Total Maximum Daily Load (TMDL) Documentation for Chlordane in Baltimore Harbor

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FOR CHLORDANE IN BALTIMORE HARBOR
Basin Code: 02-13-09-03

PREFACE

Section 303(d) of the federal Clean Water Act (CWA) directs states to identify and list waters, known as water quality limited segments (WQLSs), where current, required controls of a specified substance are inadequate to achieve water quality standards. For each WQLS, the State is to establish a Total Maximum Daily Load (TMDL) of the specified substance that the waterbody can receive without violating water quality standards.

On the basis of fish tissue data associated with portions of the Baltimore Harbor, the entire waterbody was identified on the 1998 additions to Maryland's 303(d) list of WQLSs as being impaired by the pesticide chlordane. This report documents the establishment of a proposed chlordane TMDL for Baltimore Harbor.

Once approved by the U.S. Environmental Protection Agency (USEPA), the TMDL will be documented according to procedures described in the State's Continuing Planning Process. In the future, the established TMDL will support monitoring activities required to track restoration of the impaired resource with the eventual goal of lifting the associated fish consumption advisory.

EXECUTIVE SUMMARY

Chlordane, a pesticide no longer authorized for use in the United States, has been detected in certain Baltimore Harbor fish tissues at levels requiring issuance of a fish consumption advisory. This advisory has been in place since February 5, 1986 (Attachment 1). As a consequence of impairment by chlordane, the Baltimore Harbor was identified as a WQLS on the 1998 additions to Maryland's 303(d) list.

The Maryland Department of the Environment (MDE), thereby, proposes a TMDL of 0.00059 µg/L in the water column based on an earlier, more conservative USEPA water quality criterion for chlordane. In the absence of any defined currently active sources of chlordane, other than sporadic low-level inputs from urban runoff, there is no opportunity to allocate loadings among point and non-point sources other than bottom sediments. The State intends to periodically monitor contaminant levels in fish tissues from Baltimore Harbor to track expected gradual declines in chlordane concentrations. The goal of the monitoring program will be to identify fish tissue levels that would allow for the withdrawal of the fish consumption advisory.

1.0 INTRODUCTION

The Clean Water Act (CWA), section 303(d)(1)(C), and federal regulation 40 CFR 130.7(c)(1) direct each State to develop a Total Maximum Daily Load (TMDL) for all impaired waters on its 303(d) list. A TMDL reflects the maximum amount of the impairing substance a waterbody can receive and still meet water quality standards. A TMDL can be expressed in mass per unit time, toxicity, or any other appropriate measure (40 CFR 130.2(i)). TMDLs must take into account seasonal variations and a margin of safety (MOS) to allow for uncertainty. Maryland's 1998 additions to the 303(d) list, submitted to the U.S. Environmental Protection Agency (USEPA) by the Maryland Department of the Environment (MDE), identify Baltimore Harbor as impaired by the pesticide chlordane. Historical fish tissue data and an associated fish consumption advisory (Attachment 1), based on monitoring of the fish resources during the 1980s, prompted the 1998 listing.

Chlordane has been identified as a pollutant of concern because it is a bioaccumulative pesticide that is carcinogenic and can cause both acute and chronic toxic effects. Since its introduction in the 1940s, chlordane had been used as a broad-spectrum pesticide for agricultural, home, and commercial control of insects until it was withdrawn from the market in 1988. Its polycyclic chlorinated organic structure produces deleterious biological effects similar to those of DDT, polychlorinated biphenyls (PCBs), and other related substances.

The Maryland Department of Agriculture suspended broad-based uses of chlordane in 1975 by restricting its use to termite control. Only certified applicators were authorized to purchase quantities greater than ½ gallon after that date. The USEPA reached an agreement with the sole producer of the product on July 1, 1986, which led to the further restriction of use to the exterior of buildings, and to the ultimate termination of all sales by April 15, 1988. The USEPA officially cancelled the product's registration in 1993.

Concerns with the substance were largely brought to the State's attention through results of its fish tissue monitoring program, which has been an element of the State's water quality monitoring efforts since the 1970s. Water quality impairments in the Baltimore Harbor estuary were initially suggested as a result of fish tissue samples taken by the State of Maryland in 1981 from waters of the tidal portion of the basin. Chlordane levels were of sufficient magnitude to justify issuance of a fish consumption advisory for Channel catfish (*Ictalurus punctatus*) and American eel (*Anguilla rostrata*). All readily available data indicate that the only current source of chlordane in fish tissues is the historical accumulation of chlordane in sediments of the tidal reaches of the Baltimore Harbor estuary.

The estuary's designation as a WQLS is based upon violations of the use designation for the waterbody and the narrative standard for toxic substances in the State's regulations. Specifically, Baltimore Harbor is designated as a Use I water. The Code of Maryland Regulations (COMAR) Title 26.08.02.01 B (2) (a), requires that all Use I "waters of this State shall be protected for the basic uses of water contact recreation, fish, other aquatic life, wildlife, and water supply." In COMAR 26.08.02.01 C, the narrative statement concerning toxic pollution states that "the waters of this State may not be polluted by: . . . (3) high temperature, toxic, corrosive or other deleterious substances attributable to sewage, industrial

wastes, or other waste in concentrations or combinations which: . . . (b) are harmful to human, animal, plant, or aquatic life." Because the fish inhabiting the waters cannot be consumed without restriction, the estuary does not comply with the Use I designation and is considered to be impaired.

2.0 SETTING AND SOURCE ASSESSMENT

2.1 General Setting

Baltimore Harbor is a tidal estuary located on the western shore of the Chesapeake Bay, just south of Back River (see Attachment 2). Baltimore Harbor lies in the Patapsco watershed (Maryland Department of Natural Resources basin code 12-13-09-03) and it is estimated that 60 percent of the total freshwater entering Baltimore Harbor comes from the Patapsco River (Quirk, Lawler and Matusky Engineers, QLME, 1973). With an area of roughly 623 square miles, the Patapsco watershed straddles both the Piedmont Plateau and Coastal Plain Province geological formations, and includes all of Baltimore City, as well as portions of Anne Arundel, Baltimore, Carroll and Howard Counties (MDE 1996). Smaller tributaries feeding the Harbor are the Gwynns Falls (upper Middle Branch of the Harbor), Jones Falls (Northwest Branch of Baltimore Harbor), Bear Creek, and Curtis Creek.

The Harbor estuary is highly developed with a mix of urban residential, commercial, and industrial/manufacturing uses, which include; food and related products, chemical and allied products, electrical/electronic equipment, and primary metals' industries (MDE 1996). Land use in the large Harbor tributaries shifts from industrial/commercial to high/low density residential and eventually rural/agricultural in the uppermost reaches of some of these drainages.

The largest wastewater discharge to the Baltimore Harbor is from the Patapsco Wastewater Treatment Plant, operated by the City of Baltimore. It discharges approximately 60 million gallons per day of treated municipal and pretreated industrial wastewater to the middle tidal reaches of the estuary.

2.2 Source Assessment

This analysis divides sources into two components, external sources and internal sources (primarily bottom sediments). Based on limited available information, this analysis suggests that internal sources dominate impacts on the water quality, and that, external sources are not significant, and thus no attempt is made to quantify them. This is reasonable considering that any minute external loads eventually become internal sources as they bind strongly to the bottom sediments, and are thus accounted for as part of the internal sources (Agency for Toxic Substances and Disease Registry. 1989).

All readily available data point to *in-situ* Harbor sediments as the sole remaining source of chlordane to the estuary. Estuaries are sinks for contaminants and Harbor sediments integrate loadings from the tributaries. Due to their adsorption capacity, sediments are the most comprehensive indicators of historical and present day contamination (Agency for

Toxic Substances and Disease Registry. 1989). Equilibrium partitioning equations used in section 6.0 predict current Harbor water column concentrations below the 0.00059 µg/L benchmark adopted for this TMDL. These low concentrations predicted in the water column suggest that natural processes are converging to reduce chlordane levels in the Harbor. Future fish analyses are predicted to show decreased tissue burdens and will further confirm adherence to the proposed TMDL.

External Sources: The majority of chlordane loadings were expected to cease as of 1988 with the end of authorized commercial use. However, stocks held by homeowners could be a continuing source, as would be the erosion and transport of existing soils previously contaminated by chlordane. Based on the limited nonpoint source and point source data, presented below, there do not appear to be any significant external sources of chlordane to control or regulate at this time.

External Nonpoint Sources: Water quality information on chlordane concentrations in surface waters draining to the Harbor is limited. However, studies of urban and agricultural runoff report minute amounts of chlordane being detected in tributaries to the Harbor. These infrequent occurrences, however, do not allow for the identification of quantifiable sources.

Data from an unpublished 1994 urban runoff study by MDE (MDE draft August 1997) suggest that the occurrence of chlordane is unpredictable in spatial and temporal scope. Twelve of the fifteen samples taken from the Baltimore Harbor watershed stations (ZDE0009, ZGW0001 and GWN0015) produced chlordane levels that were either not detected (ND), or less than the level of quantification. Of the three that were measurable, one was at the level of quantification (0.02 µg/L or parts per billion - ppb) and two were at 0.03 µg/L (Table 1).

Table 1: Pesticides in Baltimore Harbor Tributaries – 1994 (units are in µg/L)

Tributary	Station	Watershed	Winter	Spring	Summer-1	Summer-2	Fall
Unnamed Trib.	ZDE0009	Stony Run	0.03	ND	ND	0.02	ND
Unnamed Trib.	ZGW0001	Gwynns Falls	<0.02[T]	ND	ND	0.03	ND
Gwynns Falls	GWN0015	Middle Branch	ND	ND	ND	ND	ND

[T]Trace – the pesticide was detected in at least one sample at a level below the quantification limits.
ND – Not detected

Another report published by MDE in 1997 (MDE 1997) analyzed stormwater discharge data for the National Pollutant Discharge Elimination System (NPDES, 1987 CWA) permit application process. Baltimore City and Anne Arundel, Baltimore, Harford, Howard, Montgomery and Prince George's counties were required to participate in the NPDES program. Monitoring sites were organized into residential, commercial and industrial categories to analyze specific landuse runoff characteristics.

Sampling was conducted at each site during three discrete storm events which had to produce at least 0.1 inches of rainfall and occur at least 72 hours after the previous rain event. Samples were collected every 20 minutes for the first 3 hours of the storm and each outfall could not be sampled more than once per month. A total 107 storm events were sampled during the NPDES study, 21 of which were in tributaries to Baltimore Harbor. Chlordane detection levels were 0.014 µg/L using USEPA method 608. No chlordane was detected during this study.

Point Sources: Chlordane is not an expected substance in point source discharges. If it were to occur in municipal discharges, it would be from intermittent, illicit, and generally untraceable sources. If such sources exist, they are not generally considered controllable by waste water treatment plants.

Chlordane has not been detected in discharges from the Patapsco River wastewater treatment plant (personal communication – John Martin, Baltimore City DPW). For meaningful reference, however, the nearby Back River wastewater treatment plant produced no detectable chlordane during pesticide surveys in 1989 or 1998. The detection levels in 1998 were 0.086 µg/L (personal communication – John Martin, Baltimore City DPW).

Internal Sources: The only significant internal source of chlordane in the Baltimore Harbor is the bottom sediments, which are considered to be a nonpoint source from the perspective of load allocations. Computations provided within this report indicate that current sediment concentrations should not lead to the elevation of chlordane in fish tissue; however, older fish may have elevated levels due to past exposure. MDE continues to monitor fish tissue to verify these expectations.

Harbor sediments are the most probable continuing source of chlordane. The most recent sediment data collected in the estuary are from the "Spatial Mapping of Sedimentary Contaminants from the Baltimore Harbor/Patapsco River/Back River System" (Baker *et al.* 1997). The mean concentration of chlordane detected in this study was 5.62 ng/g dry weight. An earlier study conducted by Eskin *et al.* (1996) in the Harbor found mean chlordane sediment concentrations of 2.56 ng/g dry weight. Instead of averaging the values from these two studies, the higher chlordane concentration of 5.62 ng/g from the Baker study is assumed for the calculations in this study. This adds a margin of safety to the analysis by using the highest mean sediment concentrations currently available for calculating associated chlordane in the water column.

3.0 WATER QUALITY IMPAIRMENT

Fish tissue samples collected since 1976 as part of a statewide fish tissue monitoring program serve as the sole source of data used to justify placement of the Baltimore Harbor on Maryland's 303(d) list of water quality limited segments for chlordane. Under this state program two or more fish species, representing bottom feeders and higher trophic level predators, are targeted for collection at each monitoring location. Species having a wide range of occurrence are targeted to allow for regional comparisons in addition to the temporal trends at each monitoring station. Chlordane has been identified in almost every fish tissue

sample collected from all basins under the State's fish tissue monitoring program. The fish tissue monitoring program currently consists of a network of over thirty monitoring locations where triennial sampling allows for statewide trend assessments. This network is supplemented with additional monitoring sites in areas of concern.

Statewide, most fish tissue chlordane levels have been well below the 0.3 mg/kg action level established by U.S. Food and Drug Administration (USFDA) guidelines. Elevated levels of chlordane in fish tissue have appeared most commonly in urban areas, especially those located near the head of tidal influence. Among the sites of greatest accumulation were Baltimore Harbor (Patapsco River), Back River, and Lake Roland (an impoundment on Jones Falls and a tributary to the Patapsco River). In these water bodies, the levels of chlordane in selected fish tissues frequently exceeded the USFDA action levels.

Following the initial surveys of the 1970s, where results indicated a potential for problems in selected urban areas, additional monitoring efforts were focused on the areas of greatest concern, including Baltimore Harbor. The monitoring conducted in Baltimore Harbor in 1981 substantiated contamination concerns and resulted in additional, more comprehensive monitoring in subsequent years. Because chlordane was detected in a number of fish tissue samples above the 0.3 mg/kg level, the waterbody was considered to be impaired. Results of the monitoring in the Baltimore Harbor watershed are summarized in Table 2.

Table 2: Chlordane Levels in Fish Tissue Collected in Baltimore Harbor (1976-1987)

Year	Station	Basin	Species	Tissue Analyzed	Weight (g)	Concentration (ppm)
1976	PAT0195	Patapsco River	Yellow Perch	Fillet	N/A	0.05
	XHF9502	Rock Creek	White Perch	Fillet	N/A	**0.37**
	PAT0195	Patapsco River	Bluegill	Edible Portion	419	ND
	XIE2885	Patapsco River	White Perch	Edible Portion	315	0.05
	XIE2885	Patapsco River	Spot	Edible Portion	440	0.02
	XIE2885	Patapsco River	White Perch	Edible Portion	N/A	0.11
	XIE2885	Patapsco River	White Perch	Edible Portion	343	0.07
	XIE2885	Patapsco River	American Eel	No skin, head, visc.	372	0.17
1982	XIE2885	Patapsco River	White Perch	Edible Portion	290	0.10
	XIE2885	Patapsco River	Spot	Edible Portion	540	0.10
	CUR0007	Curtis Creek	Spot	Fillet	N/A	0.07
1983	XIE2885	Patapsco River	Spot	Fillet	95.5	**0.31**
	XIE2885	Patapsco River	Spot	Fillet	86.6	**0.49**
	XIE2885	Patapsco River	Spot	Fillet	86.1	0.11
	XIE2885	Patapsco River	Spot	Fillet	108.3	0.20
	XIE2885	Patapsco River	Spot	Fillet	86.1	**0.73**
	XIE2885	Patapsco River	Spot	Fillet	76.3	0.27
	XIE2885	Patapsco River	Spot	Fillet	80	0.11
	XIE2885	Patapsco River	Spot	Fillet	95.3	**0.45**
	XIE2885	Patapsco River	Spot	Fillet	86.9	0.18
	XIE2885	Patapsco River	Spot	Fillet	89.3	**0.30**
	XIE2885	Patapsco River	Spot	Fillet	96.5	0.16
	XIE2885	Patapsco River	Spot	Fillet	83.8	**0.75**
	XIE2885	Patapsco River	Spot	Fillet	92.5	0.22
	XIE2885	Patapsco River	Spot	Fillet	91.6	0.20
1985	XIE6254	Northwest Branch	American Eel	No skin, head, visc.	260	**0.67**
	XIE6254	Northwest Branch	American Eel	No skin, head, visc.	360	0.18
	XIE6254	Northwest Branch	American Eel	No skin, head, visc.	180	**0.40**
	XIE6254	Northwest Branch	American Eel	No skin, head, visc.	220	**0.34**
	XIE6254	Northwest Branch	American Eel	No skin, head, visc.	226	**0.60**
	XIE6254	Northwest Branch	American Eel	No skin, head, visc.	208	**0.67**
	XIE6254	Northwest Branch	American Eel	No skin, head, visc.	170	**0.57**
	XIE2590	Patapsco River	American Eel	No skin, head, visc.	194	0.26
	XIE2590	Patapsco River	Channel Catfish	Fillet	813	**0.46**
	XIE2590	Patapsco River	American Eel	No skin, head, visc.	128	**0.42**
	XHF9502	Rock Creek	American Eel	No skin, head, visc.	191	0.16
	XHF9502	Rock Creek	American Eel	No skin, head, visc.	398	0.24
	XHF9502	Rock Creek	American Eel	No skin, head, visc.	251	0.26
	XHF9502	Rock Creek	American Eel	No skin, head, visc.	461	0.08
	XHF9502	Rock Creek	American Eel	No skin, head, visc.	189	0.21
	XHF9502	Rock Creek	American Eel	No skin, head, visc.	177	0.17
	XHF9502	Rock Creek	American Eel	No skin, head, visc.	134	0.19

Table 2: Continued

	XIF1629	Patapsco River	White Catfish	Fillet	305	**0.36**
	XIF1629	Patapsco River	Brown Bullhead Catfish	Fillet	195	**0.53**
	XIF1629	Patapsco River	Brown Bullhead Catfish	Fillet	127	0.02
	XIF1629	Patapsco River	Channel Catfish	Fillet	402	0.19
	XIF1629	Patapsco River	Channel Catfish	Fillet	475	**0.31**
	XIF1629	Patapsco River	Channel Catfish	Fillet	672.4	**0.86**
	XIF1629	Patapsco River	White Perch	Fillet	148	0.07
	XIF1629	Patapsco River	White Perch	Fillet	149	0.06
	XIF1629	Patapsco River	White Perch	Fillet	110	0.11
	XIF1629	Patapsco River	White Perch	Fillet	167	0.06
	XIF1629	Patapsco River	White Perch	Fillet	152	0.09
	XIF1629	Patapsco River	White Perch	Fillet	101	0.04
	XIF1629	Patapsco River	White Perch	Fillet	142	0.05
	XIF1629	Patapsco River	White Perch	Fillet	192	0.06
	XIF1629	Patapsco River	White Perch	Fillet	129	0.16
	XIF1629	Patapsco River	White Perch	Fillet	90	0.11
	XIF1629	Patapsco River	White Perch	Fillet	192	0.04
	XIF1629	Patapsco River	White Perch	Fillet	128	0.08
	XIF1629	Patapsco River	White Perch	Fillet	128	0.08
	XIF1629	Patapsco River	White Perch	Fillet	93	ND
	XIF1629	Patapsco River	White Perch	Fillet	100	0.15
	XIF1629	Patapsco River	White Perch	Fillet	83	0.05
	XIF1629	Patapsco River	White Perch	Fillet	113	0.08
	XIF1629	Patapsco River	White Perch	Fillet	89	0.08
	XIF1629	Patapsco River	White Perch	Fillet	89	**0.75**
	XIF1629	Patapsco River	White Perch	Fillet	1082	0.16
	XHE9541	Patapsco River	White Perch	Fillet	182	0.11
	XHE9541	Patapsco River	White Perch	Fillet	282	**0.61**
	XHE9541	Patapsco River	White Perch	Fillet	319	0.22
	XHE9541	Patapsco River	White Perch	Fillet	270	0.15
	XHE9541	Patapsco River	Carp	Fillet	1467	**0.33**
	XHE9541	Patapsco River	Brown Bullhead Catfish	Fillet	206	0.16
	XHE9541	Patapsco River	Brown Bullhead Catfish	Fillet	185	0.08
	XHE9541	Patapsco River	White Perch	Fillet	237	0.11
	XHE9541	Patapsco River	White Perch	Fillet	173	0.11
	XHE9541	Patapsco River	White Perch	Fillet	162	0.10
	XHE9541	Patapsco River	White Perch	Fillet	152	0.09
	XHE9541	Patapsco River	White Perch	Fillet	N/A	**0.53**
	XHE9541	Patapsco River	White Perch	Fillet	214	0.04

Table 2: Continued

	XHE9541	Patapsco River	White Perch	Fillet	179	0.18
	XHE9541	Patapsco River	Carp	Fillet	2533	**0.67**
	XHE9541	Patapsco River	Brown Bullhead Catfish	Fillet	185	0.17
	XHE9541	Patapsco River	Brown Bullhead Catfish	Fillet	162	0.11
	XHE9541	Patapsco River	Brown Bullhead Catfish	Fillet	187	0.21
1986	CUR0007	Curtis Creek	White Perch	Fillet	170.1	0.17
	CUR0007	Curtis Creek	White Perch	Fillet	170.1	0.17
	CUR0007	Curtis Creek	White Perch	Fillet	155.9	-0.02
	CUR0007	Curtis Creek	White Perch	Fillet	184.3	ND
	CUR0007	Curtis Creek	White Perch	Fillet	141.8	ND
	CUR0007	Curtis Creek	White Perch	Fillet	198.4	ND
	CUR0007	Curtis Creek	White Perch	Fillet	192.8	ND
	CUR0007	Curtis Creek	White Perch	Fillet	170.1	ND
	CUR0007	Curtis Creek	White Perch	Fillet	184.3	ND
	CUR0007	Curtis Creek	White Perch	Fillet	175.8	ND
	CUR0007	Curtis Creek	White Perch	Fillet	184.3	ND
	CUR0007	Curtis Creek	White Perch	Fillet	221.1	**0.49**
	CUR0007	Curtis Creek	White Perch	Fillet	155.9	0.11
	CUR0007	Curtis Creek	White Perch	Fillet	170.1	**0.33**
	CUR0007	Curtis Creek	White Perch	Fillet	192.8	0.02
1987	XIF2929	Old Road Bay	Brown Bullhead Catfish	Fillet	680	0.02

N/A – Information not available
ND – Not detected
Concentrations in bold exceed the USFDA guidance level of 0.3 mg/kg

4.0 TARGETED WATER QUALITY GOALS

Although the State has not adopted a numeric water quality criterion for chlordane, it does take action on environmental contaminants that significantly increase the risk to public health. The level of significance generally used by the State in these analyses for carcinogenic endpoints is the level that produces an increased risk greater than one in 100,000 of the population. This is often expressed as a risk greater than 1.0×10^{-5}. Assuming that the public has a risk of cancer from all causes of at least 25%, or 25,000 in 100,000, the threshold of concern for a single substance would increase the risk to 25,001 in 100,000.

The USFDA has established specific guidance levels for fish tissue in the commercial market (0.3 mg/kg). This level was employed in the setting of the original fish consumption advisory for Baltimore Harbor. The USEPA currently supports a purely risk based approach for developing fish consumption advisories. Using USEPA default assumptions: CSF_o (0.35/mg/kg/d), the average adult daily consumption of fish (6.5 grams/day), the average body weight of an adult (70 kg) and a risk factor of 10^{-5}, yields a fish tissue concentration of 0.3 mg/kg. This means that a fish tissue concentration of 0.3 mg/kg approximates a 10^{-5} risk level. Since both USEPA and USFDA support the same fish tissue concentration, this weight-of-evidence leads Maryland to conclude that an average fish tissue level of 0.3 mg/kg is reasonable for the purpose of deciding whether a fish consumption advisory may be warranted. The current USEPA ambient water quality criteria for the protection of human health from the consumption of contaminated fish is calculated similarly, but is conservatively based on a 10^{-6} risk level instead of 10^{-5}. This adds a factor of 10 safety margin to the most current USEPA water quality criteria of 0.0022 µg/L. Therefore, the endpoint for the control or mitigation of chlordane as it affects the edibility of fish taken from Baltimore Harbor would be linked to achieving a reduction of chlordane in the targeted fish tissues to a level of 0.3 mg/kg or less.

Because chlordane was banned nearly 15 years ago, chlordane loadings from sources other than existing bottom sediments are believed to be negligible; consequently, the bottom sediments are assumed to be the dominant present day source of chlordane in Baltimore Harbor water and fish tissue[1]. Therefore, the rate of reduction of chlordane concentrations in the biologically active sediment layer will ultimately control water column and fish tissue concentrations. Chlordane concentrations in sediments are reduced by a number of processes, including:

- Burial/dilution of contaminated sediments;
- Dissolution into, followed by vaporization from, the water column;
- Uptake by biota living in the sediment;

[1] This expectation is also supported by the well-established propensity of chlordane to adsorb to sediments (Agency for Toxic Substances and Disease Registry, 1989). Based on calculations provided in section 5.0 Technical Methods, current sediment concentrations of chlordane in Baltimore Harbor have declined below levels that are expected to result in elevated fish tissue concentrations (See also Section 2.2 Source Assessment).

- Chemical degradation;
- Biological degradation; and
- Hydrologic transport from the system.

The dominant processes are likely burial and/or dissolution followed by volatilization from the water body. Howard (1991) provides estimated volatilization half-lives from a representative environmental pond, river and lake as 8-26, 3.6-5.2, and 14.4-20.6 days, respectively. Howard also states that adsorption to sediments can significantly affect the importance of volatilization.

Water quality criteria for chlordane have been developed by USEPA (USEPA 1999) to protect marine aquatic life from toxic effects (0.004 µg/L) and to protect humans from the consumption of contaminated aquatic organisms (0.0022 µg/L). These superceded the earlier water quality criteria developed by USEPA; 0.0043 µg/L (toxicity to marine aquatic life) and 0.00059 µg/L (human health) (EPA 1999). As a conservative assumption of the TMDL analysis, the earlier and more strict ambient water quality criteria for the protection of human health was employed, which includes an additional built-in margin of safety.

5.0 TECHNICAL METHODS

Following the steps provided below, an equilibrium approach, using the USEPA 1993 sediment criteria development methodology, was employed to provide an upper estimate of the dissolved water column concentration based on recent sediment concentrations.

First, the log K_{oc} is estimated from the log K_{ow} using the empirically derived equation provided below.

$$\log K_{oc} = 0.00028 + 0.983 \times \log K_{ow}$$

where:

K_{ow} = octanol/water equilibrium partition coefficient
K_{oc} = octanol/organic carbon equilibrium partition coefficient (L/kg)

Substituting the experimentally determined log K_{ow} chlordane (5.54) from Howard (1991) into this equation yields:

$$\log K_{oc} = 0.00028 + 0.983 \times 5.54$$

$$\log K_{oc} = 5.45$$

$$K_{oc} = 279{,}000 \text{ L/kg}$$

The concentration of chlordane in water in equilibrium with the sediment can be estimated by the equation provided below. It should be emphasized that this equation represents the pore water concentration or the concentration in the water present between bottom sediment particles. The overlying water column is expected to be subject to a much greater degree of

dilution, resulting in even lower chlordane concentrations. Using this methodology provides an additional margin of safety by estimating the maximum concentration of chlordane potentially present in the overlying water column.

$$C_w = C_s / (f_{oc} \times K_{oc})$$

where:

C_w = concentration in water (µg/L)
C_s = concentration in sediment (g/kg)
f_{oc} = fraction organic carbon (unitless)
K_{oc} = organic carbon/water equilibrium partition coefficient (L/kg)

Recent measurements of Baltimore Harbor sediments (Baker *et al.* 1997) indicate an average concentration of 5.62 ng/g (dry weight) for chlordane and 4.36% total carbon. Applying these values in the following equation yields a predicted water column concentration of 0.000462 µg/L (4.62 x 10^{-4} µg/L)., lower than the more conservative water quality criteria (0.00059 µg/L) being used in this TMDL analysis.

$$C_w = C_s / (f_{oc} \times K_{oc})$$

$$C_w = 5.62 \text{ µg/kg} / (0.0436 \text{ g/g} \times 279{,}000 \text{ L/kg})$$

$$C_w = 0.000462 \text{ µg/L} = 4.62 \times 10^{-4}$$

The multiple margins of safety used in the above calculations ensure that the predicted water column concentration (4.62 x 10^{-4} µg/L) of chlordane in Baltimore Harbor represents the maximum concentration possible based upon available data. These calculations predict that the current concentration of chlordane in the water column (4.62 x 10^{-4} µg/L) is still approximately twenty five percent lower than the most conservative (5.9 x 10^{-4} or 0.00059µg/L) USEPA water quality criteria adopted for the Baltimore Harbor TMDL. In addition, since there are no discernible continuing sources of chlordane to the Harbor, continued fish monitoring and the expected gradual declines in tissue burdens below the 0.3 mg/kg level will strongly suggest that water column concentrations fall below the 0.00059 µg/L water quality standard adopted for the Harbor TMDL.

6.0 TOTAL MAXIMUM DAILY LOADS AND LOAD ALLOCATIONS

Chlordane is a persistent substance, which has a high affinity for fine sediments and generally settles to the bottom with the sediment in the estuary. Water column concentrations are thus generally extremely low and difficult to measure in a manner that would allow adequate characterization of a large estuarine system. Sediment analyses are costly and provide information only on the precise location where sampling occurred. Fish tissue accumulates and integrates bioaccumulative contaminants, such as chlordane, and is, therefore, the logical endpoint for assessing environmental contamination.

6.1 Water Quality Endpoint

The water quality endpoint for this TMDL is expressed in terms of achieving the specific criterion for which Baltimore Harbor was identified on the 303(d) list. The current USFDA guidance level for fish tissue concentrations of 0.3 mg/kg was used to determine the need to list Baltimore Harbor as being impaired by chlordane. A water quality endpoint equivalent to the most conservative of the USEPA's water quality criteria for chlordane (0. 00059 µg/L) should, therefore, be sufficient to attain fish tissue concentrations below the guidance level.

6.2 Total Maximum Daily Load

The computations provided above establish a linkage between the fish tissue endpoint of 0.3 mg/kg and a water column concentration of 0.00059 µg/L (USEPA 1980) that includes a factor of 30 margin of safety (see Margin of Safety section). Thus, MDE is establishing a concentration of 0.00059 µg/L as the appropriate measure for the Baltimore Harbor chlordane TMDL.

6.3 Seasonal Variations and Critical Conditions

The TMDL is represented as a concentration level that is protective against toxic human health effects *at all times*. Implicitly, the TMDL accounts for seasonal variations since it is protective throughout the year (i.e., "at all times"). This situation does not present an issue of controlling for critical conditions for several reasons. First, the notion of "critical conditions" does not arise in the traditional sense for this TMDL. The allowable concentrations of chlordane are based on human fish consumption over a long time period, which averages out any critical events. Additionally, the TMDL is founded upon human health standards which account for critical sub-populations that might be more susceptible to toxic risk. Second, the TMDL is protective at all times, which implies that any "critical conditions" within that timeframe are considered. Finally, the TMDL levels established to be protective of human health are more conservative than the chlordane levels established to protect environmental resources, implying that critical conditions for environmental resources are also addressed by the previous logic that applied to human health.

6.4 TMDL Allocation

The studies referenced above suggest that the transient events, in which minute levels of chlordane have been observed in association with point and non-point sources, are too insignificant to support the quantification of meaningful allocations to these sources. Furthermore, the bottom sediments integrate other sources. All readily available data indicate that chlordane present in the bottom sediment layer of the estuary is the only significant source causing elevated fish tissue concentrations. Therefore, the sole allocation of chlordane is to the existing bottom sediments of the Baltimore Harbor estuary.

6.5 Margin of Safety

The USEPA's TMDL guidance requires each TMDL to include a margin of safety (MOS) that accounts for uncertainty in a manner that is conservative with respect to environmental protection. The USDA fish tissue guidance level, which serves as the water quality measurement endpoint, identified the specific need for a TMDL. The older and more conservative USEPA ambient water quality standard for the protection of humans from the ingestion of contaminated aquatic organisms (0.00059 µg/L) serves as the basis of the TMDL. This is more conservative than the current USEPA ambient water quality criterion (0.0022 µg/L) and was employed to add a margin of safety of a factor of 3. Additionally, the current USEPA water quality criterion of 0.0022 µg/L was calculated at a 10^{-6} risk level, whereas Maryland typically uses a 10^{-5} risk level for water quality criteria for the protection of human health due to fish ingestion. This adds an additional margin of safety by a factor of 10. When combined, these two margins of safety amount to a protection factor of 30.

The equation used in section 6.0 to predict water column concentrations of chlordane based upon current Inner Harbor sediment concentrations also has a built-in margin of safety. It predicts concentrations expected in the sediment pore water rather than the water column overlying the sediments. When considering sediments as the sole source of contamination, the pore water between sediment particles frequently has higher contaminant concentrations than the overlying water column, which is subject to mixing and dilution.

As a third margin of safety, the maximum mean chlordane concentration among the most recent sediment analyses was used to calculate the existing water column concentration.

6.6 TMDL Summary

Based on the previous discussion, the TMDL for chlordane may be summarized as follows:

TMDL	=	WLA	+	LA	+	MOS
0.00059	**=**	**0**	**+**	**0.00059**	**+**	**built-in**

(µg/l – at all times). No future allocation is provided.

Where, WLA is Waste Load Allocation (Nonpoint Sources)
LA is Load Allocation (Point Sources), and
MOS is Margin of Safety

7.0 ASSUREDNESS OF IMPLEMENTATION

The State of Maryland is committed to protecting the State's rivers, streams, lakes, wetlands, and estuaries. Chlordane concentrations in Baltimore Harbor sediments are expected to decline over time due to natural recovery of the estuary, through gradual biodegradation, dispersal, and natural burial by sedimentation. The computations provided in Section 6.0 suggest that current sediment concentrations of chlordane are below levels expected to result in elevated fish tissue concentrations. No observations of fish tissue are currently available

to confirm this, and older fish may continue to have elevated levels due to past bioaccumulation.

Chlordane has not been commercially available since the late 1980s. It is, therefore, an intermittent contaminant the source of which is most likely stormwater or illegal disposal. Local governments are promoting efforts to enhance source reductions by offering "household hazardous chemical disposal days." These efforts have been ongoing since the late 1980s and are continuing to provide local citizens with an environmentally acceptable means of disposal. Similar efforts have been extended to farmers for disposal of agricultural chemicals no longer suitable for use.

Aside from the processes of natural recovery, physical removal of the bottom sediments from this estuary would be the only other means of removing the chlordane-contaminated sediments. Environmental concerns, coupled with the high costs associated with dredging and dredged material disposal, place chlordane impairment in Baltimore Harbor in the category of "Extremely Difficult Problems" as defined in Chapter 6 of the Report of the Federal Advisory Committee on the TMDL Program (USEPA 1998a).

Biologically available chlordane levels in Baltimore Harbor sediments are expected to decline over time due to natural processes including biodegradation, redistribution, and natural burial by sedimentation. Maryland has a fish tissue monitoring program in place that collects and analyzes samples for contamination in Baltimore Harbor on a regular basis. Maryland is proposing triennial monitoring of the fish and surficial sediments in the Harbor to track the natural attenuation of chlordane. An evaluation of the required sampling frequency will be considered each year as information from the statewide monitoring network is developed. As contamination levels decline and appear low enough to protect human health and the environment, these data and results from additional samples will be evaluated to determine if the consumption advisory should be modified or withdrawn.

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NEWS RELEASE
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February 5, 1986

DHMH ISSUES HEALTH ADVISORY

Adele Wilzack, R.N., M.S., Secretary of the Department of Health and Mental Hygiene, today issued a health advisory concerning recreational fishing and the consumption of black crappie, carp, channel catfish and american eels from certain waters in the urban Baltimore area.

"This advisory is limited in nature," Ms. Wilzack said. "No health risk exists with the general consumption of oysters, crabs or finfish from Maryland waters, and commercial fisheries are not affected."

A recently concluded intensive investigation in Lake Roland, the Baltimore Harbor and Back River found that average chlordane concentrations in certain fish exceeded the FDA action level of 0.3 ppm.

Chlordane is an insecticide whose use in Maryland is now limited to subterraneous application to protect homes from termites. However, in the past, chlordane was also used as an insecticide in agriculture and was sprayed in homes and gardens. Chlordane remains for long periods of time in the environment and can become concentrated in fish. It has a relatively low acute toxicity, compared to other insecticides, but because it is a suspected carcinogen, continuing long-term exposure is considered a risk.

M O R E

DHMH ISSUES HEALTH ADVISORY

"Individuals are advised to limit their consumption of carp and black crappie from Lake Roland," Ms. Wilzack said. "We are also advising residents to limit their consumption of channel catfish and american eels from both the Baltimore Harbor and Back River."

These fish should not be used as a substantial part of the daily diet and should be avoided by women of childbearing age, infants or children. To further reduce health risks, Secretary Wilzack recommends removal of the belly flap, skin and dark meat, because chlordane is most likely to be concentrated in fatty protions of fish. Secretary Wilzack indicated that other fish were tested in each body of water, but that the average chlordane levels in them were not found to exceed the FDA action level for chlordane.

To protect the consumer, the Food and Drug Administration has established a chlordane "action level" of 0.3 parts per million for fish. The possible lifetime cancer rish associated with consumption of over 100 lbs. of fish containing chlordane levels of 0.3 ppm. over a person's lifetime has been estimated at 1 in 100,000 for the average individual.

To give this value some perspective, it can be compared to the lifetime cancer risk for a person sharing an office with a smoker, which is 70 in 100,000 or the lifetime cancer risk from cosmic radiation associated with taking one transcontinental airplane flight annually, which is 3.5 in 100,000. To illustrate this another way, a person is at a 3.5 times greater risk from taking one such flight annually than from eating 100 lbs. of fish containing 0.3 ppm chlordane over a lifetime.

M O R E

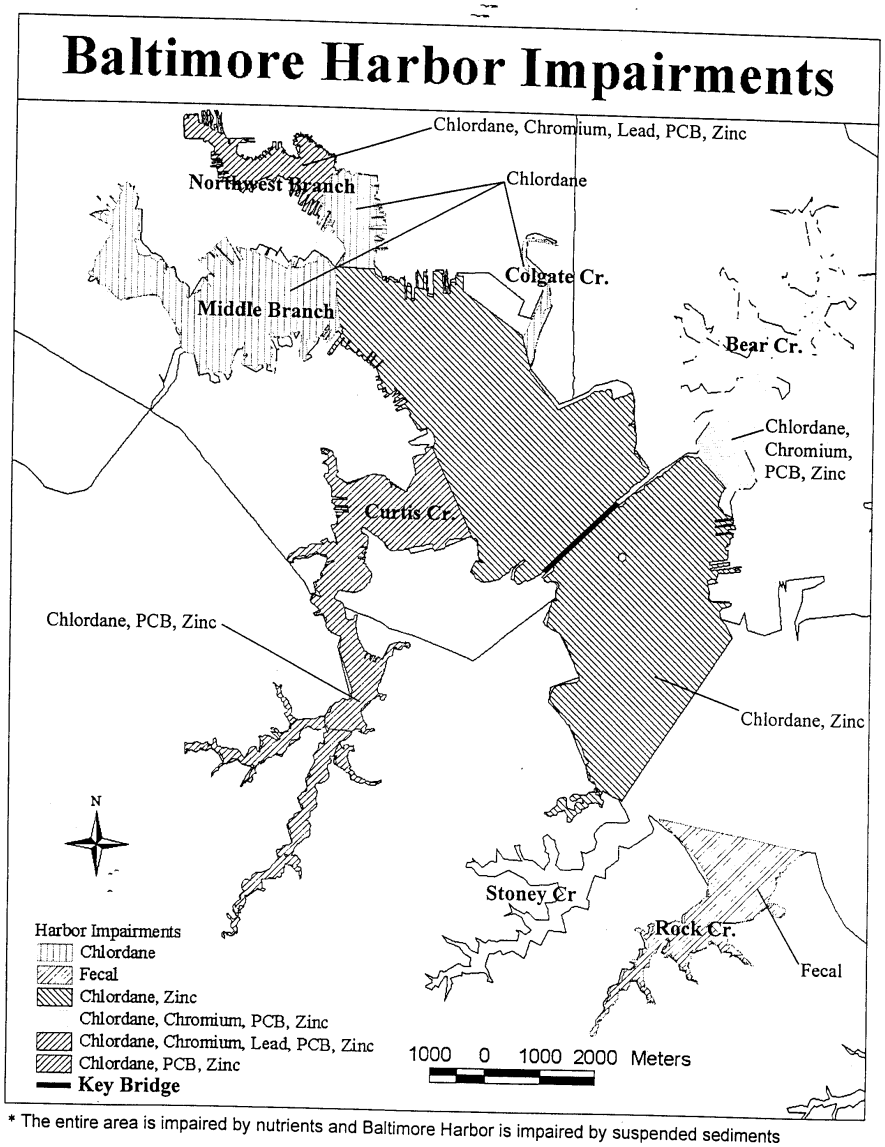
DHMH ISSUES HEALTH ADVISORY

"Similar advisories concerning chlordane have been issued in New York, New Jersey, Mississippi, Missouri, Illinois and Wisconsin," said Ms. Wilzack, who again emphasized that continual surveillance of Maryland fish, crabs and shellfish indicates there is no health risk associated with the general consumption of oysters, crabs and finfish from Maryland waters.

Indiviuaals desiring further information may contact Dr. Katherine Farrell, M.D., M.P.H. at (301) 225-5753.

# # #

Attachment 1



* The entire area is impaired by nutrients and Baltimore Harbor is impaired by suspended sediments

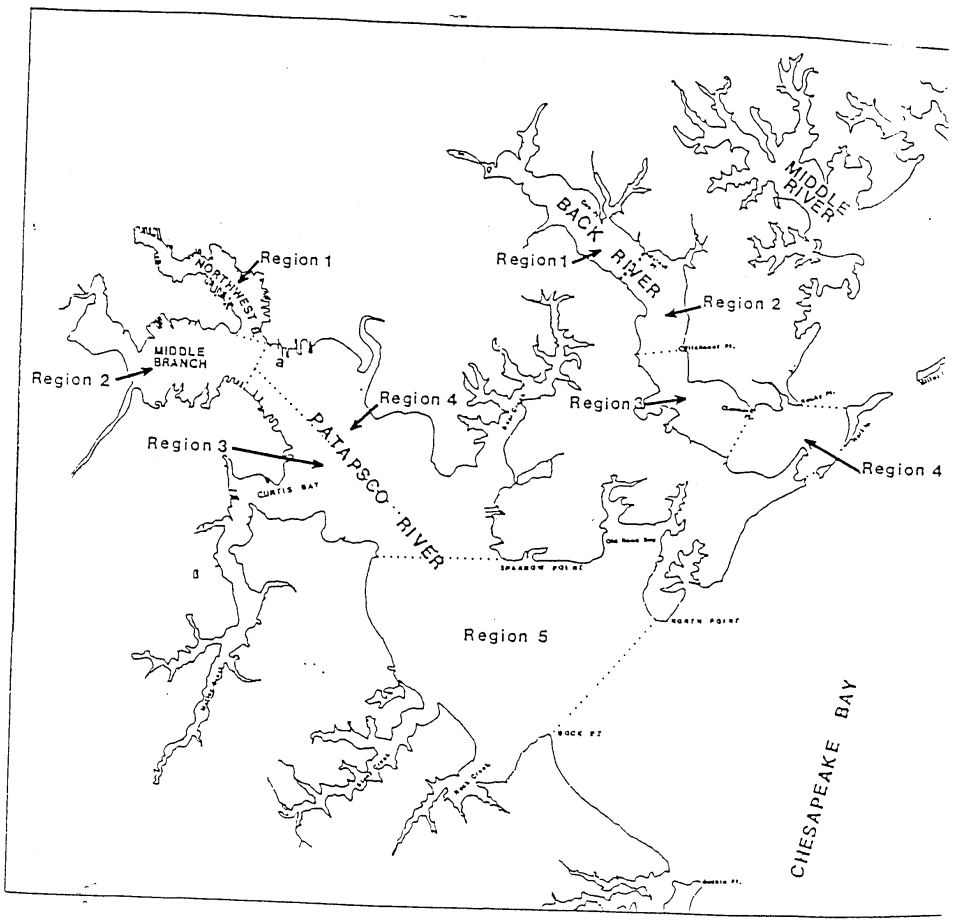


Figure 1. Finfish sampling regions in the Patapsco and Back River Estuaries.

MDE *Facts About . . .*

Maryland Department of the Environment

CONTAMINANTS AND TOXICITY

BACKGROUND

In describing the estuarine and marine environment, the terms "contaminant" and "toxic" are widely used and often misunderstood. The detection or presence of contaminants or toxic substances does not mean a threat exists to either human health or the health of the water body.

- All substances have the potential to be contaminants and to cause toxicity.
- Even substances considered relatively harmless or even beneficial, such as water and vitamin C, may be harmful if consumed in very large quantities or on a too frequent basis. Alcohol is another example; one drink per week is considered harmless, while several drinks per day can cause liver disease.
- Whether or not a substance exerts toxicity depends on both the concentration (dose) and duration of exposure. For example, because of the difference in alcohol content (dose), consumption of a shot glass of whiskey each day is more harmful than consumption of a shot glass of beer each day. Similarly, consumption of a shot glass of whiskey each day is more harmful than drinking same amount each week.
- In assessing the health of Maryland surface waters, substances which are evaluated include metals, such as lead and cadmium, and organic substances, such as pesticides and PCBs. These substances are frequently not present or only present in natural waters at very low concentrations, often below analytical detection levels. Therefore, water sampling is not cost effective and is seldom performed. Since these substances may accumulate in fish and shellfish tissue or sediment, tissue or sediment are the media of choice for sample collection and analysis. Sediment data are used to determine historical discharges or environmental trends, but are not appropriate for evaluating human health risk.

SWIMMING

The presence of toxic substances is generally not important in evaluating the health risk associated with swimming. Exceptions are the rare situation when there may be excessive discharges of acids or alkalis or the presence of marine toxin producing algal blooms. These situations do not occur in Maryland. During swimming, the potential for exposure to heavy metals at concentrations and frequencies sufficient to cause a problem is negligible, when compared to other daily sources such as ingesting food or drinking water.

Although a swimmer might accidentally swallow water during swimming, the amount of a chemical that would be ingested in this manner would be much too small to pose a health risk. Therefore, there is no significant health risk from exposure to chemical contaminants during recreational swimming. Skin contact, during swimming is of no consequence either, since metals are not readily absorbed through the skin.

CONSUMING FISH

Fish have the potential to accumulate heavy metals or organic chemicals in their tissue, even when these materials cannot be measured in the water column. This makes fish good indicators of environmental pollution in a body of water. For this reason, MDE monitors chemical contaminants in fish tissue. Monitoring fish tissue also allows the Maryland Department of Environment to determine if contaminant levels in fish are within limits established as safe for human consumption.

MDE has monitored contaminant levels in fish from Maryland waters since the 1960s and 1970s. Analysis of these data has identified only three water bodies in Maryland where contaminants in certain fish species pose a health concern to humans consuming them. These three water bodies are Lake Roland (black crappie and carp) and the Baltimore Harbor and Back River (american eel and channel catfish).

For more information contact:

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MDE

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MDE *Facts About . . .*

Maryland Department of the Environment

MONITORING CONTAMINANT LEVELS IN FISH, SHELLFISH AND CRABS

Fish and shellfish have the potential to accumulate heavy metals or organic chemicals in their tissue even when these materials cannot be measured in the water column. This makes fish good indicators of environmental pollution in a body of water. This is one of the reasons MDE monitors chemical contaminants in fish tissue. Monitoring fish tissue also allows the Maryland Department of Environment to determine if contaminant levels in fish are within limits established as safe for human consumption. In order to make this determination, MDE evaluates <u>all</u> relevant data and utilizes our professional knowledge and experience.

The relevant data include <u>not only</u> contaminant data on fish and shellfish from the area, but also information on which compounds are likely to bioaccumulate in tissue, their sources and their potential to be present in the aquatic environment at sufficient levels for bioaccumulation to levels of concern. Additional important information considered includes the seasonal variations in fish lipid levels which governs levels of many contaminants. MDE also gives careful consideration to which fish species are those likely to accumulate the highest levels of bioaccumulative contaminants; and thus pose the highest potential risk to human consumers.

<u>FISH</u>

Since the early 1970s, the Maryland Department of the Environment (MDE) has been monitoring chemical contaminant levels in fish found in Maryland waters. Currently, Maryland's monitoring program divides state waters into three groups: 1) Western Maryland watersheds, 2) Chesapeake Bay watersheds, and 3) Baltimore/Washington urban watersheds. Fish from within each of these areas are sampled each 3 years. Collections consist of 2 samples of accumulator species and one sample of game species. Of the accumulator samples, one includes whole fish, while the second includes only fillet tissue. Of the game species, only the fillet portion is analyzed. This allows water-quality managers to evaluate the relative levels of contaminants of concern accumulating in state waters, and contaminant levels in the fish to determine safety for human consumption.