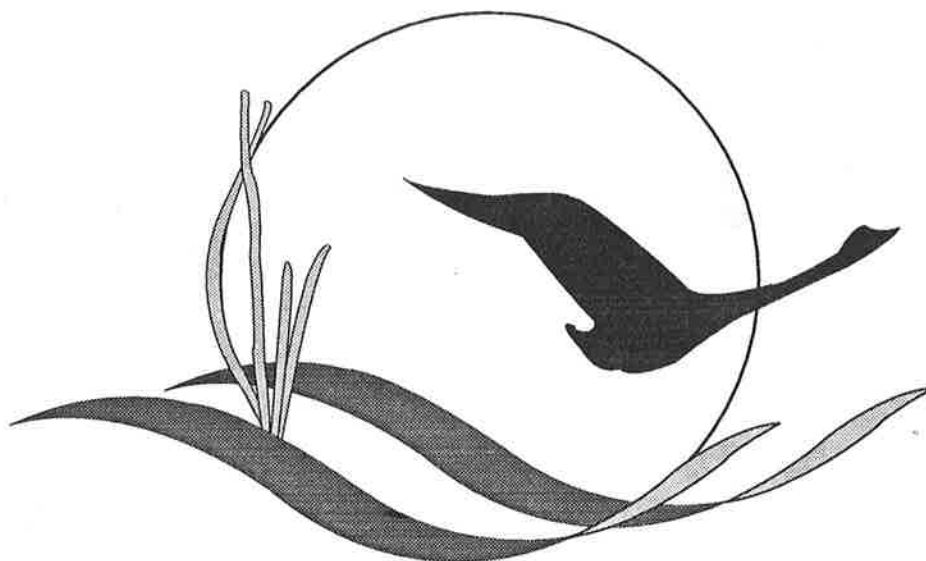


Chesapeake Bay Water Column Contaminants Critical Issue Forum Proceedings

Basinwide Toxics Reduction Strategy Reevaluation Report



Chesapeake Bay Program

Chesapeake Bay Water Column Contaminants Critical Issue Forum Proceedings

Sponsored by the
Chesapeake Bay Program Toxics Subcommittee

April 14, 1993



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**PROCEEDINGS OF THE
CHESAPEAKE BAY PROGRAM
TOXICS SUBCOMMITTEE
SPONSORED**

**CHESAPEAKE BAY WATER COLUMN CONTAMINANTS
CRITICAL ISSUE FORUM**

U.S. EPA Chesapeake Bay Program Office
Chesapeake Bay Information and Conference Center
Annapolis, Maryland

April 14, 1993

1. CRITICAL ISSUE FORUM OBJECTIVES/PROCESS

Rich Batiuk, EPA Chesapeake Bay Program Office, described the objectives of the critical issues forum, the questions posed to the forum participants by the Toxics Subcommittee, and the process for incorporating forum findings into the reevaluation of the 1988 Basinwide Toxics Reduction Strategy. The forum questions were presented as follows:

- From the critical review of available data, have we defined or can we define the relative magnitude (concentration) and extent (geographical distribution) of water column contamination within Chesapeake Bay? within the Bay basin?
- Does this definition of the magnitude and extent of water column contamination within the Bay tidal waters/Bay basin give us reason to believe this identified (potential) toxics issue is causing or can cause an adverse impact (e.g. bioaccumulation, toxicity) on the Chesapeake Bay system on a basinwide, baywide, regional or local scale?
- If there is insufficient data or information to answer the above questions, identify the additional data/research required to answer the questions.

To ensure the findings from the Chesapeake Bay Water Column Contamination Critical Issues Forum are fully considered in continuing efforts to reevaluate and revise the Basinwide Toxics Reduction Strategy, the following process will be undertaken:

- A written summary of the forum proceedings, discussions and findings will be prepared by CBPO staff and distributed for review by the forum speakers.
- The forum summary will be presented to the Toxics Subcommittee for the Subcommittee's consideration and incorporation into the continuing Strategy reevaluation.
- The forum summary will be published by the Subcommittee as a Chesapeake Bay Program

- The forum summary will be published by the Subcommittee as a Chesapeake Bay Program Technical Report.

2. STATE WATER COLUMN CONTAMINANT MONITORING FINDINGS

Representatives from the Bay basin jurisdictions presented findings from their respective water column contaminant monitoring programs, with emphasis on concentration ranges observed at Bay tidal water stations. No formal presentations of water column data from the New York, Delaware, and West Virginia portions of the Chesapeake Bay basin were made as the available data were very limited.

Pennsylvania

Rod Kime, Pennsylvania Department of Natural Resources, described Pennsylvania's Water Quality Network and the resultant water column contaminant data. The network includes 168 stations statewide; 69 stations are in the Susquehanna River basin, and 4 stations are in the Potomac River basin. Prior to 1988, most stations were sampled monthly, however, metals analyses were only conducted once a year, during the August low flows. As samples were missed during the annual sampling schedule and detection limits varied year to year, only very obvious trends could be detected with this data.

Since 1989, all stations have been sampled monthly for all parameters, including aluminum, copper, lead, nickel, and zinc. Detection limits have been fixed at the lowest possible consistent value. The trends observed in the data collected since 1989 will be reported in the upcoming 1994 Pennsylvania 305 (b) report. In addition, each station is surveyed annually for macroinvertebrates, using rapid bioassessment protocols

The metals observed are those primarily associated with acid mine drainage in the upper Susquehanna River watershed: such as aluminum, cadmium, zinc, and lead. In addition, there are also problems associated with Mirex, PCBs and dioxin, which have caused fish consumption bans to be issued for the specific stream segments in the Susquehanna River watershed where these compounds have been found: Spring Creek in Centre County (Mirex), Susquehanna River in Luzerne County (PCBs), and Codorus and South Branch Codorous Creek in York County (dioxin).

Metals data collected since 1988 from the Water Quality Network's three stations on the mainstem Susquehanna River, the Juniata River station, the Octoraro Creek station, and all four stations in the Potomac River basin were presented (Table 1). The data showed significant exceedances (10% or more of the observations) of Pennsylvania water quality standards at all nine stations for aluminum, at two stations for copper (Octoraro and Little Wills/Potomac River), and at one station for lead (Little Wills/Potomac River). Sampling for cadmium and chromium at most stations was discontinued because these metals were not detected and, therefore, determined not to be a problem.

Table 1. Summary of water column metals concentration data from selected Pennsylvania Water Quality Network Stations 1988 to 1992.

Metal	Station name	Median conc.	Maximum conc.	Percent exceeding criteria	Less than detect
Al (ug/L)	Lower Susquehanna	492.5	11600.0	46%	4%
Al (ug/L)	Lower Susquehanna	312.0	4940.0	40%	16%
Al (ug/l)	Lower Susquehanna	257.0	3600.0	25%	9%
Al (ug/L)	Juniata-Susq. Trib.	187.0	3950.0	18%	22%
Al (ug/L)	Octoraro-Susq. Trib.	278.0	5910.0	25%	9%
Al (ug/L)	Potomac-Conococheague	271.5	6850.0	24%	20%
Al (ug/L)	Potomac-Licking Creek	177.0	5320.0	13%	24%
Al (ug/L)	Potomac-Little Wills	135.0	4510.0	12%	21%
Al (ug/L)	Potomac-Rock Creek	237.5	16800.0	21%	14%
Cu (ug/L)	Lower Susquehanna	10.0	50.0	7%	30%
Cu (ug/L)	Lower Susquehanna	10.0	50.0	2%	48%
Cu (ug/L)	Lower Susquehanna	10.0	31.0	2%	34%
Cu (ug/L)	Juniata-Susq. Trib.	10.0	32.0	0%	39%
Cu (ug/L)	Octoraro-Susq. Trib.	10.0	50.0	10%	32%
Cu (ug/L)	Potomac-Conococheague	10.0	21.0	2%	41%
Cu (ug/L)	Potomac-Licking Creek	10.0	25.0	2%	50%
Cu (ug/L)	Potomac-Little Wills	10.0	29.0	10%	32%
Cu (ug/L)	Potomac-Rock Creek	10.0	32.0	2%	36%
Ni (ug/L)	Lower Susquehanna	25.0	100.0	2%	38%
Ni (ug/L)	Lower Susquehanna	25.0	88.0	0%	53%
Ni (ug/L)	Lower Susquehanna	25.0	73.0	2%	44%

Table 1. Summary of water column metals concentration data from selected Pennsylvania Water Quality Network Stations 1988 to 1992.

Metal	Station name	Median conc.	Maximum conc.	Percent exceeding criteria	Less than detect
Ni (ug/L)	Juniata-Susq. Trib.	25.0	84.0	0%	51%
Ni (ug/L)	Octoraro-Susq. Trib.	25.0	118.0	0%	40%
Ni (ug/L)	Potomac-Conococheague	25.0	108.0	2%	48%
Ni (ug/L)	Potomac-Licking Creek	25.0	85.0	2%	49%
Ni (ug/L)	Potomac-Little Wills	25.0	98.0	0%	30%
Ni (ug/L)	Potomac-Rock Creek	25.0	47.0	2%	57%
Pb (ug/L)	Lower Susquehanna	4.0	10.1	2%	37%
Pb (ug/L)	Lower Susquehanna	4.0	15.6	2%	53%
Pb (ug/L)	Lower Susquehanna	4.0	13.9	2%	51%
Pb (ug/L)	Juniata-Susq. Trib.	4.0	283.7	3%	46%
Pb (ug/L)	Octoraro-Susq. Trib.	4.0	6.5	0%	45%
Pb (ug/L)	Potomac-Conococheague	4.0	10.0	2%	58%
Pb (ug/L)	Potomac-Licking Creek	4.0	6.9	3%	61%
Pb (ug/L)	Potomac-Little Wills	4.0	6.6	37%	39%
Pb (ug/L)	Potomac-Rock Creek	4.0	10.9	2%	56%
Zn (ug/L)	Lower Susquehanna	17.0	70.0	2%	9%
Zn (ug/L)	Lower Susquehanna	11.0	63.0	0%	27%
Zn (ug/L)	Lower Susquehanna	15.0	145.0	2%	19%
Zn (ug/L)	Juniata-Susq. Trib.	10.0	57.0	0%	42%
Zn (ug/L)	Octoraro-Susq. Trib.	10.0	51.0	0%	29%

Table 1. Summary of water column metals concentration data from selected Pennsylvania Water Quality Network Stations 1988 to 1992.

Metal	Station name	Median conc.	Maximum conc.	Percent exceeding criteria	Less than detect
Zn (ug/L)	Potomac-Conococheague	10.0	99.0	2%	47%
Zn (ug/L)	Potomac-Licking Creek	10.0	86.0	2%	47%
Zn (ug/L)	Potomac-Little Wills	10.0	87.0	0%	34%
Zn (ug/L)	Potomac-Rock Creek	10.0	65.0	2%	40%

Maryland

Deirdre Murphy, Maryland Department of the Environment, explained that Maryland does not routinely monitor water column contaminant concentrations because the concentrations are highly variable over time, many parameters are routinely below the detection limits, and it is expensive to properly characterize water column contaminants. The state relies on sediment, tissue and biological monitoring programs for assessment of contamination problems.

Results from three specific water column contaminant studies carried out by Maryland within the past five years were discussed by Deirdre Murphy. These three studies were: a 1988-1990 monitoring project which supported the development of Maryland's 304(l) list, a 1992 pilot pesticide monitoring project, and a 1992 urban pesticide monitoring project.

304(l) Monitoring Project

The locations of sampling sites selected for the Maryland 304(l) monitoring project were based on a review and analysis of existing water column contaminants data. Sites were selected where previously collected data indicated elevated contaminant levels. A total of 237 grab samples were collected over two periods during 1988-1990 from 41 sub-basin segments, where past sample collection and analysis detected concentrations of water column contaminants. Most of the samples were surface water column samples, although some bottom water column samples were also collected for analysis. Samples were analyzed for all 126 priority pollutants, except for dioxin and asbestos. Samples were not filtered so results were for whole water samples.

Detection limits (or ranges) for classes of organic priority pollutants are given below in ug/L.

Organochlorine Pesticides	0.02 - 0.1
PCB Aroclors	0.5 - 1
PAHs	2 - 10
Chlorinated Benzenes	2 - 10

Chlorinated Ethanes/Ethylenes	1 - 5
Halo Ethers	2 - 10
Phenols	10
Halomethanes	2 - 10
Nitrosamines	1 - 10
Phthalates	5 - 10
Other Organics	1 - 200

No detectable quantities of the organic priority pollutants were found in any of the 237 samples at the above ranges of detection limits. As three different laboratories conducted the sample analyses, there was some variation in detection limits. The total recoverable metals analyses did yield some detectable results, however, the number of samples with detectable levels varied among the metals (Table 2).

Table 2. Percent detections of metals in water column samples collected from 1989-1990 during the Maryland 304(l) Monitoring Project.

Metal	% Detection	Metal	% Detection
Aluminum	91%	Iron	99%
Arsenic	5%	Lead	17%
Antimony	< 1%	Mercury	9%
Beryllium	18%	Nickel	19%
Cadmium	8%	Selenium	10%
Chromium	16%	Silver	5%
Chromium(+6)	1%	Thallium	1%
Copper	14%	Zinc	68%

Those metals closely associated with soils, aluminum, iron, and zinc, were detected in most samples. The majority of the metals, however, were detected in less than 20 percent of all samples collected. In the case of several metals, the detections were 1 percent or less of the samples (e.g. antimony, hexavalent chromium, and thallium). Such results may be related to the range of the detection levels, as well as the contaminant levels in the samples. In most cases, the detection levels were not below the relevant EPA water quality criteria.

Of the total recoverable metals concentrations detected, some exceeded EPA water quality criteria. The primary contaminants for which this occurred were copper and cadmium at the freshwater sites. These sites were added to Maryland's 304(l)a(ii) list. The results of the 304(l) monitoring project provided conservative estimates of locations where total recoverable contaminant concentrations approached or exceeded EPA water quality criteria on the occasion sampled. As EPA's criteria are more directly relevant to dissolved metal concentrations, the availability of

dissolved metals data would have provided a better assessment of criteria exceedances.

1992 Watershed Pesticide Monitoring Project

The 1992 Maryland pilot watershed pesticide monitoring project assessed water column pesticide concentrations at a total of eleven stations in three regions: Eastern Shore (Little Northeast Creek, East Fork of Langford Creek, Morgan Creek, and German Branch), Central (White Marsh and Honeygo runs), and Western (Monocacy River, Big Pipe Creek, and Fishing Creek (control site)).

All stations were sampled on 4 to 5 occasions - during the late winter, spring, summer, and fall. Samples were analyzed for triazines and their metabolites, organochlorines, chlorpyrifos, carbofuran, pyrethroids, diflubenzuron, alachlor, and metolachlor, using EPA methods where available. These pesticides were chosen on the basis of use patterns within the sampled watersheds, potential toxicity, water solubility, and their presence on the Chesapeake Bay Toxics of Concern List.

Detection limits (or ranges) for these classes of pesticides are given below in ug/L:

Organochlorine Pesticides	0.01 - 1.0
Triazines	0.1 - .44
Alachlor, Metolachlor	0.01 - 0.1
Carbofuran	1.50
Diflubenzuron	0.025
Pyrethroids	0.2 - 1.0

No detectable levels of organochlorine pesticides, pyrethroids, or diflubenzuron were found at any of the eleven sample stations. Of the pesticides that were detected (Table 3), all concentrations were below all available EPA surface water criteria and drinking water criteria.

Table 3. Number of 1992 Maryland pilot watershed monitoring stations at which pesticides were detected in water column samples.

Pesticide	Number of stations at which pesticides were detected	Sampling events during which detectable concentrations were reported
Alachlor	2	spring and summer
Atrazine	2	spring, summer, and fall
Carbofuran	1	spring
Chlorpyrifos	1	spring
Cyanazine	2	spring

Pesticide	Number of stations at which pesticides were detected	Sampling events during which detectable concentrations were reported
Metolachlor	8	all collections at least 1 station
Simazine	3	spring and summer

Urban Watershed Pesticide Monitoring Project

The Maryland Urban Pesticide Monitoring Project, which is in its initial stages, involves determining pesticide use and monitoring pesticide concentrations in stream baseflow and storm runoff within three Baltimore City sub-watersheds. A pesticide use survey, which was conducted during the summer of 1992, was followed by limited sample collection and analysis efforts to screen for detectable concentrations of pesticides. From this information, a list of pesticides targeted for analysis was compiled. Followup sampling based on this list will be conducted this year.

Although Maryland does not routinely monitor for water column contaminants, but rather relies on sediment, tissue, and biological monitoring programs for water quality assessments. Water column monitoring is done only as part of more focused assessment efforts, such as the 304(l) and pesticides monitoring projects previously described.

While Maryland has only limited water column data, and those data indicate contaminant concentrations in the water column are ephemeral, more intensive sampling is necessary to get a broader picture of water column contamination.

In the discussion that followed, Deirdre Murphy stated that one limitation to the 304 (l) list was that entire river segments often get identified, because of contaminant data for a single site. About half of the sites sampled during the 1988-1990 monitoring project were placed the 304 (l) list. Other sites on Maryland's 304(l) list were identified from evaluations of existing ambient and effluent data.

District of Columbia

Anita Key, District of Columbia Department of Consumer and Regulatory Affairs, described the District of Columbia's water column toxics monitoring program. Since October 1982, water column samples have been collected quarterly from the following locations: Potomac River and its tributaries, Anacostia River and its tributaries, Washington Ship Channel, Rock Creek, C & O Canal, Kingman Lake, Watts Branch, and the Tidal Basin. Samples are analyzed for arsenic, cadmium, chromium, copper, iron, lead, mercury, selenium, and zinc.

The assessment of heavy metal contamination in the District of Columbia waters has been restricted by the level of detection achievable by the analytical laboratory relative to the concentration criterion specified in the District's water quality standards (Table 4). A substantial portion of water column metals results have been reported as below detection limits, likely due to high detection limits. Determination of whether results were often above certain criteria was not possible

particularly with the detection limits for lead, mercury, cadmium, and copper.

A review of metals data collected from the Potomac and Anacostia Rivers in 1989 and 1990 showed that chromium and zinc concentrations were at levels exceeding the District's water quality standards. In 1989, chromium concentrations were found to be in violation on two dates in the Potomac River and on three dates in the Anacostia River. In comparison, zinc concentrations were found to be in violation twice in 1989 and once in 1990 in the Potomac. In the Anacostia River, zinc levels were in violation of the water quality standard on four dates in 1989 and on two dates in 1990.

Water column concentrations of iron were also above the District's water quality standard of 1000 ug/L on several occasions in both the Potomac and Anacostia rivers in 1989 and 1990. Clay deposits in the Potomac watershed are rich in iron. Water samples containing clay particles have been found, at times, to exceed the District's water quality standard for iron.

Table 4. District of Columbia water quality standards and detection limits for metals monitored through the District's water column toxics monitoring program.

Metal	District water quality standard (ug/L)	Range of detection limits (ug/L)
Arsenic	90	
Cadmium*	1.17 (1989) 1.33 (1990)	5 - 100
Chromium	10	10 - 100
Copper*	12.23 (1989) 14.01 (1990)	10 - 100
Iron	1000	25 - 2,000
Lead*	3.34 (1989) 4.1 (1990)	50 - 1,000
Mercury	0.012	0.2 - 20.2
Selenium	40	
Zinc	50	10 - 2,000

Criteria calculation for: Cadmium ($e^{(0.7852 \ln(\text{hardness}) - 3.490)}$ ug/L); Copper ($e^{(0.8545 \ln(\text{hardness}) - 1.465)}$ ug/L); Lead ($e^{(1.2730 \ln(\text{hardness}) - 4.705)}$ ug/L); where hardness = 104 (1989) or 122 (1990).

Virginia

John Kennedy, Virginia Department of Environmental Quality, presented findings from Virginia's water column monitoring efforts based on data contained in two reports: "Comprehensive

Review of Selected Toxic Substances - Environmental Samples in Virginia, 1990", and the "Elizabeth River Toxics Initiative First Biennial Progress Report, 1990." Copies of either report are available upon request from the Virginia Department of Environmental Quality.

Ambient Network Synthesis Report

The review and synthesis of data from the past twenty years from Virginia's Ambient Water Quality Monitoring Network focused on the analysis of data for arsenic, beryllium, cadmium, copper, lead, mercury, aldrin, chlordane, DDT, dieldrin, and PCBs. These toxic substances were selected from an initial list of 88 contaminant parameters. Through this review process, baseline levels of water column contaminants were established for present and future comparisons, areas for recommended source identification were identified, and recommendations for future ambient monitoring were established.

Summaries of the water column contaminant results reported in "Comprehensive Review of Selected Toxic Substances - Environmental Samples in Virginia, 1990" for statewide data are provided below.

- Arsenic: Majority of the data (86%) were below detection limits; more than 99% of the data were below EPA and Virginia chronic water quality criteria.
- Beryllium: Only 2% of the data were above detection limits; all data were below EPA and Virginia acute and chronic water quality criteria.
- Cadmium: Majority of the data (94%) were below detection limits; a limited number of data exceeded acute chronic water quality criteria for freshwater and saltwater.
- Copper: Approximately 35% of the data were above detection limits, with 20% of the data exceeding the acute freshwater or saltwater criteria.
- Lead: About 50% of the values were below detection limits, with a limited number of exceedances of EPA freshwater acute criteria.
- Mercury: Majority of the data (94%) were at or below the applicable detection limits; all the reported detection limits were above the EPA water quality criteria.
- Aldrin: Majority of the data (94%) were below detection limits; a limited number of data exceeded Virginia's acute water quality criteria.
- Chlordane: Majority of the data (98%) were below detection limits; a very limited number of data exceeded EPA and Virginia chronic water quality criteria.
- DDT: Majority of the data (>99%) were below detection limits, with most of the detections from samples collected prior to the ban on DDT use.
- Dieldrin: Majority of the data (95%) were below detection limits; a limited number of data

exceeded Virginia and EPA chronic water quality criteria.

PCBs: Majority of the data (95%) were below detection limits; all the data above the detection limits exceeded EPA and Virginia chronic water quality criteria for freshwater and saltwater.

Elizabeth River Initiative

Through the Elizabeth River Initiative, water column total recoverable and dissolved concentrations of priority pollutant metals and organics were measured in March and June of 1989 at 12 stations. Detection limits for the metals analyzed were: cadmium - 9.3 ug/L; chromium - 50 ug/L; copper - 2.9 ug/L; lead - 5.6 ug/L; nickel - 10 ug/L; silver - 0.05 ug/L; zinc - 58 ug/L; and selenium - 54 ug/L; and mercury - 0.25 ug/L. In most cases the detection limits are set at the Virginia water quality criteria, which is also the EPA criteria. In the case of mercury, however, the detection limit is 0.25 ug/L, the state criteria is 0.10 ug/L and the EPA marine chronic criteria is 0.025 ug/L.

Results from the metals analyses were as follows:

- Total recoverable copper was detected during both sampling events at all stations, with concentrations ranging from 3.0 to 19.4 ug/L. These values were all above the Virginia water quality criteria of 2.9 ug/L.
- Total recoverable lead was detected at one Eastern Branch station at a concentration of 6.6 ug/L; this value exceeded the Virginia water quality criteria of 5.6 ug/L.
- Data from one Southern Branch station indicated levels of mercury above the Virginia water quality criteria of 0.10 ug/L.
- Total recoverable and dissolved nickel concentrations were detected at every monitoring station during the June sampling event.

The analyses for priority and non-priority organic contaminants resulted in the detection of very few compounds in the water column, with the concentrations detected being relatively low. Light weight aromatic compounds, typical of refined petroleum products, were detected at one station in the Elizabeth River and one station in the Southern Branch during June. These stations are in the vicinity of the Craney Island Naval Fuel Facility, the Craney Island Coast Guard Base and the Virginia Power Chesapeake Plant, respectively. Polynuclear aromatic hydrocarbons were found in samples from one station in the Elizabeth River (February sampling period only) as well as all five Southern Branch stations. The only other contaminants identified were plasticizers, or phthalates, observed at one Elizabeth River station and three Southern Branch stations.

Other Water Column Monitoring Programs

The majority of Virginia's continuing ambient monitoring efforts are focused on sediment and fish tissue sample collection and analysis and not on water column sampling. Two programs directed

at specific water column contaminants are the James River kepone monitoring program and tributyltin (TBT) monitoring in Hampton Roads.

The TBT monitoring program has been in effect for almost two years. Although its use has been restricted, TBT is still being detected in concentrations in excess of the Virginia water quality standard. This is probably due to the fact that TBT-based paints can be used legally on boats over 25 meters and on outboard motor shafts. In addition, in-place sediments may still be a source of TBT to the overlying water column.

3. FALL LINE TOXICS CONCENTRATION FINDINGS

Geological Survey

Linda Zynjuk, U. S. Geological Survey (USGS), presented findings from the Chesapeake Bay Fall Line Toxics Monitoring Program and the USGS National Stream Quality Accounting Network (NASQAN) program for concentrations of toxics substances measured at the Bay's major fall lines. The fall line is the geological point at which the piedmont meets the coastal plain; where free flowing freshwater streams and rivers meet tidally influenced surface waters. Concentrations of toxic substances measured at the fall line reflect the cumulative inputs of all point and nonpoint sources from the above fall line watershed, providing an ideal place at which to measure fluvial transports of toxic substances into the Bay's tidal waters.

Through the Chesapeake Bay Fall Line Monitoring Program, baseflow and storm events samples have been collected and analyzed at the Susquehanna and James River fall line stations since 1990 and at Potomac River fall line station since 1991. Combined, these rivers comprise 80 percent of the freshwater entering the Bay and, therefore, are fairly representative of majority of fall line loadings of toxic substances to the Bay. Additional quarterly sampling of metals has been conducted through the USGS NASQAN program at the Susquehanna, Patuxent, Potomac, Choptank, Rappahannock, Pamunkey, Mattaponi, James and Appomattox river fall lines over the past 13 years.

USGS NASQAN Program

Through a review of the USGS NASQAN data, Linda Zynjuk presented the following findings. In the data summary provided below, values below detection limits were set to the detection limit for calculation of the mean concentrations. All data are total recoverable (metals) or total (pesticides, organics) water column measurements.

- Mean chromium concentrations were highest at the Choptank, Rappahannock and Pamunkey River fall lines, where mean concentrations ranged from 17-21 ug/L in both cases. Mean chromium concentrations were the lowest at the Susquehanna and James River fall lines, where concentrations were less than 8 ug/L.
- No water quality criterion exists for total recoverable chromium. However, for the trivalent and hexavalent forms the EPA water quality criteria is 210 ug/L and 11 ug/L, respectively. The majority of total recoverable chromium is in the trivalent form, in which case the highest concentrations observed (60 ug/L) are low relative to the criteria.

- Mean copper concentrations ranged from 3.5 - 7.6 ug/L, all below the EPA water quality criteria of 12 ug/L. The highest value recorded (84 ug/L) was at the James River fall line.
- Mean lead concentrations ranged from 4.9 - 59.2 ug/L among all the river fall lines, except for the Appomattox River fall line which had a mean concentration of 3.0 ug/L. The EPA freshwater chronic water quality criterion for lead is 3.2 ug/L.
- Atrazine concentrations were not analyzed for at the Appomattox, Mattaponi, Rappahannock, or Patuxent River fall lines. The Susquehanna River fall line had the highest concentration (1.2 ug/L), with mean concentrations ranging below 0.18 ug/L. While there is no water quality criterion for atrazine, the EPA drinking water criterion is set at 3 ug/L.

Note: During the resultant discussion, Lenwood Hall mentioned that most of the atrazine in the water column is not available to organisms. Much higher levels than what were reported here would be needed for organismal effects.

- Mean total PCB concentrations ranged from 0.02 - 0.9 ug/L. The EPA freshwater chronic criterion for total PCB is 0.014 ug/L. Total PCB concentrations were not analyzed at the Appomattox, Mattaponi, Rappahannock, or Patuxent River fall lines.
- The range of mean Chlordane concentrations was 0.01 - 0.09 ug/L. The EPA freshwater chronic criterion is 0.0043 ug/L. Chlordane concentrations were not analyzed for at Appomattox, Mattaponi, Rappahannock, or Patuxent River fall lines

Bay Fall Line Toxics Monitoring Program

Linda Zynjuk also presented a summary of trace metal and pesticide concentration data collected at the Susquehanna River at Conowingo, Maryland during the 1990-1991 (Tables 5 and 6). Elevated lead and copper concentrations were measured, however, the observed concentrations were close to the EPA freshwater criteria. Chromium concentrations were low enough not to indicate a problem. Seasonal-based temporal patterns were observed for atrazine.

Trace metals and pesticide data from the James River at Cartersville, Virginia for the period of 1990-1991 showed that elevated levels of copper and lead occurred during the two year period, significantly exceeding the EPA freshwater chronic criteria for both metals (Tables 5 and 6). Chromium concentrations did not indicate a problem. Patterns in atrazine concentrations were related to season and high flow.

Metropolitan Washington Council of Governments

Adrienne Nemura, Metropolitan Washington Council of Governments, presented pesticide, PCB, and trace metal data, collected from March through September of 1992, for the Potomac, James and Susquehanna Rivers fall lines. The data collection was a cooperative effort between the Maryland Department of the Environment, the U. S. Geological Survey, the Occoquan Watershed Monitoring Laboratory, George Mason University, and the Metropolitan Washington Council of Governments. One important aspect of the sampling program was the development of appropriate

detection limits for all parameters to increase the number of detects. Adrienne Nemura presented both the percent of observations which were greater than the detection limits, as well as the maximum observed concentration for most of the parameters that were sampled. It was stressed that the data collection was only for six months and represented only a limited range for both storm and base flows.

The application of ultraclean field sampling technique at the Susquehanna River fall line station resulted in below detection limit data for the following previously detected metals: arsenic, barium, cadmium and mercury. However, for some metals, such as zinc, chromium, lead, nickel and copper, ultraclean sampling may not have been necessary. Organonitrogen and organophosphorus pesticides data were presented for all three fall lines. Of the pesticides which were screened, only simazine, atrazine, alachlor, metolachlor, and cyanide were present in measurable quantities. Preliminary loading estimates for trace elements for Potomac River fall line revealed a wide range in loading estimates, depending on how measurements below the detection limits are treated. Simazine, metolachlor, cyanazine, and especially atrazine all had a wide range of concentrations, which could be season and flow dependent.

Dissolved organic concentrations of organochlorine pesticides were highest at the Susquehanna river fall line, although a high dissolved concentration of oxy-chlordane was measured at the Potomac River fall line. Aldrin, oxychlordane, gamma-chlordane, alpha-chlordane, and dieldrin were present in all three rivers in both the dissolved and particulate forms. Permethrin, fenvalerate, and 4,4'-DDT were not present in measurable amounts in any river sampled. PCBs (112 congeners) were present in both dissolved and particulate forms in all three rivers, with the highest total PCB concentration of 39 mg/L was measured in a storm flow sample collected at the Potomac River fall line.

Reliable load estimates could not be developed using the present 6 month data set as correlations with flow and season are crude at best. The additional three months of data being collected will still only provide order of magnitude estimates. In order to gain confidence in load estimates, it is necessary to know if the detection limits are consistent with the bulk of the observed concentrations. Additional data is needed for most parameters to draw any conclusions about confidence in load estimates.

Ms. Nemura summarized the researchers' preliminary recommendations on future fall line toxics monitoring, which included: (1) comparison of discrete and automated sampling, (2) increased base flow monitoring, (3) increased number of storm events sampled, (4) increased sampling of organics in April through June, and (5) a special study of toxic substances present in sediments behind the dams on the Susquehanna River. Preliminary program recommendations included: (1) continuation of sampling programs on all three rivers to extend data set, (2) expanding the sampling program to include other representative tributaries, (3) assess possible cost savings (from dropping parameters consistently below detection limits), and (4) assess future data needs reflecting revised Bay Program directions for reducing toxics.

Table 5. Summary of combined 1990-1991 fall line trace metal concentration data collected the Susquehanna River at Conowingo Dam, Maryland and the James River at Cartersville, Virginia. Diss = dissolved, TR = total recoverable.

Metal	Susquehanna River		James River	
	Percent detections	Concentration range (ug/L)	Percent detections	Concentration range (ug/L)
Aluminum, Diss	85 %	< 10 - 70	92 %	< 10 - 260
Arsenic, Diss	17 %	< 1 - 1	0 %	< 1
Arsenic, TR	4.8 %	< 1 - 1	3.8 %	< 1 - 3
Barium, TR	25 %	< 100 - 100	6.7 %	< 100 - 100
Cadmium, Diss	17 %	< 1 - 1	0 %	< 1
Cadmium, TR	0 %	< 1	1.9 %	< 1 - 1
Chromium, Diss	18 %	< 1 - 2	15.4 %	< 1 - 2
Chromium, TR	79 %	< 1 - 10	72 %	< 1 - 18
Copper, Diss	98 %	< 1 - 8	88 %	< 1 - 9
Copper, TR	100 %	2 - 11	98 %	< 2 - 84
Iron, Diss	86 %	< 3 - 67	100 %	50 - 150
Iron, TR	100 %	160 - 690	100 %	30 - 7000
Lead, Diss	30 %	< 1 - 5	56 %	< 1 - 5
Lead, TR	95 %	< 1 - 17	100 %	1 - 96
Lithium, TR	0 %	< 1	0 %	< 1
Magnesium, Diss	100 %	3.6 - 14	100 %	3.1 - 8.3
Manganese, TR	100 %	90 - 190	94 %	10 - 450
Mercury, Diss	20 %	< .1 - .2	0 %	< .1
Mercury, TR	17 %	< .1 - .1	3.6 %	< .1 - .1
Nickel, Diss	98 %	1 - 5	59 %	< 1 - 6
Nickel, TR	100 %	2 - 23	94 %	< 1 - 18
Selenium, TR	0 %	< 1	1.9 %	< 1 - 1

- To measure a suite of inorganic and organic contaminants in the water column at each station during the toxicity tests.

Ambient toxicity tests were conducted in the Elizabeth (1990), Patapsco (1990, 1991), Wye (1990, 1991), and Potomac (1990, 1991) rivers. The organisms used were *Eurytemora affinis*, *Palaemoneta pugio*, *Cyprindon variegatus*, *Ceriodaphnia* sp., and *Pimephales promelas*; however, not all organisms were used at all stations.

The 1990 ambient toxicity water column data reflect significant mortality in two of the test species in the Elizabeth River, one of three test species in the Patapsco River, and no effects from the three species in the Wye River. Generally, no effects were reported in the three tidal fresh stations in the Potomac River. Significant mortality was reported from one of the three tests at both the Morgantown and Dahlgren (saltwater) stations in the Potomac River.

In presenting the water column metals data collected during the 1990 ambient toxicity tests, Lenwood Hall noted values which exceeded the EPA chronic saltwater water quality criteria. In the Elizabeth River, copper (3.3 ug/L, 3.7 ug/L) and mercury (0.22 ug/L) exceeded the criteria. At the Patapsco River sites, nickel (10.8 ug/L) exceeded the criterion. For the Wye River, copper (5.4 ug/L) and nickel (18 ug/L) were above the EPA criteria. Other exceedances were: Indian Head - cadmium (1.32 ug/L); Freestone Point - cadmium (1.48 ug/L); and Morgantown - mercury (.29 ug/L), nickel (8.4 ug/L).

The 1990 water column data were summarized as follows:

- The number of potentially toxic concentrations of metals was highest at the Elizabeth River site where the greatest number of toxic effects were reported from toxicity tests.
- The second most toxic area, the Patapsco River, also contained potentially toxic concentrations of metals in the water column.
- Toxic effects in the Potomac River were reported in ambient toxicity tests with and without measured concentrations of toxic substances at levels associated with adverse effects (i.e. concentrations elevated above EPA water quality criteria).

Testing continued in 1991 using the mysid shrimp in addition to *Eurytemora affinis*, sheepshead minnow, and grass shrimp. Four stations were tested two times each.

In 1991, exceedances of EPA water quality criteria were found at the following stations: Dahlgren - copper (3.4, 4.5, 3.7 ug/L); Morgantown - copper (5.5, 4.2 ug/L); Wye River - copper (2.9 ug/L), nickel (9.3 ug/L); Patapsco River - copper (3.7, 3.7 ug/L).

The 1991 water column data are summarized as follows:

- Significant mortality occurred during the first sheepshead minnow larval test at the Wye River concurrently with the presence of potentially toxic concentrations of metals and a suspected toxic dinoflagellate.

- Significant mortality of another test species at the Wye River site (*Eurytemora affinis*) occurred without concurrent measurement of concentrations of toxic substances above EPA water quality criteria.
- A sublethal effect, reduced growth of sheepshead minnows, was reported at both Potomac River sites with the presence of elevated levels of toxic substances.

5. REVIEW OF BAY WATER COLUMN METALS CONCENTRATIONS

Fritz Riedel, Benedict Estuarine Research Laboratory, presented an overview of the ranges of metal concentrations observed in Bay waters during the past decade, including data from ongoing work supported by the Chesapeake Bay Toxics Research Program. Most of the data presented were collected in the mainstem Bay, with some data available for the tidal tributaries.

From the data collected in the Bay mainstem, it appears that observed copper and lead concentrations most closely approach EPA water quality criteria (Table 7). For lead, this reflects a single sample which was probably contaminated. However, copper has often been seen at these levels in a variety of habitats in the Chesapeake Bay, primarily the upstream estuarine portions of tributaries. A few very high concentrations of iron and manganese, probably caused by flux from sediment into anoxic bottom waters, were reported.

Table 7. Dissolved metals concentration ranges reported in the Chesapeake Bay mainstem.

Metal	Range of Dissolved Concentrations (ug/L)	EPA Chronic Freshwater Criteria	EPA Marine Criteria
Arsenic	0.1 - 2	190	36
Cadmium	0.001 - .09	1.0 *	9.3
Cobalt	0.002 - .2		
Chromium	0.02 - 1.5	150 *	50
Copper	0.08 - 2.0	10 *	2.9
Iron	0.09 - 100		
Lead	0.01 - 1.5	2.0	8.5
Mercury	0.00005 - 0.0005	0.012	0.025
Manganese	0.4 - 400		
Molybdenum	0.6 - 7		
Nickel	0.8 - 3	100	8.3

Metal	Range of Dissolved Concentrations (ug/L)	EPA Chronic Freshwater Criteria	EPA Marine Criteria
Tin	0.01 - 1.5		
Selenium	0.02 - 0.1	5.0	71
Zinc	0.1 - 10	70	86

* Actual value depends on water hardness, value shown fits within expected hardness range for Chesapeake Bay.

In discussing levels of trace metals, Fritz Riedel explained that it is important to determine whether the source is natural or anthropogenic in origin. Sources of trace metals might include "natural" weathering and runoff, wastewater treatment plants and industrial discharges, agriculture, and seawater. Air inputs could come from dry deposition, wet deposition, or gas phase metals, such as mercury. Sediment related sources of metals entering the water column include anoxic reduction and release of iron, manganese, and arsenic, and oxidation of organics and diagenesis resulting in the release of copper and chromium.

Several metals have different chemical forms which may be present simultaneously, although with different geochemical behavior and toxicity. Several examples are given below.

- **Arsenic**

Arsenate	More toxic to plants
Arsenite	More toxic to animals
Monomethyl arsenate	Highly toxic
Dimethyl arsenite	Less toxic

- **Chromium**

Hexavalent Chromium	Soluble, highly toxic
Trivalent Chromium	Particle reactive, less toxic

- **Copper, Cadmium, Zinc (maybe others)**

Organically complexed	Not biologically available
Free ion	Biologically available

- **Mercury**

Inorganic Mercury	Highly toxic
Methyl mercury	Very highly toxic, biomagnifying

- Selenium

Selenate	Toxic, bioaccumulative
Selenite	More toxic, bioaccumulative, more toxic to animals
Organic Selenium	Less toxic, bioaccumulative?

The monomethyl and dimethyl forms of arsenic are produced by organisms. Over 99% of copper is originally complexed, as is 50% of cadmium and zinc. Mercury is toxic in very low concentrations; methyl mercury is a neurotoxic, and is truly biomagnified (i.e. concentrations in tissue tend to increase with each step in the food chain).

In presenting data for arsenic speciation in the Patuxent River estuary, Fritz Reidel stated that dinoflagellates and other algae metabolize arsenate to the dimethyl arsenite form. Arsenate has been shown to have effects on phytoplankton species composition at concentrations approaching those found in the Bay. The effect generally consists of a shift of species from larger diatoms to smaller diatoms and other small algae, such as flagellates. Such shifts have the potential of altering trophic relationships, probably in a deleterious manner, by shifting carbon away from the "standard" food chain model (e.g. algae, copepod, fish) and toward the "microbial loop" (alga, microzooplankton, bacteria).

Data for dissolved arsenic in the Patuxent River from July 1992 were presented. Differences in bottom versus surface samples show a benthic flux in arsenic. Copper was measured at 0.5-3 ug/L in the Patuxent River. These values were high, but do not reflect gross contamination. High levels of copper, silver, and cadmium in Patuxent River oysters may be due to a low salinity regime. Oysters have the tendency to uptake much higher levels of metals at low salinities than at higher salinities, at a constant metal exposure, unlike some other shellfish such as mussels. This presents a problem in using oysters as an indicator of toxic metal contamination. Although mercury levels in water were found to be 3 or 4 orders of magnitude less than other metals, this may represent a problem due to mercury's extreme toxicity and tendency bioaccumulate.

In addressing the forum questions, Fritz Riedel offered the following analysis.

Have we defined the relative magnitude and extent of water column contamination in the Chesapeake Bay System ?

"Yes, no, and maybe, depending on the metal and the site. By and large the data suggest that there is not serious widespread contamination in the mainstem Bay. Clearly, some metals are elevated in some tributaries, and industrial areas. However, for many elements at many sites it is unclear whether present concentrations are 'natural' or 'contaminant'."

Does this give us reason to believe that toxic trace elements are causing or can cause an impact (bioaccumulation or toxicity) on any scale?

"Yes, bioaccumulation of several metals (cadmium, copper, mercury and silver)

occurs in selected sites and organisms around the Bay. However, it is very difficult to demonstrate that trace elements are having a deleterious effect (toxic?) on organisms."

What additional data or research are needed to answer questions the above questions better ?

"Analytical methods have improved since 1979 (when the majority of the data discussed were collected) both in sensitivity and specificity (form of the element). We are at a stage where detailed attempts to examine the behavior of trace elements seasonally and over specific areas will better tell us whether the levels present are 'contaminants' or 'natural'. The costs will not be trivial. Improved biological techniques will be required to test for and detect toxicity at 'ambient' levels."

6. REVIEW OF BAY WATER COLUMN ORGANICS/TBT CONCENTRATIONS

Mike Unger, Virginia Institute of Marine Science, presented an overview of organic contaminant concentrations observed in Bay waters during the past decade. Findings from past and continuing water column monitoring of tributyltin concentrations were also discussed.

Several problems associated with making water column measurements of organic contaminants were outlined:

- Hydrophobic compounds readily partition to sediments and biota.
- Most organic compounds exist at concentrations below conventional analytical detection limits (i.e. sub ppb level).
- Reported laboratory toxicity values often exceed the solubility of the organic compound because of the use of solubility enhancers to introduce the compound into the toxicity test vessel.

The available water column for organic contaminants for the Chesapeake Bay, above detection limits, was so limited an effective summary of the information could not be presented.

Tributyltin

Because of the extreme toxicity of tributyltin (TBT), analytical capabilities to measure concentrations down to 1 part per trillion were developed. This enhanced analytical capability lead to TBT monitoring programs in the mid 1980s and the subsequent enactment of legislation limiting TBT use (1987-1988).

Recent data show an obvious decrease in TBT concentrations over time. For some areas, however, such as Old Point Comfort and Sarah Creek in the York River, TBT levels have remained fairly constant. One explanation for these stable concentrations is that TBT sorbs to sediments, then later desorbs, reentering the water column. In this way, sediments can act as a source of TBT.

Mike Unger discussed laboratory data which show the absorption isotherm for TBT. These data showed that TBT reestablished equilibrium concentrations after only 2 hours. The half life of TBT in water is 7-14 days. In sediments, however, the half life is much longer.

There are areas in the Chesapeake Bay, near marinas and drydocks, where TBT concentrations approach levels which have been shown to be toxic to estuarine organisms in acute and chronic laboratory studies, but these concentrations have been decreasing. Summarizing six years of TBT monitoring data, Mike Unger concluded the following:

- TBT concentrations are highest near marinas.
- Concentrations have declined in Chesapeake Bay since legislation for TBT has been enacted.
- Concentrations may be leveling off in some areas.
- In-place sediments may be important sources of TBT.
- Legal use (painting of large vessels) of TBT may increase, however, new paints have lower leaching rates than paints used prior to legislation in 1988.

7. DISCUSSION

The four critical issue forum questions were addressed by the participants as part of the effort to define the extent and magnitude water column contamination in the Chesapeake Bay basin. Two major points were made and reiterated throughout the discussion: 1) existing data are insufficient (i.e. spatially, temporally, and geochemically limited) to determine the nature, magnitude, and extent of water column contamination in the Chesapeake Bay basin; and 2) because the analysis of water column samples is expensive and available resources are limited, the focus of future monitoring or assessment of Bay basin water column contamination needs to be determined. At present, water column metals data for Bay tidal waters are limited; water column organic for Bay tidal waters are very limited or rare.

Another important point raised throughout the discussion was that there are two different purposes for collecting water column contaminants data: 1) to understand processes and transport of chemicals in the water column and their relative bioavailability; and 2) as a basis for states to determine if water quality standards are being met. When water column contaminants data are collected for these two distinctly different purposes, further issues arise. Water column metals data are often collected and reported in two different forms - dissolved for understanding processes and total recoverable for assessing violations of water quality standards - which cannot be directly compared.

Water column data routinely collected and analyzed for regulatory purposes is often analyzed using methods with very high detection limits, yielding many nondetect values. Contamination of the samples during sample collection and handling is also an inherent problem.

Water column data collected for the purpose of understanding processes is often of better

quality (lower detection limits, use of collection and handling procedures resulting in less sample contamination), leading to a better general understanding of the geochemistry of trace elements and organics in the water column. Forum participants suggested that it may be beneficial to utilize water column processes directed research for this purpose, rather than rely on basinwide monitoring efforts to address these needs.

Several forum participants pointed out there is little chance that more sensitive analytical methods for detecting contaminants in the water column will be developed without some impetus to drive the resource intensive methods development process. In the past, efforts to develop and refine analytical methods that can detect small concentrations of substances have been chemical specific.

For example, large investments of time and resources were to improve the methods for detecting small quantities of tributyltin (TBT). These efforts stemmed from the extreme toxicity of this compound, as was evidenced by the fact that toxicity was observed when the concentrations of TBT were below the existing detection limits. Researchers had to develop more sensitive analytical methods to detect TBT in the parts per trillion range, the concentration range TBT was determined to be toxic to estuarine and marine organisms. This work, however, was mostly funded by the U.S. Navy, and driven by the extreme toxicity of TBT. This type of intensive methods development might be difficult to replicate for other substances.

Very few routine monitoring programs target repeated sampling of water column contaminants, particularly in the Bay's tidal waters. The result is there are few areas with a sufficient temporal record to show larger scale patterns and trends.

With limited resources available, forum participants recommended a determination be made as to whether and how resources should be directed towards further studying metals and organics contamination in the water column. Copper and arsenic were suggested as priority elements for more intensive assessment. Copper has been seen repeatedly in high concentrations and exhibits toxic effects. According to work done by Jim Sanders, chronic low levels of arsenic killed some species of Bay phytoplankton and has been incorporated into higher trophic levels through consumption of contaminated phytoplankton.

It was suggested as selenium contamination has had serious consequences in other systems at relatively low concentrations, due to its bioaccumulative nature, it should be further investigated in Chesapeake Bay. Because water column testing is so expensive, and many areas do not appear to have problems, specific substances, such as mercury, or processes, such as sediment fluxes, should be targeted because there is concern or evidence that there could be a problem in Chesapeake Bay. There was general consensus that water column processes do need to be understood, and that perhaps the focus should be on both a chemical and regional basis, rather than on maintaining broad monitoring programs.

The general question of the usefulness of water column contaminants data, as opposed to sediment or fish tissue contaminants data, was raised. Water column analysis of contaminants is expensive and, therefore, the need for it must be well substantiated. Several supporting reasons to do water column work were: 1) for metals, comparisons cannot be made between water column and sediment concentrations; 2) bioavailability cannot be determined from sediment concentrations; and

3) at this time, fish tissue residue data only reflect human health issues, therefore, water column testing is also needed to look at ecosystem health.

It was generally agreed that the data are spatially and temporally limited, and that the extent and magnitude of the problem cannot be characterized based on this data. Although limited, existing data do suggest problems, substances, or areas where there is a need to focus water column sampling efforts.

When asked whether a level of concern can be derived from a review of the available data, relative to the water column habitat, the general consensus of the forum participants was that the available data were too limited to answer this question. Several additional points emerged in response to this discussion:

- Long term chronic levels of water column contaminants may have adverse effects.
- More information is needed concerning low levels of contamination over longer periods of time.
- Water quality criteria are not always sufficient to prevent effects.
- A concerted effort is needed to establish water quality criteria specific to the Chesapeake Bay.
- There is a great need to focus research on a chemical specific and region specific basis.
- There is a need to determine what constitutes a problem for water column habitats.
- Over the past several years, there has been a reduction in point source effluent toxicity as evidenced by Maryland's effluent toxicity testing program.
- Nonpoint sources of water column contamination remain largely unknown.

The question of whether the Toxics Subcommittee should recommend specific sampling, handling, and analytical methodologies protocols for future water column contaminants monitoring throughout the Bay basin was raised for further consideration during the reevaluation of the Basinwide Toxics Reduction Strategy.

Roster of Participants
Chesapeake Bay Water Column Contaminants
Critical Issue Forum

April 14, 1993

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