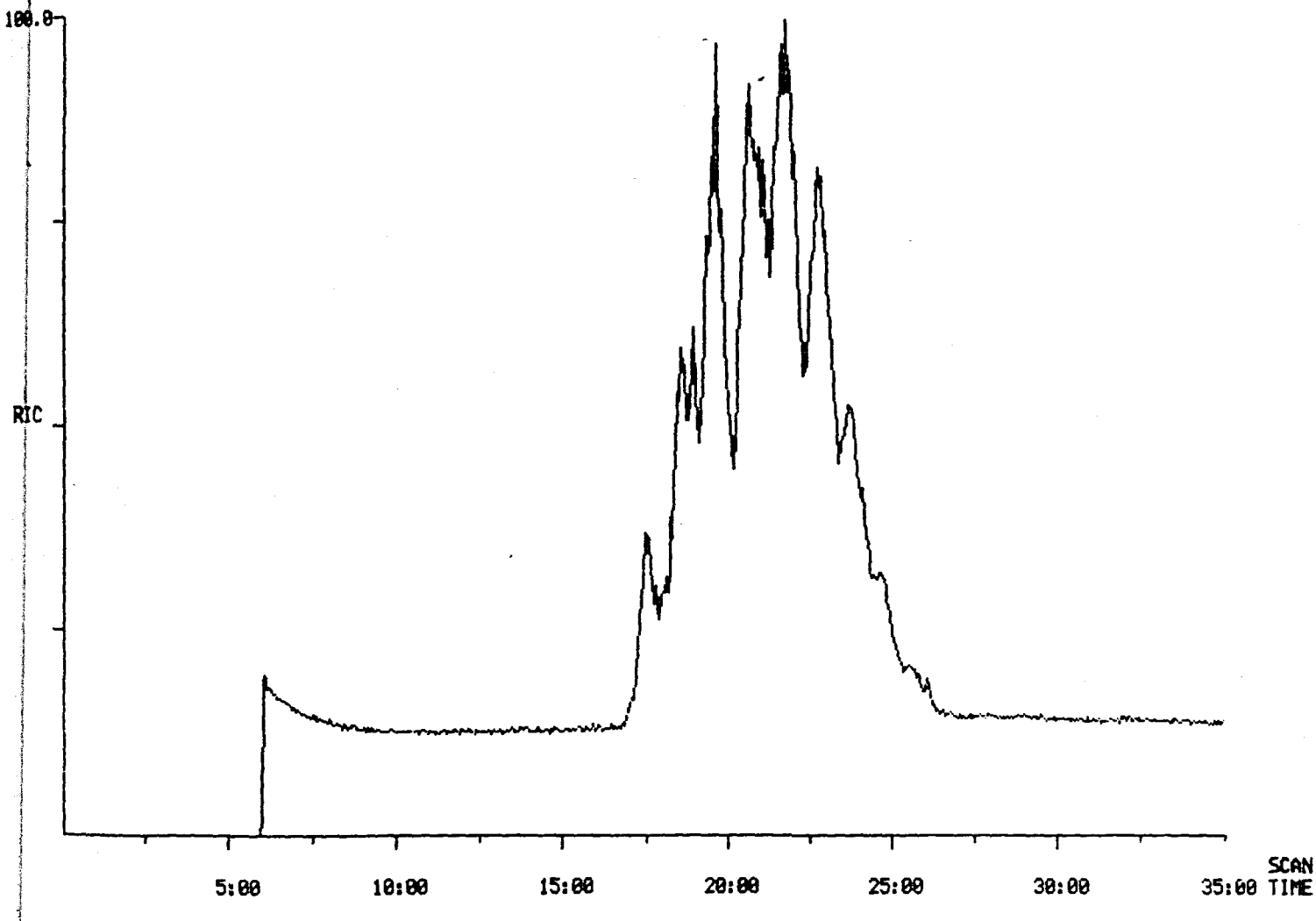

FIG. 10 HRGC/NCIMS Determination of Chlorinated Paraffin Standards in Trip-Spiked Water Sample. Sugar Creek, Station L_1. The spiking level was 50 ppb. (Midwest Research Institute)

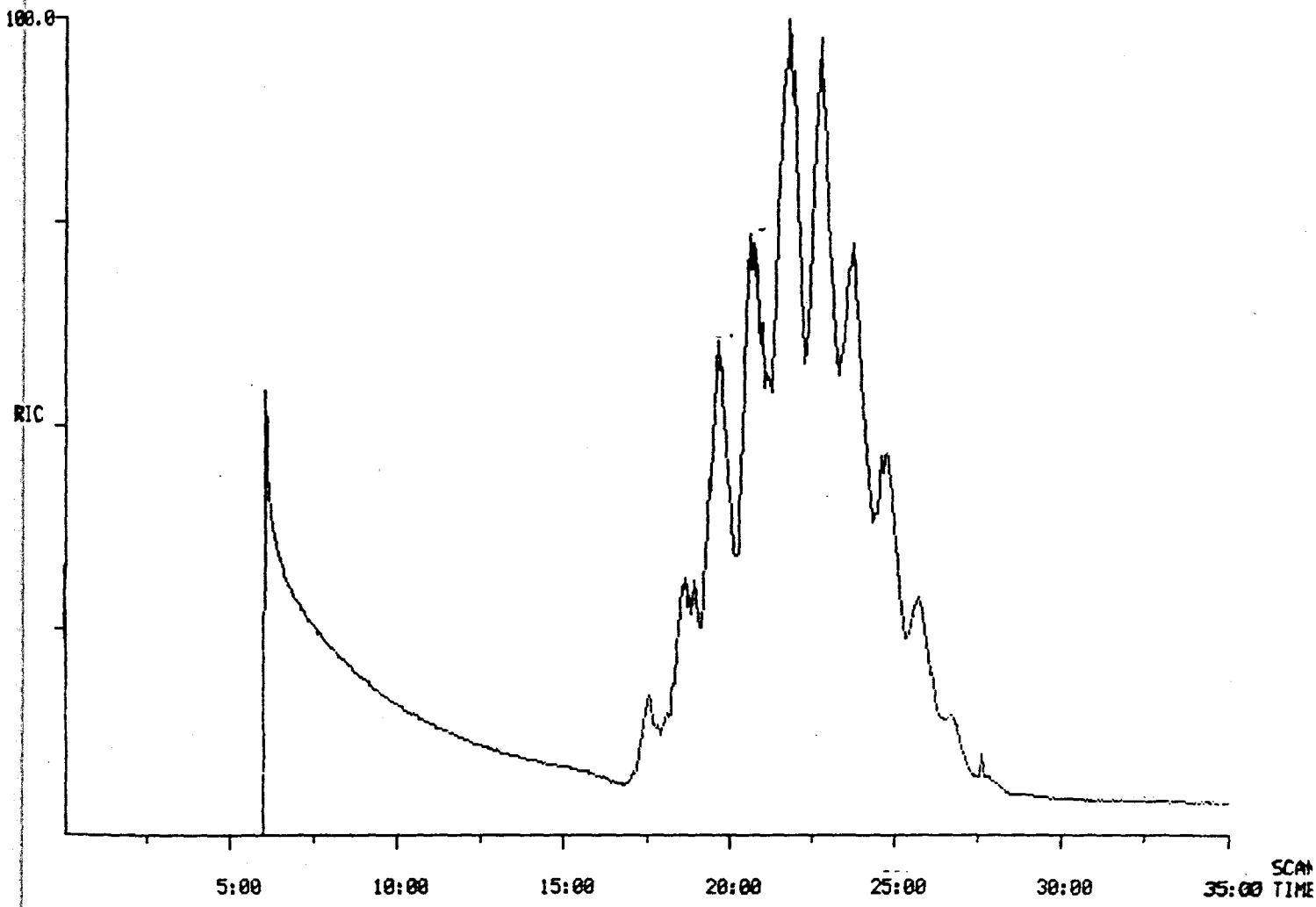

FIG. 11 HRGC/NCIMS Determination of Chlorinated Paraffins Standards, Paroil 1160, Paroil 152, and Paroil 142. (Midwest Research Institute)

of the extracts and to the methane environment in the mass spectrometer source; it appears to be an unavoidable characteristic of the source. The decline in sensitivity and short filament life were successfully accounted for by systematically analyzing external standards with the environmental samples. A reliable internal standard needs to be developed to facilitate the routine CP analysis of environmental sample extracts.

STANDARDS PREPARATION

The chlorinated paraffins measured at Sugar Creek and in the S.K. Wellman wastewater were quantitated using three standards provided by the Dover Chemical Corporation. These were Paroil 1160 (C_{10}-C_{12}), 50-60% Cl; Paroil 152 (C_{14}-C_{17}), 50-60% Cl; and Paroil 142 (C_{20}-C_{30}), 40-50% Cl (See Figure 11). These standards came very close to duplicating the three CPs (See Fig. 1), which were of interest to this study. While the CPs in the environmental samples were quantitated against these three standards, it is recognized that some CPs represented by adjacent cells in the 9-cell matrix (see Figure 1) and present in the samples could be quantitated unintentionally. The nominal concentrations of these solutions are listed in Appendix A, Table A-2.

METHODOLOGY

At the beginning of the study, the following five objectives were established for selecting an analytical procedure for this study. The analytical procedure must be able to:

- discriminate specific CPs (see Figure 1).
- reach a limit of detection at or lower than 5 ng/g (low ppb range).
- obtain CP concentrations for replicate spike samples with a range percent (precision) of less than 30% of the mean of these values.
- measure CP concentrations with a percent difference (accuracy) of less than 30% of the actual CP concentration.
- establish a recovery efficiency in the range of 70-130%.

For the most part, these five objectives were met by the study.

Method Selection

A computerized literature search revealed two methods which were capable of determining CPs in environmental media. The first (Hollies et al., 1979) was a Thin Layer Chromatography (TLC) method with argentation of the chlorine atoms for visualization and quantitation. This method is chlorine dependent and has a limit of detection of 0.5 ppb for water and 50 ppb for semisolid matrices. This method can distinguish long-chain (C_{20}-C_{30}) and shorter chain-length (C_{13}-C_{17}) CPs with chlorine contents of 42-45% (w/w). This method combines solvent extraction/partition and column chromatography followed by TLC. It has been used by some investigators (Campbell et al, 1980) to study CPs in environmental media.

The second method (Schmid and Müller, 1985) appeared to better meet the study objectives because it could differentiate between various chain lengths and chlorine content CPs and would be less affected by uncontrollable interferences. This detection and quantification method combines High Resolution Gas Chromatography/Negative Chemical Ionization Mass Spectrometry with Selected Ion Monitoring (HRGC/NCIMS/SIM). It was developed using a C_{14}-C_{18}, 52% chlorine CP (Witachlor 352). This quantification method has a limit of detection in the low nanogram range, and has been used by its authors to demonstrate the presence of CPs in sewage sludge, human adipose tissue, and sediment. However, the method had not been characterized as to precision and accuracy.

After carefully reviewing both methods, the Schmid and Müller procedure was selected for the study. Steps were then initiated to validate the method around the parameters imposed by the study objective and using available standards.

METHOD DEVELOPMENT AND VALIDATION STUDIES

A full description of the method validation studies and a statistical evaluation of their results is included in Appendix B.

In validating this method, two questions arose concerning the chemical and thermal stability of CPs during sample preparation and analysis using this method. The first concerned the effect of an H_2SO_4 treatment on the integrity of the CP compounds. The second concerned the stability of CPs when encountering the

high temperatures of the GC/MS analysis. Studies were, therefore, initiated to answer these questions. The results of these studies showed that neither the H_2SO_4/silica chromatography step (Figure 1, Appendix A) nor the GC/MS analysis had a deleterious effect on the recovery of CP standards.

In the sulfuric acid digestion experiment, the mussel samples collected from Sugar Creek were digested for one hour using 40% sulfuric acid on silica gel. The effect of this acid treatment on CPs was investigated by digesting standard solutions of CPs in hexane for periods up to 2 hours. No detectable loss of CPs was noted, as determined by GC/MS analysis of the solutions before and after acid treatment.

In the thermal decomposition experiment, decomposition of CPs was observed during preliminary studies using a heated inlet. This prompted a change to ambient on-column injection, which was incorporated in the final method. Although there are heated zones in the GC/MS interface, the atmosphere is inert. The calibration curves clearly demonstrate that instrument response is linear with respect to CP concentration, indicating that significant decomposition did not occur.

The original sample preparation and method was modified, (See Appendix A), prior to method validation. The validation procedure was based on actual field samples obtained from Sugar Creek except mussels, which were purchased. The method validation indicated that some modification of the method was needed before the actual field samples were analyzed. For samples of suspended solids, a smaller final extract volume, larger injection volumes or compositing was necessary to reach the desired sensitivity. For tissue samples, a more vigorous H_2SO_4 treatment was necessary in order to more effectively remove interferences. No modifications were necessary for water and sediment samples.

CHAPTER VI. RESULTS AND DISCUSSION

As described earlier, the design strategy for the chlorinated paraffin field study in both the Sugar Creek and Tinkers Creek study areas called for the collection of three duplicate sets of water and sediment samples (plus available biological samples) and the analysis of samples, one set at a time, until sufficient data had been derived to meet the previously stated study objectives. In following this strategy, only the first set of samples from each area was analyzed. The Sugar Creek data, because of consistency in analytical results, are judged to be adequate to demonstrate the release of CPs into the receiving stream and to provide quantitative measurements of those levels and of CP concentrations in samples from the stream environment.[1]

Analysis of Tinkers Creek samples was curtailed after one set when other industrial pollutants, largely halogenated aromatics, were found to be present in the sampled material at concentrations which masked any CPs that may have been present.

SUGAR CREEK STUDY AREA

The Sugar Creek Study Area evaluation is based on a total of 29 residue analyses among 19 field samples, coupled with confirmatory analyses of 13 quality control samples. This effort comprises 16 analyses among 8 water samples (8 each of particulates and filtered water), 8 analyses of as many sediment samples, and 5 analyses among 3 composite mussel samples.

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[1] Given the retentive nature of the Dover Chemical surface impoundment lagoon and the array of CP products which are currently being produced or have in the past been produced, CPs other than those addressed by this study, are expected to be present in the sediments and the particulates. In addition, weathering of the three CPs that were measured may have also occurred. These considerations would lead to the conclusion that, while CPs are definitely present, the quantitated levels should be considered as estimates of the total CP concentration. Because the lagoon retains the Dover Chemical discharge, no direct temporal relationship can be drawn between the CP concentrations found in Sugar Creek and the CPs produced by Dover Chemical during the time of the field study.

The analytical results from the sampling at Sugar Creek indicate that chlorinated paraffins, represented in this study as short-chain C_{10-12} 50-60% Cl; medium-chain C_{14-17} 50-60% Cl; and long-chain C_{20-30} 40-50% Cl, were generally present in the low parts-per-billion range in most of the samples collected from the surface impoundment, the drainage ditch; and downstream from the drainage ditch in Sugar Creek.

Long-chain CPs were reported in the low parts-per-billion range in two upstream sediment samples. Also, short-chain CPs were found in the low parts-per-billion range in one water particulates sample immediately upstream of the drainage ditch. With these exceptions, chlorinated paraffin concentrations were not measured in quantifiable amounts in Sugar Creek upstream of the drainage ditch.

The highest concentrations of CPs were found in the impoundment sediment and in the biological samples collected downstream from the drainage ditch. Quantifiable concentrations were also measured in the particulate matrices. Where CPs were detected in the filtered water (filtrate), they were found, inconsistently, only in the impoundment and the drainage ditch water and only at low parts-per-billion levels.

Of the three CPs addressed by this study, the long-chain CP (C_{20-30}, 40-50% Cl) was generally found at the highest levels. These findings are consistent with the available literature which reports that the microbial degradation of paraffins appears to be related to the carbon chain length and percent chlorination. Higher chlorinated (above 50%) and long-chain C_{20-30} compounds resist degradation. Short-chain (C_{10-13}) 49% Cl degrade most readily (Madeley and Birtley, 1980). Also, these results are consistent with studies of CPs which indicated that CPs readily adsorb to sediments and particulate matter (Campbell and McConnell, 1980, and Ramm, 1978).

Because it acts as a natural sink for particulate matter, the highest CP concentrations in the study area were found, within media, in the surface impoundment lagoon, especially its sediment (Figure 12, Tables 7 and 8). Residues in sediment were reportedly highest at the inflow end of the lagoon (L_2) (See Figure 13) and lowest at the outflow end (L_1). At all sampling stations, the long-chain C_{20-30}, 40-50% CP predominated, with sediment concentrations as high as 170,000 µg/kg. Concentrations

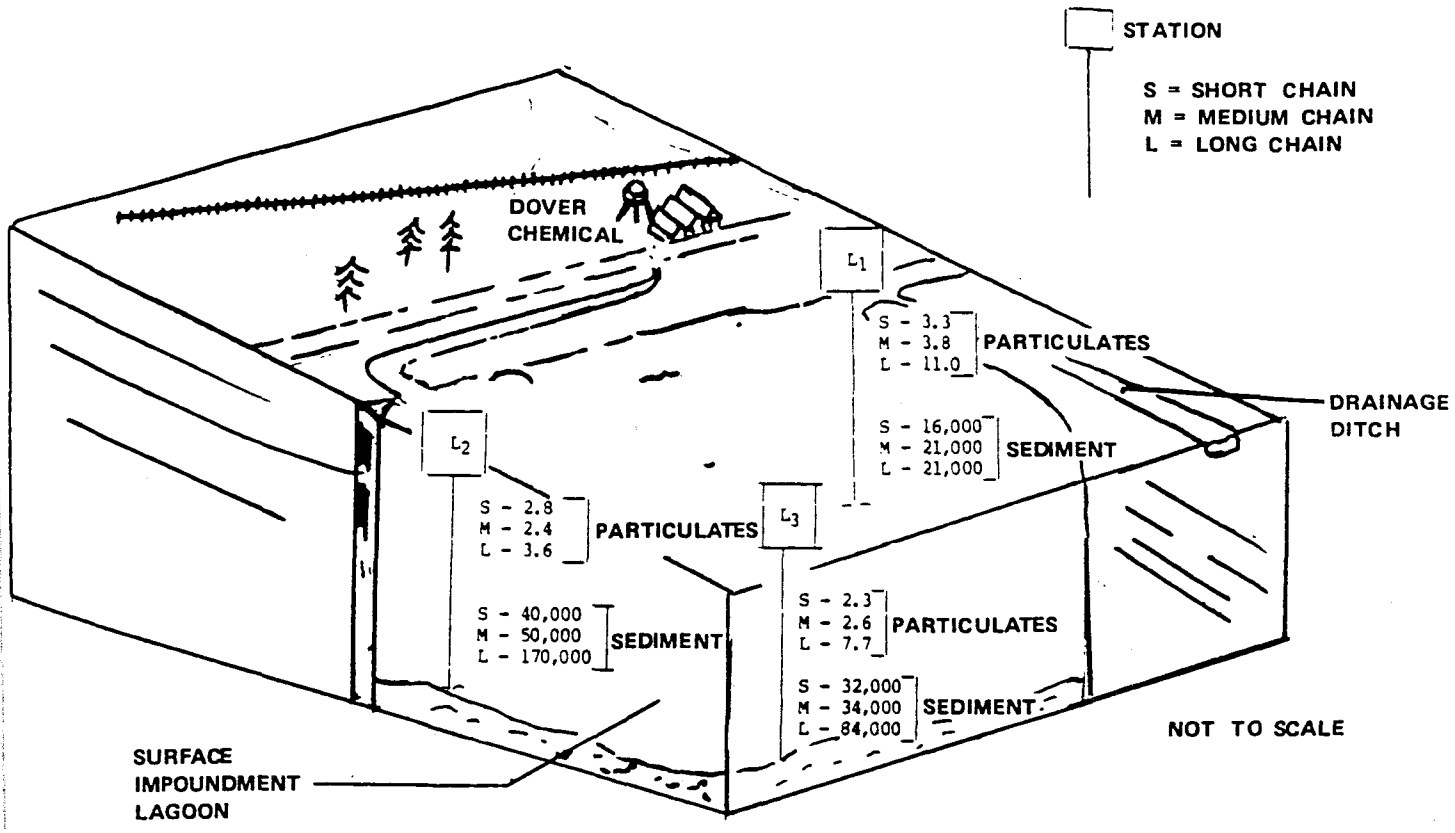

FIG. 12 CP Concentrations in the Dover Chemical Surface Impoundment Lagoon. Values are not adjusted for method recovery. Sediment Concentrations are in ug/kg; Particulates concentrations are in ug/L.

Table 7 CP Concentrations (ug/kg) in Sediment* of the Lagoon and Drainage Ditch, by Carbon Chain-length Groups and Cumulative Mass Ranges (parenthesized)

Sampling Location	Number of Samples	$C_{10} - C_{12}$ (323-329; 357-363; 365-399)	$C_{14} - C_{17}$ (399-419; 439-453; 475-487)	$C_{20} - C_{30}$ (496-506; 512-517)
L1	1	16,000	21,000	21,000
L2	1	40,000	50,000	170,000
L3	1	32,000	34,000	84,000
D	1	1,200	760	3,600

* CP concentrations are based on dry weight of sediment after removal of rocks. Values are not adjusted for method recovery.

Table 8 CP Concentrations* (µg/L), in Filtrate and Particulates, from Filtered Impoundment and Drainage Ditch Water, by Carbon Chain-Length Groups and Cumulative Mass Ranges (parenthesized)

Sampling Location	Number Of Samples	Matrix	C_{10}- C_{12} (323-329; 357-363; 365-399)	C_{14}- C_{17} (399-419; 439-453; 475-487)	C_{20} - C_{30} (496-506; 512-517)
L1	1	Filtrate	Tr**	ND***	ND
		Particulates	3.3	3.8	11
		Sum	3.3.+Tr	3.8	11
L2	1	Filtrate	0.25-0.51	Tr	ND
		Particulates	2.8	2.4	3.6
		Sum	3.0-3.3	2.4+Tr	3.6
L3	1	Filtrate	0.39-0.57	Tr	0.61
		Particulates	2.3	2.6	7.7
		Sum	2.7-2.9	2.6+Tr	8.3
D	1	Filtrate	Tr	Tr	Tr
		Particulates	2.3	1.5	3.7
		Sum	2.3+Tr	1.5+Tr	4.0

* = Values are not adjusted for method recovery.
*Tr = Trace (Conc. between 0.15 and 0.50 µg/L).
**ND = Not detected (Conc. <0.15 µg/L);

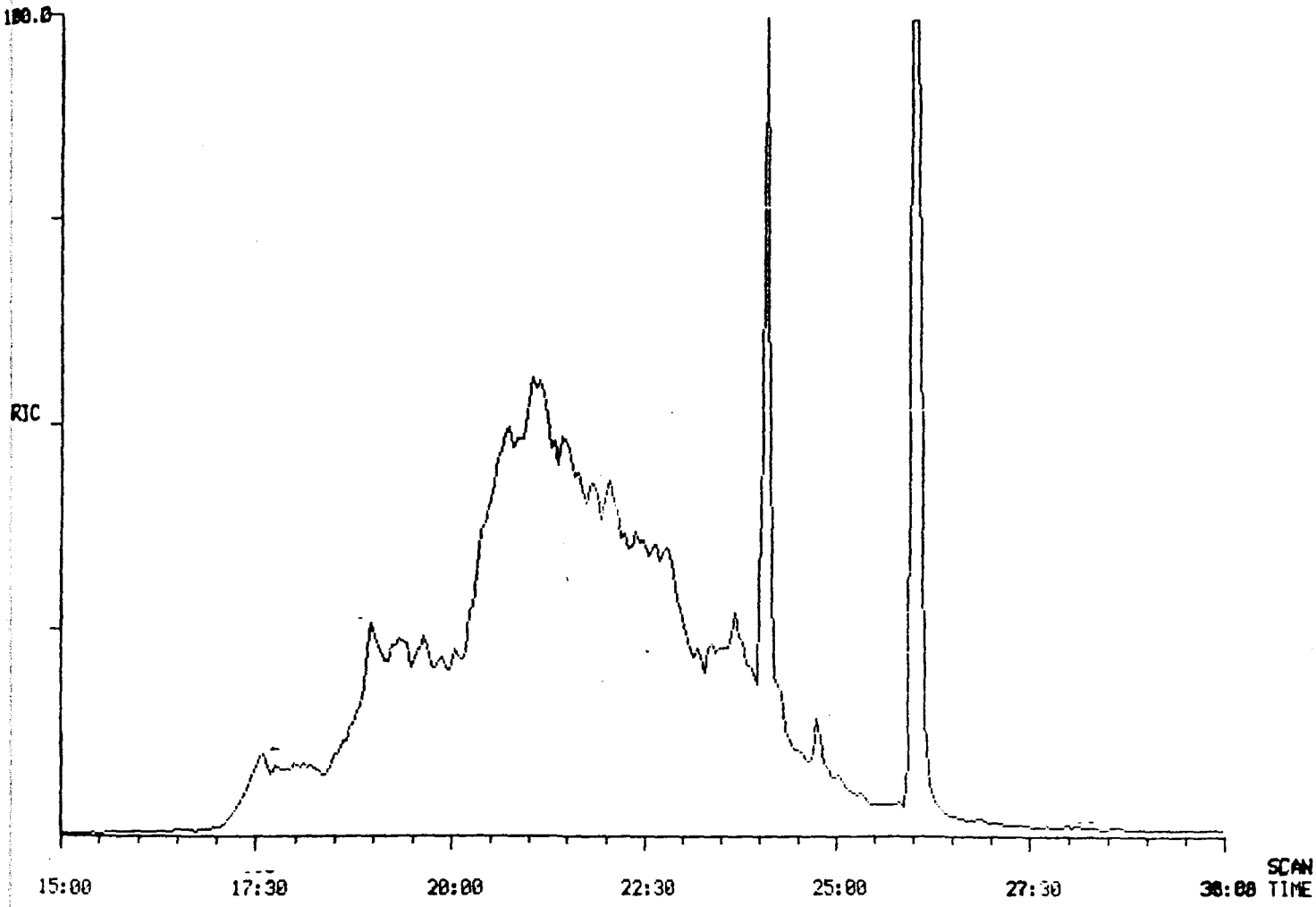

FIG. 13 HRGC/NCIMS Determination of Chlorinated Paraffins in Sediment Sample Collected from Station L_2, Surface Water Impoundment Lagoon, Sugar Creek. (Midwest Research Institute)

Note: The 2 peaks to the right of the Chlorinated Paraffin mass range are non-CP interferents.

were intermediate for the medium-chain CP and lowest for the short-chain CP.

Concentrations adsorbed to particulates filtered from the depth-integrated water samples collected from the lagoon were also highest for the longer chain CP, the highest concentration being 11 µg/L at station L_1. There was no discernible correspondence between residue levels in water particulates and those in sediment from the respective sampling stations.

Water samples collected from the lagoon were composites of discrete grab samples integrated from depths of 2, 10, and 17-20 ft. Temperatures recorded at each station and at these depths ranged from 21.5°C to 22°C. The water was clear to slightly cloudy at all locations. The sediment was mostly black to dark gray, a fine silt with some but not a strong odor. Two of the three sediment samples collected from station L_3 were a light brown fine silt with no odor.

Chlorinated paraffin concentrations measured in the filtered water fraction of the lagoon samples were near or below the level of quantitation but were still reported for at least one chain length in all samples. There was no discernible correspondence between residue levels in particulate material and in the respective filtrate of the lagoon water samples. No mussels were available for analysis from the lagoon.

In the ditch, which served as the drainage conduit for the lagoon and therefore represented Dover Chemical Corporation's point source discharge to Sugar Creek, CPs were detected in each matrix analyzed (Figure 14, See Tables 9 and 10). Again, the long-chain CP predominated with the highest concentration (3,600 µg/kg) found in the sediment. Quantifiable concentrations were found in the particulates, and trace or marginally quantifiable concentrations were found in the filtered water column. The water temperature at this station was 23.5°C. The flow was reported as 1.2 cfs. In Sugar Creek, the receiving stream, CPs were largely not detected above its confluence with the Dover Chemical drainage ditch, but were measured in quantifiable levels at stations downstream from this drainage ditch (Tables 9, 10, and 11).

At the far upstream station (station B), the only quantified value was 11 µg/kg of the long-chain CP found in the sediment matrix. No CPs were detected either in the filtered water fraction or the tissue of mussels (which were collected along the west bank of the stream). A second analytical run of mussels collected from this station revealed

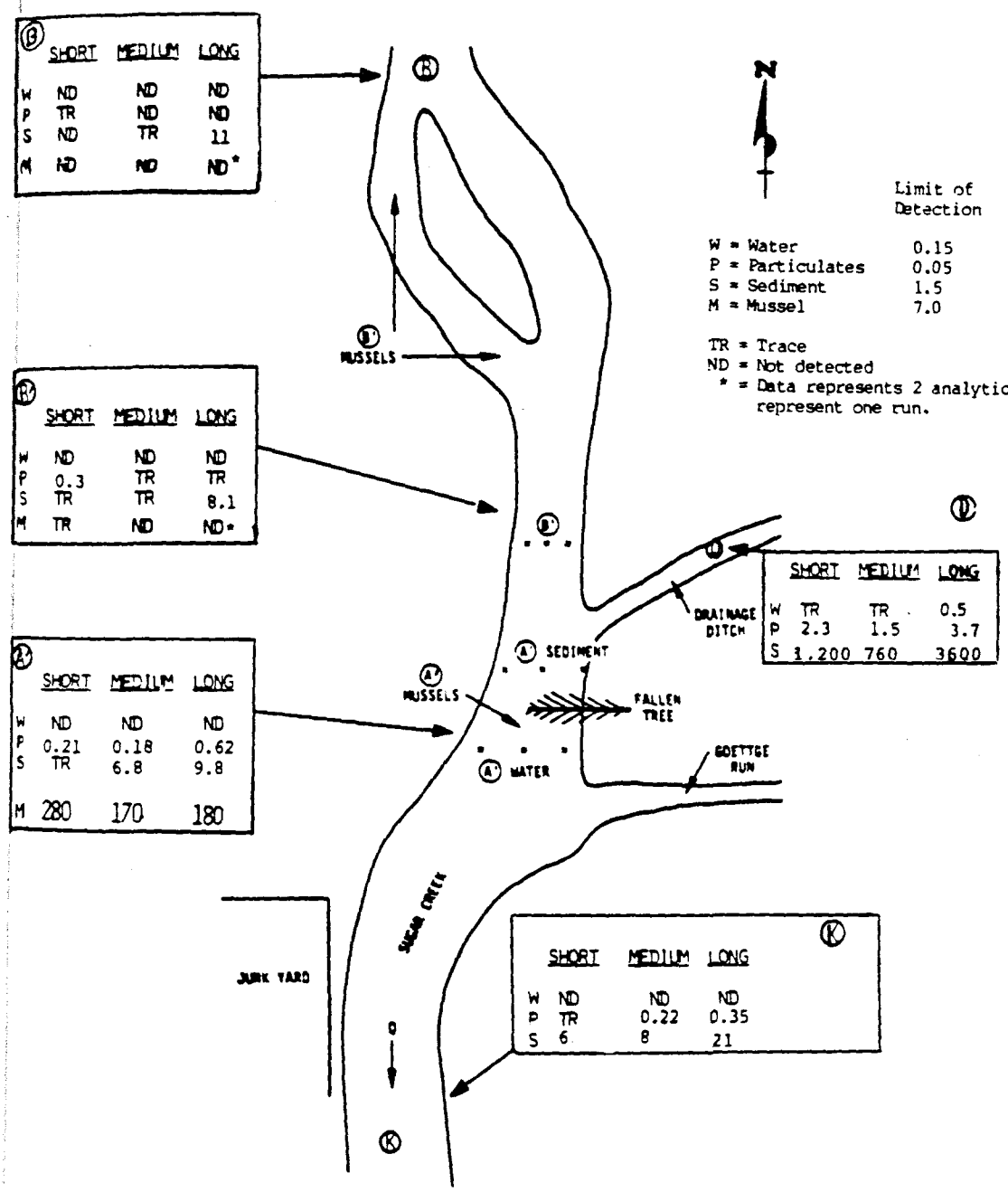

FIG. 14 CP Concentration in the Dover Chemical Drainage Ditch and Sugar Creek. Values are not adjusted for method recovery.

Table 9 CP Concentrations (µg/kg) in Stream Sediment*, by Carbon Chain-length Groups and Cumulative Mass Ranges (parenthesized)

Sampling Location	Number Of Samples	$C_{10} - C_{12}$ (323-329; 357-363; 365-399)	$C_{14} - C_{17}$ (399-419;439-453; 474-487)	$C_{20} - C_{30}$ (496-506; 512-517)
B	1	ND***	Tr***	11
B'	1	Tr	Tr	8.1
A'	1	Tr	6.8	9.8
K	1	5.5-7.3	8.2	21

* CP concentrations are based on dry weight of sediment after removal of rocks. Values are not adjusted for method recovery.

** ND = Not detected (Conc. <1.5 µg/kg)

*** Tr = Trace (Conc. between 1.5 and 5.0 µg/kg)

Table 10 CP Concentrations (μg/L), Particulates*, from Filtered Stream Water, by Carbon Chain-Length Groups and Cumulative Mass Range, (parenthesized)

Sampling Location	Number of Samples	$C_{10} - C_{12}$ (323-329; 357-363; 365-399)	$C_{14} - C_{17}$ (399-419; 439-453; 475-487)	$C_{20} - C_{30}$ (496-506; 512-517)
B	1	Tr**	ND ***	ND
B'	1	0.27-0.30	Tr	Tr
A'	1	0.20-0.23	0.16-0.20	0.62
K	1	Tr	0.20-0.24	0.35

* Values are for particulate contributions only. CP residues were not detected in filtered Stream Water (filtrate) samples. Values are not adjusted for method recovery.

** Tr = Trace (Conc. between 0.05 and 0.17 μg/L)
*** ND = Not detected (Conc. <0.05 μg/L)

Table 11 CP Residues* (µg/kg) in Composite Mussel Samples from Sugar Creek, by Carbon Chain-length Groups and Cumulative Mass Ranges (parenthesized)

Sampling Location	Number of Composite Samples	Mussels Per Composite	$C_{10} - C_{12}$ (323-329; 357-363; 365-399)	$C_{14} - C_{17}$ (399-419; 439-453; 475-487)	$C_{20} - C_{30}$ (496-506; 512-517)
B	1	1	ND**	ND	ND
B'	1	1	Tr***	ND	ND
A'	1	2	280	170	180
K	0	-	-	-	-

* = Values are not adjusted for method recovery.

** ND = <7 µg/kg

*** Tr = >7<22 µg/kg

trace levels of both the short and medium-chain CPs. Trace amounts of the short-chain and medium-chain CPs were found in the particulates and sediment matrices, respectively.

Water temperature at station B was 20.5°C. The flow ranged from 127-150 cfs. The flow at this station was greater than that measured the day before at downstream stations, probably because of the contribution of precipitation occurring in the upstream drainage basin.

At station B', located just upstream of the drainage ditch confluence, a quantified concentration (8.1 µg/kg) of the long-chain CP was reported in the sediment sample, and a low part-per-billion (0.3 µg/L) residue of short-chain CP was reported for particulates in the water column. Otherwise, concentrations in all matrices were reported as trace (Tr) or not detected (ND). No CPs were detected in the filtered water fraction. A trace value of the short-chain CP was found in the composite mussel sample collected from this site. These mussels were collected from a small portion of the stream situated on the west side of a small island about 150 ft upstream of the location where the water and sediment samples were collected. A second analytical run of mussels collected from this station did not detect CPs of any chain length. The water temperature at this station was 20.5°C.

Below the influence of the drainage ditch, quantifiable concentrations of CPs wre measured in all matrices except the filtered water fraction. At station A', which was located just downstream from the drainage ditch but above the influence of Goettge Run, quantifiable concentrations of each of the three CPs were measured in the composite mussel sample collected from this site: 280 µg/kg of the short-chain CP, 170 µg/kg of the medium-chain CP, and 180 µg/kg of the long-chain CP. In the sediment matrix, concentrations of 6.8 and 9.8 µg/kg were reported for the medium and long-chain CPs, respectively. Trace levels were reported for the short-chain CP in this matrix. Because only coarse gravel and cobble were present at station A', the sediment samples were collected approximately 15 ft upstream of the point where water samples were collected.

In the particulates matrix, quantifiable concentrations were found for each chain length (0.21, 0.18, and 0.62 µg/L for short-, medium-, and long-chain CPs, respectively). The water temperature at station A' was 20.5°C.

At the far downstream station (station K), CP concentrations were also evident. As at all stream stations, no CPs were detected in the filtered water matrix; however, quantifiable concentrations were found in the particulates and sediments. In the particulates fraction, while only trace levels of the

short-chain CP were found, 0.22 µg/L and 0.35 µg/L of the medium, and long-chain CPs, respectively, were measured. In the sediments, 6, 8 and 21 µg/kg of the short, medium, and long-chain CPs were reported, respectively. The sediments at this station were gravel to fine brown silt with no odor. No mussels were available for analysis from this site. The water temperature was 20.5°C.

Statistical Evaluation of the Sugar Creek Data

As stated in Chapter I., the objective of this study was to determine, preliminarily, if chlorinated paraffins exist in selected water environments [here, the Sugar Creek study area] and, if so, at what concentrations. The study data, although necessarily limited to chemical analysis of one of three replicated sets of water, particulates and sediment samples from eight sampling stations plus mussels samples from three of those stations, have been determined to be of sufficient quality to meet the study objective. The determination of sufficiency utilizes findings from the method validation chemistry presented in Appendix B plus the observed consistency of analytical results relative to the type of environment sampled (i.e., surface impoundment, etc.)

From what is known about the behavior of CPs in an aquatic environment (extremely low solubility, propensity to adsorb to suspended particulates and sediment and to bioaccumulate), one would expect that if CPs were present in the study environment as the result of effluent discharge, overall concentrations would be highest in the surface impoundment, next highest in the outflow ditch, present but at lower levels downstream from the ditch outflow, and lowest or virtually absent upstream of the outflow. This, exactly, was the outcome for reported concentrations in all sediment and particulate samples, respectively, and for the three mussel samples from Sugar Creek. Because of extremely low solubility, CPs were not detected in filtered stream water and barely so in impoundment and ditch water, a result not inconsistent with expectations.

Reported CP concentrations in impoundment sediment (Table 7) ranged from 16,000 µg/kg of the short-chain (C_{10-12}) CP (station L_1) to 170,000 µg/kg of the long-chain (C_{20-30}) CP (station L_2), with a median concentration of 34,000 µg/kg (C_{14-17} CP, station L_3). These concentrations averaged approximately 30 times the respective chain-length concentration reported in the ditch sample (Table 7). In turn, ditch sample concentrations (median 1,200 µg/kg) were from 95 to 170 times the highest concentrations reported in downstream sediment samples.

Using the working equations for the prediction of true CP concentrations in sediment ($\hat{X}$) from reported concentrations (Y) and for calculation of 95% confidence limits for those predicted values (Table B-8, Appendix B), it has been observed that there is no overlap in the lower 95% confidence limits for predicted true concentrations of the C_{10-12} and C_{14-17} CPs in impoundment samples and the respective upper 95% confidence limits for predicted true concentrations in the ditch sample. (There was some overlap of C_{20-30} confidence limits as a result of lower precision for those estimates.) Similarly, it has been determined for each carbon chain-length group that there is no overlap between the lower 95% confidence limit for the predicted true concentration in the ditch sample and the upper 95% confidence limit for the highest predicted true concentration in a downstream sediment sample (Station K, Table 9). Thus, with the exception of the C_{20-30} CP in impoundment sediment, it has been demonstrated at the 95% confidence level that true CP concentrations, as sampled, were highest in impoundment sediment, intermediate in the outflow ditch sediment, and lower downstream from the ditch than in the ditch itself. Concentrations reported in sediment samples upstream of the ditch outflow were generally numerically lower than those for downstream samples, an exception being the C_{20-30} value of 11 µg/kg for station B. (Rather than attempt to test differences between upstream and downstream sediment concentrations per se, a broader test that incorporates all sampled media will be presented.)

CP residues adsorbed to suspended particulates resulted in concentrations (µg/L) that tended to be numerically slightly higher in unfiltered water samples from the impoundment than in the sample from the ditch (Table 8). Concentrations reported for unfiltered water samples downstream from the ditch outflow were approximately one-tenth those for the ditch. With one exception (the C_{10-12} CP, Station B'), all reports for upstream samples were either "not detected" or "trace".

Concentrations reported for suspended particulates would seem to be consistent with flow and dilution factors, especially regarding the concentration decreases from outflow ditch to stream. Apparently, there has been significant transport of CPs via the impoundment as evidenced by concentrations in unfiltered ditch water and the accumulated residues in ditch sediment. Although it was not possible to develop equations for predicting true concentrations for suspended particulates, it can be shown that if there were truly no differences between impoundment/ditch concentrations and stream concentrations, the probability that analytical variation would, by chance alone, result in the highest values being reported

for the four impoundment/ditch samples and the lowest values for the four stream samples is approximately 0.01 (one chance in a hundred).

Comparison of overall differences in CP concentrations between stations upstream of vs. downstream from the ditch outflow utilizes the reported total concentration of CPs in each sediment, particulate, and mussel sample. The total concentration in each sample was derived as the sum of its C_{10-12}, C_{14-17} and C_{20-30} CP concentrations, using mid-range values for reports of "trace" and "not detected".

For upstream stations B and B' and downstream stations A' and K, respectively, total CP concentrations were 14.6, 14.5, 19.8, and 35.6 µg/kg for sediment samples; 0.16, 0.47, 1.0, and 0.68 µg/L for particulate samples; and 10, 21 and 630 µg/kg in mussel samples, with station K providing no sample. Thus, for each medium, the total of CP residue reported for each sample is consistently higher in samples from the downstream stations. If, in fact, there were no differences within media between upstream and downstream true concentrations, the probability that, by chance alone, analytical variation would consistently result in downstream samples having the higher reported concentrations is less than 0.01.

The validity of the foregoing comparisons of CP concentrations requires the assumption that results were not measurably biased either by sample collection or laboratory procedures, including the order in which samples were collected and/or analyzed. In this respect, the study protocol specified standardized sample collection, handling, and analytical procedures and, within media, that samples be processed and analyzed in random order "blind" to the analyst (i.e., the analyst did not know from which station a sample had been collected). Water and sediment samples were collected over a 3-day period and mussels within a 1-day period. It would seem unlikely that CP concentrations in sediment and mussels would have changed measurably during the respective periods or that particulate concentrations would have changed sufficiently to alter the ranking of concentrations among stations. Collection stations were not randomly located, but rather strategically located to derive data needed to best meet the study objective. Samples are considered to be representative of the study environment at the time of collection.

In summary, the data indicate that chlorinated paraffins do exist in the receiving stream in the area of the Dover Chemical Plant, and that discharge levels from the drainage ditch, plus the relative differences in residue between upstream and downstream samples, are results sufficient to

support the statement that the Dover Chemical Plant, via its surface impoundment lagoon, is a source of CP residues in Sugar Creek.

The reason that some quantifiable concentrations of CPs were found upstream of the discharge ditch is not readily apparent. There are no known CP manufacturers, processors, or users of CPs upstream at this time. Further, Sugar Creek is impounded upstream which would likely sequester any CPs adsorbed to particulate matter, should they be present. On the other hand, the Dover Chemical surface impoundment lagoon has reportedly overflowed in the past. These incidences would likely carry CP-laden particulates to the stream upstream of the discharge ditch. Also, because the lagoon is in direct contact with a shallow aquifer, CPs could be reaching Sugar Creek through ground water recharge. Additional study is needed to test these hypotheses.

Monitoring versus Modeling Results

Where environmental measurements are scant, mathematical models can oftentimes provide estimates that can bridge the information gap that exists between environmental concerns and sensible risk management decisions. This was the case in 1985, when, in an effort to supplement a limited monitoring data base on CPs, a preliminary modeling analysis was performed to estimate CP concentrations in three watercourses: Sugar Creek, Ohio; Schuykill River, Pennsylvania; and Galveston Bay, Texas (Versar 1985, GSC 1985). This modeling effort, based on reasonable production estimates and professional judgment, produced estimates of environmental CP concentrations that were generally consistent with available environmental monitoring data.

The 1986 Sugar Creek field study, because it measured actual environmental release information from a CP manufacturer, provided an opportunity to repeat the modeling analysis for Sugar Creek, using measured environmental release information. It also provided an opportunity to compare, directly, estimated results generated by the model with actual field measurements.

The following discussion first describes the 1985 modeling effort in Sugar Creek and then compares this preliminary analysis with the 1986 effort using new monitoring information.

The 1985 modeling analysis was performed to estimate CP loadings to Sugar Creek based on CP release estimates (PEI, 1984) and best engineering judgment. The CP release estimates did not differentiate the chlorinated paraffins of various carbon chain length and degree of chlorination.

The Exposure Analysis Modeling System (EXAMS) was used to estimate the concentrations of CPs in surface water, sediment, and biota. Two compartments were assumed for modeling purposes: (1) Sugar Creek before it enters the Tuscarawas River (3000 m long with a mean stream flow of 330 cfs) and (2) the Tuscarawas River downstream from the confluence of Sugar Creek (13,000 m long with a mean stream flow of 1,740 cfs). The model assumed complete and uniform mixing within each compartment. The model was run under controlled (CP removal during waste treatment) and uncontrolled (no CP removal) release scenarios.

Two CPs were selected for modeling based on their physico-chemical properties. These were the short-chain (C_{12}), highly chlorinated CP Chlorowax 500-C and the long-chain (C_{24}), highly chlorinated CP Chlorowax 70.

The controlled release rates of Chlorowax 500-C and Chlorowax 70 were derived individually by multiplying the estimated uncontrolled release rate (1.7904 kg/yr) by a removal factor based upon the organic carbon partition coefficient. The estimated controlled releases of Chlorowax 500-C and Chlorowax 70 were 63.06 and 0.35 g/day, respectively (Versar 1985, GSC 1985).

The modeling analysis was then repeated using the actual environmental releases of short-chain and long-chain CPs, measured during the 1986 EPA field study at Sugar Creek. The field data used for this analysis were the CP releases measured at station D, the drainage ditch which carries the Dover Chemical plant's waste discharge to Sugar Creek. The releases (loadings) measured during the 1986 field study were 0.97 and 1.46 g/day for the short-chain and long-chain CPs respectively. The measured loading of the short-chain CP is significantly lower than the estimated loading (63.0 g/day) used in the 1985 preliminary modeling study by GSC. Although no statistical significance can be attributed to these data, the results showed that the model estimates were comparable with the monitoring data.

A comparison of the 1985 preliminary modeling estimates, the modeling estimates using input from the 1986 field study and the actual concentrations measured in the field is given in Tables 12 and 13 for the short-chain and long-chain CPs, respectively. While too few field data were available for this to be considered a full validation of the model, the correspondence between model predictions and field measurements suggests that the modeling approach provides a reasonable measure of CP concentrations in the receiving water environment.

TABLE 12 - Comparison of Preliminary Modeling, Field Sampling Data and Modeling Results Using Field Estimates of Chlorinated Paraffins Loadings (C_{10-12}, Short Chain)

	Load (g/day)	Water Column (µg/L)	Suspended Particulates (µg/kg)	Benthic Sediments (µg/kg)	Biota (µg/kg)
Original Model Estimates in 1985 GSC Report[1]	63.0	0.007	23.1	125.0	9,690
Model Estimates Using Input from 1986 Field Sampling [2]	0.97	0.001	0.37	1.98	155
1986 Field Sampling Data	0.97	ND[3]	Trace[4]	6.4	280

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[1] Based on Best Engineering Judgment

[2] Loading Based on Conc. of CPs Dissolved in Water and Sorbed to Suspended Solids Being Released to Sugar Creek

[3] Detection Limit = 0.15 µg/L

[4] Trace = 0.05 - 0.17 µg/kg

TABLE 13 - Comparison of Preliminary Modeling, Field Sampling Data and Modeling Results Using Field Estimates of Chlorinated Paraffin Loadings (C_{20-30}, Long-chain)

	Load (g/day)	Water Column (µg/L)	Suspended Particulates (µg/kg)	Benthic Sediments (µg/kg)	Biota (µg/kg)
Original Model Estimates in 1985 GSC Report[1]	0.35	8.06E-05	4.64	25.07	15,300
Model Estimates Using Input from 1986 Field Sampling[2]	1.46	3.37E-04	19.4	105.00	64,000
1986 Field Sampling Data	1.46	ND[3]	0.35	21.0	180

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1 Based on Best Engineering Judgment

2 Loading based on concentrations of CPs dissolved in water and sorbed to suspended solids being released to Sugar Creek

3 Detection Limit = 0.15 µg/L

Due to the scant field data, it is also not possible to determine the reasons for the differences that exist between the field measurements and model estimates.

The comparison of the 1986 monitoring data with the updated modeling estimates using measured releases illustrates that, given a correct CP discharge loading, the model is a predictive tool that can be used with some confidence in other aquatic systems, where monitoring data are lacking. Until further study is made, this predictive ability must be considered limited to the chlorinated paraffins of the types considered by this report and the water/solids systems of the kind dealt with by this study.

TINKERS CREEK STUDY AREA

The analytical results of the Tinkers Creek samples indicate that chlorinated paraffins, represented by the short-chain C_{10-20}, 50-60% chlorine, the medium-chain C_{14-17}, 50-60% chlorine and long-chain C_{20-30}, 40-50% chlorine CPs, could not be detected in any of the samples collected from the S.K. Wellman NPDES outfalls or waters receiving direct discharge from the plant. These waters included the network of tributaries which make up the Deerlick Run drainage network and Tinkers Creek. Most of these samples, especially the sediment samples, contained a variety of organic constituents at high enough concentrations to mask the presence of any CPs. These interferences, largely halogenated aromatics, essentially raised the limit of detection of the method. In other words, if CPs were present, they could not be resolved. These interferences could be attributed to the highly industrialized nature of the Tinkers Creek area. (Water temperatures measured in the area ranged from 9 to 14°C. The substrate consisted of fine silt or gravel with no odor. Flow was immeasurably slow in the tributary network. Flow was measured as 90 to 140 cfs in Tinkers Creek.)

Chlorinated paraffins, however, were detected in the sample collected from the process wastestream inside the S.K. Wellman plant. This sample was collected near the end of the assembly process just before the wastestream is discharged from the plant to the main POTW interceptor. CP concentrations were measured as follow: short-chain CP, 8.1 µg/L; medium-chain CP, 1.3 µg/L; and long-chain CP, 2.2 µg/L.

CHAPTER VII. REFERENCES

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APPENDIX A

ANALYTICAL METHOD

TABLE OF CONTENTS

1. SCOPE AND APPLICATION

This method provided procedures for the detection and semiquantitative measurement of chlorinated paraffins in water, suspended solids, sediment, and mussel tissue. Chlorinated paraffins measured with this method are C_{10}-C_{12}, 50-60% Cl ; C_{14}-C_{17}, 50-60% Cl; and C_{20}-C_{30}, 40-50% Cl.

2. SUMMARY OF METHOD

Figure A-1 presents a schematic of the analytical procedures used for determining chlorinated paraffins in water, sediment, suspended solids, and mussel tissue. The method requires sample preparation, extraction of chlorinated paraffins, cleanup, concentration, and determination by high resolution gas chromatography/negative chemical ionization mass spectrometry/selected ion monitoring (HRGC/NCIMS/SIM).

3. DEFINITIONS

3.1 Concentration Calibration Solutions

Solutions containing known amounts of analytes. These calibration solutions are used to determine instrument response of the analytes as a function of mass.

3.2 Sample Batch

A sample batch consists of up to 10 environmental samples of the same matrix, one laboratory method blank, and two internal quality control samples (one spiked and one unspiked). Additional QC samples (e.g., field QC samples, trip QC samples) may be added to a sample batch where appropriate.

3.3 Laboratory Method Blank

This blank is prepared in the laboratory and contains all of the analytical reagents in required quantities and is carried through the performance of all analytical procedures except addition of a sample aliquot to the extraction vessel. A minimum of one laboratory method blank will be analyzed with each batch of samples.

3.4 Laboratory Method Spike

This sample consists of an aliquot of matrix to which a known amount of analyte is added. All analytical procedures are performed on this spike. A minimum of one laboratory spike is analyzed with each batch of samples to monitor recovery for that batch.

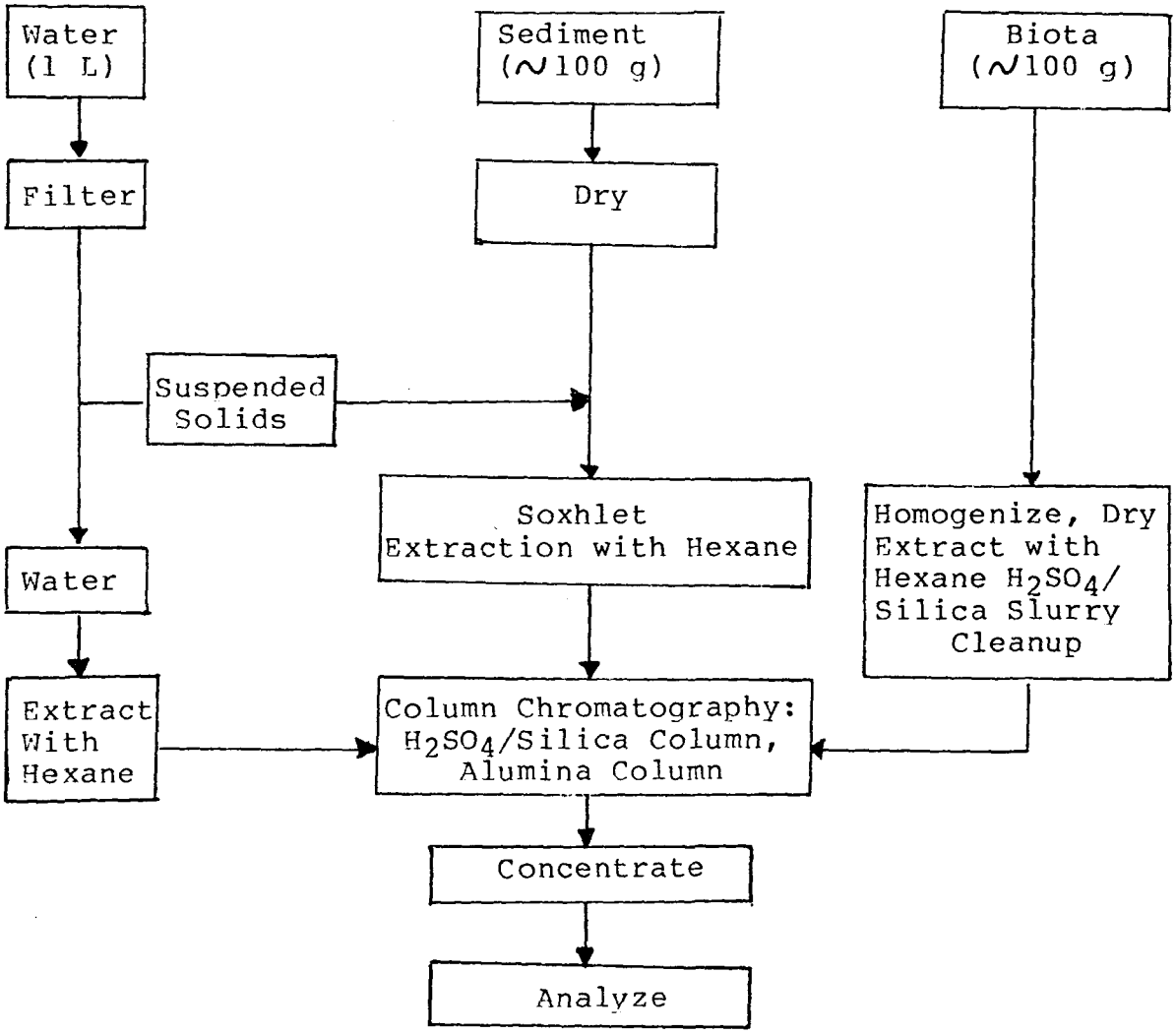

FIG. A-1 Extraction and Clean-Up Procedures for Chlorinated Paraffins

3.5 Field QC Samples

A sample collected in the field, homogenized, and divided into four aliquots. Two of the aliquots are spiked in the field (field spikes) and two are left unspiked (field blanks). The field blanks are spiked in the laboratory at the same level as the field spikes, analyzed, and compared to the field spikes to monitor analyte behavior during transportation and storage.

3.6 Trip QC Samples

Blank matrix samples prepared in the laboratory, taken and maintained on the sampling trip. Half of the samples are spiked in the field and the remaining half left unspiked. The samples are transported, stored, and analyzed in the laboratory in the same manner as the environmental samples. These samples are used to monitor contamination of the environmental samples. For this method, deionized water served as the trip sample matrix.

3.7 Performance Sample

A standard solution of analytes prepared by the work assignment Quality Control Coordinator (QCC) at a concentration unknown to the analyst. This sample was analyzed by the analyst and the results reported to the QCC for evaluation. This sample was designed to measure instrument performance.

4. INTERFERENCES

Chemicals which elute from the HRGC column within the retention time windows of the chlorinated paraffins and produce ions within the mass ranges scanned are potential interferences. Because low levels (sub ppb) of chlorinated paraffins were anticipated, the elimination of the interferences was essential. High purity reagents and solvents were used and all equipment was thoroughly cleaned. Because chlorinated paraffins are used as plasticizers, contact with plastics (except polyethylene) was avoided. Polyethylene gloves were worn during sample preparation to avoid contamination of the samples. Laboratory method blanks were analyzed to demonstrate the absence of contamination that would interfere with the measurement of

the chlorinated paraffins. Column chromatographic procedures were used to remove co-extracted sample components; these procedures were performed carefully to minimize loss of chlorinated paraffins during attempts to increase their concentration relative to other sample components.

5. APPARATUS AND EQUIPMENT

5.1 The GC/MS system was a Finnigan MAT 4000 equipped with an Incos 2400 data system. Operating conditions and parameters are listed in Table A-1.

5.2 HRGC Column

A 30-m x 0.25-mm i.d. fused silica capillary column coated with DB-5 (0.25 μm) was used for analysis of chlorinated paraffins.

5.3 Miscellaneous Equipment

5.3.1 Nitrogen evaporation apparatus with variable flow rate.

5.3.2 Balance capable of accurately weighing to 0.01 g.

5.3.3 Balance capable of accurately weighing to 0.0001 g.

5.3.4 Water bath equipped with concentric ring cover and capable of being temperature controlled.

5.3.5 Stainless steel spatulas or chemical spoons.

5.3.6 Magnetic stirrers and stir bars.

5.4 Glassware

5.4.1 Separatory funnels, 2-L

5.4.2 Kuderna-Danish (KD) apparatus

5.4.3 Soxhlet apparatus

5.4.4 Erlenmeyer flasks

5.4.5 Minivials

2-ml borosilicate glass with conical-shaped reservoir and screw caps lined with Teflon-faced silicone disks.

Table A-1 HRGC/NCIMS Operating Conditions for CP Analysis

Mass spectrometer	
Mode:	negative chemical ionization
Ionization gas:	methane
Ionizer pressure:	0.7 torr
Electron energy:	70 eV
Emission current:	0.3 mA
Electron multiplier voltage:	-1700 V
SEV:	10^{-7}
Source temperature:	170°C
Overall SIM cycle time:	3 sec
Gas chromatograph	
Column coating	DB-5
Film thickness:	0.25 μm
Column dimensions:	30 m x 0.25 mm ID
Helium linear velocity:	~ 25 cm/s
Helium head pressure:	8 psi
Injection type:	on-column
Injector temperature:	ambient
Interface temperature:	300°C
Injection size:	1 μL
Initial temperature:	80°C
Initial time:	2 min
Temperature program:	80°C to 320°C at 10°C/min

5.4.6 Powder funnels--glass

5.4.7 Chromatographic columns for the silica and alumina chromatography--champagne minicolumns with 30 mL reservoirs (Supelco).

5.4.8 Carborundum boiling chips; extracted for 6 h in a Soxhlet apparatus with benzene and air dried.

5.4.9 Glass wool, silanized (Supelco); extracted with methylene chloride and hexane and air dried.

5.4.10 Glassware Cleaning Procedure

The glassware was cleaned using the procedures outlined in Appendix B, section 4.3 of the Chlorinated Paraffin Environmental Field Study Quality Assurance Project Plan (QAPP) (Appendix D).

6. REAGENTS AND STANDARD SOLUTIONS

6.1 Column Chromatography Reagents

6.1.1 Alumina Woelm B (Woelm Pharma) activated at 130°C for 48 h or longer.

6.1.2 Silica Gel

High purity grade, type 60, 70/230 mesh. The silica gel was extracted in a Soxhlet apparatus with methylene chloride for 10 h (minimum of two cycles per hour). It was then air dried and activated by heating in a foil-covered glass container for at least 24 h at 130°C.

6.1.3 Silica gel impregnated with 40% (by weight) sulfuric acid. Two parts (by weight) concentrated sulfuric acid was added to 3 parts (by weight) silica gel (extracted and activated) in a glass screw cap bottle. It was tumbled for 5 to 6 h, shaking occasionally until free of lumps.

6.1.4 Sulfuric acid, concentrated; ACS grade, specific gravity 1.84.

6.2 Sodium sulfate, granular, anhydrous. Extracted with methylene chloride for 16 h (minimum of 2 cycles per hour) air dried and then heated for longer than 4 h in a shallow tray at 400°C. It was cooled in a desiccator and stored in a 130°C oven.

6.3 Solvents

High purity, distilled in glass; methylene chloride, hexane, diethyl ether, acetone, and isooctane. High purity solvents were dispensed from Teflon squirt bottles.

6.4 Concentration Calibration Solutions

Three chlorinated paraffin standard materials (Paroil 142, Paroil 152, and Paroil 1160) were required. Portions of the standards were accurately weighed and dissolved in isooctane to produce concentration calibration solutions at the concentrations shown in Table A-2.

7. GC/MS PERFORMANCE CRITERIA

Single run limited mass range selected ion monitoring analyses of the chlorinated paraffins were carried out with the instrumental conditions and parameters outlined in Table A-1. All nine mass ranges given in Table A-3 were sequentially scanned in a single run with a total elapsed time of approximately 3 s.

7.1 Tuning and Mass Calibration

The mass spectrometer was tuned on a daily basis prior to sample analysis using perfluorotributylamine (FC-43). For reproducibility of the relative abundance measurements, the abundance ratio of the m/z 414: m/z 633 ion was adjusted to 1:3 (±10%).

7.2 Initial Calibration for Chlorinated Paraffin Analysis

Initial calibration was required before any samples were analyzed for chlorinated paraffins. Initial calibration was also required if any routine calibration did not meet the required criteria listed in Section 7.3.

7.2.1 Tuned and calibrated the instrument with FC-43 as outlined in Section 7.1.

7.2.2 The four concentration calibration solutions listed in Table A-2 were analyzed for the initial calibration phase.

7.2.3 Using the HRGC and MS conditions in Table A-1 and the SIM monitoring parameters given in Table A-3, 1 μL of each of the four concentration calibration solutions were analyzed.

Table A-2 Concentration Calibration Solutions

CP	Concentration in calibration solutions (µg/mL)			
	CS1	CS2	CS3	CS4
Paroil 142	100	50	20	10
Paroil 152	100	50	20	10
Paroil 1160	100	50	20	10

Table A-3 SIM Mass Ranges for CP Analysis

Mass range	Nominal scan time (s)	CP
324-329	0.34	C_{10-12}
359-364	0.34	
367-372	0.34	
393-401	0.34	
401-420	0.35	C_{14-17}
441-454	0.34	
477-488	0.36	
498-503	0.36	C_{20-30}
514-518	0.34	

7.2.4 The response factors for each mass range were computed using the computational method in Section 13.1.

7.2.5 The mean RF and the standard deviation were then calculated.

7.3 Criteria for Acceptable Initial Calibration

7.3.1 The standard error (%) of the mean RFs for the four calibration standards were:

323-329	357-363	365-371	391-399
7.4	7.6	5.6	4.4

399-419	439-453	475-487	496-502
7.2	7.5	4.8	6.6

512-517
16.5

7.3.2 The SIM traces for all ions used for quantitation must present a signal-to-noise (S/N) ratio of $\geq$3 as measured from the integrated areas in the appropriate retention time windows.

7.4 Routine Calibration

Routine calibration was performed at the beginning of every day before actual sample analyses were performed and after all samples for the day were analyzed. Additional calibration during the day may have been employed if instrument instability was suspected.

7.4.1 One (1) µL of concentration calibration solution CS2 was injected as the initial calibration check on each analysis day.

7.4.2 The RF for each ion range in the concentration calibration solution was computed.

7.5 Criteria for Acceptable Routine Calibration

7.5.1 The measured RF for all cells was within ±30% of the average mean calculated in Section 13.1.1.

7.5.2 If this criterion was not met, a second attempt was made before repeating the entire initialization process.

8. QUALITY CONTROL PROCEDURES

8.1 Summary of QC Analyses

8.1.1 Initial and routine calibration and instrument performance checks.

8.1.2 Analysis of a batch of samples with accompanying QC analyses: up to 10 environmental samples of one matrix type plus QC analyses including one method blank, and one spiked blank. Additional QC samples, including field spikes, field blanks, trip spikes, and trip blanks may be included in a batch of samples.

8.2 Performance Evaluation Solutions

Prior to sample analysis, a solution provided by the work assignment quality control coordinator containing known amounts of chlorinated paraffins was analyzed. The accuracy of measurement for performance evaluation samples was in the range of 70-130% of true value.

8.3 Laboratory Method Blanks

A minimum of one laboratory method blank was generated with each batch of samples. The method blank was generated by performing all steps detailed in the analytical procedure using all reagents, standards, equipment, apparatus, glassware, and solvents that would have been used for a sample analysis. For sediment, suspended solids, and biota samples, the matrix was omitted. Deionized water was substituted for environmental water.

8.3.1 An acceptable method blank exhibited no positive response in the characteristic ion ranges monitored.

8.3.1.1 If the above criterion was not met, solvents, reagents, apparatus, and glassware were checked to locate and eliminate the source of the contamination before any further samples were extracted or analyzed.

8.3.1.2 If new batches of reagents or solvents contained interfering contaminants, they were purified or discarded.

8.4 Spiked Samples

8.4.1 Method Spikes

A minimum of one method spike was generated with each batch of samples. A method spike is generated by performing all steps detailed in the analytical procedure using all reagents, standards, equipment, apparatus, glassware, and solvents that would be used for a sample analysis. For sediment, suspended solids, and biota samples, the matrix was omitted. Deionized water was substituted for environmental water. These samples were spiked with known amounts of chlorinated paraffins prior to extraction.

8.4.2 Field Spikes

Field spikes were analyzed using the method at the frequency specified in the experimental design contained in the main body of the QAPP (Appendix D).

8.4.3 Trip Spikes

Trip spikes were analyzed using this method at the frequency specified in the experimental design contained in the main body of the QAPP.

9. SAMPLE PRESERVATION AND HANDLING

Water and sediment samples were maintained at 8°C or lower until extraction. Mussel samples were maintined at -20°C until extraction. Sample extracts were stored at 8°C or less until analysis.

0. SAMPLE PREPARATION AND EXTRACTION

10.1 Extraction of Water Samples

10.1.1 Filter water through a 0.45 μ filter (Type HA, Millipore, 47 mm) in a millipore filtration apparatus. Use a 2-L suction flask to receive the filtrate. Use suction by aspiration to facilitate the process.

10.1.2 Rinse the sample jar with a 250-mL portion of the filtrate and pass through the filter again. Note: For samples with a large amount of particulate, more than one filter may be needed if filtration becomes slow.

10.1.3 Measure the volume of the filtrate using a 500-mL graduated cylinder and pour back into the sample jar.

10.1.4 Transfer the filter to a clean 4-oz jar using forceps. Retain for determination of suspended solids as detailed in section 10.4.

10.1.5 Transfer 1,000 mL of the filtrate into a 2-L separatory funnel.

10.1.6 Add 60 mL of hexane, stopper, invert and vent the funnel. Shake the funnel for 2 minutes vigorously enough to form an emulsion.

10.1.7 Allow the phases to separate, drain the aqueous phase into a 1,000-mL Erlenmeyer flask and the hexane phase into a 250-mL Erlenmeyer flask.

10.1.8 Transfer the aqueous phase back into the 2-L separatory funnel and add another 60 mL of hexane to the 1,000 mL Erlenmeyer flask to rinse the flask. Add the rinse to the separatory funnel and shake again for 2 min.

10.1.9 Repeat step 10.1.7.

10.1.10 Discard the aqueous phase.

10.1.11 Add enough (10-20 g) anhydrous sodium sulfate to the hexane extract to remove the water.

10.1.12 Transfer the hexane extract to a 250-mL Kuderna Danish (KD) flask equipped with either a 5- or 10-mL receiver. Complete the transfer with three rinses of hexane, 10-20 mL each.

10.1.13 Add several carborundum chips and place a 3-ball Snyder column into position.

10.1.14 Concentrate the hexane to about 5 mL on a steam bath.

10.1.15 Transfer the concentrated hexane extract to a 4-dram vial using a Pasteur pipette. Complete the transfer using three rinses of hexane (about 0.5 mL each).

10.1.16 Proceed to the sulfuric acid/silica cleanup (Section 11.1).

10.2 Extraction of Sediment Samples

10.2.1 Transfer the sediment sample (1 kg) to a clear Pyrex baking dish (12 in x 12 in x 2 in) with a stainless steel spatula.

10.2.2 Drain and discard the excess water.

10.2.3 Dry the sediment by placing it in an oven (65-70°C) for 48-60 h. Stir the sediment occasionally to facilitate drying and to break up large clumps.

10.2.4 Break the sediment into a fine powder using a mortar and pestle, if necessary. Remove large rocks with a pair of forceps.

10.2.5 If necessary, sift the sediment through a screen to remove particles greater than 1 mm.

10.2.6 Weigh 100 g (±0.1 g) of the sediment into a clean 8 oz jar.

10.2.7 Add 100 g (±0.1 g) of anhydrous sodium sulfate to the sediment sample and mix with a spatula.

10.2.8 Load the sediment/sodium sulfate mixture into a Soxhlet flask containing a pad of glass wool.

10.2.9 Add 200 mL of hexane to a 200-mL round bottom flask, add several carborundum chips and extract the sample for 16 h.

10.2.10 Allow the apparatus to cool and manually cycle any remaining hexane in the sediment. Remove the 250-mL flask from the apparatus. Discard the sediment.

10.2.11 Transfer the hexane to a 250-mL KD flask. Complete the transfer with three 10-mL rinses of hexane. Concentrate to about 5 mL and transfer to a 4-dram vial using a Pasteur pipette. Complete the transfer with three 0.5-mL rinses of hexane. Cap with a Teflon-lined lid.

10.2.12 Proceed to the sulfuric acid/silica cleanup (Section 11.1).

10.3 Preparation and Extraction of Mussel Samples

10.3.1 Open the mussel with a sharp knife by cutting the muscles attached to the shell next to the hinge.

10.3.2 Scrape and transfer the tissue to a tared 500-mL beaker.

10.3.3 Drain off any residual water and remove any plant tissue.

10.3.4 Open and add enough mussels to obtain at least 100 g of tissue.

10.3.5 Homogenize the tissue in a Waring blender. A homogeneous viscous liquid should be obtained.

10.3.6 Transfer the tissue homogenate to a clear Pyrex dish (12 in x 12 in x 2 in) using a stainless steel spatula.

10.3.7 Slowly add 3 times the sample weight of anhydrous sodium sulfate to the homogenate, stirring frequently with a spatula.

10.3.8 Allow the mixture to dry until it is free flowing. This step may take several days.

10.3.9 Load the tissue/sodium sulfate mixture into a Soxhlet flask to an equivalent weight of 100 g of mussel tissue. Extract for 16 h with 450 mL of hexane.

10.3.10 Cool and remove the round bottom flask. Discard the tissue/sodium sulfate mixture.

10.3.11 Add 10-20 g of anhydrous sodium sulfate to dry the extract.

10.3.12 Add 20 g of 40% (w/w) sulfuric acid on silica gel, and let stand for 1 h with occasional swirling.

10.3.13 Transfer the extract to a 250-mL KD flask. Complete the transfer with three 20-mL rinses of hexane. Concentrate to about 5 mL.

10.3.14 Transfer the concentrated extract to a 4-dram vial. Complete the transfer with three 0.5-mL rinses of hexane.

10.3.15 Concentrate the extract to about 0.5 mL with a gentle stream of nitrogen. Cap with a Teflon-lined lid.

10.3.16 Proceed to the alumina cleanup step. (Section 11.2)

10.4 Extraction of Suspended Solids

10.4.1 Weigh the filters obtained in step 10.1.4 to the nearest 0.1 mg.

10.4.11 Load the filters into a Soxhlet flask containing a pad of glass wool.

10.4.2 Proceed with extraction and cleanup beginning with step 10.2.9.

11. CLEANUP PROCEDURES

11.1 Sulfuric Acid/Silica Cleanup

11.1.1 Prepare the columns (champagne minicolumns with 30-mL reservoir, Supelco Inc.) by inserting a small pad of pesticide-grade glass wool (DCMS treated, Alltech Associates).

11.1.2 Rinse the columns and glass wool with three aliquots each of acetone and hexane in that order.

11.1.3 Add 1.0 g of 40% (w/w) sulfuric acid/silica to the column. Layer about 1 cm of anhydrous sodium sulfate on top of the bed.

11.1.4 Wet the column with enough hexane to saturate the bed. DO NOT ALLOW THE COLUMN TO DRAIN FAR ENOUGH TO EXPOSE THE BED OF SILICA.

11.1.5 Transfer the sample to the column using a Pasteur pipette. Complete the transfer with three 0.5-mL rinses of hexane. Collect the eluent in a 6-dram vial.

11.1.6 Allow the sample extract to flow through the column and add 5 mL of hexane into the vial.

11.1.7 Allow the column to run dry and rinse the tip with about 1 mL of hexane into the vial.

11.1.8 Concentrate the eluate to about 0.5 mL with a gentle stream of nitrogen. Cap with a Teflon-lined lid.

11.2 Alumina Cleanup

11.2.1 Prepare the columns as described for the sulfuric acid/silica columns (Section 11.1.1). Use 1.0 g of basic alumina prepared as described in Section 6.1.1.

11.2.2 Wet the column with enough hexane to saturate the bed. DO NOT ALLOW THE SOLVENT LEVEL TO FALL BELOW THE TOP OF THE ALUMINA BED.

11.2.3 When the solvent level has reached the bed, add the sample extract with a Pasteur pipette.

11.2.4 Measure 10 mL of 1% (v/v) diethyl ether in hexane into a graduated cylinder. Complete the transfer of the sample extract to the column with three rinses of the 1% ether in hexane mixture when the sample extract has completely drained into the alumina bed. Add the remaining 1% ether in hexane. Collect the eluate in a 4-dram vial.

11.2.5 When the 1% ether in hexane has reached the top of the bed, add 10 mL of 50% diethyl ether in hexane to the column. Collect the eluate in a fresh 4-dram vial. Discard the 1% ether eluate.

11.2.6 After the 50% ether in hexane fraction has completely eluted and the column drained dry, rinse the tip of the column with about 1 mL of hexane and concentrate the sample to about 0.5 mL with a gentle stream of nitrogen.

11.2.7 Transfer the sample with a Pasteur pipette to a 2-mL conical reaction vessel (Supelco). Complete the transfer with one rinse of hexane and two rinses of acetone (about 0.5 mL each). Reduce the sample to dryness with a gentle stream of nitrogen.

11.2.8 Cap with a Teflon-lined lid and store for analysis by mass spectrometry.

11.2.9 Prior to analysis, the analyst will add a 50 uL (or other volume) aliquot of isooctane to the sample and sonicate for 30 sec.

12. INSTRUMENTAL PROCEDURES

12.1 Once routine calibration criteria were met, the instrument was ready for sample analysis. Prior to the first sample, a blank injection of isooctane was analyzed to document system cleanliness. If any evidence of system contamination was found, corrective action was taken and another isooctane blank analyzed.

12.2 The typical daily sequence of injections is shown in Table A-4.

Table A-4 Typical Daily Sequence for CP Analysis

1. Tune and calibrate mass spectrometer with FC-43.
2. Inject concentration calibration solution.
3. Inject isooctane blank.
4. Inject samples.
5. Inject concentration calibration solution.

13. DATA REDUCTION

In this section, the procedures for data reduction are outlined for the analysis of chlorinated paraffins in environmental samples.

13.1 Quantitative Calculations

13.1.1 Calculation of Response Factors

Response factors for each mass range were calculated from the data obtained during the analysis of concentration calibration solutions using Equation 13.1.

$$RF = \frac{Astd}{Cstd \times Vstd} \qquad \text{EQ. 13.1}$$

Where:
Astd is computer generated area for a mass range
Cstd is the concentration of the standard (ng/μL)
Vstd is the volume of sample injected in (μL)

13.1.2 Calculation of Chlorinated Paraffin Concentrations

Chlorinated paraffin concentrations were calculated for each mass range using Equation 13.2.

$$\text{Concentration (ppb)} = \frac{Aex \times Vex}{RF \times Vinj \times M} \qquad \text{EQ. 13.2}$$

Where:
Aex is the computer generated area of the mass range in the extract
RF is the response factor calculated in Equation 13.1.
Vinj is the volume of extract injected (μL)
Vex is the final volume of the extract (μL)
M is the mass of sample taken for analysis (g)

13.2 Estimated Method Detection Limit

Estimated method detection limits were calculated in situations where (1) no response was noted for a specific mass range and (2) where a response was quantitated as a trace value, that is, where the response is between 3 and 10 times the signal to noise ratio. These two cases are discussed below.

13.2.1 For samples in which no signal was detected above the baseline, the estimated minimum detectable concentration was calculated. The background (σ) was determined by integrating the ion abundances for the mass ranges in the appropriate regions and relating the area to an estimated concentration that would produce that area. The formula is given in Equation 13.3.

$$EDL = \frac{3 \times Aex \times Vex}{RF \times Vinj \times M} \qquad \text{EQ. 13.3}$$

Where:
EDL is the estimated detection limit (ppb)
Aex is the computer generated area of the mass range in the extract
RF is the response factor calculated in Equation 13.1
Vinj is the volume of extract injected (uL)
Vex is the final volume of extract (uL)
M is the mass of sample taken for analysis (g)

13.2.2 If a response for a specific mass range was quantitated as a trace value [signal to noise is greater than or equal to 3 (σ) but less than 10 (σ)], the analyst also provided an estimated method detection limit. This was accomplished by using the integrated area with in the retention window and calculating as given in Equation 13.3.

APPENDIX B

ANALYTICAL METHOD VALIDATION RESULTS

TABLE OF CONTENTS

TABLE OF CONTENTS (CONT'D)

1. Summary

The method validation phase of this work was designed to assess the precision, accuracy, and recovery of the method. Matrix samples (except mussel tissue, which was obtained commercially) for the validation were obtained from Sugar Creek (Dover, Ohio) sampling stations A and B during the reconnaissance trip conducted on August 12, 1986. Station A is located downstream from the Dover Chemical Plant and Station B is located upstream. Station B samples provided the basis for method assessment, while station A samples were run to obtain a preliminary indication of downstream CP concentrations and were used to prepare the spiked environmental samples.

Overall, the methodology for analysis of CPs in water and sediment was well-behaved for quantification of the C_{10-12} and C_{14-17} carbon chain-length groups, providing stable recovery rates of predictable precision. The methodology provided generally useable C_{20-30} quantification, but of somewhat lower predictability than for the C_{10-12} and C_{14-17} carbon chain-length groups.

A statistical summary of the validation phase follows:

- CPs were not identified in unspiked filtered stream water although present in particulates and sediment from the same sampling stations. Values reported for filtered stream water (0.003-0.157 µg/L) were comparable to those for distilled water (0.005-0.11 µg/L) and were indistinguishable from procedural noise.

- The numerical values reported for unspiked filtered stream water and distilled water were statistically significantly highest for C_{10-12} and lowest for C_{20-30}, suggesting a higher limit of detection for C_{10-12} than for C_{20-30} for CP analysis of water.

- Recovery percentages for CPs spiked in filtered stream and distilled water were significantly higher statistically for C_{10-12} ($\bar{X} \doteq 100\%$) than for C_{14-17} ($\bar{X} \doteq 75\%$). Recovery of C_{20-30} was too variable for meaningful comparison.

- CP residues were reported in unspiked stream and sediment both upstream of and downstream from the Dover Chemical Plant outflow ditch, with downstream concentrations significantly higher than upstream concentrations. Within stations, the lowest residues were reported consistently for C_{10-12} and the highest for C_{20-30}. There was no overlapping of values among the three carbon chain-length sets.

- Evaluation of recovery data for spiked sediment is confounded, to some extent, by the presence of CPs in the unspiked sediment from Station A prior to spiking. An attempted

arithmetic correction to estimate recovery of spiked CPs alone was not fully effective.

- Contrary to recoveries reported for spiked water, those for the C_{10-12} and C_{14-17} were essentially equal among all three spiking levels for sediment, the six recovery values ranging from 56.3% to 63.5%. Recovery of C_{20-30} from the 500 and 1,000 µg/kg sediment spikes ($\bar{X}$ unadjusted = 84.4%) was significantly higher than was recovery of C_{10-12} or C_{14-17} for those spikes. (C_{20-30} recovery data for the 200 µg/kg spike was too variable for meaningful comparison as the result of two apparently false negative reports.)

- Concentrations reported for the single downstream particulate sample were decidedly higher than for the single upstream sample, being highest for C_{20-30} (4.2 µg/L water).

- Of the 45 water, sediment and method blank samples analyzed (Tables 10 and 11), there were 14 samples that might have resulted in false positive reports for C_{10-12}, C_{14-17}, and C_{20-30}, and the remaining 31 samples that might have resulted in false negative reports. Among these quantifications, there was one apparent false positive report (13.89 µg/kg of C_{20-30} for an unspiked method blank for sediment) and two false negative reports (0.048 and 0.052 µg/L of C_{20-30} for stream water spiked at 1 µg/L). There were no false positives or false negatives for analyses of C_{10-12} or C_{14-17}. The false positive frequency for C_{20-30} was 1 in 14 analyses, and the false negative frequency 2 in 31 analyses (see Section 6.6).

- Statistical analysis of the water and sediment spiking recovery data provided least squares estimates of overall method recovery and accuracy. Estimates for recovery and, equivalently, accuracy for quantification of CPs in sediment averaged 61%, ranging from 57% for C_{14-17} to 66% for C_{20-30}. Recovery and accuracy for CP quantification in water was essentially 100% for C_{10-12}, 75% for C_{14-17} and not calculated for C_{20-30}.

- Precision estimates as coefficients of variation, or relative standard deviation, for individual spiking levels are presented in Tables B-3, B-4 and B-5. Coefficients of variation for quantification of CPs in water averaged approximately 12% for C_{10-12}, 25% for C_{14-17} and 73% for C_{20-30} (8 degrees of freedom per average; derived from Table B-3). For quantification of CPs spiked in stream sediment (excluding method blanks), coefficients of variation averaged approximately 26% for C_{10-12}, 23% for C_{14-17} and 34% for C_{20-30} (6 degrees of freedom per average; derived from Table B-5).

- Regression equations to derive "best estimates" of true CP concentrations in water and sediment samples for given reported concentrations, and their statistical confidence limits, were developed using methods of inverse prediction.

2. Experimental Design

The experimental design for the method validation phase of this study is outlined in Table B-1. The design is broken down into two phases. The first phase was designed to measure background (L_0) levels of CPs in the matrices and to provide a basis for setting spiking levels (L_1-L_3) for phase II. The phase II analyses were used to assess method accuracy, precision, and recovery. A batch of samples consists of four validation samples and associated quality control samples. A laboratory method blank and a spiked control sample for water and a laboratory method blank for sediment were incorporated. Since control sediment was not available, spiked control sediments were not included in the design.

3. Analytical Procedures

The validation samples were analyzed according to the procedures detailed in Appendix A. The Chlorinated Paraffin concentrations measured in these samples and used in this statistical analysis are given at the end of this Appendix as Tables B-10 and B-11.

4. Data Quality Assessment

Precision, accuracy and recovery were determined for three spiking levels for each of the three cells.

4.1 Precision

Precision was assessed as relative standard deviation, or coefficient of variation, within each cell. Precision is expressed as relative standard deviation as defined in Section 9.1 of the QAPP.

4.2 Accuracy

The accuracy of the method was assessed within each cell. Accuracy is expressed as A% as defined in Section 9.2 of the QAPP. Method overall accuracy was assessed using regression estimates of recovery for known spiking levels.

4.3 Recovery

Recovery was assessed within each cell. The measure of recovery is percent recovery as defined in section 9.3 of the QAPP. Method overall recovery was assessed using the same procedures as for method accuracy.

TABLE B-1 Experimental Design for the Method Validation Study

WATER MATRIX		Upstream "B" Pool	Downstream "A" Pool				Method Blank	Spike Control
PHASE	BATCH NO.	L_0	L_0	L_1	L_2	L_3	S_0	S_1
I	1	2X	2X	-	-	-	1X	1X
II	2	-	1X	1X	1X	1X	1X	1X
II	3	-	1X	1X	1X	1X	1X	1X
II	4	-	-	1X	1X	1X	1X	1X
Total # of Analyses		2	4	3	3	3	4	4

SEDIMENT MATRIX		Upstream "B" Pool	Downstream "A" Pool				Method Blank (no sediment)
PHASE	BATCH NO.	L_0	L_0	L_1	L_2	L_3	S_0
I	5	2X	2X	-	-	-	1X
II	6	-	1X	1X	1X	1X	1X
II	7	-	1X	1X	1X	1X	1X
II	8	-	-	1X	1X	1X	1X
Total # of Analyses		2	4	3	3	3	4

Note 1: 1X = single analysis; 2X = replicate analysis
Note 2: Each sample in the above table went through the extraction process.
Note 3: One solvent blank and one calibration check at the L_2 spiking level was run per day for instrument check.
Note 4: Spiking level S_1 for the distilled water spike check was 10 times the estimated LOQ (i.e., 5 ppb for water).

5. Method Development and Validation Study Results

5.1 Spiked Recoveries

5.1.1 Sediment Blank Spike Recoveries

The method development and validation studies indicate that acceptable recoveries from spiked sediments are obtained using the analytical method. However, spiked method blanks analyzed with the sample sets did not yield recoverable CPs. It is thought that the loss of analyte from these samples is the result of lack of matrix. The method development and validation studies were performed with Missouri River sediment and Sugar Creek sediment, respectively. These sediments were spiked and dried by mixing with equal portions of sodium sulfate at moderate temperatures until free-flowing mixtures were obtained. This was done to prevent plugging of the Soxhlet apparatus during extraction. The method spikes consisted of sodium sulfate only. It would appear that CPs are bound to the sodium sulfate tightly enough that Soxhlet extraction will not recover them. It is recommended for future analyses that a control sediment be identified and used for spiked recovery determinations during sample analysis.

5.1.2 Water and Particulate Field Spikes

The environmental spike samples (field and lab) were designed to show differences upon transport and storage of the environmental samples. The analytical results showed generally consistent results between the field and lab spikes, indicating that sample degradation was not a serious problem; however, low extraction efficiencies were obtained for these samples. This is not surprising considering the complex nature of these samples and the difficulty in generating four samples containing the same amount of particulates from a single source at each QA station.

The trip spike and spiked DI water (both 50 ppb) also exhibited low recoveries, which were in general agreement with the environmental water spikes. This was expected since these spikes did not contain particulates, which was thought to contribute heavily to the low recoveries.

Several experiments, using the chlorinated paraffin standards were carried out to isolate the cause of the low recoveries. These included experiments to isolate various possible aspects of the extraction procedure, in particular, adsorption to glassware, losses during transfers, and losses by filtration. Adsorption to glassware or loss during transfers were not thought to be

the cause of the low recoveries; these would have been evident during the method validation study, which incorporated these steps. The Sugar Creek validation water was filtered prior to spiking to remove the particulates; the environmental water samples were spiked, then filtered; and the trip spike and lab spike DI water were extracted unfiltered.

The results of these experiments indicate that losses to adsorption and filtering are not significant. However, the results obtained do indicate that the solubility of chlorinated paraffins is less than 50 ppb, as evidenced by recoveries from DI water spiked at 50 ppb, extracted with hexane, and analyzed. The recoveries obtained were consistent with those obtained for the trip and lab spikes.

This spiking level was chosen prior to the Sugar Creek sampling effort without knowledge of the CP and particulate levels which would be encountered. This level is an order of magnitude higher than the highest validation level and was chosen in an effort to provide a concentration which could be measured above the existing environmental levels. This spiking level was maintained for the Tinkers Creek study as analytical data was not available from the Sugar Creek study to form a basis for change.

The analytical results for the environmental samples indicate that no significant concentration of chlorinated paraffins is contained in the filtered water fractions, even above sediments which contain relatively large amounts of chlorinated paraffins, as in the Dover Chemical lagoon. For future analyses, it is recommended that spiking levels be reduced to 5 ppb or less.

5.2 Mussel data

It is noted in the QAPP and preliminary draft of the final report that 10 mussels were to be considered a sample of mussels. This estimate was based on the size of the mussels purchased for the methods development and validation work. It was found, however, that the mussels collected in Sugar Creek were significantly larger, requiring only one to two mussels to generate 100 g of tissue for analysis.

As previously discussed, the first set of mussels presented extraction problems, e.g plugging of the Soxhlet extractor, followed by storage of the extracts at room temperature. The analytical results of the spiked blank, which was stored under the same conditions indicate that the ambient storage did not have an adverse effect on the chlorinated paraffins in the field samples. The results obtained for the upstream mussel samples indicated nondetectable levels of CPs; measurable CP levels were found in the downstream mussel samples. Additional mussel tissue was available for the two upstream sites and the analysis

was repeated with results consistent with the first analysis. However, no tissue from the downstream site was available to confirm the original analysis. Although the quality assurance data would indicate that the original analysis of the downstream sample is valid, the CP level measured should probably be considered a minimum value, due to possible incomplete extraction.

6. Statistical Evaluation of the Method Validation Data

To review, the chloroparaffin method validation study is based on quantification data from analyses of spiked and unspiked samples of sediment and filtered water from Sugar Creek, Ohio, of unspiked particulates filtered from that water, and of spiked and unspiked method blanks analyzed concurrently with those samples. The water and sediment samples, collected during the reconnaissance survey (August, 1986) were taken both upstream (Station B) and downstream (Station A) of the outflow ditch from the Dover Chemical Plant lagoon.

Three separate levels of spiking were used for water and sediment samples. The spiked samples and their respective method blanks were prepared in replicate: generally three replicates for the spiked series and either two or four replicates for the sets of unspiked samples and their method blanks. Particulate material filtered from the stream water samples was of insufficient quantity to provide replicate particulate samples.

Statistical analyses of the data were conducted to examine and evaluate various aspects of the method as related to carbon chain length groups and sampled media. Although intended to provide an overall evaluation of the method, separate statistical analyses were necessarily conducted of the water and sediment data for spiked and unspiked samples. Specifically, the analyses compare reported levels and precision among unspiked samples and their method blanks to evaluate method sensitivity, and they quantify and evaluate recovery characteristics among spiked samples.

6.1 Statistical Evaluation of the Unspiked Water Data

The unspiked water samples were derived from the filtered composite water samples collected at upstream station B and downstream station A. Two replicate samples were taken from the station B composite and four replicates from the station A composite. The four method blank replicates comprised distilled water.

Means and standard deviations for the replicated unspiked water samples are presented, by stations and carbon chain length groups, in Table B-2. Analysis of variance (split-plot) of the total set of data failed to demonstrate statistical differences among stations (considering method blanks as a station) ($F_{2,7df} = 0.978$). The result indicates that the reported values

Table B-2. Reported CP Concentrations (µg/L) in Unspiked Samples of Filtered Stream Water

Sampling Station	Replicates	Statistic	Carbon Chain-length Group C_{10-12}	C_{14-17}	C_{20-30}	Total CPS
B		$\bar{X}$	0.110	0.006	0.004	0.120
(Upstream)	2	(s.d.)	(0.066)	(0.008)	(0.006)	(0.052)
A		$\bar{X}$	0.042	0.014	0.009	0.065
(Downstream)	4	(s.d.)	(0.015)	(0.012)	(0.007)	(0.034)
Method Blank	4	$\bar{X}$	0.053	0.039	0.002	0.094
		(s.d.)	(0.043)	(0.042)	(0.004)	(0.055)
Stations Combined	10	$\bar{X}$	0.060	0.022	0.005	0.087
		s.d.	(0.044)	(0.029)	(0.006)	0.047
		$\bar{X}$ + 3 s.d.	0.192	0.109	0.023	

are apparently not distinguishable from "noise" in the methodology and are therefore not properly attributable to CPs.

There were statistically significant differences among carbon chain-length groups in those reported values, being highest for the C_{10-12} group ($x = 0.060$ µg/L) and lowest for the C_{20-30} group ($x = 0.005$ µg/L), suggesting a higher noise level for the former than for the latter group.

Table B-2 presents values for the mean plus three standard deviations for each of the C-groups as estimates of minimum levels of CP detection in water.

6.2 Statistical Evaluation of Reported CP Concentrations in Spiked Water Samples

Subsamples from the composite water sample collected from station A were used to prepare the spiked samples of filtered stream water. Three spiking levels were used: 1, 2.5, and 5 µg/L for each of the carbon chain-length groups. Thus a sample spiked at "1 µg/L" contained 1 µg/L each of C_{10-12}, C_{14-17}, and C_{20-30} "standard", for a total of 3 µg of CPs/L of water. Method blanks of distilled water spiked at 5 µg/L were also included. All samples were prepared and analyzed in triplicate.

Table B-3 presents the replicate means and standard deviations of the reported CP concentrations, by carbon chain-length group and spiking level, and the means and standard deviations of the respective recovery percentages. The coefficients of variation for reported concentrations and recovery percentages are algebraically identical and thus are presented once in the table to represent both variables.

Analyses of variance of recovery percentages for the C_{10-12} and C_{14-17} groups indicated that within each group, numerical differences among spiking levels were not statistically significant ($F_{3,8df} = 1.09$ and 1.63 respectively.) Analyses were conducted only after Bartlett's test for homogeneity of variances indicated that variances of the C_{10-12} and C_{14-17} sets were not heterogeneous ($X^2_{7df} = 8.769$; $P>0.25$). Bartlett's test indicated statistically significant heterogeneity for replicate variances when the C_{20-30}, 1 µg/L cell was included (reported recoveries of 5.2%, 309.2%, and 4.8%); that cell was therefore excluded from further statistical comparisons as being anomalous. Recovery rates among the remaining C_{20-30} cells, as within the C_{10-12}, and C_{14-17} groups, did not differ statistically.

Analysis of variance indicated that overall differences in recovery percentages between the C_{10-12} groups ($\bar{X} = 102.6\%$) and the C_{14-17} group ($\bar{X} = 76.9\%$) were statistically

Table B-3. Reported CP Concentrations (µg/L) in Spiked Samples of Filtered Stream Water, and Recovery Percentages

Sampling Station	Spike (µg/L)	Replicates	Statistic	C_{10-12} µg/L	C_{10-12} %Recov.	C_{14-17} µg/L	C_{14-17} %Recov.	C_{20-30} µg/L	C_{20-30} %Recov.
A	1.0	3	$\overline{X}$	0.996	99.6	0.701	70.1	1.064	106.4
			(s.d.)	(0.104)	(10.45)	(0.093)	(9.32)	(1.756)	(175.63)
			C.V.(%)	10.4		13.3		165.0*	
A	2.5	3	$\overline{X}$	2.293	91.7	1.555	62.2	1.330	53.2
			(s.d.)	(0.162)	(6.47)	(0.521)	(20.83)	(0.498)	(19.97)
			C.V.(%)	7.1		33.5		37.4	
A	5.0	3	$\overline{X}$	5.605	112.1	4.806	96.1	5.983	119.7
			(s.d.)	(1.286)	(25.73)	(1.736)	(34.71)	(3.203)	(64.07)
			C.V.(%)	22.9		36.1		53.5	
MB	5.0	3	$\overline{X}$	5.343	106.9	3.952	79.0	2.342	46.8
			(s.d.)	(0.357)	(7.15)	(0.605)	(12.08)	(0.814)	(16.25)
			C.V.(%)	6.7		15.3		34.8	

* Variability is significantly greater($P < 0.025$) than that of remaining cells.

highly significant ($F_{1,3df}$ = 61.8). A tendency for the recovery percentage for the C_{20-30} group to be lower than the C_{10-12} and possibly the C_{14-17} groups could not be substantiated because of high recovery values in two of the three C_{20-30}, 5 µg/L replicates (178%, 130%, 51%).

Comparison of coefficients of variation (CVs) across carbon chain-length groups reveals that within each spiking level (viewing MB as a separate level), CVs were always lowest for the C_{10-12} group and highest for the C_{20-30} group (see Table B-3). The probability of this being a chance event is approximately 0.0008 (1 in 1,296 chances), indicating an inverse relationship between analytical precision and carbon chain-length group for CP analysis in water. This relationship was not evident for sediment analysis (see Table B-5).

6.3 Statistical Evaluation of Unspiked Sediment Samples

The unspiked sediment samples were derived from the composite sediment sample collected at upstream station B and that collected at downstream station A. Two replicate samples (subsamples) were derived from the station B composite sample and four replicates from the station A composite sample. The method blanks consisted of a mixture of all the reagents used in the sediment extraction process, but did not include sediment per se.

Replicate means, standard deviations, and coefficients of variation are presented in Table B-4. The table also includes values for the method blank "mean-plus-three standard deviations" for each of the carbon chain-length groups, as estimates of minimum detection levels.

Chemical analysis indicated levels of CPs in the sediment samples collected at both stations that were well in excess of "noise" present in the method blank analyses. Analysis of variance (split-plot using log-transformed data to stabilize variances) of the A and B replicates showed differences in reported levels between the two stations to be statistically highly significant ($F_{1,4df}$= 52.84), the higher levels occurring at downstream station A, as might be expected. The reported "levels" in the method blanks were obviously lower than those for stream sediment and were excluded from the analysis of variance so as not to obfuscate results.

Analysis of variance showed statistically significant differences among carbon chain-length groups, the lowest levels being reported for the C_{10-12} group and the highest levels for the C_{20-30} group.

Table B-4. Reported CP Concentrations (μg/kg) in Unspiked Samples of Sediment

Sampling Station	Replicates	Statistic	Carbon Chain-length Group C_{10-12}	C_{14-17}	C_{20-30}	Total CPS
B	2	$\overline{X}_B$	4.56	13.39	65.08	83.02
(Upstream)		(s.d.)	(2.737)	(3.033)	(21.99)	(16.22)
		C.V.(%)	60.1	22.7	33.8	20.0
A	4	$\overline{X}_A$	30.55	58.14	162.93	251.62
(Downstream)		(s.d.)	(11.724)	(10.155)	(32.539)	(50.620)
		C.V.	38.4	20.2	20.0	20.1
Method Blank	4	$\overline{X}_{MB}$	0.18	0.22	3.47	3.37
		(s.d.)	(0.281)	(0.440)	(6.945)	(7.352)
		C.V.	158.1	200.0	200.0	190.0
		$\overline{X}_{MB}$ + 3 s.d.	1.02	1.54	24.31	-

Table B-5. Reported CP Concentrations (µg/kg) in Spiked Samples of Stream Sediment, and Recovery Percentages

Sampling Station	Spike (ug/kg)	Peplicates	Statistic	C_{10-12} µg/kg	C_{10-12} %Recov.	C_{14-17} µg/kg	C_{14-17} %Recov.	C_{20-30} µg/kg	C_{20-30} %Recov.
A	200	3	$\overline{X}$	113.02	56.5	124.01	62.0	253.34	126.7
			(s.d.)	(40.285)	(20.14)	(42.304)	(21.15)	(154.795)**	(77.4)**
			C.V.(%)	35.6		34.1		61.1	
A	500	3	$\overline{X}$	301.17	60.2	304.36	60.9	415.29	83.1
			(s.d.)	(63.930)	(12.75)	(52.874)	(10.57)	(72.443)	(14.50)
			C.V.	21.2		17.4		17.4	
A	1,000	3	$\overline{X}$	635.27	63.5	587.69	58.8	855.89	85.6
			(s.d.)	(141.881)	(14.17)	(96.268)	(9.62)	(199.881)	(19.81)
			C.V.	22.3		16.4		23.1	
MB	50	1	$\overline{X}$	37.53	75.1	24.49	49.0	15.44	30.9
MB	1.000	3	$\overline{X}$	645.39	64.5	507.53	50.7	371.92	37.2
			(s.d.)	(111.028)	(11.07)	(37.303)	(3.73)	(68.593)	(6.86)
			C.V.	17.2		7.3		18.4	

** Bartlett's test for homogeniety of variances is highly significant ($p<0.01$) when cell 200: C_{20-30} is included, but not so ($p<0.50$) when it is excluded.

The outcomes of higher reported CP levels in sediment downstream from the lagoon ditch outfall and of a low to high progression of levels from the C_{10-12} group to the C_{20-30} group are consistent with results of the Sugar Creek field study.

6.4 Statistical Evaluation of Reported Concentrations in Spiked Sediment Samples

Subsamples of the composite sediment sample from station A were used to prepare the spiked sediment samples. Three spiking levels were used for each of the carbon chain-length groups: 200, 500 and 1,000 µg/kg of sediment. Thus samples spiked, say, at 200 µg/kg were spiked so as to contain that concentration of each of the carbon chain-length "standards." All spiked sediment samples were prepared and analyzed in triplicate. Method blanks spiked with an equivalent of 1,000 µg/kg were also prepared and analyzed in triplicate, and a single method blank spiked at an equivalent of 50 µg/kg was included.

Table B-5 presents the replicate means and standard deviations of the reported CP concentrations in spiked sediment, by chain-length group and spiking level and the means and standard deviations of the respective recovery percentages. Also, the coefficient of variation is presented for each replicate cell.

Evaluation of the recovery data for spiked sediment is complicated somewhat by the reported levels of CPs in the unspiked sediment from station A. Adjustment of average reported concentrations and recovery percentages for spiked samples has been attempted by subtracting average reported concentrations in unspiked samples from those for spiked samples and recalculating average recovery percentages based on the adjusted concentrations values. The adjusted concentrations and recovery percentages are presented in Table B-6.

The adjusted recovery values are presented for review and consideration only. Comparison of the adjusted recovery percentages with those for the method blanks indicates that adjustment is warranted for the C_{20-30} averages and possibly for the C_{14-17} averages. Adjustment of the C_{10-12} averages, however, is apparently not warranted and may well be counter-productive. Because of apparent inconsistencies in the adjustment results, statistical evaluation presented here is restricted to the unadjusted data. This decision should not affect estimates of method precision, since the adjustment procedure merely multiplied each value in a replicate set by a constant.

Contrary to results for spiked water samples, average recovery percentages among the three C_{10-12} spiking sets for sediment were virtually equal to those among C_{14-17} sets ($\bar{X}$ = 60.3%, range 56.3% to 63.5%; unadjusted values). Recovery

Table B-6. CP Recovery Percentages for Spiked Sediment Samples, Adjusted for Pre-spiking CP Concentrations Reported for Sediment

Station	Spike (µg/kg)	Mean Values	C_{10-12} µg/kg	C_{10-12} %Recov.	C_{14-17} µg/kg	C_{14-17} %Recov.	C_{20-30} µg/kg	C_{20-30} %Recov.
A	200	Spike	113.02	56.5	124.01	62.0	253.34	126.7
		Pre-Spk	-30.55		-58.14		-162.93	
		(Adj.)	(82.47)	(41.2)	(65.87)	(32.9)	(90.41)	(45.2)
A	500	Spike	301.17	60.2	304.36	60.9	415.29	83.1
		Pre-Spk	-30.55		-58.14		-162.93	
		(Adj.)	(270.62)	(54.1)	246.22	(49.2)	(252.36)	(50.5)
A	1,000	Spike	635.27	63.5	587.69	58.8	855.89	85.6
		Pre-Spk	-30.55		-58.14		-162.93	
		(Adj.)	(604.72)	(60.5)	529.55	(53.0)	(693.0)	(69.3)
MB	50	-	37.53	75.1	24.49	49.0	15.44	30.9
MB	1,000	-	545.39	64.5	507.53	50.8	371.92	37.2

for the 500 and 1,000 µg/kg spikes was significantly higher for the C_{20-30} group ($x = 84.4$), contrary to results for spiked water samples. (The C_{20-30}, 200 ug/kg data were excluded because of variance heterogeneiety.) It should be noted that adjustment of the recovery data (Table B-6) tended to diminish these differences, reducing especially the C_{20-30} recovery values after subtraction of the relatively high pre-spiking levels of that chain-length group.

Recovery among the method blanks followed a pattern similar to that of the method blanks for water, showing highest recovery values for the C_{10-12} group (67.2%), intermediate for C_{14-17} (50.3%) and lowest for C_{20-30} (35.7%). The differences are statistically significant ($p<0.05$).

6.5 Evaluation of Unspiked Particulate Data

Because the quantity of particulate material filtered from the single composite water sample from either station A or B was insufficient to construct replicate samples or undertake spiking tests, a single analysis of each sample's particulates was conducted. The Station B particulates of 0.23874 g were filtered from 10.02 L of stream water, and those from Station A of 0.60645 g were from 19.25 L. Quantitation levels are reported as ug CP and as µg/10 L, by carbon chain-length groups (Table B-7).

CP extraction was performed on the particulates-plus-filter to avoid the problem of completely removing and extracting only the particulates. Thus an "unspiked blank" was created by extracting and quantifying a filter only, and recovery efficiency was measured by spiking a filter with 5 ug of each chain-length standard, followed by extraction of the filter and quantification of the extract. Method blank results are also presented in Table B-7. Presented also in the table are residue and recovery data adjusted for "noise" present in the unspiked method blank analysis.

While these results are based only on four analyses, there is consistency in the results in that the highest levels appear in the downstream sample (A) and, in particular, in the C_{20-30} group as is consistent with field study results. In contrast, the levels reported for the three remaining samples (B, MB and MB_5) show the highest values for the C_{10-12} group and the lowest values for the C_{20-30} group, which is consistent with noise level estimates for filtered stream water (Table B-2) and, in general, with recovery from spiked filtered water.

Table B-7. Reported CP Concentrations (μg and μg/10 L) in Stream Water Particulates

Station	Filtered Water (L)	Total Particulates (g)	Particulates (g) Per 10 L	μg CPs			μg CPs/10 L H_2O		
				C_{10-12}	C_{14-17}	C_{20-30}	C_{10-12}	C_{14-17}	C_{20-}
B	10.02	0.23874	0.2383	0.778	0.091	0.005	0.776	0.091	0.005
A	19.25	0.60645	0.3150	1.626	1.495	4.172	0.845	0.777	2.167
MB_0	(filter only)	-	-	0.254	0.073	0.011			
MB_5	(filter + 5μg CPs)	-	-	3.345	2.193	0.749			
A D J U S T E D D A T A									
B - MB_0				0.524	0.018	nd	0.523	0.018	nd
A - MB_0				1.372	1.422	4.161	0.712	0.739	2.162
MB_5 - MB_0				3.091	2.120	0.738			
Unadjusted % recovery (MB_5)				66.9	43.9	15.0			
Adjusted % recovery (MB_5 - MB_0)				61.8	42.4	14.8			

6.6 Frequency of Classification Errors

There was a possibility for false positive reports to occur for C_{10-12}, C_{14-17}, and/or C_{20-30} quantifications among 14 samples: 4 unspiked method blanks for water, 6 unspiked samples of stream water and 4 unspiked method blanks for sediment (Tables 10 and 11). There was only one report that could be considered a false positive, that of 13.89 µg/kg of C_{20-30} in a sediment method blank. Otherwise, reports were either "n.d." or trivial values attributable to "noise". Thus, there were no false positive reports among 14 analyses each for C_{10-12} and C_{14-17}. The observed false positive frequency for C_{20-30} was 1 in 14 analyses.

There was a possibility for false negative reports to occur for C_{10-12}, C_{14-17}, and/or C_{20-30} in a total of 12 spiked water samples (9 stream water and 3 distilled water, Table 11), and in a total of 19 sediment samples (9 spiked stream sediment, 4 method blanks for sediment and 6 unspiked but contaminated stream sediment samples, Table 10). There were only two apparent false negative reports: those of 0.048 and 0.052 µg/L of C_{20-30} in two of the three stream water samples spiked at 1 µg/L, reported values that could be attributed to procedure noise. Thus, there were no false negative reports among 31 analyses each for C_{10-12} and C_{14-17}. The false negative frequency for C_{20-30} was 2 in 31 analyses, essentially the same frequency as that for false positive reports.

6.7 Regression Analysis of CP "Concentrations Reported" on "Concentrations Added"

Regression analyses of CP "concentrations reported" (Y) on "concentrations added" (X) were performed for each carbon chain-length set of sediment and water method validation data. The analyses generated least squares regression statistics for measuring overall method accuracy and precision and for developing predictive equations, and 95% confidence limits, for estimation of $\hat{Y}$ for known X values and, in particular, for estimation of $\hat{X}$ for known Y values by means of inverse prediction.

Because of apparent direct proportionality between the means and standard deviations of reported recoveries as spiking levels increased (i.e., coefficients of variation did not vary significantly within carbon chain-length groups), both water and sediment data were transformed to logarithms (natural logarithms) for regression analysis. The resulting log-linear model, $\ln Y_i = \ln a + b \ln X + \ln e_i$, proved to be satisfactory, stabilizing standard deviations and providing correlation coefficients (r) that ranged from 0.95 to 0.99 for all but the C_{20-30} sets, which were 0.85 for sediment

and 0.73 for water. The model for Y (untransformed) is $Y_i = aX^b e_i$, the random error component e_i being multiplicative rather than additive. Plots of Y on X, with 95% confidence bounds for individual measurements, are shown for C_{10-12}, C_{14-17} and C_{20-30} in sediment in Figures B-1, B-2 and B-3, respectively, and for C_{10-12} and C_{14-17} in water in Figures B-4 and B-5. (The plot for C_{20-30} in water is not presented because of erratic data for the 1 µg/L spiking level.)

Working equations for calculating the predicted value of a reported concentration ($\hat{Y}$) for a given spiked concentration (X) and of a true concentration ($\hat{X}$) for a given reported concentration (Y), with respective 95% confidence limits, are presented for sediment in Table B-8 and for water in Table B-9, for each carbon chain-length group. (Confidence limits incorporate the 2-tail, 0.05 value of t with n - 2 degrees of freedom.) The equations are used in the following manner:

- To determine $\hat{Y}$ for a given value of X, first solve for $\ln \hat{Y}$ by inserting the value of ln X in the right side of the $\ln \hat{Y}$ equation. The antilog of $\ln \hat{Y}$, or exp $\ln \hat{Y}$, is $\hat{Y}$, the best estimate of the concentration Y that will be reported for a single analysis of a sample spiked at concentration X.

- To determine upper and lower 95% confidence limits for Y, first determine those limits for $\ln \hat{Y}$ by inserting the values for ln X and the now-determined ln Y in the respective equation and solving first for the upper (+) and then for the lower (-) confidence limit. The antilogs of those values are the upper and lower 95% confidence limits for Y.

- To determine values for $\hat{X}$, the best estimate of the true CP concentration in a sample whose reported concentration from a single analysis is Y, and the 95% confidence limits for X (the true concentration), the procedure is as above in solving for $\hat{Y}$ and the confidence limits for Y, except that the values of ln Y and, once solved, of $\ln \hat{X}$ are inserted as required. The antilog of $\ln \hat{X}$ is X, and the antilogs of the upper and lower confidence limits for $\ln \hat{X}$ are those limits for X.

Approximate values for the above calculations may be derived directly from Figures B-1 through B-5. Values for predicted Y ($\hat{Y}$ and 95% confidence limits for Y) for a given value of X are read conventionally on the Y-axis by extending horizontal lines to that axis from the points at which a line extended vertically from a selected value on the X-axis intersects the regression line for Y on X and the lines for the upper and lower confidence limits for individual measurements. Values for predicted X ($\hat{X}$ and the 95% confidence limits for X) are read on the X-axis by extending vertical

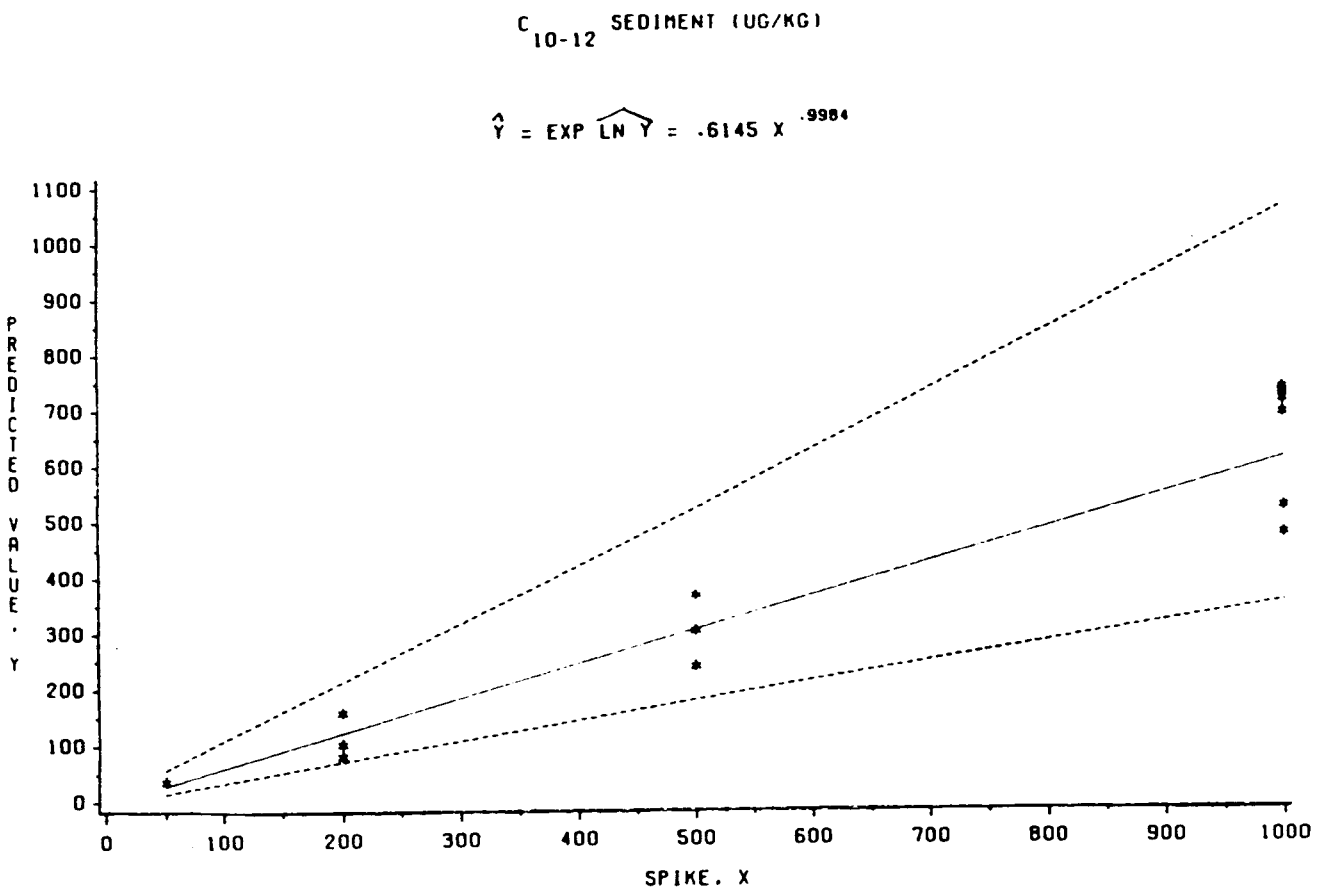

FIGURE B-1. 95% CONFIDENCE INTERVAL FOR SINGLE OBSERVATION OF Y

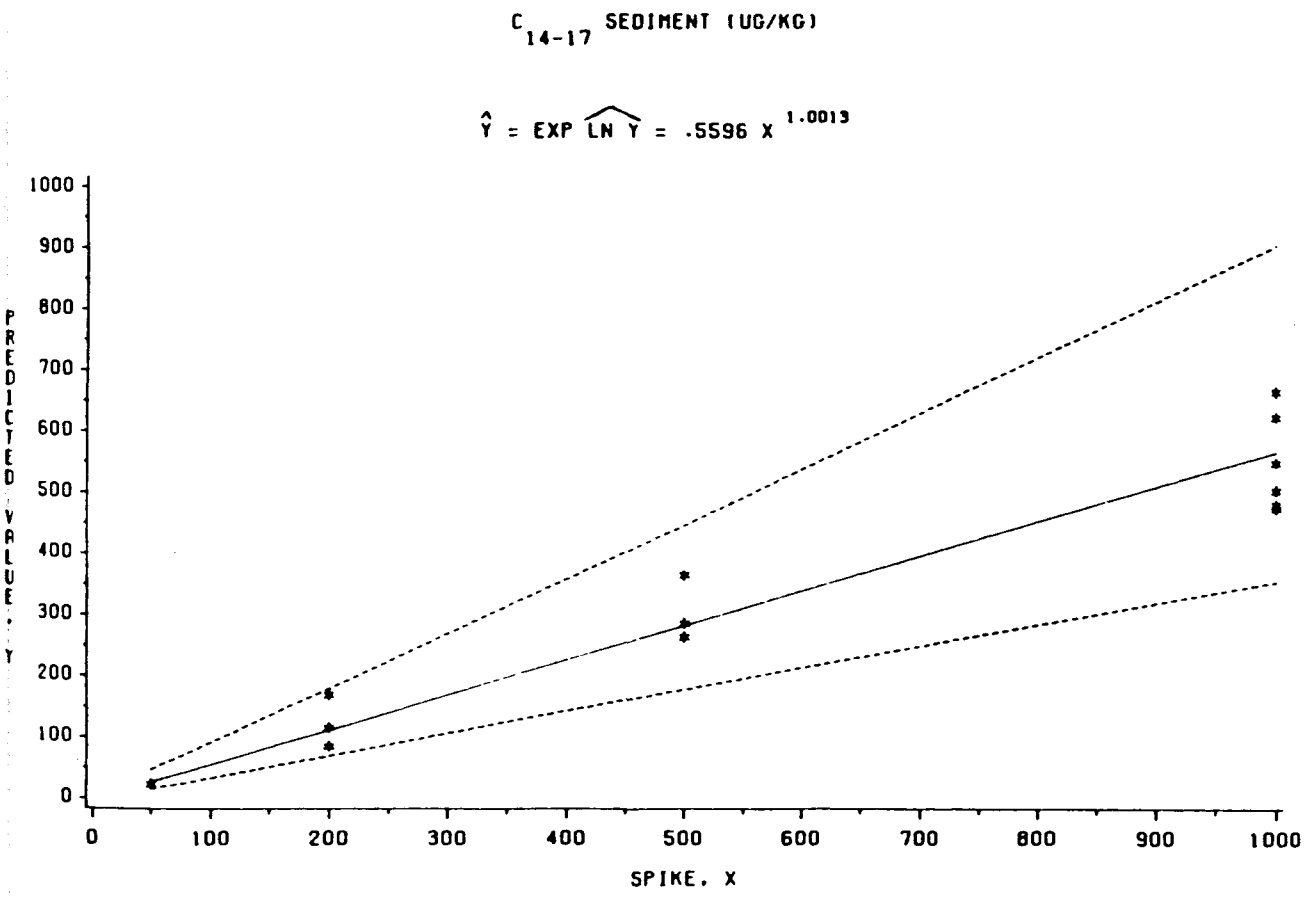

FIGURE B-2. 95% CONFIDENCE INTERVAL FOR SINGLE OBSERVATION OF Y

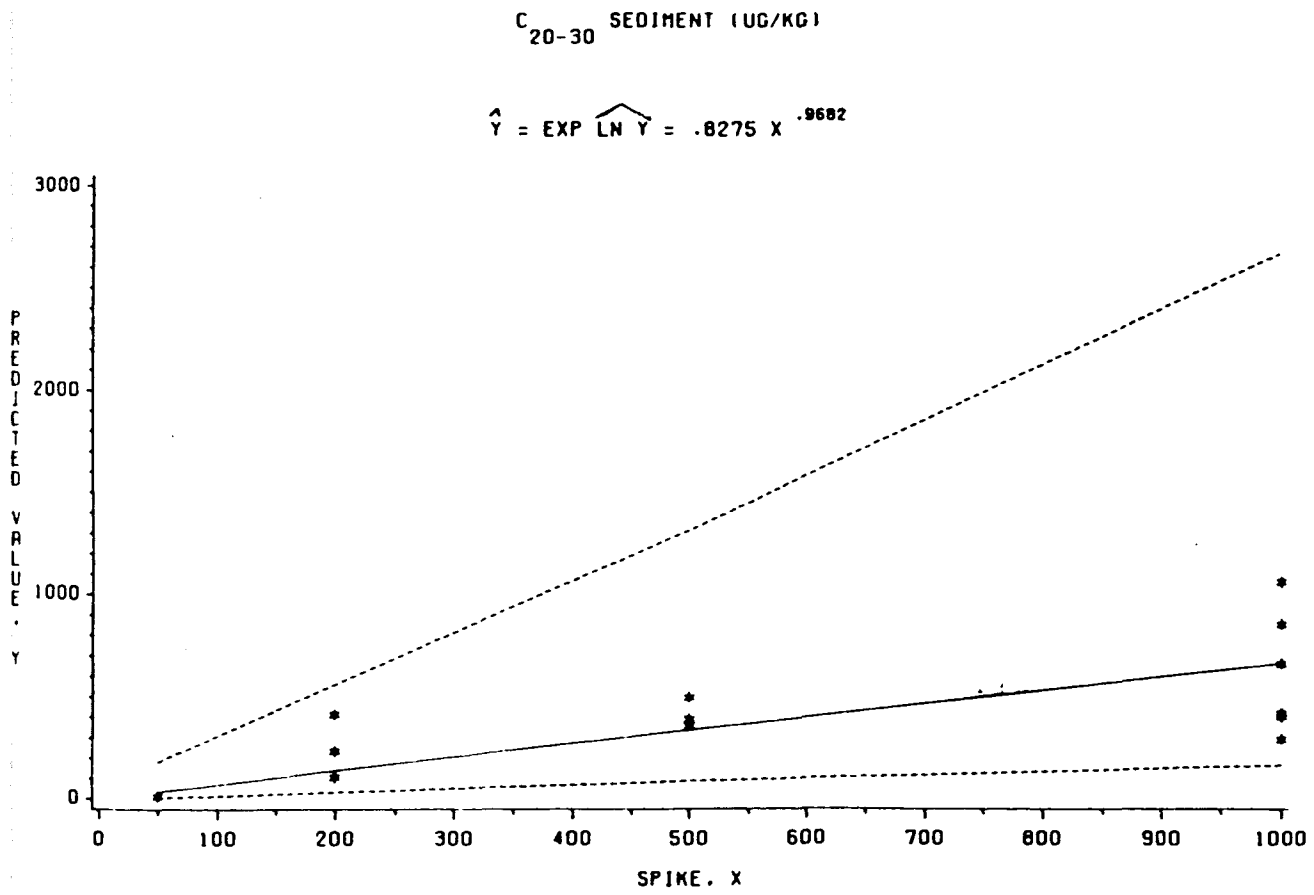

FIGURE B-3. 95% CONFIDENCE INTERVAL FOR SINGLE OBSERVATION OF Y

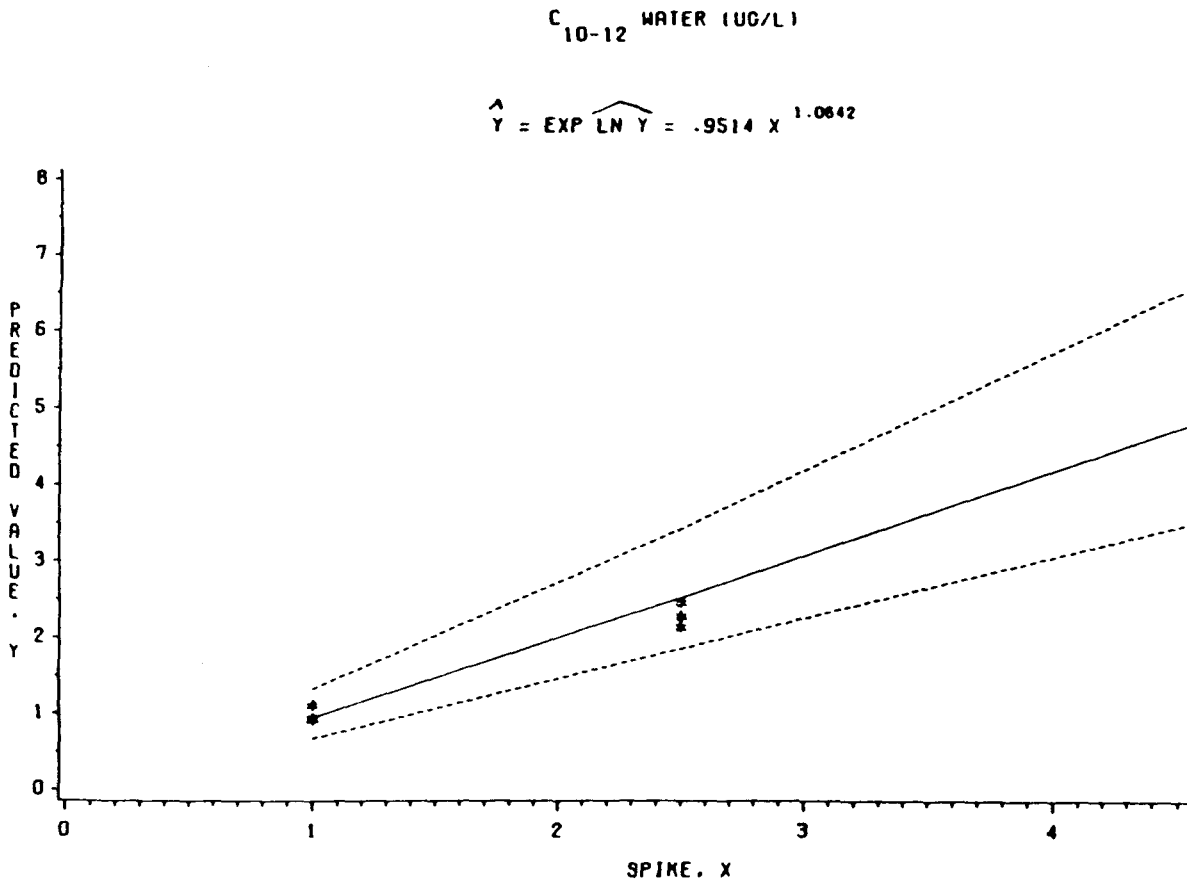

FIGURE B-4. 95% CONFIDENCE INTERVAL FOR SINGLE OBSERVATION OF Y

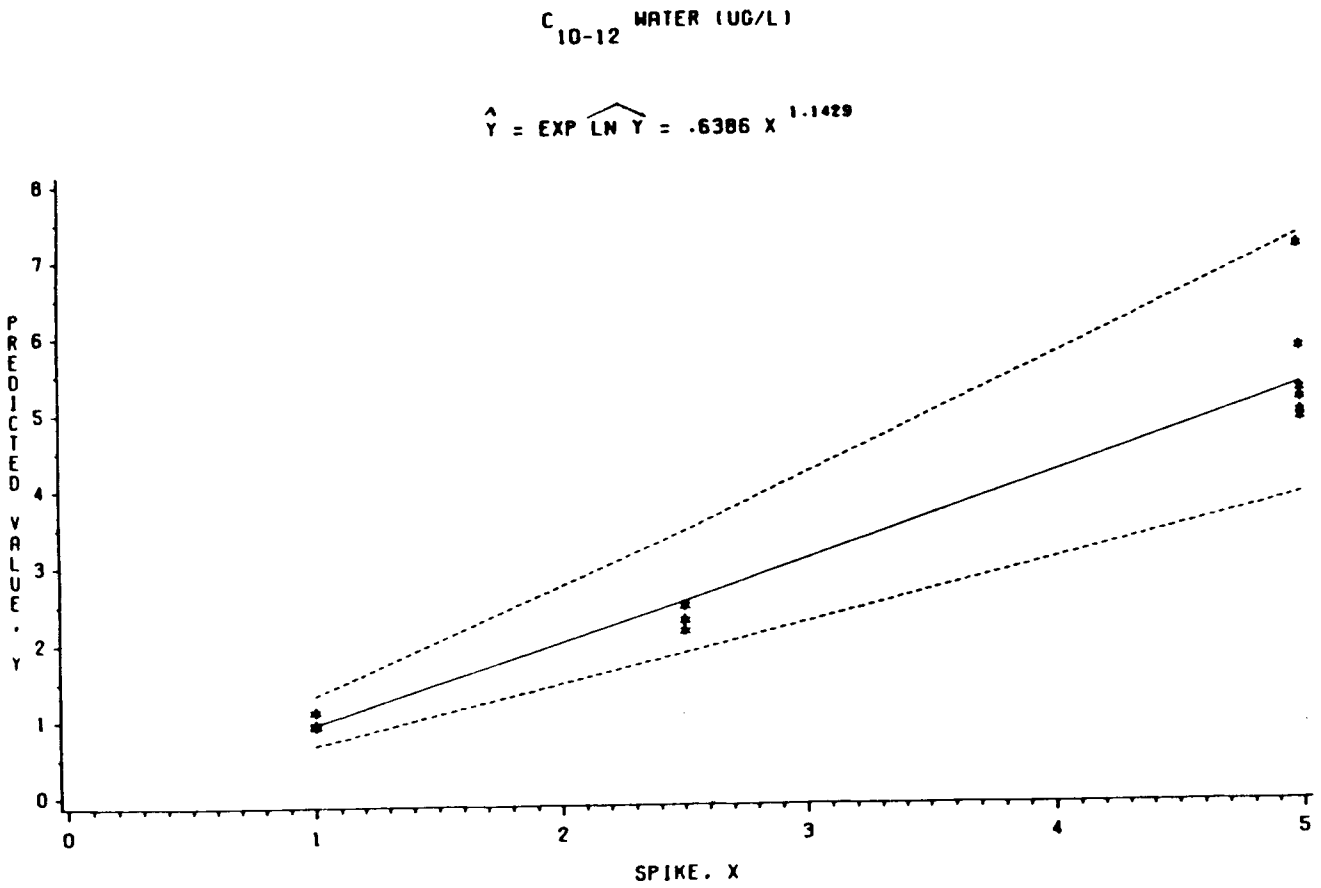

FIGURE B-5. 95% CONFIDENCE INTERVAL FOR SINGLE OBSERVATION OF Y

lines to that axis from the points at which a line extended horizontally from a selected point on the Y-axis intersects the regression line for Y on X and the lines for the individual confidence bounds. (Note that in reading from a plot, the line that provides the upper 95% bound for predicted Y provides the lower 95% bound for predicted X, and vice versa.)

6.8 Estimation of True CP levels (X) in Individual Samples, Using Inverse Prediction from Regression Analysis

From the working equations for $\hat{X}$ and the 95% confidence limits for X presented for sediment in Table B-8 and for water in Table B-9, a "best estimate" of the true level of each CP group in a sample, and the 95% confidence limits for that estimate, can be derived from the reported concentration (Y) for that sample. Estimation of $\hat{X}$ by inverse prediction is similar to the use of a correction factor for recovery except that $\hat{X}$ is based on least squares regression procedures that utilize recovery data from all spiking levels and provide valid statistical confidence limits for estimates of $\hat{X}$. (Procedures for using the equations are given in Section 6.7.)

It should be noted that confidence limits for inverse prediction are typically not symmetrical, being somewhat greater above than below predicted values of X. This lack of symmetry is increased for CP confidence limits because the CP model for $\hat{X}$ is multiplicative rather than additive.

Because the equations are necessarily based on recoveries for spiked samples, their validity for use in environmental studies requires the assumption that extraction of CPs from unspiked environmental samples will be of efficiency comparable to that for spiked CPs.

6.9 Estimation of Method Recovery, Accuracy, and Precision

Measures of overall method recovery and accuracy (both expressed as percentages) can be derived directly from the regression of Y on X, recovery being measured as $\hat{Y}/X \times 100$ and accuracy as $(1 - |\hat{Y} - X|/X) \times 100$, which is equivalent to recovery for values of $\hat{Y}$ less than X. The regression values $\hat{Y}$ and its respective X provide the necessary input values, $\hat{Y}$ being a function of recoveries for all spiking levels rather than a single level.

Regression estimates for accuracy and, equivalently, for recovery for analysis of CPs in sediment averaged 61%, ranging from 57% for the C_{14-17} group to 66% for the C_{20-30} group. (Estimates are comparable to those for arithmetic averages of recovery data in Table B-5.) Accuracy and

Table B-8. Working Equations[1/] for Predicted Values, and 95% Confidence Limits (C.L.), for Reported ($\hat{Y}$) and True ($\hat{X}$) CP Concentrations in Individual Sediment Samples

Log-Linear Predictive Equation (Natural Logarithms)	Predicted Concentration[2/] (µg/kg)
C_{10-12}	
$\ln \hat{Y} = 0.9984 \ln X - 0.4869$	exp $\ln \hat{Y}$
C.L. $\ln Y = \ln \hat{Y} \pm \sqrt{0.2888 + 0.0252 (\ln X - 6.1459)^2}$	exp C.L. ln Y
$\ln \hat{X} = 1.0016 (\ln Y + 0.4869)$	exp $\ln \hat{X}$
C.L ln X = 1.0259 $\ln \hat{X}$ - 0.1594 $\pm \sqrt{0.2974 + 0.0266 (\ln \hat{X} - 6.1459)^2}$	exp C.L. ln X
C_{14-17}	
$\ln \hat{Y} = 1.0013 \ln X - 0.5805$	exp $\ln \hat{Y}$
C.L. $\ln Y = \ln \hat{Y} \pm \sqrt{0.2079 + 0.0181 (\ln X - 6.1459)^2}$	exp C.L. ln Y
$\ln \hat{X} = 0.9987 (\ln Y + 0.5805)$	exp $\ln \hat{X}$
C.L. ln X = 1.0184 $\ln \hat{X}$ - 0.1133 $\pm \sqrt{0.2112 + 0.0188 (\ln \hat{X} - 6.1459)^2}$	exp C.L. ln X
C_{20-30}	
$\ln \hat{Y} = 0.9682 \ln X - 0.1893$	exp $\ln \hat{Y}$
C.L. $\ln Y = \ln \hat{Y} \pm \sqrt{1.8243 + 0.1592 (\ln X - 6.1459)^2}$	exp C.L. ln Y
$\ln \hat{X} = 1.0329 (\ln Y + 0.1893)$	exp $\ln \hat{X}$
C.L. ln X = 1.2046 $\ln \hat{X}$ - 1.2573 $\pm \sqrt{2.3445 + 0.2464 (\ln \hat{X} - 6.1459)^2}$	exp C.L. ln X

1/ Derived from regression analysis of ln spiked sample recovery data, method validation study. Equations for $\ln \hat{Y}$ are logarithmic transformations of the respective multiplicative regression equations ($\hat{Y}=aX^b$) shown in Figures B1-B3. Logarithmic confidence limits incorporate "t" values for $\alpha = 0.05$, $n - 2 = 11$ degrees of freedom.

2/ exp ln Y reads $e^{\ln Y}$ or the antilog of ln Y, where e = 2.71828....

Table B-9. Working Equations[1/] for Predicted Values and 95% Confidence Limits (C.L.) for Reported ($\hat{Y}$) and True ($\hat{X}$) CP Concentrations in Individual Water Samples

Log-Linear Predictive Equation (Natural Logarithms)	Predicted Concentration (µg/L)
C_{10-12}	
$\ln \hat{Y} = 1.0642 \ln X - 0.0498$	exp $\ln \hat{Y}$
C.L. $\ln Y = \ln \hat{Y} \pm \sqrt{0.0937 + 0.0165 (\ln X - 1.0338)^2}$	exp ln C.L.Y
$\ln \hat{X} = 0.9396 (\ln Y + 0.0498)$	exp $\ln \hat{X}$
C.L. $\ln X = 1.0148 \ln \hat{X} - 0.0153 \pm \sqrt{0.0840 + 0.0150 (\ln \hat{X} - 1.0338)^2}$	exp ln C.L. X
C_{14-17}	
$\ln \hat{Y} = 1.1429 \ln X - 0.4485$	exp $\ln \hat{Y}$
C.L. $\ln Y = \ln \hat{Y} \pm \sqrt{0.4290 + 0.0756 (\ln X - 1.0338)^2}$	exp ln C.L. Y
$\ln \hat{X} = 0.8749 (\ln Y + 0.4485)$	exp $\ln \hat{X}$
C.L. $\ln X = 1.0615 \ln \hat{X} - 0.0635 \pm \sqrt{0.3486 + 0.06523 (\ln \hat{X} - 1.0338)^2}$	exp ln C.L. X

[1/] Derived from regression analysis of ln spiked sample recovery data, method validation study. Equations for $\ln \hat{Y}$ are logarithmic transformations of the respective multiplicative regression equations ($\hat{Y}=aX^b$) shown in Figures B-4 and B-5. Logarithmic confidence limits incorporate "t" values for $\alpha = 0.05$, $n - 2 = 10$ d.f.

NOTE: Recovery of C_{20-30} spikes in water samples was too variable to provide useful predictive equations.

recovery for water analysis were essentially 100% for the C_{10-12} group and 75% for the C_{14-17} group. The percentages are comparable to the arithmetic averages of the respective replicate recoveries presented in Table B-3. (As mentioned, regression analysis of the C_{20-30} water data was not utilized because of anomalous results at the 1 µg/L spiking level.)

Precision was assessed for each set of replicated samples as the standard deviation expressed as the percentage of their mean, i.e., as the "coefficient of variation" (CV) or, equivalently, as the "relative standard deviation" (Tables B-3, B-4 and B-5). For replicated spiked water samples (Table B-3), CVs ranged from 6.7% to 53.5% (excluding an aberrant 165%), with a median CV of approximately 28% (2 degrees of freedom (d.f.) per CV). Precision was consistently higher for quantification of C_{10-12} than for C_{20-30}, CVs ranging from 6.7% to 22.9% for the former and from 34.8% to 165% for the latter. CVs for C_{14-17} quantification were of intermediate values.

For replicated unspiked and spiked sediment samples (excluding method blanks as potentially atypical because they could not be prepared from sediment), CVs ranged from 16% to 61%, with a median CV of approximately 23% (1 and 3 d.f. per CV for unspiked replicates and 2 d.f. per CV for spiked replicates). There were no discernible differences in analytical precision between unspiked and spiked samples or among carbon chain-length groups.

Table B-10 Chlorinated Paraffin Concentrations, by Carbon Chain-length Group, Reported for Spiked and Unspiked Sediment Samples[1/] and Method Blanks: Method Validation Study

Sample Source	Spike (µg/kg)	Replicate	Reported Concentrations (µg/kg) C_{10-12}	C_{14-17}	C_{20-30}
Station B	0	1	2.62	11.24	80.63
		2	6.49	15.53	49.53
		(mean)	(4.56)	(13.39)	(65.08)
Station A	0	1	16.21	52.67	126.19
		2	36.93	73.02	184.48
		3	26.32	50.81	145.55
		4	42.71	56.06	195.49
		(mean)	(30.55)	(58.14)	(162.93)
Method Blank	0	1	0.12	0.88	13.89
		2	0.59	nd	nd
		3	nd[2/]	nd	nd
		4	nd	nd	nd
		(mean)	(0.18)	(0.22)	(3.47)
Station A	200	1	157.86	169.54	415.95
		2	101.35	116.56	236.30
		3	79.87	85.92	107.77
		(mean)	(113.02)	(124.01)	(253.34
Station A	500	1	365.23	364.05	496.91
		2	300.92	285.59	390.36
		3	237.37	263.42	358.61
		(mean)	(301.17)	(304.36)	(415.29)
Station A	1,000	1	709.44	621.58	850.22
		2	724.70	662.43	1056.55
		3	471.68	479.06	660.91
		(mean)	(635.27)	(587.69)	(855.89)
Method Blank	50	1	37.53	24.49	15.44
Method Blank	1,000	1	730.41	502.14	293.27
		2	685.99	547.23	403.17
		3	619.78	473.21	419.33
		(mean)	(645.39)	(507.53)	(371.92)

[1/] Sediments from Sugar Creek, Stations A and B near Dover, Ohio: Reconnaissance Survey, August 12, 1986

[2/] nd = not detected; assigned value of 0

Table B-11 Chlorinated Paraffin Concentrations, by Carbon Chain-length Group, Reported for Spiked and Unspiked Stream Water[1/] Samples and Distilled Water Method Blanks: Method Validation Study

Sample Source	Spike (µg/kg)	Replicate	Reported Concentrations (µg/kg) C_{10-12}	C_{14-17}	C_{20-30}
Station B	0	1	0.064	0.011	0.008
		2	0.157	nd[2/]	nd
		(mean)	(0.110)	(0.006)	(0.004)
Station A	0	1	0.039	0.011	0.010
		2	0.047	0.010	0.009
		3	0.060	0.031	0.017
		4	0.023	0.003	nd
		(mean)	(0.042)	(0.014)	(0.009)
Method Blank	0	1	0.014	0.096	nd
		2	0.110	0.044	0.007
		3	0.062	0.010	nd
		4	0.026	0.005	nd
		(mean)	(0.053)	(0.039)	(0.002)
Station A	1.0	1	0.928	0.694	0.052
		2	0.943	0.797	3.092
		3	1.116	0.611	0.048
		(mean)	(0.996)	(0.701)	(1.064)
Station A	2.5	1	2.277	1.947	1.221
		2	2.139	0.964	1.874
		3	2.462	1.754	0.896
		(mean)	(2.293)	(1.555)	(1.330)
Station A	5.0	1	7.089	6.810	8.900
		2	4.823	3.769	6.493
		3	4.902	3.840	2.556
		(mean)	(5.605)	(4.806)	(5.983)
Method Blank	5.0	1	5.749	4.641	3.282
		2	5.080	3.510	1.859
		3	5.199	3.704	1.885
		(mean)	(5.343)	(3.952)	(2.342)

[1/] Water from Sugar Creek, Stations A and B near Dover, Ohio: Reconnaissance Survey, August 12, 1986

[2/] nd = not detected; assigned value of 0

APPENDIX C

SAMPLE COLLECTION PROTOCOL

TABLE OF CONTENTS

The sample collection protocol for the field studies for Sugar Creek near Dover, Ohio, and Tinkers Creek near Bedford, Ohio, is given below.

1. Parameter Coverage

In addition to Chlorinated Paraffin determinations, temperature (°C), flow (cfs) and depth in feet (ft) were recorded at each sampling station.

2. Sample Collection

All samples were collected and handled using procedures that are fully approved by EPA. A duplicate set of samples (except mussels) from the Sugar Creek site was provided to the Dover Chemical Corporation for their independent analysis. A duplicate sample of the process water from the S.K. Wellman Company in the Tinkers Creek site was provided to that facility's management.

All samples from both sites, with the exception of the lagoon samples collected from the Sugar Creek site, were collected by wading in the stream. For the lagoon, two canoes were lashed together with three 2 in x 3 in x 8 ft studs to form a stable catamaran platform. All lagoon samples were collected from this platform.

Sampling in Sugar Creek was done in a downstream to upstream direction in order to avoid unnatural disturbances and thereby minimize contamination of the samples.

2.1 Sample Preparation

All water column and sediment samples were collected in glassware that had undergone the following cleaning steps:

- Surface residuals were removed.
- A hot, soapy soak was used to loosen and flotate most of the residue.
- A hot water rinse was used to flush away floating residue.
- A soak with deep penetrant or oxidizing agent was used to destroy traces of organic residue.
- A hot water rinse was used to flush away materials loosened by deep penetrant soak.
- A rinse with deionized water was used to remove metallic deposits from the tap water.

- The glassware was then rinsed with high purity methanol followed by high purity methylene chloride.

Glassware was handled using polyethylene gloves to avoid contact with hands.

2.2 Water Column Samples

Each water column sample collected at stations A', B, B', D and K in Sugar Creek and stations A, B and C in Tinkers Creek was a composite of single grab samples collected from at least three equidistant points along a stream transect. A 0.5 gallon glass jar was triple rinsed with stream water at the location the sample was to be collected. The jar was then submerged in the stream until all air was replaced by a water sample (Figure C-1). The water sample depth was half way between the surface and the bottom of the stream. The samples collected along the stream transect were then composited to form a single sample.

Water samples collected at stations D, E, F, and G at Tinkers Creek were collected as a single grab in 0.5 gallon glass jars.

Water samples collected at stations L_1, L_2, and L_3 at the Sugar Creek site were depth-integrated with discrete samples collected from three depths per station: near the bottom (17-20 ft), at mid-depth (10 ft) and near the surface (2 ft). To avoid outside contamination, a stainless steel Kemmerer sampler (Figure C-2) with non-rubber stoppers was used.

All jars were capped with Teflon-lined lids. The water samples required no preservatives.

Each sample jar was labeled with a barcode label.

2.3 Sediment Samples

All sediment samples were collected in 500 mL glass jars. At stations A', B, B', D, and K at Sugar Creek and stations A, B, and C at Tinkers Creek, a stainless steel scoop was used to remove sediment from the same equidistant points along the same stream transect that the water column samples were collected. These discrete samples were then composited to form a single sample.

At stations D, E, and F at Tinkers Creek, the sample was a single grab using a stainless steel scoop.

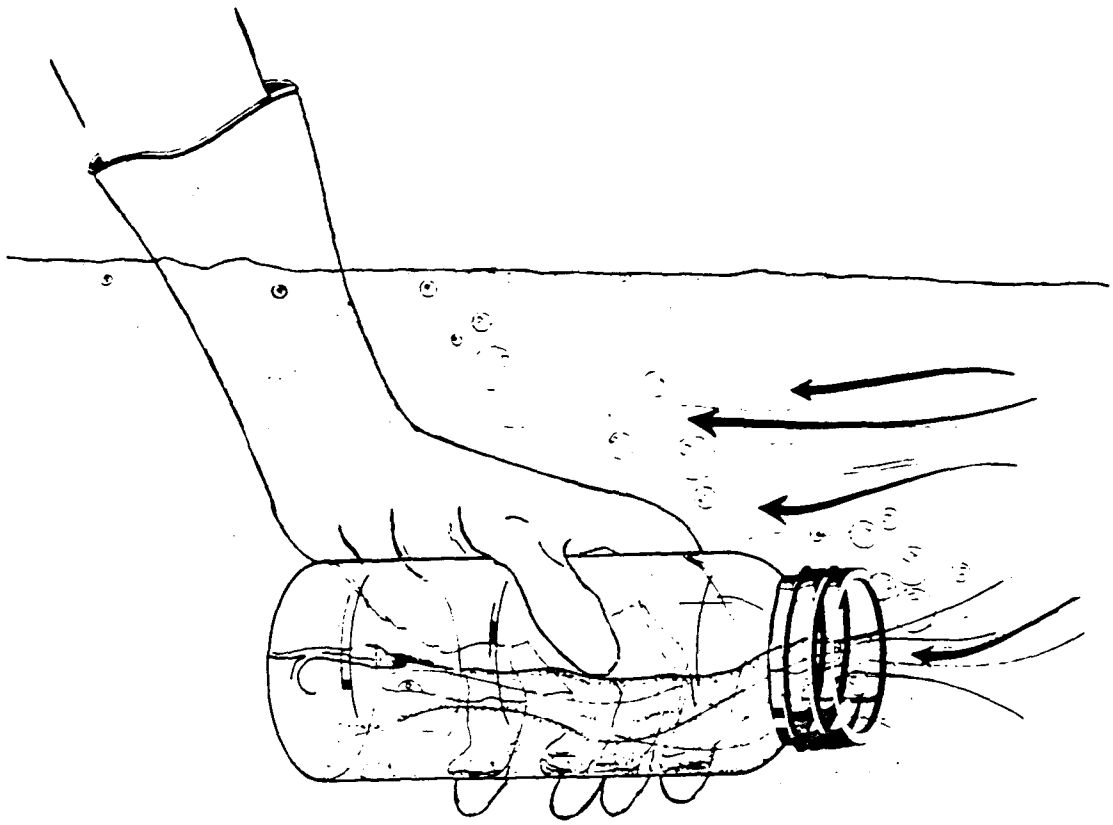

FIG. C-1 Demonstration of Technique Used in the Grab Sampling of Waters and Wastewaters

At stations L_1, L_2, and L_3 in Sugar Creek, sediment samples were collected using an Ekman dredge (Figure C-2).

Large rocks were removed before placing the samples in the jars. All jars were capped with Teflon-lined lids. Sediment samples required no preservatives. Each sample jar was labeled with the same information as described above. The stainless steel scoop and the Ekman dredge were triple rinsed with distilled water prior to filling a sample collection jar.

2.4 Tissue Samples

Mussel samples (where available) were collected from the Sugar Creek stations by hand and placed on ice in the coolers.

In accordance with the permit obtained by the field crew from the Ohio Department of Natural Resources, no more than 10 mussel specimens were collected from any of the stations in Sugar Creek.

At the Tinkers Creek study site, attempts were made to collect biological organisms from the stream bottom at each of the field stations. Sediment scoops were sieved using a standard No. 30 sieve in search of invertebrate larvel forms, especially chironomid larvae. None were found after several hours of sampling.

All sample jars were kept in coolers out of direct sunlight and transported in ice-filled coolers with sufficient packaging material to reduce the possibility of breakage. The mussels collected during the Sugar Creek study were also placed in an ice-filled cooler. This kept the mussels alive during transport to the laboratory in Kansas City. All water, sediment, and mussel samples were shipped via overnight delivery service to MRI's Kansas City laboratory.

3. Field Quality Control

Monitoring for chlorinated paraffins requires demanding quality control procedures because of the potential for contamination. During this study, special precautions were made to avoid any contamination. These included using polyethylene gloves in the field and in the laboratory to avoid possible contamination by hands, avoiding seals and paints that may contain CPs, and avoiding PVC and plastic and rubber materials which may contain CPs.

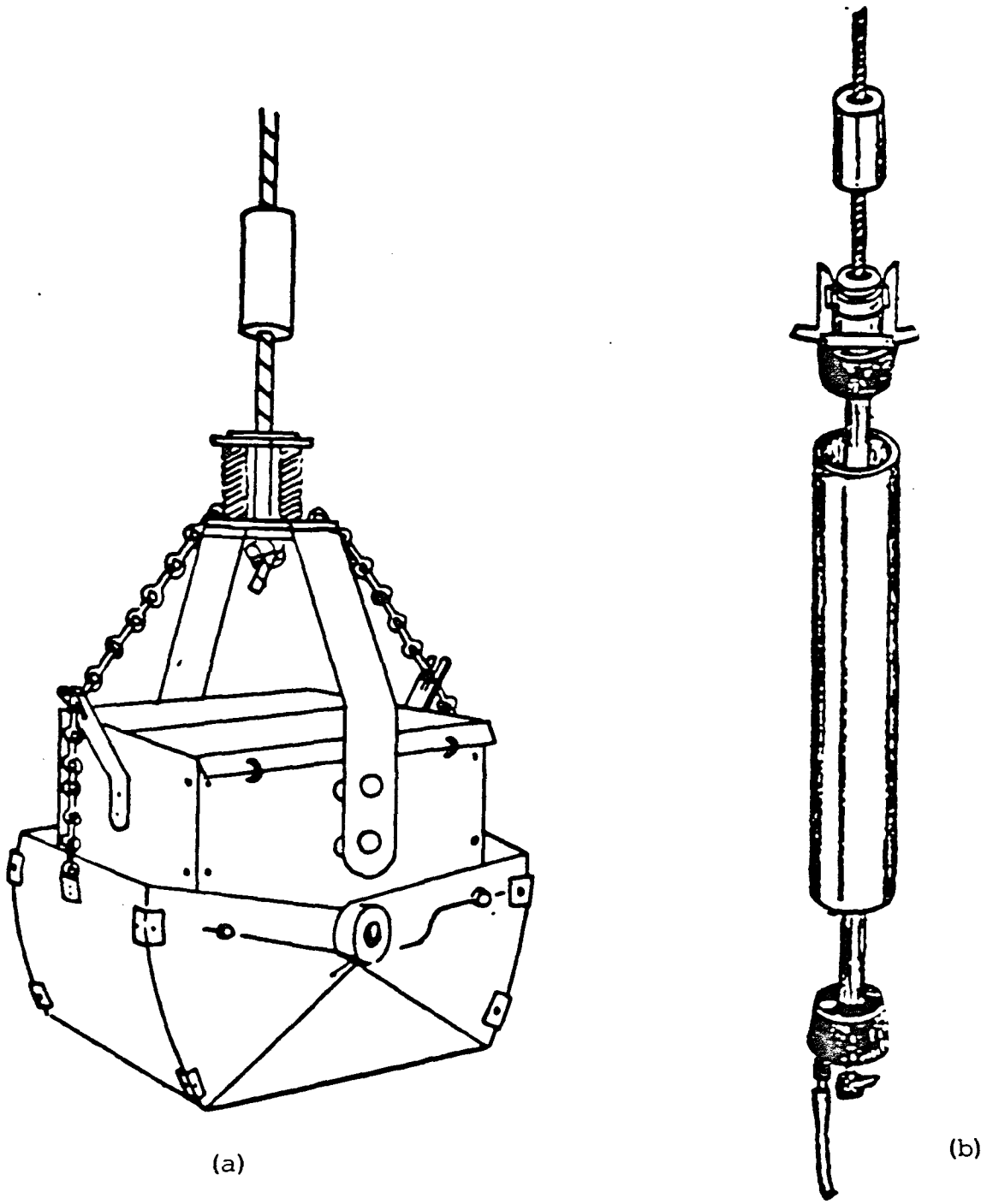

FIG. C-2 Water and Sediment Samplers Used in the Study Sites
(a) Ekman Dredge (b) Kemmerer Sampler

A Field Study Site Observation Sheet (Figure C-3) was completed for each sampling station deployed in the field. The field study crew used this sheet to describe each sampling station site, weather conditions at the time of sampling, and the like. Also, for each sample collected at a station, the field crew completed Sample Data Sheets (Figure C-4). The field crew used these sheets to record sample information such as the time of collection, depth of sample collection, and the like.

3.1 Sample Traceability

All samples were uniquely identified with preprinted barcode labels. These labels (printed as a set of six) were used to physically track samples for this project. One of the labels was affixed to the sample container and a second to a Sample Data Sheet. The remaining labels were affixed in the laboratory.

The MRI sample traceability protocol was followed for sample tracking for this project. Traceability records started with sample collection and the completion of the lower portion of the Sample Data Sheets. Upon receipt at MRI, the samples were inventoried by the project sample custodian (See Tables C-1 and C-2). The water and sediment samples were stored in a locked cold room. This room is accessible only through the cold room custodian, who maintains records of room temperature and staff accessing the room. The mussel samples were individually wrapped in aluminum foil and stored in a freezer. Further transfer of samples was documented by the sample custodian.

3.2 Quality Control Checks

Spiked water samples were prepared at two stations in the Sugar Creek site (stations B and L_1) and two stations at the Tinkers Creek site (stations A and D). Water samples collected at these stations were spiked at 50 ppb. The water sample collected from station L_1 at the Sugar Creek site was taken at mid-depth for spiking.

The QC field samples were collected in three 4-L glass jugs and transferred to 0.5 gallon glass jugs for spiking. Separate sets of 4-L jugs were provided for stations B and L_1. Homogenization and spiking was done according to the following procedures.

FIELD STUDY OBSERVATION SHEET

Site ID: _____ Date: _____ Time: _____

Signature: _____ Title: _____

Sampling Station Description: _____

_____

_____

_____

_____

_____

_____

Weather Conditions: _____

_____

_____

_____

Personal Observations: _____

_____

_____

_____

_____

_____

_____

Dover CP production during Field Study: _____ lbs.

FIG. C-3 Field Study Observation Sheet

SAMPLE DATA SHEET

Field Study: SUGAR CREEK DOVER, OHIO	Contract Number 68-02-4252	Date (Mo/Da/Yr)
Station ID:	Work Assignment No.	Substance Monitored: Chlorinated Paraffin
Flow (cfs): Field: Calculated:	Samples collected by:	

Sample No.	Type of Sample 1 = water 2 = sediment 3 = mussel	Comp. or Grab	Temp. C°	Time	Depth (ft)	Remarks

Samples relinquished to:_____ by:_____ on:_____ (Date)

to:_____ by:_____ on:_____ (Date)

FIG. C-4 Sample Data Sheet

Table C-1 Correlation of Sample Identity with Barcode Numbers, Sugar Creek (Midwest Research Institute)

STATION ID	MATRIX	SAMPLE TYPE	BARCODE LABEL
A'	Water	Composite	01681
	Water	Composite	01682
	Water	Composite	01683 **
	Water	Composite	01684 *
	Sediment	Composite	01685 **
	Sediment	Composite	01686
	Sediment	Composite	01687
	Sediment	Composite	01688 *
	Mussel	Composite	01704 **
B'	Water	Composite	01647 **
	Water	Composite	01648
	Water	Composite	01649
	Water	Composite	01650 *
	Sediment	Composite	01675
	Sediment	Composite	01676 **
	Sediment	Composite	01677
	Sediment	Composite	01678 *
	Mussel	Composite	01703 **
B	Water	Composite	01669
	Water	Composite	01670 **
	Water	Composite	01679
	Water	Composite	01680 *
	Sediment	Composite	01729
	Sediment	Composite	01730 *
	Sediment	Composite	01701
	Sediment	Composite	01702 **
	Mussel	Composite	01718 **
B (QC)	Water	Field Spike	01711 **
	Water	Field Spike	01712
	Water	Lab Spike	01713 **
	Water	Lab Spike	01714
	Water	Trip Spike	01715 *
	Water	Trip Spike	01716
	Water	Trip Blank	01717
L_1	Water	Composite	01631
	Water	Composite	01632 **
	Water	Composite	01633
	Water	Composite	01634 *
	Sediment	Composite	01635 **
	Sediment	Composite	01636
	Sediment	Composite	01637
	Sediment	Composite	01638 *

Table C-1 (continued)

STATION ID	MATRIX	SAMPLE TYPE	BARCODE LABEL
L_2	Water	Composite	01657 **
	Water	Composite	01658
	Water	Composite	01659
	Water	Composite	01660 *
	Sediment	Composite	01661
	Sediment	Composite	01662
	Sediment	Composite	01663 **
	Sediment	Composite	01664 *
L_3	Water	Composite	01639 *
	Water	Composite	01640
	Water	Composite	01651 **
	Water	Composite	01652
	Sediment	Composite	01653
	Sediment	Composite	01654 **
	Sediment	Composite	01655
	Sediment	Composite	01656 *
L_1 (QC)	Water	Trip Spike	01641 **
	Water	Field Spike	01642 **
	Water	Field Spike	01643
	Water	Trip Blank	01644 **
	Water	Field Blank	01645 **
	Water	Field Blank	01646
D	Water	Composite	01665 **
	Water	Composite	01666
	Water	Composite	01667
	Water	Composite	01668 *
	Sediment	Composite	01671 *
	Sediment	Composite	01672
	Sediment	Composite	01673 **
	Sediment	Composite	01674
K	Water	Composite	01721
	Water	Composite	01722 **
	Water	Composite	01723
	Water	Composite	01724 *
	Sediment	Composite	01725 **
	Sediment	Composite	01726
	Sediment	Composite	01727
	Sediment	Composite	01728

* Split samples for the Dover Chemical Corporation
** Analyzed at MRI

Table C-2 Correlation of Sample Identity with Barcode Numbers, Tinkers Creek (Midwest Research Institute)

STATION ID	MATRIX	SAMPLE TYPE	BARCODE LABEL
A	Sediment	Composite	01787 **
	Sediment	Composite	01788
	Sediment	Composite	01789
	Water	Composite	01790 **
	Water	Composite	01791
	Water	Composite	01792
	Fish	Composite	01834
B	Sediment	Composite	01793 **
	Sediment	Composite	01794
	Sediment	Composite	01795
	Water	Composite	01796
	Water	Composite	01797
	Water	Composite	01798 **
C	Sediment	Composite	01799
	Sediment	Composite	01800 **
	Sediment	Composite	01801
	Water	Composite	01802 **
	Water	Composite	01803
	Water	Composite	01804
	Fish	Composite	01833
D	Sediment	Grab	01805 **
	Sediment	Grab	01806
	Sediment	Grab	01807
	Water	Grab	01808
	Water	Grab	01809
	Water	Grab	01810 **
E	Sediment	Grab	01811 **
	Sediment	Grab	01812
	Sediment	Grab	01813
	Water	Grab	01814
	Water	Grab	01815
	Water	Grab	01816 **
F	Water	Grab	01817
	Water	Grab	01818
	Water	Grab	01819 **
	Sediment	Grab	01820 **
	Sediment	Grab	01821
	Sediment	Grab	01822

Table C-2 (continued)

STATION ID	MATRIX	SAMPLE TYPE	BARCODE LABEL
A (QC)	Water	Lab Spike	01781 **
	Water	Lab Spike	01782
	Water	Field Spike	01783 **
	Water	Field Spike	01784
	Water	Trip Spike	01785 **
	Water	Trip Blank	01786 **
D (QC)	Water	Field Spike	01771 **
	Water	Bad Blank	01772
	Water	Lab Spike	01773 **
	Water	Field Spike	01774
	Water	Field Blank	01775
	Water	Trip Spike	01776
G	Water	Grab	01826 **
	Water	Composite	01827
	Water	Composite	01828 **
	Water	Grab	01831 *
	Water	Composite	01832 *

* Split samples for the S.K. Wellman Company
** Analyzed at MRI

The 4-L glass jugs were etched in the laboratory at the 3-L level. The 0.5-gallon jugs were etched in the lab at the 475, 950, and 1,425 mL levels. In the field, the 4-L jugs were filled to the 3-L marks with the water sample. The first jug was shaken thoroughly and the contents poured into the 0.5 gallon jugs to the first mark (475 mL). The second and third 4-L jugs were used to fill the 0.5-gallon jugs to the second and third marks respectively. Two of the four samples for each station were spiked at the 50 ppb level. This was done by adding 1.0 mL of a chloroparaffin standard (approximately 70 μg/mL each cell) in methanol. The remaining field QC samples were spiked at the same level immediately before extraction in the laboratory.

Extraction and analysis of the eight QC samples (four samples from each of the two stations), constituting 16 analyses (8 filtrate and 8 suspended solids fractions) was done at the same time the field samples were analyzed.

In addition to these field QC samples, trip QC samples were prepared as follows:

Two samples of laboratory deionized water (volume = 1,425 mL) were prepared for each of the four QC stations, i.e. stations B and L_1 (Sugar Creek) and stations A and D (Tinkers Creek). These samples were then transported to the field. At each of the designated QC stations a set of two of these samples were removed from the cooler and one of these per QC station selected, at random, and spiked at 50 ppb (a total of four samples). The other sample from each set of two was not spiked but was returned to the lab and analyzed along with its spiked counterpart.

Just prior to analysis, an additional sample per QC station (a total of four samples) was prepared, again using laboratory deionized water and spiked at 50 ppb.

Because the rate of adsorption of CPs to suspended solids may differ between environmental and spiked samples and between field-spiked and laboratory-spiked samples, CP recovery is expressed in a weight/volume basis (μg/L) after summing the weights of CP in the filtered water sample and its respective solids. (It is similarly meaningful to express CP residues in water samples in the same way, especially when comparing residues in samples containing different amounts of suspended solids. For example, residue levels in the solids of two samples might be quite similar on weight CP/weight solids basis, whereas total weight of CP would be considerably greater in the water sample having the higher concentrations of suspended solids.)

50272-101

REPORT DOCUMENTATION PAGE	1. REPORT NO. 560/5-87-012	2.	3. Recipient's Accession No

4. Title and Subtitle
Chlorinated Paraffins: A report on the Findings From Two Field Studies, Sugar Creek, Ohio and Tinkers Creek, Ohio

5. Report Date January 22, 1988

6.

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10. Project/Task/Work Unit No.

11. Contract(C) or Grant(G) No.
(C) EPA 68-02-4252
(G) EPA 68-02-4243

12. Sponsoring Organization Name and Address
Environmental Protection Agency
Office of Toxic Substances
Exposure Evaluation Division
401 M St. S.W., Washington D.C. 20460

13. Type of Report & Period Covered
Final Report
1986 - 1987

14.

15. Supplementary Notes
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16. Abstract (Limit: 200 words)

This report presents the results of two field studies conducted in 1986 by the Environmental Protection Agency's Office of Toxic Substances (EPA/OTS) under the existing chemicals program to screen selected waterbodies for the presence of chlorinated paraffins. Chlorinated paraffins are saturated straight-chain hydrocarbons ranging from 10 to 30 carbons in length and containing 20 to 70% chlorine by weight. The information gained from these field studies will be coupled with that from other environmental hazard and environmental exposure studies and collectively contribute to an EPA risk assessment for this chemical.

The report also develops an analytical method for chlorinated paraffins in different environmental matrices and includes a rigorous statistical analysis of the data used to validate the method.

17. Document Analysis a. Descriptors

Chlorinated Paraffins, lubricating oils, survey design, HRGC/NCIMS/SIM analytic method, statistical assessment of method validation studies.

b. Identifiers/Open-Ended Terms

Literature review	Chromatography
Extraction	Cleanup
Mass spectrometry	Statistical analysis

c. COSATI Field/Group

18. Availability Statement
Release Unlimited

19. Security Class (This Report) Unclassified

21. No. of Pages 65 plus App.

20. Security Class (This Page) Unclassified

22. Price

(See ANSI-Z39.18) See Instructions on Reverse

OPTIONAL FORM 272 (4-77)
(Formerly NTIS-35)
Department of Commerce