Surface Microlayer Sampling Results for the Chesapeake Bay

Spring 1988



Surface Microlayer Sampling Results for the Upper Chesapeake Bay: Spring 1988

Prepared by:

Hermann Gucinski Anne Arundel Community College

Ronald Preston
U.S. Environmental Protection Agency

Robin J. Laird
U.S. Environmental Protection Agency
Chesapeake Bay Program Office

ABSTRACT

An exploratory study was conducted during the spring of 1988 to examine the surface microlayer zone of the Chesapeake Bay for the presence of contaminants, to measure ambient toxicity of the microlayer, and to characterize the microlayer biotic community. This study was also conducted to compare the seasonal variations of the contaminant concentrations to a previous surface microlayer investigation conducted during the autumn of 1987 (U.S. EPA, 1988a). This investigation included: chemical analysis scans for pesticides, organics and metals; neuston collection and community composition; and, screening acute toxicity testing using Menidia beryllina.

Trace quantities of contaminants (pesticides, organics, metals) were detected in the microlayer. In several cases, the concentrations were greater than detected in the water column. However, the values for the spring 1988 sampling generally indicated less contaminant concentration in the surface microlayer than was found in previous sampling during the late summer of 1987. The neuston community was dominated by the genera <u>Bosmina</u>, <u>Eurytemora</u>, and <u>Acartia</u>. Other organisms observed included <u>Gammarus</u>, <u>Diaphanosoma</u>, <u>Daphnia</u> and fish eggs. The screening toxicity tests of surface microlayer samples with the silver minnow (<u>Menidia beryllina</u>) did not produce acute toxic responses.

The field conditions and observations indicated a general lack of coherent surface films. The low concentrations of microlayer contaminants found in this study correlate well with the presence or absence of such microlayer 'slick' occurrences.

ACKNOWLEDGEMENTS

Analytical support was obtained through contract laboratory services of the Industrial Technology Division, Office of Water Regulations and Standards, U.S. EPA; field sampling and neuston analysis by the Environmental Center, Anne Arundel Community College, Annapolis, Maryland; the screening toxicity tests were conducted by the Biology Laboratory staff, Environmental Services Division, Region III, U.S. EPA; a portion of the field sampling and metal analyses were performed by Lenwood Hall and his staff of the Applied Physics Laboratory, Johns Hopkins University.

We would also like to thank Richard Batiuk of the U.S. EPA Chesapeake Bay Program Office and Ellen Horvath, Computer Sciences Corporation, for their continuous efforts in finalizing this document for publication.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRAC	T i
ACKNOWL	EDGEMENTS i i
LI	ST OF TABLES v
LI	ST OF FIGURES vi
IN	TRODUCTION 1
ME	THODS AND MATERIALS 1
	Field Sampling Design and Sampling Locations 1
	Surface Microlayer Sample Collection and Handling 2
	Surface Tension and Pressure Analyses 7
	Chemical Analyses 9
	Biological Analyses
	Toxicity Testing 9
	Neuston Collections
	Surface Microlayer Sampler Design 12
RE	SULTS AND DISCUSSION 12
	Surface Microlayer Contamination
	Physical Analyses 12
	Chemical Analyses 22
	Biological Results 25
	Toxicity Tests
	Neuston Analyses 25
CO	NCLUSIONS 29
BI	BLIOGRAPHY 31

APPENDICES

APPENDIX A	A:	Freeman Surface Microlayer Sampler Design Specifications
APPENDIX I	B:	<pre>Menidia beryllina Toxicity Testing: Survival, Physical and Chemical Data B-1</pre>
APPENDIX (C:	Neuston Species and Abundance Data C-1
APPENDIX I	D:	List of Organic Compounds Scanned for in the Surface Microlayer and Bulk Water Samples
APPENDIX E	E:	List of Pesticides Analyzed for the Surface Microlayer and Bulk Water Samples E-1

LIST OF TABLES

		<u> I</u>	Page
Table	1.	Surface Microlayer Sample Collection Stations in Upper Chesapeake Bay	. 3
Table	2.	Surface Microlayer/Bulkwater Sample Collection Stations in Northern Chesapeake Bay - Metal Analyses Only	. 5
Table	3.	Analytical Methods Used for Contaminant Analyses of Surface Microlayer and Bulk Water Samples	. 8
Table	4.	Summary of Physical Observations made during Surface Microlayer Sample Collection	. 14
Table	5.	Organic Compounds Detected in the Surface Microlayer and Bulk Water Samples	. 23
Table	6.	Pesticide (Tributyltin) Detected in the Surface Microlayer and Bulk Water Samples	. 23
Table	7.	Metals, Dibutyltin, and Tributyltin (TBT) Concentrations in the Surface Microlayer and Bulk Water Samples	. 24
Table	8.	Summary of Menidia beryllina Toxicity Tests Results	26

LIST OF FIGURES

		<u>P</u>	age
Figure	1.	Surface Microlayer/Bulk Water Sample Collection Stations in Upper Chesapeake Bay	. 4
Figure	2.	Surface Microlayer/Bulk Water Sample Collection Stations in Upper Chesapeake Bay - Metal Analyses Only	. 6
Figure	3.	Freeman Surface Microlayer Sampler	13
Figure	4.	ATR Infrared Spectrum from the Choptank River Surface Microlayer	16
Figure	5.	ATR Infrared Spectrum from the Choptank River Surface Microlayer (Deionized Water Leach)	17
Figure	6.	ATR Infrared Spectrum from the Susquehanna River Surface Microlayer	19
Figure	7.	ATR Infrared Spectrum from the Susquehanna River Surface Microlayer (Deionized Water Leach)	20
Figure	8.	Zisman Contact Angle Plot - Choptank River Station	21
Figure	9.	Zisman Contact Angle Plot - Susquehanna River Station	21
Figure	10.	Neuston in the Surface Waters of the Choptank River Station	27
Figure	11.	Neuston in the Surface Waters of the Potomac River Station	27
Figure	12.	Neuston in the Surface Waters of the mid-Chesapeake Bay Mainstem Station	28
Figure	13.	Neuston in the Surface Waters of the Susquehanna River Station	28

INTRODUCTION

Analyses of surface microlayer samples in previous investigations have revealed elevated levels of contaminants in the surface microlayer of the Chesapeake Bay compared to the rest of the water column (bulk water). An exploratory study conducted in the autumn of 1987 (U.S. EPA, 1988a) found detectable or higher levels of 24 pesticides, 14 aromatic hydrocarbons, 22 saturated hydrocarbons and organotin in the surface microlayer at 6 upper Chesapeake Bay stations. The relatively high contaminant levels found in the Potomac and Susquehanna rivers during the study suggested that these sites be revisited. The mixed contaminant loads found at the mid-Chesapeake Bay and the Choptank River sites also suggested repeat sampling. The selection of these stations for analysis was an attempt to verify the seasonal variations in microlayer contaminant concentrations, and to evaluate the threat that might exist in important living resource habitat areas. Another recent study in the Chesapeake Bay (Hardy et. al., 1987) also found elevated levels of organics contaminants and metals in the surface microlayer.

The microlayer sampling survey described here was designed to follow up these earlier studies. The survey objectives were to:

- Test the hypothesis that higher concentrations of some pesticides are expected during spring application periods compared to autumnal runoff periods, leading to increased surface microlayer contamination;
- Analyze the spring surface microlayer samples for other organics and metals contamination;
- Sample the neuston community and identify species potentially exposed to surface microlayer contamination; and,
- Explore the potential toxicity of collected surface microlayer samples to finfish.

METHODS AND MATERIALS

Field Sampling Design and Station Locations

The survey was designed to maximize the information gained from the few stations sampled. Sample quantity constraints, dictated by available resources, allowed for collection of fewer bulk water (10 cm below the water column surface) than microlayer samples. Characterizing potential impacts required that station selection include important living resource areas as well as zones

with the potential for high contamination. Four stations were selected - Susquehanna River at Havre de Grace, mid-Chesapeake Bay at Matapeake, Choptank River at Cambridge, and the Potomac River at Hedge Neck - all located in northern Chesapeake Bay (Table 1, Figure 1). At two of the stations - Hedge Neck and Havre de Grace - bulk water samples were also collected concurrently with the surface microlayer samples.

The Havre de Grace station represented the input point from the large Susquehanna River drainage area, with the potential for contaminants from agricultural and urban sources within the basin. The Matapeake station represented an area that typifies the conditions in the upper Chesapeake Bay mainstem. The Choptank River at Cambridge station represented an upper Bay tributary with important living resource habitats. The Potomac River at Hedge Neck station, immediately downstream of the urban Washington DC metropolitan area, is representative of a potentially contaminated area. These stations were a subset of stations previously sampled for surface microlayer contamination in the fall of 1987 (U.S. EPA 1988a).

In addition to the metal analyses conducted from these four stations, metal analyses were also conducted for a set of surface microlayer/bulk water samples collected from six other Chesapeake Bay locations: three on the Potomac River, one on the Elk River, one on the Sassafras River and one on the Susquehanna River (Table 2, Figure 2). The Johns Hopkins University, Applied Physics Laboratory, performed the sampling and analyses.

Surface Microlayer Sample Collection and Handling

The surface microlayer samples and neuston tows were sampled over a zone that was determined by towing speed and duration. To minimize tidal current effects, tows were bi-directional, and typically covered a distance of 50 to 60 meters. Physical observations were made simultaneously with the surface microlayer sample collections, and the neuston tows performed last.

The collection of surface microlayer samples required a sampler towed by an outrigger from the beam of a small craft (Figure 3). For speed and efficiency, a small craft was propelled by an electric motor in an upwind or crosswind direction when possible, with the sampler towed outside of the boat's wake.

The microlayer drum sampler was used with the following protocol: the drum was washed with detergent, rinsed with sampling water, and allowed to turn for 10 minutes prior to sample collection in order to complete the rinsing and equilibration

Table 1. Surface Nicrolayer and Bulk Water Sample Collection Stations in Upper Chesapeake Bay

Mid-Chesapeake Bay at Matapeake	Choptank River at Cambridge	Susquehanna River Havre de Grace	Potomac River at Hedge Neck	Station Name
12	1 4	ça		Station Number
5/12/88	5/10/88	5/11/88	5/13/88	Date
38 57/30"	38 35'17"	39 33/16"	38 43/29*	Latitude
76 21'56"	76 04'40"	76 05'00"	77 02'00"	Longitude
Microlayer	Microlayer Bulk water	Microlayer Bulk water	Microlayer Bulk water	Sample Type
Approximately 1/2 to 2/3 mile from eastern shore and about 2 miles south of Chesapeake Bay Bridge, depth 12-18 feet; residential and some agricultural use.	Approximately 1/3 mile from western shore of Cambridge; residential land use with commercial use within 1-1.5 miles.	Approximately 1/4 mile south of railroad at bridge near river mouth, western channel; light industrial/commercial land use.	Approximately 1 mile north of Ft. Washington, deep central channel; agricultural/residential land use.	Station Location Description

^{*} Station numbers reflect the selection of a subset of the twelve stations sampled in the Fall, 1987 survey (U.S. EPA, 1988a). Only Stations 3, 8, 11 and 12 were sampled in this study.

^{**} Limited funding did not allow for chemical analysis on bulk water samples at all stations. Previous investigations document that the surface microlayer concentrates chemical compounds in greater amounts than bulk water concentrations.

Figure 1. Surface Microlayer and Bulk Water Sample Collection Stations in Upper Chesapeake Bay

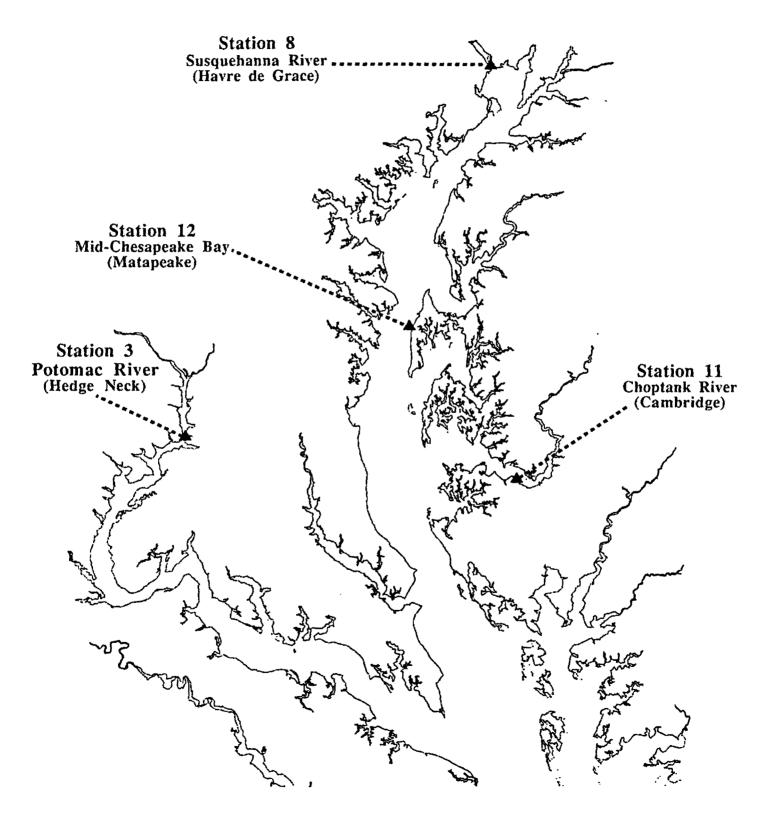
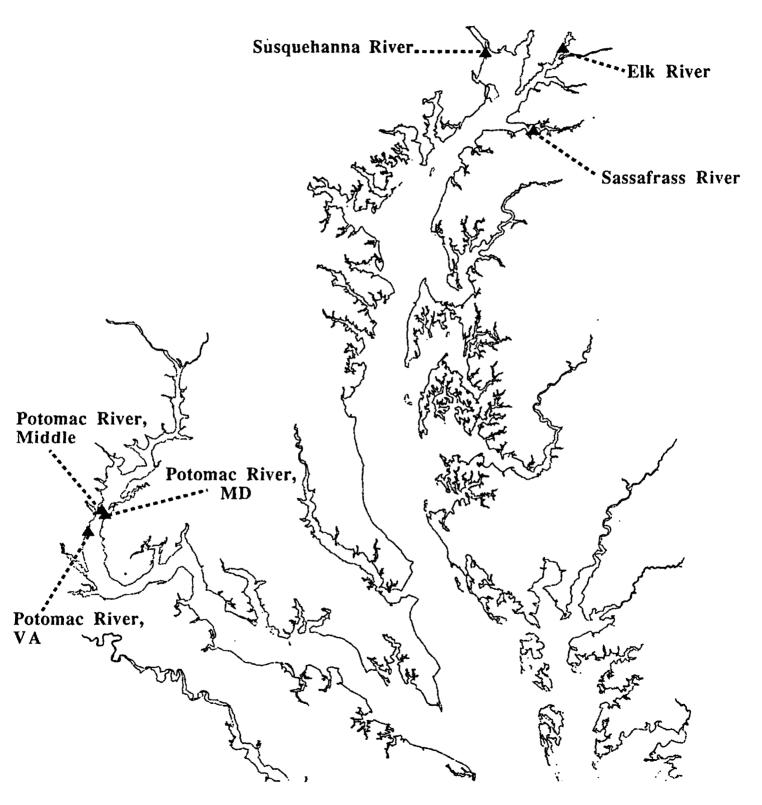


Table 2. Surface Microlayer Sample Collection Stations in Upper Chesapeake Bay - Metal Analyses Only*

Station Name Potomac River, MD	Sample Date 4-26-88	Latitude	Longitude	Sample Type Microlaver	Station Location Description Marvland side of the F
Potomac River, MD	4-26-88	38 31' 42'' N 38 31' 42'' N	77 15' 23'' W 77 15' 23'' W	Microlayer Bulk water	Maryland side of the Potomac River near the power lines at Possum Point (near Moss Point).
Potomac River-Middle	4-26-88	38 32' 23'' N 38 32' N	77 15' 54'' W	Microlayer Bulk water	Middle of the Potomac River
Potomac River, VA	4-125-188 8-8-8-8-8-8-8-8-8-8-8-8-8-8-8-8-8-8	38 29' 26'' N 38 29' 26'' N	77 18: 25: W 77 18: 25: W	Microlayer Bulk water	Virginia side of the potomac River near the power lines at Possum Point.
Elk River	5 1 1 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	39 33' N 33' N N N	75 52' W 75 52' W 75 52' W	Microlayer Bulk water Filt. Bulk	.5 kilometer south of Plum Pt.
Sassafrass River	5-20-88 5-20-88 5-20-88	39 22' N 39 22' N 39 22' N	75 58' W 75 58' W 75 58' W	Microlayer Bulk water Filt. Bulk	At the end of the community pier at Kentmore Park.
Susquehanna River	5-20-88 5-20-88	39 33' N	76 5.5' W 76 5.5' W	Microlayer Bulk water	100 meters from Have de Grace Marina, .5 kilometer south of Garrett Island.

^{* (}Station information from Lenwood Hall, University of Maryland - Wye Institute, Queenstown, MD)

Figure 2. Surface Microlayer and Bulk Water Sample Collection Stations in Upper Chesapeake Bay—Metal Analyses Only



cycle. A half-gallon glass sampling bottle (with a teflon lined cap) was used for all collections. Aliquots were taken for metals, volatile organics, tributyltin (TBT), and bioassay analyses from the first bottle. Separate bottles were used for the organics and pesticide scans. All samples were stored on ice until they were taken to the lab by air-express or local transportation within the holding time specified in the analytical methods references (see Table 3). This same collection procedure was maintained throughout the sampling effort.

Sample collections were accompanied by physical observations of: surface tension using the Adam spreading oil technique (Adam, 1937); Germanium prism dips for characterizing the organic composition of the microlayer (Gucinski, 1981 and Baier et al., 1974); sea surface and air temperature (bucket thermometer); salinity (refractometer); windspeed (hand held anemometer), and wind direction (small boat compass). Table 6 contains a summary of the physical observations made during surface microlayer sample collections.

The collection times for surface microlayer sampling were extremely long when the concentration of surfactants (surface active agents) was too low to produce measurable surface pressure changes at the air-water interface. When sample collection periods exceeded 10 minutes for the collection of two liters of microlayer water, the field crew maximized these collection efforts by following windrows of bubbles because they indicate the zones of convergence where microlayer thickness and enrichment may not reflect truly average sea surface conditions.

Surface Tension and Pressure Analyses

Chemical bonds of dominant organic molecules were identified using Attenuated Total Reflection (ATR) Infra-Red spectroscopy (Gucinski et al., 1981; Baier, 1974; Harrick, 1967). Optically flat, trapezoidal prisms of Germanium (50x20x1 mm) were vertically lowered and retrieved through the interface, relying on the Langmuir-Blodgett transfer of surface active substances to the Gesubstratum. The method is sensitive to about 5 nanograms of sample and does not appear selective for "wet" surfactants (Gucinski et al., 1981).

Surface tension was measured after Adam (1937), in which mixtures of mineral oil of zero spreading pressure and dodecyl alcohol of high intrinsic spreading pressure are calibrated for several spreading pressure ranges. Dropper application of mixtures with increasing alcohol strength quickly yielded a point of visible droplet spreading against the ambient surfactant pressure, allowing

Table 3. Analytical Methods Used for Contaminant Analyses of Surface Microlayer and Bulk Water Samples

Parameter	Method	Number Number	Method Reference
Aluminum	Atomic Emission - ICP	200.7	U.S. EPA 1982
Arsenic	Atomic Absorption - Hydride	206.3	U.S. EPA 1979
Cadmium	Atomic Absorption - Furnace	213.2	U.S. EPA 1979
Chromium, Total	Atomic Absorption - Furnace	218.2	U.S. EPA 1979
Copper	Atomic Absorption - Furnace	220.2	U.S. EPA 1979
Lead	Atomic Absorption - Furnace	239.2	U.S. EPA 1979
Nickel	Atomic Absorption - Furnace	249.2	U.S. EPA 1979
Selenium	Atomic Absorption - Hydride	270.3	U.S. EPA 1979
Tin	Atomic Absorption - Furnace	282.2	U.S. EPA 1979
Zinc	Atomic Absorption - Direct Aspiration	289.1	U.S. EPA 1979
Dibutyltin and Tributyltin	Gas Chromatography - Flame Photometric Detector	1	Unger et al., 1986
Organics and Volatile Organics	Isotope Dilution GC/MS	1624C 1625C	U.S. EPA 1988b U.S. EPA 1988c
Organo-halide and organo- phosphorus pesticides and phenoxy-acid herbicides	Capillary column GC	1618	U.S. EPA 1988d

(see Appendices D and E for a complete listing of the detaction limits for each compound)

a quick determination of a narrow range of sea-surface tension values.

By measuring the contact angles of a series of ultra-pure liquids of known surface tension, one may plot the cosine of these angles against the liquid's surface tension. The intercept at the cos 00 = 1 axis of the least square fit of the data gives a numeric value termed the critical tension or critical surface energy by Zisman (1964) who, with coworkers, developed the technique. The concept provides an empirical description that closely relates to the substrate's surface energy, and has proven to be an excellent predictor of wetability and adhesion.

Chemical Analyses

Chemical analyses on the surface microlayer and bulk water samples were performed for the following categories by contract laboratories:

Analyses	Laboratory
----------	------------

Organics Midwest Research Institute
Pesticides Colorado State University
Metals/Tributyltin Johns Hopkins University, Applied
Physics Laboratory

The methods and quality assurance procedures used for these analyses are described in the method references provided in Table 3. The isotope dilution gas chromatography/mass spectrophotometry (GC/MS) (U.S. EPA Methods 1624C and 1625C) was used to scan over 300 organic compounds. A gas chromatography capillary column was used to search for 79 pesticides (U.S. EPA Method 1618). U.S. EPA procedures for atomic emission and atomic absorption were used to analyze for eleven metals. Dibutyltin and tributyltin were analyzed for using gas chromatography with flame photometric detection according to Unger et al., 1986.

Biological Analyses

Toxicity Testing

The EPA protocol (U.S. EPA 1988e) was used to conduct toxicity tests on the surface microlayer and bulk water samples. The test protocol calls for a daily renewal (during the seven-day test period) of the test media to which the fish are exposed and recommends renewal with fresh samples collected each day. Protocol options allow for the use of one sample (large enough to obtain

daily renewal aliquots) kept cool (at four degrees centigrade to minimize deterioration) during the test period and used as source for the daily renewal. This option was chosen because of the lack of resources required to collect daily surface microlayer samples at four widely separated geographical locations. Also, relatively large volumes of surface microlayer samples (over four liters) were difficult to obtain due to the lack of surface forming "slicks." Therefore, the volume of a sample did not permit the chronic test to be run for the routine seven days; the results of the four-day test are valid for measuring acute response.

The static renewal test protocol recommends using 7-11 dayold silverside minnows (<u>Menidia beryllina</u>). When the sample
collection and testing began for the toxicity response test,
however, only 19-23 day-old fish were available in sufficient
numbers for the designed test. While the protocol authors theorize
that <u>Menidia beryllina</u> may be less sensitive to contaminant effects
as the fish age beyond the post-larvae stage, such comparable data
for 19-23 day old fish are not available. Cultured test organisms
are less variable in many ways than 'wild' fish and, therefore,
even though the test fish were 12 days older than recommended,
their potential response to controlled test conditions was presumed
more beneficial than not conducting this screening toxicity test
at all.

A sample of laboratory source control water (15 ppt salinity) was obtained from the U.S. EPA's Gulf Breeze Laboratory. A control was set up with each group of samples because the age of the fish changed as the study progressed. Comparisons between control and exposure tests should only be made among samples set up on the same day. Using commercial artificial sea salts, the salinities of the microlayer and bulk water samples were adjusted to the salinity range in which the test organisms were acclimated. A control was set up on May 10, 1988 using these artificial salts to demonstrate that these salts do not adversely affect the survival and growth of Menidia beryllina.

Menidia beryllina was chosen because it is one of the species identified in the standardized EPA method manual for marine toxicity tests. It also is an estuarine species that inhabits the Chesapeake Bay. The Menidia beryllina used for these tests were obtained from the U.S. EPA's Gulf Breeze Laboratory. They were shipped air freight on May 9, 1988 and arrived at the mobile laboratory the next day. The fish were cultured in the laboratory control water at 23-25 degrees centigrade with a salinity of 15 ppt. On the day that testing was initiated (May 10, 1988), they were 19 days old. The remaining fish were held in culture water to be used in the samples set up on May 12, and May 14, 1988 and were 21 and 23 days old, respectively. While being held, the

<u>Menidia</u> <u>beryllina</u> were fed concentrated brine shrimp nauplii twice daily.

After the water samples arrived at the laboratory, the temperatures were adjusted up to the test temperature (24 degrees centigrade +/- 2). The salinities were then adjusted to within 5 ppt salinity of the culture/holding water. The pH, temperature, salinity and dissolved oxygen were measured in each test solution. The dissolved oxygen was measured in one of the replicate test containers every day thereafter for the duration of the test.

Each sample was set up in triplicate in 125 X 65 mm glass containers with 500 ml of test solution in each. For the samples set up on May 10 and 12, ten fish were placed in each replicate for a total of 30 per sample. Due to a reduced supply of fish during the testing period, only six fish were placed in each replicate of the samples set up on May 14 for a total of 18 fish per sample.

One hundred microliters of concentrated brine shrimp nauplii were dispensed to each replicate every morning. The test organisms were allowed to feed before the containers were cleaned. Each replicate test chamber was cleaned daily by siphoning the water and any debris out of it, filtering the water through a brine shrimp net and returning the water to the test container. The test organisms were then fed again.

All tests were terminated after four days of testing. The tests set up on May 10 and 12 were terminated in the mobile laboratory. The samples set up on May 14 were transferred from the mobile laboratory to the U.S. EPA's Wheeling Laboratory on May 16 and terminated on May 18. Results of the control exposure indicated no adverse effect of this transfer. At termination, the test organisms were euthanized and preserved in 70% alcohol. The fish from each replicate were dried and weighed to determine their mean dry weight. The survival and weight data were analyzed using Dunnett's Procedure.

Neuston Collections

The neuston population density, composition and diel variation were all sampled from the same sampling stations using dual nets - a neuston net immersed 5 - 10 centimeters during tows and a subsurface net sampling at the 30-50 centimeters depth.

The dual net consisted of two rectangular-mouth (0.56 X 0.17 meter) zooplankton nets with a mesh size of 200 micrometers. Ten minute tows were made at a boat speed of one nautical mph, retracing a marked path or towing in a large circle to avoid

current bias in the estimated sampling volumes. The towed distance was 315 meters (0.17 nautical mile) and the sampling volume of the partially immersed upper net, was 7.6 cubic meters while the lowered net sampling volume was 25.8 cubic meters.

Nighttime collections were made no sooner than 3.5 hours after sunset, and were generally completed at least two hours before sunrise. Daytime collections rarely began before 10:00 a.m., or generally at least 4.5 hours after sunrise, and were always completed at least three hours before sunset.

Identification was made by counting aliquots of the sample in a Durrel trough using aliquot volumes of 5 - 10 milliliters and increasing the volumes until consistent concentrations for identified species were obtained. Dissecting scopes and low power (X40) inverting microscopes were used as required. The major literature sources for taxonomic identification include Ward and Whipple (1966); Versar, Inc. (1987), and Lippson and Moran (1974).

Surface Microlayer Sampler Design

The surface microlayer sampler (Figure 3) was constructed to provide the Chesapeake Bay Program with an evaluated device for surface microlayer sample operations. This device incorporates modifications of existing surface microlayer samplers to improve the design of the sampler in the following areas:

- collection of sample volumes sufficient for chemical analysis;
- high collection efficiency;
- shallow, nominal/sampling depth;
- reasonably light weight;
- ease of repair and disassembly; and,
- facility for use from small boats.

Appendix A gives the design specifications and notes.

RESULTS AND DISCUSSION

Surface Microlayer Contamination

Physical Analyses

The presence of either naturally occurring surfactants or surface active contaminants is reflected in the observed surface pressure changes (Table 4) from the nominal surface tension value of 72.4 mN/m (milli Newton per meter) of freshwater at 20 degrees centigrade. Surface pressure measurements, using the Adam

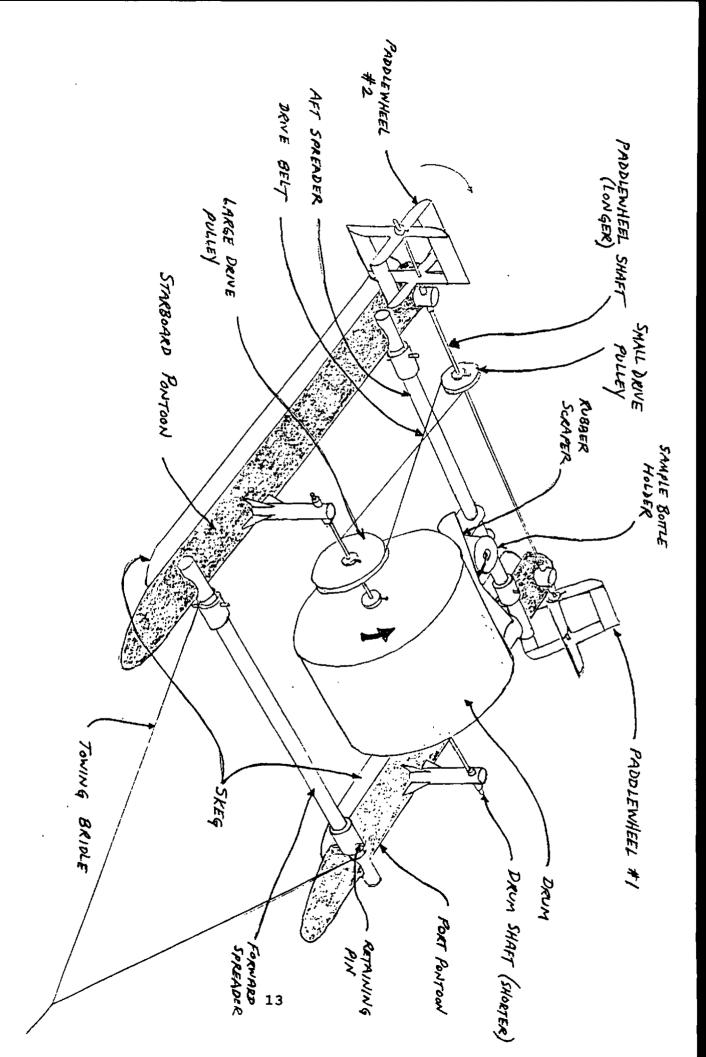


FIGURE 3. THE FREEMAN MICROLAYER SAMPLER

8-24-08

•

.

Table 4. Summary of Physical Observations made during Surface Microlayer Sample Collections

** 1 - Toxicity testing 2 - Metals 3 - Volatile organics 4 - Organics/Pesticides	* milli Newton per meter	Mid-Chesapeake Bay at Matapeake	Choptank River at Cambridge	Susquehanna River at Havre de Grace	Upper Potomac River at Hedge Neck	Station
nics fordes	eter	10	10	10	.0	Neuston Tow (Min.)
		16.5	16.5	16	2	Water Temp.
		9.5	12	0	0	Salinity 0/00
		N	w	w	N	Wind Beaufort Scale
		MNM	w	ene	S.	Wind Beaufort Direction Scale
		0.83	0.83	9.25	0.83	Surf. Pressure (mN/m)* Non/slick
		16	5 0	<u>مر</u> س	Ø.	C011
		32	30	7	111	Microlayer Sampler Collection Times (minutes) Sample Type ** 1 2 3 4
		13	জ 6	15	36	yer Sami imes (mi Type **
		28	27	10	69	nutes)

spreading oils which rely on surface pressure sensitivity, did not vary more than 1 mN/m from the nominally clean value. A surface pressure change greater than 1 mN/m correlates with sufficiently close molecular packing of surfactants to produce interfacial effects such as capillary wave suppression; it also produces the appearance of surface slicks (Katsaros et al., in press; Huhnerfuss et al., 1985). Thus, a measured spreading pressure of 9.25 indicates the clean surface tension of 72.4 mN/m had dropped to 63.15 mN/m.

In the spring 1988 sampling effort, few surface slicks were observed; the majority appeared as windrows, bands of foam or bubbles, with only a narrow zone of obvious capillary wave damping. The highest surface pressure of 9.25 mN/m was recorded at the Susquehanna site at giving a nominal sea surface tension of 63.2 mN/m. By comparison, in the autumn 1987 sampling effort, the same stations gave slick surface pressures as high as 16 mN/m, with slicks observed at all but two of the sites (data were missing at two other sites) (U.S. EPA, 1988a). Slick surface pressures averaged 7.5 mN/m. In both the spring 1988 and the autumn 1987 sampling efforts, the non-slick values were never lower than 0.83 mN/m.

We interpret the findings as follows: when no deviations in surface tension are found (e.g. 72.4 mN/m at 20 C), surface pressure is zero, and the water surface is essentially free of surface-active contaminants. Low surface pressure (e.g. values less than 1 mN/m), indicates the presence of natural or man-made surfactants in very low concentrations, insufficient to produce even a layer one molecule thick (see, for example, Adamson 1974). Our measurements, and the work of others (Baier et. al., 1974), have shown that biogenic surfactants are ubiquitous on natural waters, typically at low concentrations. Higher surface pressures indicate higher surfactant concentrations at the interface, and these may be toxic, anthropogenic surfactants, or more likely, biogenic materials that in turn have a high potential for trapping or adsorbing potentially toxic contaminants (Hardy, 1987 and Hardy et. al., 1987b, 1987c).

The presence of organic substances at the air-water interface is further verified by two infrared analyses done on Germanium prism dips at the Choptank and Susquehanna stations. Figures 4 and 5 show the infrared spectrum of the surfactants recovered, analyzed by attenuated total reflection (ATR) unprocessed, and after gently leaching with high purity deionized water, respectively. The leaching removes soluble components, especially salts. Figure 4 highlights 5 peaks. These are:

- the broad peak centered at 3350 1/cm indicating the presence

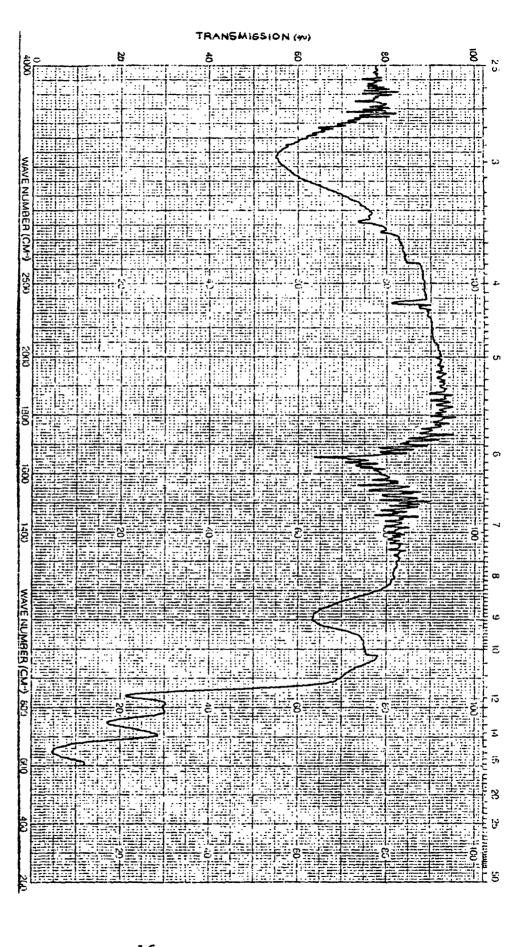
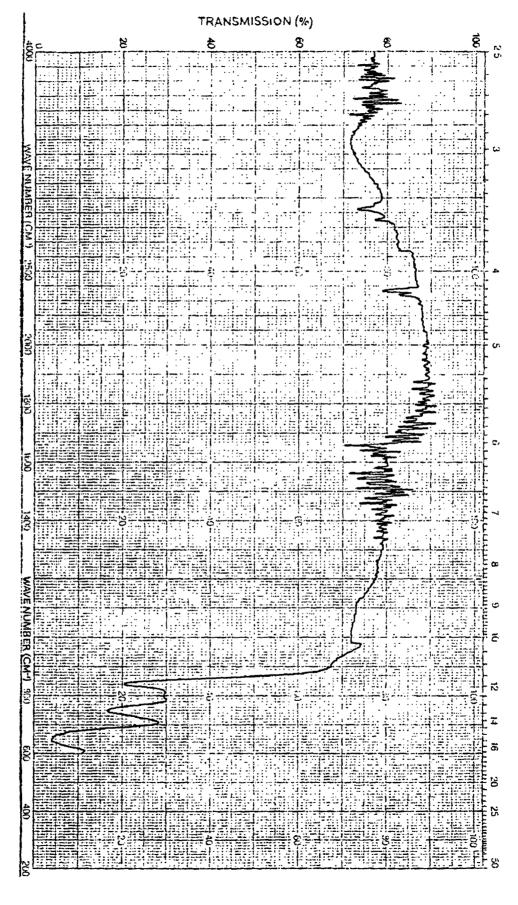


Figure 4. ATR Infrared Spectrum from the Choptank River Surface Microlayer



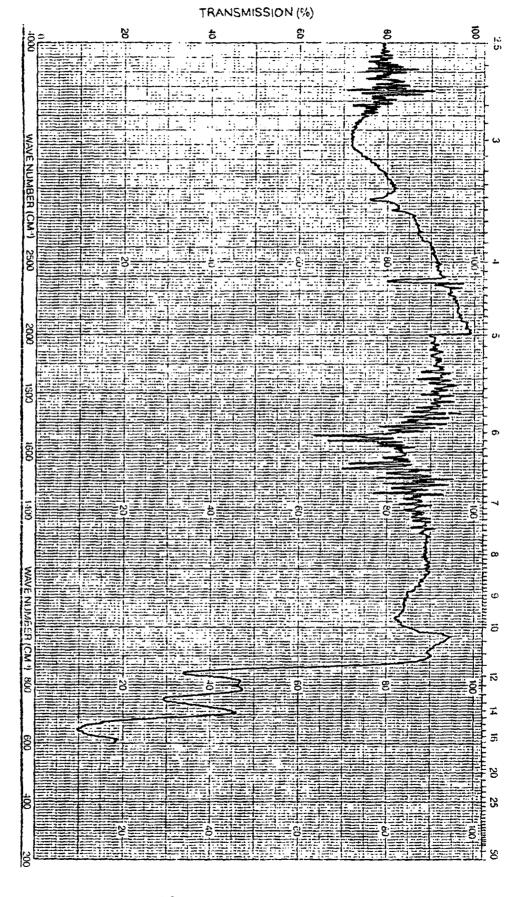
of both bound water and molecules having an N-H bond;

- a peak produced by methyl and CH2 groups of aliphatic hydrocarbons, occurring free or bound as side chains of larger molecules;
- a peak reflecting atmospheric CO2 in the sample chamber of the spectrophotometer, a sign of sensitive instrument performance;
- the broad, noise peak(s) centered at 1660 1/cm reflecting the presence of amide bonds found in proteins and their breakdown products; and,
- the peak centered at 1310 1/cm which is produced by bonds both of the sulfate radical and the hydroxyl groups bound in polysaccharides.

The removal by the peaks at 3350 and 1310 1/cm indicated these constituents were not firmly bound and partially water soluble. What remains, likely a significant component of the surface microlayer, is protein-derived material and some hydrocarbons. The latter are most probably man-made inputs (e.g. fuels etc.), for these bands are rarely seen at that strength in waters remote from human influence (see Baier, 1974; Gucinski et. al., 1981; and, Sieburth, 1983).

Figures 6 and 7 contain similar information with the following differences. The hydrocarbon signature is weaker, while the protein related peaks are more distinctly defined. Moreover, all three peaks - hydrocarbon, protein-like, and possible polysaccharide-like - are changed minimally by leaching the sample, indicating low solubility, and suggesting large molecular size. Finally, the remaining peak at 3300 l/cm after leaching correlated well with the presence of amide bonds, further confirming proteinaceous material to be present.

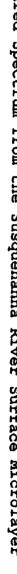
Figures 8 and 9 further confirm the presence of a microlayer organic matrix, as shown by contact angle analysis. The intercept of the Zisman Plot least squares fit gives a critical surface tension of 21.8 mN/m for the Choptank data (Figure 8), and 29.4 mN/m for the Susquehanna data (Figure 9). The former value is consistent with one obtained in spreading a film mixture of glycoprotein and a little oil onto the prism. The latter value, somewhat higher, suggests a less coherent and less intact film, shown by the changes seen upon leaching. Both sets of contact angle data were taken after the prism had been leached and analyzed by infrared scans. These data indicate that small concentrations of natural surface-active substances are present at the air-water



TRANSMISSION (%)

Figure ATR Infrared Spectrum from the Susquehanna River Surface Microlayer

(Deionized Water Leach)



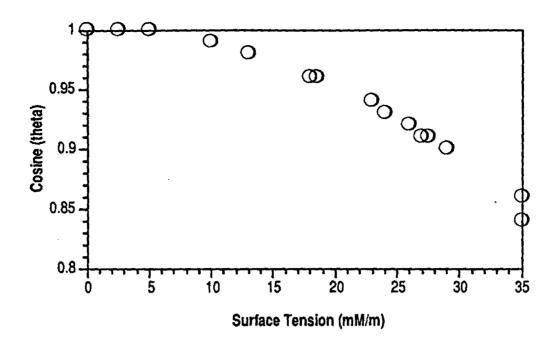


Figure 8. Zisman contact angle plot from the Choptank River at Cambridge, May 10, 1988. (leached in deionized water for 10 seconds. HG 6N epi 1328, gamma - C = 21.8)

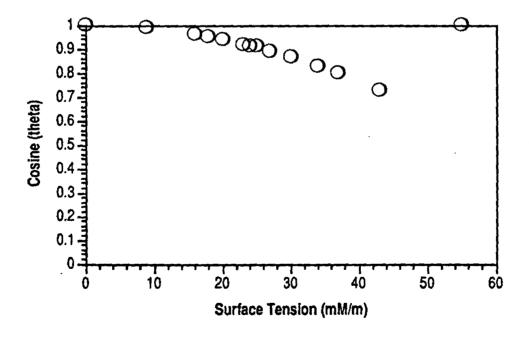


Figure 9. Zisman contact angle plot from the Susquehanna River at Harve de Grace, May 11, 1988. (leached in deionized water for 10 seconds. HG 2R epi 1327, gamma - C = 28.8)

interface even in the absence of slicks. The potential to trap other substances including toxic contaminants exists. The absence of well-defined slicks of moderate to high spreading pressure during our sampling suggests that enrichment of trapped contaminants under these conditions is only moderate at best.

Chemical Analyses

Over 300 organic compounds were scanned for (Appendix D), but only four compounds were detected in microlayer and bulk water samples. These compounds were three low molecular weight solvents and a plasticizer (Table 5). The autumn 1987 study (U.S. EPA, 1988a) detected a larger number of organic compounds including saturated and aromatic hydrocarbons. These same compounds were not detected during the spring 1988 survey. Sixteen pesticides were detected (Table 6) in trace quantities out of the 79 screened (Appendix E) by GC/MS. The autumn 1987 study (U.S. EPA, 1988a) detected a greater variety of pesticides at slightly higher concentrations than the present study.

The results of the metals analyses (Table 7) indicated concentrations of several metals in the surface microlayer samples exceeded the U.S. EPA marine or freshwater water quality chronic values. While the microlayer itself is not 'water,' its close association to the water column justifies comparing the measured concentration to these chronic values.

The following marine chronic values were exceeded in the microlayer at stations in the Elk, Sassafras and the Susquehanna rivers: copper - 2.9 ug/l; lead - 5.6 ug/l and nickel - 8.3 ug/l). The zinc marine chronic value (86 ug/l) was exceeded in the Sassafras River.

The freshwater chronic values were exceeded in the microlayer for the following: copper (12 ug/l) at two of the Potomac River's three freshwater locations; lead at all three Potomac River freshwater locations; and zinc at two of the three Potomac River freshwater locations. The aluminum analytical results were high for the Potomac (middle station), Elk, Sassafras and Susquehanna stations. These values exceed the water quality criteria for freshwater organisms. Depending on hardness and pH, the values reported here are potentially capable of producing toxic effects on aquatic life.

The butyltin concentrations (Table 7) were much less than those observed in the exploratory studies conducted in the autumn 1987 study (U.S. EPA, 1988a). Several of the values from the spring 1988 study are in the range reported to produce sublethal effects: .015 ug/l for dibutyltin (DBT) and .016 ug/l for tributyltin (TBT)

Table 5. Organic Compounds Detected in the Surface Microlayer and Bulk Water Samples (ug/l)

	Datection	Susquehanna River at Harve de Grace Micro- Bulk	na River de Grace Bulk	Choptank River at Cambridge Wirro- Bulk	k River cidge	Potomac River at Hedge Neck	Mid~Bay at Matapeake
Chemical Name	Limit	layer	2000	layer water	Water	Microlayer	Microlayer
Methylene chloride	10	< 10	< 10	20	v 10	21	< 10
Bromoform	0 1 0	< 10	< 10	· 10	14	13	13
Di~N-Butyl Phthalate	10	< 10	< 10	53	53 < 10	138	38
trans-1,2-dichloroethene	10	< 10	۷ 10	< 10 < 10	< 10	11	< 10

Table 6. Pesticides Detected in the Surface Microlayer and Bulk Water Samples (ug/l)

PCNB	Nitrofen (TDK)	Methoxychlor	Isodrin	Reptachlor epoxide	Heptachlor	Endrin	Endosulfan I	Dieldrin	Dichlone	4,4'-DDE	Captan	gamma-BHC	delta-BHC	beta-BHC	alpha-BHC	Chemical Name	
0.05	0.13	0.13	0.03	0.05	0.05	0.03	0.03	0.03	0.25	0.13	0.13	0.03	0.03	0.03	0.03	<u> Limit</u>)))))
TR TR																layer water	Susquehanna River at Harve de Grace
															.03 < 0.03		
< 0.05																Anter	Choptank River Po
< 0.05	TM	< 0.13	TR	TR	72	다 X	TR	^ 0.03	< 0.25	< 0.13	< 0.13	< 0.03	< 0.03	12	78.	Microlayer	Potomac River at Hedge Neck
(0.05	## H	< 0.13	TH	TR	TR	TR	< 0.03	< 0.03	72	< 0.13	< 0.13	TR	< 0.03	rx	< 0.03	Microlayer	Mid-Bay at Matapeake

 $exttt{TR} exttt{ o} exttt{Trace} residue slightly greater than the listed detection limit, but not quantifiable.$

Table 7. Metals, Dibutyltin (DBT) and Tributyltin (TBT) Concentrations in the Surface Microlayer and Bulk Water Samples.

of at ion	Sample Type	Date	A	≯s	C d	Cr	Metal	Metals/But	yltins (ug/l) Ni Se Sn	se (ug,	Sn (1)	Zn	DBT	TBT
Susquehanna River at Havre de Grace (1)	Microlayer Bulk water	5-11-88	960 200	ââ	۵۵	4. W	12 3	20 <3	26	ωû	£15	12	.007	.005
Choptank River at Cambridge (1)	Microlayer Bulk water	5-10-88	60	۵۱	۵۱	۵۱	۱۵	۵í	⇔)	û	\$15	ωi	.071	.009
Potomac River at Hedge Neck (1)	Microlayer Bulk water	5-13-88	1 4 4 0	۱ ۵	1 2	įω	1 W	1 🍒	Įω	1 45	~ \$15	27	1 1	1 1
Mid-Ches. Bay at Matapeake (1)	Microlayer Bulk water	5-12-88	200	۱۵	ا ش	ı û	1 2	1 3	1 6	1 3	÷15	12	.015	910.
Susquehanna River (2)	Microlayer Bulk water	5-20-88 5-20-88	950 <60	<u>۵</u> 1	۵۵	æω	ar ivi	۵۵	8 7	ŝŝ	\$15 \$15	9 8	.010 <.002	.028 <.002
Sassafras River (2)	Microlayer Bulk water Filt. bulk	5-20-88 5-20-88 5-20-88	5,830 410 24	28 11	۵۵۵	322	101 4	\$\$£	146 9	232	225	353 20 42	<.002 <.002	<.002 <.002
Elk River (2)	Microlayer Bulk water Filt. bulk	5-1-19-1-8-8 5-1-19-1-8-8 8-8-8-8	3,270 2,950 60	ଡ଼ଡ଼ୣ	۵۵۵	û 6 8	10 9	ω̂ ဖ ∪ π	20 39 13	۵۵۵	\$15 \$15	554 66 67	<.002 <.002	<.002 <.002
Potomac River - Maryland (2)	Microlayer Bulk water	4-26-88	350 340	۵۵	£ Ĝ	ω 4.4	ω 65	μą	ωû	۵۵	\$15 \$12	99 37	<.002 <.002	<.002 <.002
Potomac River - Middle (2)	Microlayer Bulk water	4-26-88	3,300 730	ââ	<u>ه</u> ۵	æ û	20 4	20 7	û .	ûû	\$15 \$15	242 86	<.002	<.002 <.002
Potomac River - Virginia (2)	Microlayer Bulk water	4-25-88	730 330	ជំជ	۵۵	۵۵	21 5	34	<u>.</u> 10	۵۵	£15	491 30	<.002 <.002	<.002 <.002

(2) — Samples collected by John Hopkins University Applied Physics Laboratory personnel; toxicity tests not performed on these samples.

^{(() =} at or less than the detection limit. (-) = not sampled for and/or not analyzed for.

in the Matapeake; .071 ug/l for DBT and .009 ug/l for TBT in the Choptank; .010 ug/l DBT and .028 ug/l TBT in the Susquehanna.

Biological Results

Toxicity Tests

The <u>Menidia beryllina</u> toxicity tests were terminated after four days because insufficient volumes of surface microlayer samples were obtained. The results of these tests (surface microlayer and bulkwater samples for four stations) are summarized in Table 8 and fully listed in Appendix B.

No mortality with larval <u>Menidia beryllina</u> was observed in any of the ambient water samples. The control exposures (Gulf Breeze water and an artificial sea salt water) also recorded high survival (100% survival in nine exposures, 89% survival in one exposure). The four-day growth rate response parameter (final mean weight) was not significantly different in any of the sample tests when compared to the sample set controls. The growth rate response parameter in the endpoint of the standardized chronic test protocol is designed for a seven-day period. Insufficient sample volumes precluded completion of the seven day chronic test, and therefore, the four-day test results record an acute toxicity response.

Neuston Analyses

The results of the neuston analyses are summarized by station in Figures 10-13 and fully listed in Appendix C. The neuston concentration (number of organisms per cubic meter) and percent abundance for the top 5 cm and for a 20 cm interval sampled between the 30 and 50 cm water depth are listed for each station.

Both day and night tows were made to better characterize the diel differences. The values reported as the averages of two replicated tows (with the exception of the mid-Chesapeake Bay at Matapeake station where a top tow sample was not collected). Unfortunately, the nighttime neuston samples for the Potomac River at Hedge Neck station were invalidated due to a labeling error.

The nighttime total organism density exceeded the daytime density at all stations, as did the density of the single most abundant species. Nighttime total organism density exceeded daytime values by as little as a factor of two at the Susquehanna station, up to a factor of 50 at the mid-Chesapeake Bay at Matapeake station. One might expect greater organism densities at the lower depth compared to the surface layer in daytime and this is borne out at all stations. It is not clear whether a nighttime

Table 8. Summary of Menidia beryllina Toxicity Test Results

Total Number of Surviving Organisms Beginning Day Day Day Day Percent Sample Test Date __1 __2 __4 Rep. Survival 5-10-88 Gulf Breeze A Control В С Sea Salt 5-10-88 A Control R C Choptank River 5-10-88 A at Cambridge В Bulk water C Choptank River 5-10-88 A at Cambridge B Microlayer C Gulf Breeze 5-12-88 A Control В С Susquehanna River 5-12-88 A at Havre de Grace В Bulk water C Susquehanna River 5-12-88 A at Havre de Grace В Microlayer C Mid-Chesapeake Bay 5-12-88 A at Matapeake B Bulk water C Mid-Chesapeake Bay 5-12-88 A at Matapeake В Microlayer Ç Gulf Breeze 5-14-88 A Control В С Potomac River 5-14-88 A at Hedge Neck В Bulk water C Potomac River 5-14-88 б A at Hedge Neck В б

C

Microlayer

Figure 10. Neuston in Surface Waters of the Choptank River - Spring 1988

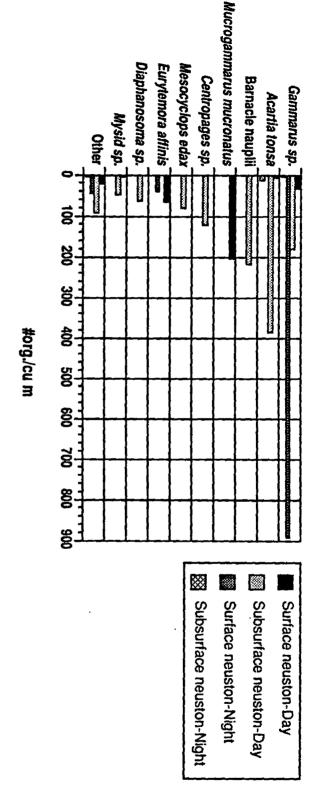


Figure 11. Neuston in Surface Waters of the Potomac River - Spring 1988

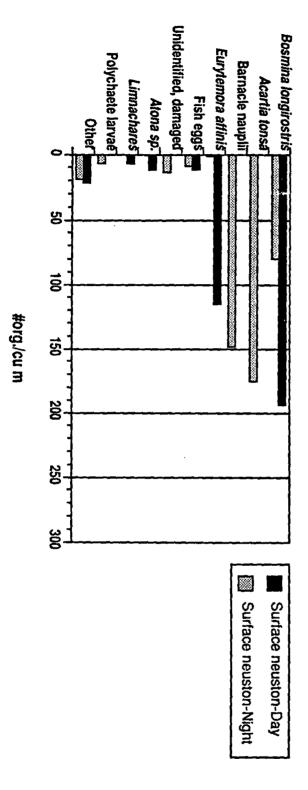
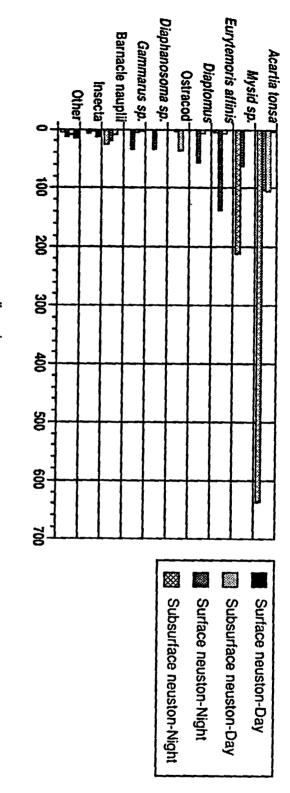
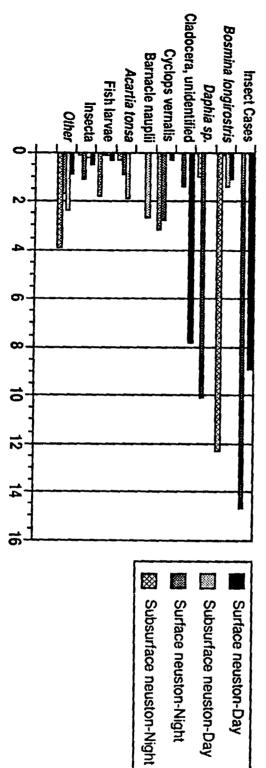


Figure 12. Neuston in Surface Waters of the Chesapeake Bay (Matapeake) - Spring 1988



#org./cu m

Figure 13. Neuston in Surface Waters of the Susquehanna - Spring 1988



#org./cu m

Surface neuston-Night Subsurface neuston-Day Surface neuston-Day reversal is expected, yet a clearly evident case was observed at the Choptank River at Cambridge station. Here a single species <u>Gammarus</u> sp., accounted for the high density (97% abundance) in the surface layer at night, although fish eggs were also more abundant than at subsurface depths.

At a number of sites, several species occurred in greater abundance within the surface layer compared to the deeper layer, even if that species did not dominate the total population density. For example, at the Potomac River at Hedge Neck station, Bosmina sp. (a cladoceran) and Eurytemora sp. (a copepod) occurred in greater numbers in the surface layer, while the total population density was driven by the slightly greater abundances of Acartia sp. (a copepod) and barnacle nauplii in the subsurface layer. At the mid-Chesapeake Bay at Matapeake station, Acartia sp., mysid shrimp, and barnacle nauplii were more abundant below the surface, but Eurytemora sp. was more dense within the surface layer and Diaphanosoma sp. (a cladoceran), and Gammarus sp. (an amphipod) and fish eggs were more abundant within the surface layer. At the Susquehanna River at Havre de Grace station, only Daphnia sp. were more dominant in the surface layer compared to the subsurface volume sample in this work.

The greater abundance of some zooplankton species in or near the surface microlayer, especially at night, along with the high abundance of a few species assemblages in that zone at other times, suggest highly dynamic behavior in these populations. Our data are too sparse to allow deductions about variables that shape the zooplankton density at any one level. Certainly vertical motility plays a role, as do physical mixing processes. But the sum total of the effects suggests that contact with the microlayer as part of the diel changes is likely for some fraction of these animals.

Copepods, cladocerans, and amphipods are important prey for fishes and shellfish of resource value. These species may directly assimilate potential toxicants when the surface microlayer is contaminated. No knowledge has come to our attention concerning the possibility of increased grazing by these opportunistic species in slick-covered enriched areas.

CONCLUSIONS

The absence of coherent surface films or slicks and the infrequency and low concentration of surface microlayer contaminants found in this spring 1988 sampling correlate well with the autumn 1987 higher "slick" abundance and higher surface microlayer contaminant loading. This correlation supports the hypothesis that biogenic surfactants form a pollutant trapping matrix. No data have been found that allow prediction of the

frequency, distribution, and coherence of film or the trapping potential they represent.

The toxicity test results agree with the organic and pesticide analyses - no observable toxic responses with low concentrations of contaminants. Several metal concentrations (copper, lead, nickel and zinc) exceeded the marine water quality criteria chronic values. These chronic values were based on the lowest observed effective concentration and, therefore, observed concentrations near these values would not necessarily produce direct acute or short-term responses. A broader scoped sample and analysis design is required for verification of the observed variability of the surfactants and their potential effects.

BIBLIOGRAPHY

- Adam, N.K. 1937. A rapid method for determining the lowering of tension of exposed water surfaces, with some observations of surface tension of the sea and inland waters. Proc. Royal Soc. (B) 122:134-139.
- Adamson, A.W. 1967. Physical Chemistry of Surfaces. Interscience, New York, pp. 747.
- Baier, R.E., D.W. Goupil, S. Perlmutter, R. King. 1974. Dominant chemical composition of sea-surface films, natural slicks, and foams. J. Res. Atmosph. 8: 571-600.
- Gucinski, H., D.W. Goupil, and R.E. Baier. 1981. The Sampling and Composition of the surface microlayer. In: <u>Atmospheric Pollutants to Natural Waters</u>. S. Eisenreich, Ed., Ann Arbor Press.
- Hardy, J.T. 1988. Anthropogenic alteration of the sea-surface. Guest Editorial. Marine Env. Res. 23: 223-225.
- Hardy, J.T., E.A. Crecelius, L.D. Antrim, S.L. Kiesser and V.L. Broadhurst. 1987. Aquatic surface microlayer contamination in Chesapeake Bay. Contract to Maryland Dept. of Natural Resources, Energy Administration, Power Plant Research Program, Annapolis, MD. 39 pp.
- Hardy, J.T., E.A. Crecelius, C.W. Apts and J.M. Gurtisen. 1988. Sea-surface contamination in Puget Sound: Part I. Toxic effects on fish eggs and larvae. Marine Env. Res. 23: 227-249.
- Hardy, J.T., E.A. Crecelius, C.W. Apts and J.M. Gurtisen. 1988. Sea-surface contamination in Puget Sound: Part II. Concentration and distribution of contaminants. Marine Env. Res. 23: 251-271.
- Harrick, N. J. 1967. Internal Reflection Spectroscopy. Interscience, New York.
- Huhnerfuss, H., P.A. Lange, W. Walter. 1985. Relaxation effects in monolayers and their contribution to water wave damping. I. Wave-induced phase shifts. J. Colloid Interf. Sci. 108(2): 430-431.
- Katsaros, K.B., H. Gucinski, S.S. Atakturk, R. Pincus. Effects of reduced surface tension on short waves at low wind speeds in a fresh water lake. (in press.)
- Lippson, A.J. and R.L. Moran. 1974. Manual for identification of early developmental stages of fishes of the Potomac River Estuary. Maryland Dept. of Natural Resources, Power Plant Siting Program. PPSP-MP-13. 282 pp.

- Seiburth, J. McN. 1983. Microbiological and organic-chemical processes in the surface and mixed layers. In: P.S. Liss, W.G.N. Slinn. <u>Air-Sea Exchange of Gases and Particles</u>. NATO ASI Series 108, Reidel Publ. Co., Boston.
- U.S. Environmental Protection Agency. 1979. Methods for chemical analysis of water and wastes. U.S. EPA, Washington, DC. EPA 600/4-79-020.
- U.S. Environmental Protection Agency. 1982. Methods for chemical analysis of water and wastes. U.S. EPA, Washington, DC. EPA 600/4-79-020.
- U.S. Environmental Protection Agency, Chesapeake Bay Program. 1988a. Review of Technical Literature and Characterization of Aquatic Surface Microlayer Samples. Contract Report prepared by J.T. Hardy, Battelle Marine Research Laboratory, Sequim, WA, and Hermann Gucinski, Anne Arundel Community College, Annapolis, MD.
- U.S. Environmental Protection Agency. 1988b. Method 1624C Revision B Volatile Organic Compounds by Isotope Dilution GC/MS. Office of Water Regulations and Standards/Industrial Technology Division (ITD) Methods. 6/89. Washington, D.C.
- U.S. Environmental Protection Agency. 1988c. Method 1625C Revision B Semivolatile Organic Compounds by Isotope Dilution GC/MS. Office of Water Regulations and Standards/Industrial Technology Division (ITD) Methods. 6/89. Washington, D.C.
- U.S. Environmental Protection Agency. 1988d. Method 1618 Organo-Halide Pesticides, Organo-Phosphorus Pesticides, and Phenoxy-Acid Herbicides by Wide Bore Capillary Column Gas Chromatography with Selective Detectors. U.S. EPA, Washington, DC. June 1989.
- U.S. Environmental Protection Agency. 1989. Office of Water Regulations and Standards/Industrial Technology Division (ITD) Methods, Method 1618. 6/89. Washington, D.C.
- Unger, M.A., W.G. MacIntyre, J. Greaves and R.J. Huggett. 1986. GC determination of butyltins in natural waters by flame photometric detection of hexyl derivatives with mass spectrometric confirmation. Chemosphere 15:461-470.
- Versar, Inc., July, 1987. Chesapeake Bay Water Quality Monitoring Program Meso-Zooplankton Component: August 1984 December 1986. Maryland Dept. of Health and Mental Hygiene, Office of Envir. Programs, Baltimore, MD. 21201.
- Ward, H.B. and G.C. Whipple. 1966. Freshwater Biology. 2nd ed. John Wiley, New York. 1248 pp.
- Zisman, W.A. 1964. Relation of equilibrium contact angle in liquid and solid constitution. Advances in Chemistry 43:1.

APPENDIX A

FREEMAN SURFACE MICROLAYER SAMPLER DESIGN SPECIFICATIONS

The microlayer sampler (Figure 3) incorporates the advantages of previous models in order to provide the Chesapeake Bay Program with an upgraded, evaluated collecting device. The upgrades to the microlayer sampler include:

- collection of large sampling volume;
- high collection efficiency;
- shallow, nominal, sampling depth;
- reasonable light weight;
- ease of repair and disassembly; and
- facility of use from small boats.

Design specifications for the microlayer drum sampler were submitted for bid to several contractors. These specifications include:

The drum material should be metal and thick enough to retain stiffness. It does not have to be made of stainless steel. Aluminum is acceptable if the coating extends over all surfaces. Tolerance of the drum barrel surface should be within 1/32 inch or 2 mm. The drum coating should be teflon (polytetrafluoroethylene), preferably non-dyed, with sufficient thickness so that minor scratches will not expose the metal. The teflon should be tested and must provide water contact angles of at least 108 degrees and critical surface tension of 16-18 milli newtons per meter. The teflon finish coat should be characterized by infrared spectroscopy and contact angle analysis. The drum shaft should be made from a non-corrosive material or coated from corrosion.

The floats may consist of either foam floatation with a suitable watertight outer layer or PVC (poly vinyl chloride) pipe of adequate diameter to ensure towing qualities. Buoyancy requirements must support the sampler, its attached sampling bottles and immerse the drum 2-4 inches during towing operations. The float separation must be sufficient to minimize float wake effects on the drum sampler.

The supporting structure may be made of PVC or corrosion-protected metal. It must provide lateral and transverse stability to withstand waves of up to 3 feet, handling and shipping stress, and overboard launching and retrieval. Easy disassembly and reassembly is preferred. The structure must support a wiper and drain system and provide a secure platform for the sampling bottles. A maximum sampling bottle capacity of 1 U.S. gallon and a minimum capacity of 125 milli liters is required.

An automatic drive is preferred to propel the sampler forward using the water's motion to turn the drum so that the forward face of the drum is rising and the after face is descending. Drum rotation rate should be set so that the drum's rim tangential velocity is equal to the sampler's forward motion via a paddle wheel, propeller, or other drive mechanism. If this set up is not achievable, then an electric drive that is fear or belt driven is acceptable. The electric drive must use a 12 volt DC motor run from a standard 12 volt car or marine lead-acid battery (i.e. a duty cycle with a 24 amp. hour battery), to allow for an adjustable drum rotation rate consistent with a tangential velocity equal to a sampler tow speed of 1 to 2.5 knots.

The wiper and drain assembly must have a flexible blade so that it maintains contact with the drum at all times. The use of teflon coating is preferred to prevent sample contamination, but siliconized rubber may be used with minimum reliability. The drain assembly may be made of PVC piping or an equivalent, but must have a teflon or silicon coating to prevent sample contamination.

Freeman Associates, in Berlin, Maryland, was selected as the contractor. Their design sketch, in Figure 3, is similar to a design developed by Battelle Marine Science Lab (see Hardy, et al., 1988) except for these differences:

- Except for the drum shafts, and pulleys constructed of T6061 aluminum, construction is almost entirely of PVC with commercially available grade pipe sizes. Simplicity and ease of repair and assembly was emphasized allowing maintenance on-site with a simple PVC repair kit.
- The drive is unique in that it synchronizes the drum rotation rate with the forward motion of the sampling rig, ensuring the proper drum advancement and the fresh surface layer to be lifted from the water. This drive system avoids the problems caused by a fixed speed tow where the tow speed may exceed or lag behind the drum rotation rate.

A higher tow speed in respect to the drum rotation rate will collapse the surface film ahead of the drum, collecting too much surface layer in the presence of a slick. Too slow of a tow speed will initially remove the surface film present, but will subsequently remove subsurface water, causing a dilution effect in the sample collection. These risks should be minimized by the chosen design.

APPENDIX B

<u>Menidia</u> <u>beryllina</u> Toxicity Testing: Survival, Physical and Chemical Data

Menidia beryllina Larval Survival and Growth Test Toxicity Data

Sample Source: Ch Beginning Date: 5			Numbe rviving Or	· -	ay
Observation Time:		1033	1414	1045	1300
		Day	Day	Day	Day
Exposure	Repl.	_1	_2	_3	4
Gulf Breeze	A	10	10	10	10
Control	В	10	10	10	10
	С	10	10	10	10
Observation Time:		1046	1425	1056	1304
_		Day	Day	Day	Day
Exposure	Repl.	_1_	_2	_3	_4
Sea Salt	A	10	10	10	10
Control	В	10	10	10	10
	С	8 of 9	8 of 9	8 of 9	
Observation Time:	<i>f</i>	1100	1438	1109	1310
		Day	Day	Day	Day
Exposure	Repl.	1	2	3	4
Choptank	A	10	10	10	10
Bulk water	В	10	10	10	10
	С	10	10	10	10
Observation Time:		1131	1446	1142	1317
		Day	Day	Day	Day
Exposure	Repl.	_1	2	3	4
Choptank	A	10	10	10	10
Microlayer water	В	10	10	10	10
	С	10	10	10	10

APPENDIX B

Menidia beryllina Larval Survival and Growth Test Toxicity Data (continued)

Sample Source: Chesapeake Bay Beginning Date: 5-12-88 Number of Surviving Organisms/Day

			Daratati	y organizami	3, Day
Observation Time:		1154 Day	1418 Day	1008 Day	0853 Day
Exposure	Repl.	_1	2	_3	_4
Gulf Breeze	A	10	10	10	10
Control	В	10	10	10	J 0
	С	10	10	10	10
Observation Time:		1205	1428	1018	0906
		Day	Day	Day	Day
Exposure	Repl.	_1	_2	_3	_4
Susquehanna	A	10	10	10	10
Bulk water	B	10	10	10	10
	С	10	10	10	10
Observation Time:		1220	1437	1028	0910
-		Day	Day	Day	Dау
Exposure	Repl.	_1	_2	_3	_4
Susquehanna	A	10	10	10	10
Microlayer water	В	10	10	10	10
	С	10	10	10	10
Observation Time:		1230	1459	1038	0917
		Day	Day	Day	Day
Exposure	Repl.	_1	_2	_3	4
Mid-Bay	A	10	10	10	10
Bulk water	В	10	11	11	11
	C	10	10	10.	10
Observation Time:		1242	1509	1058	0923
		Day	Day	Day	Day
Exposure	Repl.	1	_	3	4
Mid-Bay	A	10	10	10	10
Microlayer water	B	10	10	10	10
-	С	10	10	10	10

APPENDIX B

Menidia beryllina Larval Survival and Growth Test Toxicity Data (continued)

Sample source: Chesapeake Bay

Α

В

C

Potomac

Microlayer water

Beginning Date: 5-14-88 Number of Surviving Organisms/Day Observation Time: 1108 0903 1303 1441 Day Day Day Day Repl. _1 _2 _3 4 Exposure 6 6 6 6 Gulf Breeze Α 6 6 Control В 6 6 6 C 6 6 6 0912 1300 1434 1119 Observation Time: Day Day Day Day Exposure Repl. _1 _2 _3 4 6 5 5 6 Potomac A 6 6 Bulk water В 6 6 6 6 6 C 6 1130 0925 1258 1428 Observation Time: Day Day Day Day Exposure Repl. _1 _2 _ 3 4

6

6

6

6

6

6

6

5

6

6

5

APPENDIX B

Initial Test Exposure Water Quality Data (all temperatures reported are in degrees Celsius)

Sample Source: Chesapeake Bay

Beginning Date: 5-10-88

Evnogura	Daw.	D:	issol [.]	ved 0:	xygen 3	 4	กษ	Temp.	Salinity
Exposure Gulf Breeze Control	Day.	8.1	7.1	7.2	6.8	7.1	7.7	25.8°	18
				ved 0:					
Exposure Sea Salt Control	Day:	8.7	7.2	7.1	<u>3</u> 6.7	$\frac{4}{7.0}$	<u>рН</u> 8.6	Temp. 23.8°	Salinity 16
		D:	issol	ved 0:	xygen				
Exposure Choptank Bulk water	Day:	8.2	1 7.2	<u>2</u> 7.2	<u>3</u> 6.5	<u>4</u> 6.9	<u>рн</u> 6.8	Temp. 25.5°	<u>Salinity</u> 15
		D:	issol	ved 0	xygen				
Exposure Choptank	Day:	<u>0</u> 8.5	$\frac{1}{7.2}$	<u>2</u> 6.6	<u>3</u> 6.6	<u>4</u> 6.9	<u>рн</u> 7.8	Temp. 24.4°	Salinity 14
Microlayer w	ater								
Sample Sourc Beginning Da				Bay					
		D:	issol	ved 0	xygen				
Exposure Gulf Breeze Control	Day:	<u>0</u> 7.8	<u>1</u> 7.1	<u>2</u> 7.0	<u>3</u> 6.5	$\frac{4}{7.0}$	<u>рн</u> 7.7	Temp. 24.1°	Salinity 15
		D:	issol	ved 0	xygen				
Exposure Susquehanna Bulk water	Day:	<u>0</u> 8.6	1 7.0	<u>2</u> 6.9	<u>3</u> 6.5	<u>4</u> 6.9	<u>рн</u> 8.4	Temp. 23.0°	Salinity 15
		D	issol	ved 0	xygen				
Exposure Susquehanna Microlayer	Day:	<u>0</u>	<u>1</u>	2	3	4		Temp. 23.4°	Salinity 15

APPENDIX B

Initial Test Exposure Water Quality Data (continued)
(all temperatues reported are in degrees Celsius)

Sample Source: Chesapeake Bay

Beginning Date: 5-12-88 (continued)

--Dissolved Oxygen--

Exposure Day: 0 1 2 3 4 pH Temp. Salinity Mid-Bay 8.4 6.7 6.7 6.1 6.9 7.9 24.2° 14

Bulk water

--Dissolved Oxygen--

Exposure Day: 0 1 2 3 4 pH Temp. Salinity Mid-Bay 8.3 6.8 6.9 6.2 6.9 7.9 24.2° 14

Microlayer

Sample Source: Chesapeake Bay

Beginning Date: 5-14-88

--Dissolved Oxygen--

Exposure Day: 0 1 2 3 4 pH Temp. Salinity Gulf Breeze 7.8 6.7 7.3 6.4 5.2 7.6 23.7° 16

Control

--Dissolved Oxygen--

Exposure Day: 0 1 2 3 4 pH Temp. Salinity Potomac 8.0 4.5 6.8 6.6 5.6 8.2 22.5° 14

Bulk water

--Dissolved Oxygen--

Exposure Day: 0 1 2 3 4 pH Temp. Salinity
Potomac 8.2 4.3 7.0 6.2 5.4 8.3 22.6° 14

Microlayer

Appendix C. Neuston Species and Abundance Data

Sample Location: Station No.: 3 Potomac

Relicate No.: Water segment: Day/Night:

TAXA:

Density #/cu. m.

Abund.

Density #/cu. m.

Abund.

Eurytemora affinis Fish eggs Atona sp. Limnachares

Bosmina longirostris

Gammarus sp. Chironomid sp.

Cyclops vernalis

Insecta

Ostracod

Microlayer Day 5-13-88 Ave (2)

Subsurface Day 5-13-68 Ave (2)

0.0	0.0	0.0	0.0	0.0	0.5	0.5	0.7	0.9	0.9	1.0	1.4	1.8	3.2	3.2	32.0	53.9
0,8	13.2	148.4	175.2	0.0	8.3	5.7	4.13	0.0	0.0	0.0	0.0	0.2	0.0	8 .3	1.6	80.3
0.2	2.9	32.8	38.7	0.0	1.8	1.3	0.9	0.0	0.0	0.0	0.0	0.0	0.0	1.8	0.3	17.7

Fish larvae
Illyocryptus spinifer
Mucrogammarus mucronatus
Acartia tonsa
Barnacle nauplii
unidentified, damaged
Polychaete larvae

Total Spider

360.3

100.0

453.0

100.0

Sample Location: Susquehanna River Station No.: 8

Total	Ostracod	Diaptomus	unidentified, damaged	Cyclops sp.	Barnacle nauplii	Mysid sp.	Insect larvae	Gammarus sp.	Illyocryptus spinifer	Fish larvae	Limnachares	Eurytemora affinis	Polychaete larvae	Diaphanosoma sp.	Centropages sp.	Harpactacoid sp.	Cyclops bicuspidatus	Bosmina longirostris	Chironomid sp.	Atona sp.	Fish eggs	Acartia tonsa	Insecta	Cladocera, unid.	Cyclops vernalis	Daphnia sp.	Insect cases		TAXA:	Replicate No.:	Date:	Day/Night:	Water segment:	
19.9	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.4	1.1	0.1	0.1	0.0	0.0	0.5	7.8	0.3	0.0	8.9	# cu. m.	, Density	Ave	5-11	D	Micro	
100. o	0.7	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.7	1.3	0.0	0.0	0.0	0.0	0.0	0.0	2.0	5.3	0.7	0.7	0.0	0.0	2.6	39.1	1.3	0.0	45.0	æ	Abund.	Ave (1)	5-11-88	Day	Microlayer	
8.7	0.0	0.0	0.1	0.3	2.7	0.0	0.0	0.0	0.0	0.1	0.0	0.0	1.1	0.0	0.1	0.0	0.8	1.4	0.0	0.0	0.0	1.9	0.2	0.0	0.0	0.0	0.0	ou. m.	Density	Ave (2)	5-11-88	Day	Subsurface	
100.0	0.0	0.0	0.9	2.9	31.0	0.0	0.0	0.0	0.4	1.6	0.0	0.0	12.2	0.4	1.1	0.0	8.6	15.5	0.0	0.2	0.4	22.2	2.2	0.0	0.2	0.0	0.0	ðР	Abund.	(2)	-88	Y	rface	
32.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.4	0.4	0.9	1.1	1.4	2.8	10.1	14.7	# CU. B.	Density	¥	(J		MT CI	
100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.4	0.4	0.6	1.2	1.2	2.6	3.2	4.2	8.5	30.9	45.3	de	Abund.	Ave (2)	5-11-88	Night	Microlayer	
22.7	0.0	0.0	0.0	0.0	0.0	0.1	0.2	1.0	1.2	1.8	0.0	0.4	0.2	0.0	0.0	0.0	0.0	12.3	0.0	0.8	0.0	0.3	0.1	0.0	3.2	1.0	0.0	CU. m.	Density	Ave	5-1	TIN	Schoo	
100.0	0.0	0.0	0.0	0.0	0.0	0.3	0.8	4.4	5.55	8,1	0.1	1.9	0.7	0.0	0.0	0.0	0.0	54.0	0.0	3. G	0.0	1.5	0.3	0.0	14.2	4.6	0.0	de	Abund.	a (2)	1-88	ght	Subsurface	

Sample Location: Choptank River Station No.: 11

Total	Cyclops sp.	Copepod naulpii	unidentifed, damaged	Fodon polyphemoides	pisces: Leistomus sp.	Illyocryptus spinifer	Daphnia sp.	Diaptomus	Chydorius sp.	Chironomid larvae	Atona sp.	Insect larvae	Bosmina longirostris	Ostracod	Cyclops bicuspidatus	Insect cases	Cyclops vernalis	Limnachares	Eurytemora affinis	Mucrogammarus mucronatus	Spider		Paracyclops fimbratus poppei	Insecta	Fish eggs	Fish larvae	Mysid sp.	Diaphanosoma sp	Mesocyclops edax	Centropages sp.	Gammarus sp.	Barnacle nauplii	Acartia tonsa		TAKA:	Replicate No.:	Date:	Day/Night:	Water segment:	
335.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.4	0.4	0.6	0.9	1.8	2.2	3.1	3.1	3.7	64.5	204.4	0.0	0.0	0	4.2	0.0	2.6	3.2	2.0	0.0	0.0	32.5	0.0	6.1	# си. п.	Density	*	5-1		Mici	
100.0	0.0	0.0	0.0	0,0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.2	0.3	0.5	0.7	0.9	0.9	1.1	19.2	60.9	0.0	0.0	0.0	1.2	0.0	0.8	0.9	0.6	0.0	0.0	9.7	0.0	1.8	de	Abund.	Ave (3)	5-13-88	Day	Microlayer	•
1194.5	0.0	0.0	1.0	0.0	0.0	0.0	0.1	0.1	0.0	0.1	0.0	0.0	0.1	0.2	1.9	0.0	1.0	1.6	0.0	0.0	4.0	6.4	7.2	13.6	26.2	29.5	47.6	62.7	60±	122.3	181.3	218.8	387.6	# CU. m.	Density	*	5	ı	sub	
100.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0,0	0.2	0.0	0.1	0.1	0.0	0.0	0.3	0.5	0.6	1.1	2.2	2.5	40	UT (A)		10.2	15.2	18.3	32.5	æ	Abund.	Ave (3)	5-13-88	Day	Subsurface	
976.8	0.5	0.0	0.0	0.0	0.2	2.0	0.0	0.0	0.1	1.3	0.0	0.0	₩.	3.1	ω 	0.0	5.2	0.4	38.6	0.0	0.0	0.0	0.3	0.0	22.8	2.2	0.0	0.4	0.0	0.0	892.2	0.0	0.0	+ cu. m.	Density		Ų	٠	¥	
100.0	0.0	0.0	0.0	0.0	0.0	0.2	0,0	0.0	0.0	0.1	0.0	0.0	0.3	0.3	0.4	0.0	0.5	0.0	•	0.0	0.0	٠	0.0	-	2.3	0.2	•	•	•	0.0	•	0,0	0.0	. de	Abund.	Ave (3)	13-88	Night	Microlayer	•
21.9	0.1	0.2	0.2	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.2	0.0	0.0	0.0	0.0	0.0	0, 3	0.2	0.0	0.0	0,0	0.0	0.9	0.0	0.6	0.0	0.0	0.0	٠. ن	0.8	14.0	# cu. m.	Density	بيو	<i>U</i>		dus	
100.0	0.5	0.4	0.7	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	, (J	0.0	0.0	0.0	0.0	0.0	1.3	0.7	0.0	0.0	0.0	0.0	4.2	0.0	2.9	0.0	0.0	0.0	15.9	3. 5	63.7	æ	Abund.	Ave (2)	5-13-88	Might	Subsurface	i

Sample Location: Matapeake Station No.: 12

Total	pisces: Leistomus sp.	Insect larvae	Daphnia sp.	Paracyclops fimbratus poppei	Bosmina longirostris	Cyclops bicuspidatus	Polychaete larvae	Fish larvae	Podon plyphemoides	Ostracod	Insecta	Fish eggs	Barnacle nauplii	Gammarus sp.	Diaphanosoma sp.	Diaptomus	Mysid sp.	Acartia tonsa	Eurytemoris affinis		TAXA:	Replicate No.:	Date:	Day/Night:	Water segment:	
27.5	0.0	0.0	0.4	1.1	2.6	2.5	0.5	0.8	0.0	0.7	12.4	0.1	0.0	2.9	0.0	0.0	0.0	3.6	0.0	# cu. m.	Density	Àν	5-1	, p	Micz	
100.0	0.0	0.0	1.4	3.8 8	9.6	9.1	1.9	2.9	0.0	2.4	45.0	0.5	0.0	10.5	0.0	0.0	0.0	12.9	0.0	dę	Abund.	Ave (1)	5-13-88	Day	Microlayer	
180.2	0.0	0.0	0.0	0.0	0.0	0.7	1.0	7.1	0.0	35.7	2.8	0.6	8.7	4.8	0.0	5.9	0.3	105.0	7.5	♦ cu. m.	Density	Av	5~1	D	sdus	
100.0	0.0	0.0	0.0	0.0	0.0	0.4	0.6	3.9	0.0	19.8	1.5	0.4	4.8	2.7	0.0	u. w	0.2	58.3	4.2	de	Abund.	Ave (3)	3-88	Day	Subsurface	
465.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	2.0	6.3	11.1	18.8	33.2	33.4	56.6	8.19	102.9	138.2	# CT: B:	Density		Ç	١	HI.	
100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.4	1.4	2.4	4.0	7.1	7.2	12.2	13.3	22.1	29.7	æ	Abund.	Ave (2)	5-13-88	Night	Microlayer	
885.2	0.1	3.4	0.3	0.0	0.5	0.0	0.9	0.0	0.0	0.5	0.0	0.5	25.9	0.0	0.0	0.0	211.0	637.2	4.9	ou. m.	Density	ļ.	5	×	sdus	
100.0	0.0	0.4	0.0	0.0	0.1	0.0	0.1	0.0	0.0	0.1	0.0	0.1	2.9	0.0	0.0	0.0	23.8	72.0	0.6	de	Abund.	Ve (1)	13-88	Night	Subsurface	

APPENDIX D

List of Organic Compounds Scanned for in the Surface Microlayer and Bulk Water Samples *

Chemical Name	Detection Limits (ug/L)
1,1,1,2-TETRACHLOROETHANE	10
1,1,1-TRICHLOROETHANE	10
1,1,2,2-TETRACHLOROETHANE	10
1,1,2-TRICHLOROETHANE	10
1,1-DICHLOROETHANE	10
1,1-DICHLOROETHENE	10
	10, 12, OR 20
1,2,3-TRICHLOROPROPANE	10
1,2,3-TRIMETHOXYBENZENE	10, 12, OR 20
1,2,4,5-TETRACHLOROBENZENE	
1,2,4-TRICHLOROBENZENE	10, 12, OR 20
1,2-DIBROMO-3-CHLOROPROPANE	
1,2-DIBROMOETHANE (EDB)	10
1,2-DICHLOROBENZENE	10, 12, OR 20
1,2-DICHLOROETHANE	10
1,2-DICHLOROPROPANE	10
	20, 25, OR 40
1,2:3,4-DIEPOXYBUTANE	20, 25, OR 40
1,3,5-TRITHIANE	50, 62, OR 100
1,3-BENZENEDIOL (RESORCINOL)	
1,3-DICHLORO-2-PROPANOL	10, 12, OR 20
1,3-DICHLOROBENZENE	10, 12, OR 20
1,3-DICHLOROPROPANE	10
1,4-DICHLOROBENZENE	10, 12, OR 20
1,4-DINITROBENZENE	20, 25, OR 40
1,4-NAPHTHOQUINONE	99, 124, OR 198
1,5-NAPHTHALENEDIAMINE	99, 124, OR 198
1-METHYLFLUORENE	10, 12, OR 20
1-METHYLPHENANTHRENE	10, 12, OR 20
1-PHENYLNAPHTHALENE	10, 12, OR 20
2,3,4,6-TETRACHLOROPHENOL	20 OR 25
2,3,6-TRICHLOROPHENOL	10 OR 12
2,3-BENZOFLUORENE	10, 12, OR 20
2,3-DICHLOROANILINE	10, 12, OR 20
	50, 62, OR 100
2,4,5-TRICHLOROPHENOL	10 OR 12
2,4,5-TRIMETHYLANILINE	20, 25, OR 40
2,4,6-TRICHLOROPHENOL	10 OR 12
2,4-DIAMINOTOLUENE	99, 124, OR 198
2,4-DICHLOROPHENOL	10 OR 12
2,4-DIMETHYLPHENOL	10, 12, OR 20
2,4-DINITROPHENOL	50 OR 62
2,4-DINITROTOLUENE	10, 12, OR 20
2,6-DI-TERT-BUTYL-P-BENZOQINONE	
	99, 124, OR 198
2,6-DICHLOROPHENOL	10 OR 12
2,6-DINITROTOLUENE	10 OR 12 10, 12, OR 20
Z,U-DINIIROIODUENE	10, 12, ON 20

```
Detection Limits (ug/L)
Chemical Name
2-(METHYLTHIO)BENZOTHIAZOLE
                                 10, 12, OR 20
                                 10, 12, OR 20
2-BROMOCHLOROBENZENE
2-BUTANONE (MEK)
                                 50
                                 10
2-CHLORO-1,3-BUTADIENE
2-CHLOROETHYLVINYL ETHER
                                 10
                                 10, 12, OR 20
2-CHLORONAPHTHALENE
2-CHLOROPHENOL
                                 10 OR
2-HEXANONE
                                 50
2-ISOPROPYLNAPHTHALENE
                                 10, 12, OR 20
                                 20 OR 25
2-METHYL-4,6-DINITROPHENOL
                                 10, 12, OR 20
2-METHYLBENZOTHIOAZOLE
                                 10, 12, OR 20
2-METHYLNAPHTHALENE
2-NITROANILINE
                                 10, 12, OR 20
                                 20 OR 25
2-NITROPHENOL
2-PHENYLNAPHTHALENE
                                 10, 12, OR 20
3,3'-DICHLOROBENZIDINE
                                 50, 62, OR 100
                                 50, 62, OR 100
3,3'-DIMETHOXYBENZIDINE
3,5-DIBROMO-4-HYDROXYBENZONITR
                                 50 OR 62
                                 10, 12, OR 20
3,6-DIMETHYLPHENANTHRENE
3-BROMOCHLOROBENZENE
                                 10, 12, OR 20
3-CHLORONITROBENZENE
                                 50, 62, OR 100
3-CHLOROPROPENE
                                 10
3-METHYLCHOLANTHRENE
                                 10, 12, OR 20
3-NITROANILINE
                                 20, 25, OR 40
                                 20, 25, OR 40
4,4'-METHYLENEBIS(2-CHLOROANI)
                                 10, 12, OR 20
4,5-METHYLENEPHENANTHRENE
4-AMINOBIPHENYL
                                 10, 12, OR 20
                                 10, 12, OR 20
4-BROMOPHENYL PHENYL ETHER
                                 20, 25, OR 40
4-CHLORO-2-NITROANILINE
                                 10 OR 12
4-CHLORO-3-METHYLPHENOL
4-CHLOROANILINE
                                 10, 12, OR 20
                                 10, 12, OR 20
4-CHLOROPHENYL PHENYL ETHER
4-METHYL-2-PENTANONE
                                 50
4-NITROANILINE
                                 50, 62, OR 100
4-NITROBIPHENYL
                                 10, 12, OR 20
                                 50 OR 62
4-NITROPHENOL
5-CHLORO-O-TOLUIDINE
                                 10, 12, OR 20
5-NITRO-O-TOLUIDINE
                                 10, 12, OR 20
7,12-DIMETHYLBENZ(A)ANTHRACENE
                                 10, 12, OR 20
                                 10, 12, OR 20
ACENAPHTHENE
                                 10, 12, OR 20
ACENAPHTHYLENE
ACETONE
                                 50
                                 10, 12, OR 20
ACETOPHENONE
                                 50
ACROLEIN
                                 50
ACRYLONITRILE
                                 10
ALLYL ALCOHOL
                                 10, 12, OR 20
ALPHA-NAPHTHYLAMINE
                                 50, 62, OR 100
ALPHA-PICOLINE
                                 10, 12, OR 20
ALPHA-TERPINEOL
                                 10, 12, OR 20
ANILINE
                                 10, 12, OR 20
ANTHRACENE
ARAMITE
                                 50, 62, OR 100
                                 50, 62, OR 100
B-NAPHTHYLAMINE
```

```
Detection Limits (ug/L)
Chemical Name
                                   50, 62, OR 100
BENZANTHRONE
BENZENE
                                   10
                                   10, 12, OR 20
BENZENETHIOL
                                   50, 62, OR 100
BENZIDINE
                                   10, 12, OR 20
BENZO(A)ANTHRACENE
                                   10, 12, OR 20
BENZO(A)PYRENE
                                  10, 12, OR 20
20, 25, OR 40
BENZO(B) FLUORANTHENE
BENZO (GHI) PERYLENE
                                  10, 12, OR 20
BENZO(K) FLUORANTHENE
                                   50 OR 62
BENZOIC ACID
                                  10 OR 12
BENZYL ALCOHOL
                                  10, 12, OR 20
BIPHENYL
BIS (2-CHLOROETHOXY) METHANE 10, 12, OR 20 BIS (2-CHLOROISOPROPYL) ETHER 10, 12, OR 20
                                  10 OR 12
BIS (2-ETHYLHEXYL) PHTHALATE
                                  10, 12, OR 20
BIS(2-CHLOROETHYL)ETHER
BROMODICHLOROMETHANE
                                   10
                                   10
BROMOFORM
                                   50
BROMOMETHANE
BUTYL BENZYL PHTHALATE
                                  10, 12, OR 20
                                  20, 25, OR 40
CARBAZOLE
                                  10
CARBON DISULFIDE
                                  10
CARBON TETRACHLORIDE
                                  10
CHLOROACETONITRILE
                                  10
CHLOROBENZENE
                                  50
CHLOROETHANE
                                  10
CHLOROFORM
CHLOROMETHANE
                                  50
                                  10, 12, OR 20
CHRYSENE
CIS-1,3-DICHLOROPROPENE
                                  10
CROTONALDEHYDE
                                   50
                                   99, 124, OR 198
CROTOXYPHOS
DI-N-BUTYL PHTHALATE
                                  10
                                 10, 12, OR 20
DI-N-OCTYL PHTHALATE
                                 20, 25, OR 40
DIBENZO(A, H) ANTHRACENE
                                 10, 12, OR 20
DIBENZOFURAN
                                  10, 12, OR 20
DIBENZOTHIOPHENE
DIBROMOCHLOROMETHANE
                                  10
                                  10
DIBROMOMETHANE
                                   50
DIETHYL ETHER
                                  10, 12, OR 20
DIETHYL PHTHALATE
                                 10, 12, OR 20
DIMETHYL PHTHALATE
                                  10, 12, OR 20
DIMETHYL SULFONE
                                  10, 12, OR 20
10, 12, OR 20
DIPHENYL ETHER
DIPHENYLAMINE
                                   20, 25, OR 40
DIPHENYLDISULFIDE
                                   10
ETHYL CYANIDE
ETHYL METHACRYLATE
                                   10
                                   20, 25, OR 40
ETHYL METHANESULFONATE
                                   10
ETHYLBENZENE
                                   20, 25, OR 40
ETHYLENETHIOUREA
ETHYNYLESTRADIOL 3-METHYL ETHE 20, 25, OR 40
                                   10, 12, OR 20
FLUORANTHENE
```

```
Chemical Name
                                   Detection Limits (ug/L)
                                     10, 12, OR 20
10, 12, OR 20
FLUORENE
HEXACHLORO-1,3-BUTADIENE
HEXACHLOROBENZENE
                                     10, 12, OR 20
HEXACHLOROCYCLOPENTADIENE
                                     10, 12, OR 20
                                     10, 12, OR 20
20, 25, OR 40
HEXACHLOROETHANE
HEXACHLOROPROPENE
HEXANOIC ACID
                                     10 OR 12
INDENO(1,2,3-CD)PYRENE
                                     20, 25, OR 40
IODOMETHANE
                                     10
ISOBUTYL ALCOHOL
                                     10
                                    10, 12, OR 20
ISOPHORONE
                                    10, 12, OR 20
ISOSAFROLE
                                     50, 62, OR 100
LONGIFOLENE
M-XYLENE
                                     10
MALACHITE GREEN
                                    10, 12, OR 20
METHACRYLONITRILE
                                    10
METHAPYRILENE
                                    10, 12, OR 20
METHYL METHACRYLATE
                                    10
                                    20, 25, OR 40
METHYL METHANESULFONATE
METHYLENE CHLORIDE
                                    10
                                    10, 12, OR 20
N, N-DIMETHYLFORMAMIDE
                                    10, 12, OR 20
N-DECANE (N-C10)
                                    10, 12, OR 20
N-DOCOSANE (N-C22)
                                    10, 12, OR 20
10, 12, OR 20
N-DODECANE (N-C12)
N-EICOSANE (N-C20)
                                    10, 12, OR 20
N-HEXACOSANE (N-C26)
                                    10, 12, OR 20
N-HEXADECANE (N-C16)
                                    10, 12, OR 20
20, 25, OR 40
N-NITROSODI-N-BUTYLAMINE
N-NITROSODI-N-PROPYLAMINE
                                    10, 12, OR 20
N-NITROSODIETHYLAMINE
                                    50, 62, OR 100
20, 25, OR 40
10, 12, OR 20
N-NITROSODIMETHYLAMINE
N-NITROSODIPHENYLAMINE
N-NITROSOMETHYLETHYLAMINE
                                    99, 124, OR 198
N-NITROSOMETHYLPHENYLAMINE
                                    10, 12, OR 20
10, 12, OR 20
10, 12, OR 20
N-NITROSOMORPHOLINE
N-NITROSOPIPERIDINE
N-OCTACOSANE (N-C28)
                                    10, 12, OR 20
N-OCTADECANE (N-C18)
N-TETRACOSANE (N-C24)
N-TETRADECANE (N-C14)
                                    10, 12, OR 20
10, 12, OR 20
                                    10, 12, OR 20
N-TRIACONTANE (N-C30)
                                    10, 12, OR 20
NAPHTHALENE
                                    10, 12, OR 20
NITROBENZENE
O- + P-XYLENE
O-ANISIDINE
                                    10, 12, OR 20
                                    10, 12, OR 20
O-CRESOL
                                    10, 12, OR 20
O-TOLUIDINE
                                    10 OR 12
P-CRESOL
                                    10, 12, OR 20
P-CYMENE
P-DIMETHYLAMINOAZOBENZENE
                                    20, 25, OR 40
P-DIOXANE
                                    20, 25, OR 40
PENTACHLOROBENZENE
                                    20, 25, OR 40
PENTACHLOROETHANE
```

Chemical Name PENTACHLOROPHENOL PENTAMETHYLBENZENE PERYLENE PHENACETIM PHENANTHRENE	Detection Limits (ug/L)
PENTACHLOROPHENOL	50 OR 62
PENTAMETHYLBENZENE	10. 12. OR 20
PERYLENE	10. 12. OR 20
PHENACETIM	10, 12, OR 20
PHENANTHRENE	10. 12. OR 20
PHENOL	10. 12. OR 20
PHENOTHIAZINE	50, 62, OR 100
PRONAMIDE	10, 12, OR 20
PYRENE	10. 12. OR 20
PYRIDINE	10, 12, OR 20
SAFROLE	10, 12, OR 20
PHENANTHRENE PHENOL PHENOTHIAZINE PRONAMIDE PYRENE PYRIDINE SAFROLE SQUALENE STYRENE T-1,3-DICHLOROPROPENE TETRACHLOROETHENE THIANAPHTHENE THIOACETAMIDE THIOXANTHONE TOLUENE	99, 124, OR 198
STYRENE	10, 12, OR 20
T-1,3-DICHLOROPROPENE	10
TETRACHLOROETHENE	10
THIANAPHTHENE	10, 12, OR 20
THIOACETAMIDE	20, 25, OR 40
THIOXANTHONE	20, 25, OR 40
TOLUENE	10
TRANS-1,2-DICHLOROETHENE	10
TRANS-1.4-DICHLORO-2-BUTENE	50
TRICHLOROETHENE	10
TRICHLOROFLUOROMETHANE	10 10, 12, OR 20
TRIPHENYLENE	10, 12, OR 20
TRIPROPYLENEGLYCOL METHYL ETHE	99, 124, 198
VINYL ACETATE	50
VINYL CHLORIDE	10

 $[\]star$ The sample detection limits varied depending on the final dilution volume of the sample for analyses.

APPENDIX E

List of Pesticides Analyzed for in the Surface Microlayer and Bulk Water Samples

Chemical Name	<u>Detection Limits</u>	(ug/L)
CHEMI CUL HUME	DOCCOULDI. DIMITO	1 4 3 / 4 /

PHENOXYACID HERBICIDES AND	HALOGENATED	PESTICIDES:
AIDDIN	0.025	
ALPHA-BHC BETA-BHC DELTA-BHC GAMMA-BHC CAPTAFOL	0.025	
BETA-BHC	0.025	
DELTA-BHC	0.025	•
GAMMA-BHC	0.063	
CAPTAFOL	0.250	
CAPTAN	0.125	
CARBOPHENOTHION	0.500	
CHLORDANE	0.010	
CHLOROBENZILATE	0.250	
4,4'-DDD	0.125	
4,4'-DDE	0.125	
4,4'-DDT	0.050	
DIALLATE	0.250	
DICHLONE	0.250	
DIELDRIN ENDOSULFAN I ENDOSULFAN II	0.025	
ENDOSULFAN I	0.025	
ENDOSULFAN II	0.025	
ENDOSULFAN SULFATE	0.125	
ENDRIN	0.025	
ENDRIN ALDEHYDE		
ENDRIN KETONE	0.125	
HEPTACHLOR	0.050	
HEPTACHLOR EPOXIDE	0.050	
ISODRIN	0.025	
KEPONE	0.250	
METHOXYCHLOR	0.125	
MIREX	0.125	
NITROFEN (TOK)	0.125	
PCB-1016	1.0	
PCB-1221	1.0	
PCB-1232	1.0	
PCB-1242	1.0	
PCB-1248	1.0	
PCB-1254	1.0	
PCB-1260	1.0	
PCNB .	0.050	
TOXAPHENE	1.67	
TRIFULRALIN	0.125	
PHENOXY ACID HERBICIDES:		
2,4-D	0.50	
DINOSEB	0.50	
2,4,5-T	0.25	
2,4,5-TP	0.25	

Chemical Name Detection Limits (ug/L)

murannaansmu naamtainec.	
THIOPHOSPHATE PESTICIDES:	1.0
AZINPHOS ETHYL	1.0
AZINPHOS METHYL	0.5
CHLORFEVINPHOS	0.5
CHLORPYRIFOS	2.0
COUMAPHOS	1.0
CROTOXYPHOS	1.0
DEMETON .	0.5
DIAZINON	0.5
DICHLORVOS	2.0
DICROTOPHOS	-
DIMETHOATE	0.5
DIOXATHION	4.0
DISULFOTON	0.5
EPN	0.5
ETHION	2.0
FAMPHUR	0.5
FENSULFOTHION	1.0
FENTHION	0.5
LEPTOPHOS	0.5
MALATHION	0.5
METHYL PARATHION	0.5
MEVINPHOS	0.5
MONOCROTOPHOS	5.0
NALED	1.0
NALED PARATHION PHORATE	1.0
PHORATE	0.5
PHOSMET	1.0
PHOSPHAMIDON	2.0
SULFOTEPP	0.5
TERBUFOS	1.2
TETRACHLORVINPHOS	0.5
TRICHLOROFON	1.0
TRICHLORONATE	1.0
TRIAZINE HERBICIDES:	
ATRAZINE	0.8
ALACHLOR	0.2
CYANAZINE	0.4
METOLACHLOR	0.4
SIMAZINE	0.8
TRIFLURALIN	0.2