



# COMMONWEALTH of VIRGINIA

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December 27, 2006

### MEMORANDUM:

TO: The Honorable Timothy M. Kaine  
  
The Honorable Charles R. Hawkins, Chair  
Senate Agriculture, Conservation and Natural Resources Committee  
  
The Honorable M. Kirkland Cox, Chair  
House Agriculture, Chesapeake and Natural Resources Committee

FROM: David K. Paylor 

SUBJECT: The Reduction of Toxics in State Waters Report 2006

In accordance with § 62.1-44.17:3 of the *Code of Virginia*, the Department of Environmental Quality has completed its annual report on the status of the State Water Control Board's efforts to reduce the level of toxic substances in state waters.

The Department of Environmental Quality is committed to preventing the contamination of the Commonwealth's waters by toxics, monitoring State waters for the presence of toxics and implementing remedial measures to reduce and/or eliminate toxics found in State waters. The primary objective of this report is to document the Commonwealth's commitment.

The full report is being made available at [www.deq.virginia.gov/regulations/reports.html](http://www.deq.virginia.gov/regulations/reports.html). If you need further information or would like a hard copy of this report, please contact me or Rick Linker at 804-698-4195.

**The Virginia**

**DEPARTMENT OF ENVIRONMENTAL QUALITY**

# **The Reduction of Toxics in State Waters**

## **State Fiscal Year 2006**

**A REPORT TO**

**THE GENERAL ASSEMBLY OF VIRGINIA**

The complete set of tables, figures and appendices associated with this report, as well as the text document itself, are available on the WebPages of the Department of Environmental Quality at

<http://www.deq.virginia.gov/watermonitoring/>.



**COMMONWEALTH OF VIRGINIA**  
**RICHMOND**  
**JANUARY 1, 2007**

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## Table of Acronyms and Abbreviations

AMD	Acid Mine Drainage
ALU	Aquatic Life Designated Use
B4B	Businesses for the Bay Program
BDE	Bromated diphenyl ether
B-IBI	Benthic Index of Biotic Integrity
CBP	Chesapeake Bay Program
CEDS	Comprehensive Environmental Data System
CIMS	CBP Information Management System
CVs	Consensus-Based Sediment Quality Guidelines – Critical values for contaminants in freshwater sediment (replace previously utilized ER-L and ER-M values for assessment of freshwater sediment; MacDonald et al. 2000). See also PEC, below.
DCLS	Division of Consolidated Laboratory Services
DEQ	Department of Environmental Quality
DMR	Discharge Monitoring Report
EDAS	Ecological Data Application System (database)
EEC	Extreme Effects Concentration – the concentration of a contaminant above which adverse effects to sediment-dwelling organisms frequently or always occur
ELG	Effluent Limitation Guidelines
EMS	Environmental Management System
ER-L	Effects Range-Low
ER-M	Effects Range-Moderate
EPA	Environmental Protection Agency
FY	Fiscal year
IBI	Index of Biological Integrity
MEC	Midrange Effect Concentration – the concentration of a contaminant above which adverse effects to sediment-dwelling organisms frequently occur
MGD	Millions of Gallons per Day
MonPlan	Annual Water Quality Monitoring Plan
MY	Monitoring year
NOAA	National Oceanic and Atmospheric Administration
NPEP	National Partnership for Environmental Priorities
NPS	Non-Point Source (pollution)
OCP	Organochlorine Pesticide
OPP or OP2	Office of Pollution Prevention
PAH	Polycyclic Aromatic Hydrocarbon
PCB	Polychlorinated biphenyl
PEC	Consensus-based <u>Probable Effects Concentrations</u> for chemical contaminants in freshwater sediments (MacDonald et al. 2000). See also CV, above.
POTW	Publicly Owned Treatment Works
P2 or PP	DEQ’s Pollution Prevention Program
ProbMon	Probabilistic Monitoring Program
QAPP	Quality Assurance Program and Project Plan
RBP	Rapid Bioassessment Protocol
SIC	Standard Industrial Classification
SOP	Standard Operating Procedure
SPMD	Semi-Permeable Membrane Device

STORET	EPA's national ecological database (short for data 'STOrage and RETrieval' system)
SV	Screening Value
TBT	Tributyltin
TEC	Threshold Effect Concentration – the concentration of a contaminant below which adverse effects to sediment-dwelling organisms are unlikely to occur
TMDL	Total Maximum Daily Load study
TMP	Toxics Management Program
TMR	Toxics Management Regulation
TOC	Toxics of Concern
TRE	Toxics Reduction Evaluation
TRI	Toxic Release Inventory
TRISWat	Toxics Reduction in State Waters (report)
USGS	United States Geological Survey
WISE	Virginia Information Source for Energy (Website)
VDH	Virginia Department of Health
VEEP	Virginia Environmental Excellence Program
VERC	Virginia Emergency Response Council
VH2E	Virginia Hospitals for a Healthy Environment
VIMS	Virginia Institute of Marine Science
VIP2	Virginia Innovations in Pollution Prevention
VMN	Virginia Mentoring Network
VPDES	Virginia Pollutant Discharge Elimination System
VPI	Virginia Polytechnic Institute and State University
WET	Whole Effluent Toxicity
WQBEL	Water-Quality-Based Effluent Limitation
WQM	Water Quality Monitoring
WQMA	Office of Water Quality Monitoring and Assessment
WQS	Water Quality Standard(s)

## Executive Summary

On January 1<sup>st</sup> of each year, the Virginia DEQ submits the annual Toxics Reduction in State Waters (TRISWat) Report to the Governor and General Assembly of the Commonwealth in accordance with Virginia Code § 62.1 - 44.17:3.

The primary objective of the TRISWat Report is to document the Commonwealth's progress toward reducing toxics in state waters and improving water quality. This commitment includes:

1. The prevention of contamination of the Commonwealth's waters by toxics,
2. The continued monitoring of those waters for the presence of toxics and
3. The implementation of remedial measures to reduce and/or eliminate toxics found in the Commonwealth's waters.

This report serves to keep the members of the General Assembly informed of the on-going efforts to achieve these objectives and, as a public document, provides the public with objective, concise, easily assimilated information on toxics not readily available from other sources.

**Monitoring:** In 2004 DEQ revised, updated and expanded its Water Quality Monitoring Strategy to include modifications in design, adoption of new monitoring technologies, and new EPA guidelines developed since 2000. After integrating a number of suggestions received from EPA in April of 2004, a revised draft was made available for public comment in August. The final draft was submitted to EPA in September 2004. EPA subsequently indicated that the Strategy was acceptable in its revised form, and DEQ has applied its principles since the fall of 2004. The agency intends to submit an updated Strategy revision to EPA in the spring of 2007, to incorporate several minor modifications in monitoring schedules and additional water quality criteria and assessment procedures that have evolved in the interim. Tentative implementation of the revised Strategy will be initiated in January 2007.

Summer (July-September) 2006 comprised the seventh year of DEQ's estuarine probabilistic monitoring and the spring and summer of 2006 comprised the sixth year of its freshwater probabilistic monitoring (ProbMon). Sampling for dissolved trace metals, as well as sediment metals and organics, has continued at both freshwater and estuarine ProbMon sites. The results of spring (March-June) freshwater probabilistic sampling for Monitoring Year 2006 are included in this report. Results from summer (July-September) sampling in 2006 will be included in next year's report.

The results from summer 2003 Semi-Permeable Membrane Device (SPMD) sampling of dissolved organic contaminants at freshwater probabilistic sites are now available on DEQ's WebPages and are partially summarized in this Toxics Reduction Report. The success of this SPMD study and declining costs for SPMD analyses have prompted the agency to apply SPMD sampling technology in a number of PCB-related special studies.

Beginning with the 2006 Integrated 305(b)/303(d) Report, sediment chemistry, sediment toxicity and benthic taxonomic results from DEQ's Estuarine Probabilistic Monitoring Program were used for a toxics-related "Weight-of-Evidence" assessment of aquatic life use in estuarine waters. These results, primarily from minor tidal tributaries, complement those from the Chesapeake Bay Program's benthic probabilistic monitoring program, which emphasizes the mainstems of major tidal tributaries and the Bay itself.

General characterizations based on probabilistic toxics monitoring have revealed that statewide concentrations of priority toxicants (metals and organics) in sediment are generally well below established sediment screening criteria, except in previously identified hotspots that are already the focus of TMDL-related special studies. Water column monitoring of toxic organic contaminants using Semipermeable Membrane Devices (SPMDs) has revealed the same pattern. The maximum observed concentrations of

most dissolved hydrophobic organic compounds were orders of magnitude below human health criteria. The single exception was for polychlorinated biphenyls (PCBs), reflecting the cosmopolitan distribution already revealed by fish consumption advisories. Further analyses of freshwater probabilistic monitoring results in 2005 revealed that, even at low concentrations, the measured values for nine of the 20 priority organics with established water quality standards were significantly correlated with the degree of urban development in the associated watersheds. No such trends were identified for agricultural or forest land use patterns. More detailed, geographically specific conclusions about toxics-related water quality concerns were presented in the 2006 Integrated 305(b)/303(d) Water Quality Assessment Report.

**Permitting:** DEQ's Toxics Management Program (TMP) currently includes 300 facilities with 738 outfalls that have active permit-defined toxics limits in their effluents in DEQ's Comprehensive Environmental Data System (CEDS) database. The CEDS database now records Discharge Monitoring Reports (DMRs) on a monthly basis, and began accepting the electronic submission of DMRs (e-DMRs) in May of 2006. There is a link to enroll in e-DMR at the DEQ internet site. This has improved cost-effectiveness by streamlining reporting methods and reducing resource requirements for managing paper-based DMR reports. It will also improve accuracy by eliminating the potential introduction of errors resulting from manual database entry, and will improve over-all effectiveness with faster and more accurate response to data analysis, compliance assessment and decision-making.

**Toxics Release Inventory (TRI):** The most recent Virginia Toxic Release Inventory Report (2004 VIRGINIA TOXICS RELEASE INVENTORY (TRI) REPORT - March 2006) indicated that 477 Virginia facilities reported to the TRI program for the 2004 activity year. Statewide toxic releases to the water totaled approximately 9,146,470 pounds or 14.6% of the total onsite releases to all media during 2004. This quantity (~9.15 million lbs.) represents an 11.5 % increase from the 8,199,535 pounds released in 2003.

**Pollution Prevention:** Among the highlights of Pollution Prevention successes in the past year were the following:

- The total number of participants in the Virginia Environmental Excellence Program (VEEP) has now exceeded 375 facilities, with 250 at the E2 (Environmental Enterprise) level, 79 at the E3 (Exemplary Environmental Enterprise) level and 16 at the E4 (Extraordinary Environmental Enterprise) level. A review of VEEP annual performance for 2005 reported elimination of the use of 53,000 lbs and the elimination or recycling of 7450 lbs of hazardous waste. In 2006 VEEP facilities earned over \$72,000 in permit fee discounts by implementing and performing their Environmental Management Plans.
- DEQ's Voluntary Mercury Reduction Initiatives have been successful. As a result of the "Virginia Switch Out" Pilot Project for the recycling of automotive mercury switches, initiated in 2005, legislation was enacted in 2006 requiring the removal of mercury switches from end-of-life motor vehicles prior to their demolition. End of Life Vehicle Solutions (ELVS), an organization created by automotive manufacturers, has distributed collection containers for mercury switches throughout the state and is already receiving recycled switches from automotive demolition facilities.
- DEQ's Pollution Prevention in Healthcare Program and its participants received a number of awards and recognition from the national program. Participants reported the reduction of over 1000 lbs of mercury as well as 500 tons of solid waste.
- Of the 850 members (735 participants and 125 mentors) of the Businesses for the Bay (B4B) Program, forty percent are in Virginia. In 2006 they reported approximately 115 million pounds of waste reduction and cost savings of \$3.8 million due to pollution prevention efforts. Virginia's participants earned eleven B4B Excellence Awards in 2006, more than half of the total awarded.
- Virginia's National Partnership for Environmental Priorities (NPEP) program was renamed and re-energized in 2004. Milestones for 2006 included the eliminating the use of 32 lbs of mercury and 4,800 lbs of lead.

## Foreword 2006

### State FY2006 Toxics Reduction in State Waters Report (January 2007)

The Virginia Department of Environmental Quality (DEQ) plans and executes its Ambient Water Quality Monitoring Program on an annual basis. Guidelines for the program include:

- A long-term Water Quality Monitoring (WQM) Strategy, accepted by EPA in October of 2004 and currently (January 2007) being revised.
- Formal Quality Assurance Program and Project Plans (QAPPs),
- Established Standard Operating Procedures (SOPs), and
- Sampling Protocols.

Beginning in July-December of 2005, the agency's annual monitoring program plan (MonPlan) was revised to correspond with the calendar year. This will help synchronize various monitoring activities and assessment periods with the 'ecological' or 'water year'. Monitoring activities summarized in this report, however, still refer to 1 July of each year through 30 June of the following year, in order to provide complete analytical results by 1 January. This reporting period corresponds to the Commonwealth's fiscal year (FY), but was commonly referred to as the monitoring year (MY) in previous documents and reports related to water quality monitoring. The present document attempts to differentiate the terms 'monitoring year' (calendar year) and 'fiscal year,' although some occurrences of previous usage may have been overlooked.

The FY 2006 Toxics Reduction in State Waters (TRISWat-07) Report is the tenth in a continuing annual series. The general formatting of the present report follows that of the previous TRISWat Reports, with only superficial changes to the general introduction, functional definitions, and descriptions of generic water quality monitoring activities. Many of the tables, lists, and appendices relating to toxics lists, water quality criteria and standards, and so forth, are in identical form as or are only slightly modified from those of previous reports.

To minimize the physical bulk of the report, reduce production time and costs, and facilitate its distribution to interested parties, the data tables, figures and appendices of this report are presented in their complete form on the DEQ Website at <http://www.deq.virginia.gov/watermonitoring/>, and are not provided in hardcopy form. (Nor are they convenient to format to be printer friendly, because of their large sizes.) Electronic copies of the complete report, including tables, figures and appendices, are available on CD upon request.

In the Water Quality Monitoring section, data summaries of yearly monitoring results are available in both tabular and graphical forms. Graphical summaries of historical toxics monitoring results (which use statistical interval-estimates for median parameter values) will continue to appear with each annual report to assist in the visual evaluation of:

- Two- to five-year changes in water quality (short-term trends),
- Differences among drainage basins (contemporary, geographic trends) year by year, and
- Differences among years within individual basins (basin-specific, short-term temporal variations).

Eventually, as each year's results are added to the report, historical results in the form of graphed statistical interval-estimates will facilitate the visual evaluation of longer-term trends. Graphed historical summaries (FY1997 – 2006) for each major drainage basin appear in this year's report, but the short period of record and changes in methodologies and detection limits make the interpretation of trends difficult.

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## Introduction

On January 1st of each year, the Virginia DEQ submits the Toxics Reduction in State Waters (TRISWat) Report to the Governor and the General Assembly of the Commonwealth in accordance with Chapter 3.1, Title 62.1, § 62.1-44.17:3 of the Code of Virginia.

The primary objective of the TRISWat Report is to document the state's commitment to improving water quality. This commitment includes:

1. The prevention of contamination of the Commonwealth's waters by toxics,
2. The continued monitoring of the those waters for the presence of toxics, and
3. The implementation of remedial measures to reduce and/or eliminate toxics found in the state's waters.

The annual report helps keep the governor and members of the General Assembly informed of on-going efforts to achieve these objectives and, as a public document, provides the general population with objective, summarized information not readily available from other sources. Although the reduction of toxics in the state's waters is primarily the responsibility of the DEQ, various agencies and organizations, including the Virginia Department of Conservation and Recreation (DCR), the Virginia Department of Health (VDH), the U.S. EPA's Chesapeake Bay Program, and the U.S. Geological Survey participate in the process. It is not possible to unite all available data on the status of toxics in Virginia's waters in this report. Rather, the report summarizes the current results and activities directed toward toxics reduction, and provides guidance on how to access further resources and information on specific subjects. It is DEQ's hope that the continued evolution of the reporting format and the expansion of the report's comprehensiveness will increase its utility to the state's legislators and to the public in general.

DEQ submitted the first TRISWat Report in January 1998. The January 1999 report provided basic background information related to the report's objectives and a basic model for its continued evolution. The current, tenth TRISWat Report (January 2007) contains tables of both raw data and statistical summaries of FY2006 monitoring results.

DEQ has also retained the results from toxics monitoring during previous years and has made these data available at the DEQ Webpage address, both in tabular form and as graphic historical statistical summaries. DEQ anticipates that, with the accumulation of future data, these summaries will facilitate visual evaluation of mid- to long-term trends in toxics concentrations within the various drainage basins of the Commonwealth's waters.

### Functional Definitions and Lists of Toxics

**Defining "Toxicity":** The Virginia Code (Chapter 3.1, Title 62.1, § 62.1-44.17:2) defines "toxicity" as "the inherent potential or capacity of a material to cause adverse effects on a living organism, including acute or chronic effects on aquatic life, detrimental effects on human health, or other adverse environmental effects." This definition is rather broad, since low concentrations of some substances, such as oxygen, can also cause adverse effects, both acute and chronic, on living organisms. However, this report applies "toxicity" only to those substances that "in excess" are detrimental to living organisms. Furthermore, the concept of "other adverse environmental effects" must be defined in biological terms, since toxicity can

only be observed, quantified, and described in relation to living organisms. The classification of chemical substances (“a material”) within the category of “toxics” (those that cause toxicity) is always based on the observed effects of their presence on specific living organisms. In fact, the concept of “excess” itself is defined in terms of the concentrations at or above which living organisms experience detrimental effects.

**Federal Water Quality Standards:** The Federal Clean Water Act (1983) first described the scope and purpose of water quality standards and defined the authority and responsibility of the U.S. EPA and the various states in relation to the requirements for, submission of, and establishment of such standards. As early as 1990, the Chesapeake Bay Commission published its Toxics of Concern (TOC) and Chemicals of Potential Concern lists, which included 21 chemical substances and/or complexes of substances (forms or isomers of complex organic compounds) that endangered the waters of the Chesapeake Bay and its tributaries. The Chesapeake Bay Commission revised and approved these lists in 1996 with the removal of some chemicals and the addition of others, but views the current “Chemicals of Concern” list more as a watershed management tool than as a list to be widely publicized. (See Appendix A of this report for a summary of both lists). The proliferation of new chemical products in the market, as well as emerging concerns over the effects of established chemical and pharmaceutical products, makes the use of a static list inadvisable.

The Interstate Chesapeake Bay Program’s Toxics Subcommittee is currently in the process of reevaluating its list of toxic substances in order to complete a new ‘toxics characterization’ of the Bay watershed by late 2007. A ‘Toxics Characterization Workgroup’ within the Subcommittee has recently (fall 2005 – spring 2006) worked on the development and calibration of a new ‘toxics characterization matrix’ that integrates results from the evaluation of the sediment quality triad (sediment chemistry, sediment toxicity, and benthic community health), water column chemistry and toxicity, fish tissue chemical analyses, fish pathologies, and fishing advisories, and other aquatic life stress indicators to standardize this toxics characterization process. The results of the new Chesapeake Bay toxics characterization are supposed to be published by December 2007.

The U.S. government has published various lists of toxic materials for which the movement, use, and/or release into the environment must be documented or for which concentrations in the environment must be monitored and their effects assessed and subsequently controlled.

- On December 22, 1992, the U.S. EPA published a comprehensive list in the *Federal Register* of 126 chemical substances for which it had established water quality criteria related to aquatic life in freshwater and saltwater and/or to human health risks (Appendix B).
- Subsequent studies have identified additional toxics and/or resulted in the establishment of new criteria for previously defined toxics, and have modified this list considerably during the ensuing years. For example, the EPA’s publication of conversion factors in May 1995 lowered the acute and chronic freshwater criteria and the acute saltwater criteria for the dissolved metals arsenic, cadmium, chromium III and VI, copper, lead, mercury, nickel, silver, zinc, and selenium.
- The EPA provided its most recent complete list of nationally recommended water quality criteria for priority toxic pollutants in November 2002 in the publication EPA-822-R-02-047, National Recommended Water Quality Criteria, which is available in electronic form from the EPA WebPages at <http://www.epa.gov/ost/pc/revcom.pdf>. More recent updates are provided as a link from that address or at: <http://www.epa.gov/waterscience/criteria/wqcriteria.html>
- Additional modifications of existing criteria, as well as the establishment of criteria for new substances, continue to update the EPA list and help maintain or improve the quality of the nation’s waters as a whole. Detailed information on recent updates may be found at:
  - Aquatic Life: <http://www.epa.gov/waterscience/criteria/aqlife.html#final>

- Human Health: <http://www.epa.gov/waterscience/criteria/humanhealth/15table-fs.htm>
- Mercury in Fish Tissues: <http://www.epa.gov/waterscience/criteria/humanhealth/docs/>

**Virginia Water Quality Standards - WQS:** The Commonwealth of Virginia has established and has periodically revised and added to its own water quality standards (9 VAC 25-260 Virginia Water Quality Standards. Statutory Authority: § 62.1-44.15 3a of the Code of Virginia - WITH AMENDMENTS EFFECTIVE JANUARY 12, 2006), which the EPA has reviewed and approved. They serve for the regulation, environmental assessment, and enforcement of water quality criteria within the state's jurisdiction.

These state standards undergo a formal review and may be updated every three years. The Commonwealth's WQS have recently undergone their required triennial review. The adopted triennial review amendments of Virginia's Water Quality Standards are summarized in Appendix C and are available in their complete form on the DEQ-WQS WebPages at <http://www.deq.virginia.gov/wqs>. Further developments in this triennial review process and other information related to Water Quality Standards are public-noticed and/or posted on the DEQ Water Quality Standards Website at <http://www.deq.virginia.gov/wqs/rule.html> as they occur.

**Toxic Substances in the Water Column:** Water Quality Criteria, and the derived Water Quality Standards, for toxic substances in the water column are expressed on the basis of dissolved concentrations. DEQ monitors dissolved metals in the water column using specialized 'clean sampling' procedures discussed elsewhere in this document. Because of the low solubility of organic substances in the water column, traditional methods of sampling them have generally resulted in values below the detection limits of the laboratory methods used for their analysis. Consequently, DEQ began using 'Semi-Permeable Membrane Devices' (SPMDs) to sample for dissolved organic contaminants during the spring of 2003. Initially, the high cost (approximately \$5000 / sample) of this methodology limited its use to fifty statewide probabilistic sites during that first deployment. During subsequent years, other sources of support, primarily for TMDL development, have allowed the employment of SPMDs in a number of special studies related to PCB contamination in the state's waters. The transfer of SPMD preparation and extraction technologies from the USGS to private contractors during the summer of 2005, and developing the ability to analyze the extracts locally at DCLS, has further reduced the costs involved, and has permitted the increased use of SPMDs in TMDL studies. Details of this sampling methodology and the specific studies in which it has been employed are discussed elsewhere in this document.

Although DEQ has in the past monitored the ambient concentrations of total suspended metals in the water column, this practice has now been limited to special studies specifically targeting areas of known water quality problems. No criteria or water quality standards exist for total suspended contaminants, because they are generally not in a form available for uptake by aquatic organisms. Consequently, no water quality assessment can be performed on the analytical results. The data are, however, useful for locating and identifying the sources of dissolved toxics or to calculate local chemical 'translator' values, for estimating dissolved concentrations from the total amount of metal in the water column.

**Toxic Substances in Sediment:** At present, neither the EPA nor the Commonwealth of Virginia has established criteria/standards for toxic substances in sediment. In the past, the analytical results of toxics in freshwater sediments were compared to ecological effects thresholds published in 1991 by the National Oceanic and Atmospheric Administration (NOAA, 1991), and in 1992 by the EPA (U.S. EPA, 1992). Long et al. (1995) published new or refined thresholds for many metals in estuarine and marine sediments. They were derived from "Ecological Risk" assessments based on much of the same published data, from both laboratory and field studies, used by the EPA in establishing water quality criteria.

Such screening values are used for the assessment of estuarine and marine sediments. A summary of some of the Effects Range - Low (ER-L) and Effects Range - Moderate (ER-M) values for selected chemicals in sediment appears in Appendix D of this report. The specific ER-M values used for the assessment of sediments in Virginia are updated regularly, as new guidelines become available. A table of the ER-M sediment screening values used for the 2006 Integrated 305(b)/303(d) Report can currently be found in the assessment guidance for the report on DEQ's WebPages at:

<http://www.deq.virginia.gov/waterguidance/pdf/042006.pdf>.

Beginning with the 2004 305(b) Report, the agency has used more recently published 'Consensus-Based Sediment Quality Guidelines' (MacDonald, *et al.*, 2000) for the evaluation of sediment toxics parameters in freshwater environments. A listing of these new guidelines is also provided in Appendix D and in the assessment guidance for the 305(b) Report on DEQ's WebPages.

**Toxic Substances in Fish Tissues:** DEQ evaluates levels of toxics in fish tissues by comparing them with human consumption risk screening values calculated from EPA data (USEPA-IRIS). A summary table of risk-based screening values DEQ uses for fish tissue consumption appears in the agency's biennial assessment guidance documents. These screening values are adjusted as necessary, following monthly updates in the EPA IRIS database (available at <http://www.epa.gov/iris>). An updated list of the Risk-Based Tissue Screening Values (TSVs) for fish tissue used for the 2006 Integrated 305(b)/303(d) Report can be found in the PDF document "WATER QUALITY ASSESSMENT GUIDANCE MANUAL For Y2006 305(b)/303(d) Integrated Water Quality Report" at:

<http://www.deq.virginia.gov/waterguidance/pdf/042006.pdf>.

Values for specific compounds can also be found listed in the tables of fish tissue analytical results posted on the DEQ Webpage at <http://www.deq.virginia.gov/fishtissue/>.

**DEQ's Review of Pesticides and Chemicals:** DEQ's Office of Water Quality Monitoring and Assessment (WQMA) has recently reviewed and updated the list of organic chemical parameters that it will monitor in Virginia's waters, as well as the monitoring schedule and methodologies with which it does so. This review is an activity explicitly described in the Water Quality Monitoring Strategy, and is in response to the release of many new organic pesticides and/or other chemical compounds into the market annually, as well as the disappearance of others from common usage. The development of new technologies, new methodologies, and the consequent lowering of Method Detection Limits (MDLs) also dictate the need for periodic revision of monitoring protocols and parameter selection. The most recent modifications to the EPA's National Recommended Water Quality Criteria, as well as the current triennial review and revision of the Commonwealth's WQS, further confirm the necessity of such periodic modifications in the Water Quality Monitoring Program. As an example, between 2000 and 2004 DEQ expanded the number of organic contaminants analyzed in sediment samples from 13 (Parameter Group Code PES1S) to more than 200 (Parameter Group Codes AMB\_TOX plus PCS\_SIM\_MS). The Parameter Group Code AMBTOX2, recently defined through collaboration with DCLS, contains 229 organic compounds. Table 1, "DCLS Toxic Parameter Group Codes and Prices - MY2006", summarizes the specific analytes included in currently active toxics-related parameter group codes. More details of this pesticide and chemical review procedure, as well as a summary of its current status, are described in DEQ's Water Quality Monitoring Strategy.

**Federal Reporting Requirements:** In addition to the biennial 305(b)/303(d) Reports, federal law requires reporting procedures for the production, movement, storage, use, and release of many of these toxic

substances. These procedures, as well as Virginia's annual Toxics Release Inventory (TRI) Report, are discussed more fully below.

### **DEQ's Ambient Water Quality Monitoring Strategy**

The first edition of DEQ's Water Quality Monitoring Strategy document was developed and provided to EPA Region 3 for review in April 2004. Following the incorporation of several EPA suggestions, the subsequent draft was placed on the DEQ Water Quality Monitoring Website, for review by the general public (and EPA) from August 9 through September 10, 2004. The public comments received required no modifications of the document released in August and it was considered to be the final draft. In November of 2004, EPA notified DEQ that the final draft Strategy was 'acceptable'. Under the continual planning process, the document has continued to adapt to new monitoring needs as they develop. The next (minor) revision is currently scheduled for completion by the spring of 2007. Tentative implementation of the adapted strategy will begin in January of 2007, with the initiation of the new six-year watershed rotation cycle. Current planning provides for revisions at six-year intervals in the future.

The WQM Strategy provides:

- Definitions of specific types of WQM stations for specific types of data uses, and formal protocols for the selection of monitoring sites.
- Additional emphasis on those watersheds with confirmed water quality problems and those identified as having high-risk potential of Non-Point Source (NPS) pollution.
- A Probabilistic Sampling Program, ensuring that DEQ's statewide monitoring of both freshwater and tidal estuarine ecosystems is representative.

As noted above, DEQ plans and executes its Ambient Water Quality Monitoring Program on an annual basis, following guidelines provided by the agency's long-term Water Quality Monitoring Strategy, formal Quality Assurance Project Plans (QAPjPs), and established SOPs and sampling protocols. Beginning in January 2006, the annual monitoring plans (MonPlans) have corresponded to the calendar year, rather than to the Commonwealth's fiscal year (FY) as they have in the past. This modification provides synchronization with the annual planning of various monitoring activities (*e.g.*, ambient watershed, lake, trend, freshwater and estuarine probabilistic, fish tissue, biological, and beach monitoring) with the ecological / water year, as well as with 305(b)/303(d) six-year assessment windows. FY2006, which terminated on 30 June 2006, was the first year of the third watershed rotation. In order to synchronize calendar year rotations, this third two-year rotation was abbreviated to 18 months and terminated on 31 December 2006. By abbreviating the third rotation and expanding the 305(b) assessment window to six years, assessments will begin to include three complete two-year station rotations beginning with the 2008 Integrated Report. This will increase the representativeness of subsequent assessment reports by assuring that each report includes two complete years of continuous monitoring at all watershed stations statewide. This will provide the desired number of observations for a continuous two-year period at each site for assessment purposes and will include statewide coverage via the rotating watershed, lake and fish tissue programs, as well as both freshwater and estuarine probabilistic monitoring networks.

For the purpose of the Toxics Reduction Report, however, summaries will continue to be related to the fiscal year in order to assure that the results of all relevant chemical analyses are available for the year-end report.

## Review of Toxic Chemical Parameters and Their Monitoring Methodologies

Implementation of the newly developed Water Quality Monitoring Strategy has focused on toxic chemical monitoring in a more concerted effort to assess the potential impact on water quality. Toxic chemicals fall into two general classes of compounds: inorganic trace metals and synthetic organic chemicals.

With the exception of sampling at all probabilistic sites, the guidance for monitoring dissolved toxic trace metals has recently shifted focus from ambient waters to major point source discharges and other known or suspected problem areas. Monitoring at major point source discharges and other targeted Standard Industrial Classifications (SICs) based on their permit status, 303(d)<sup>1</sup> listed waters, acid mine drainage (AMD) sites, and the Elizabeth River, are prime areas where dissolved metals monitoring will continue to occur. This shift to target areas of known or suspected problems was based on results from previous ambient trace metal sampling collection efforts. Beginning in May 1997, the Ambient Water Quality Monitoring Program began “clean” trace metal sampling in freshwaters. From then until the end of 1998, 113 samples were collected at 102 separate sites in all major basins, except for the most western basin, Tennessee / Big Sandy. The results of this effort indicated that the average dissolved concentrations of trace metals in Virginia rivers are consistent with the global distributions observed by other researchers. The continued monitoring of dissolved metals at probabilistic sites has confirmed this conclusion, and will continue to provide annual summaries of the status of the Commonwealth’s waters on a statewide basis.

Prior to 2004, the WQM Strategy provided for sampling of trace organic toxic contaminants in sediments at all watershed stations once every five to six years, and once at each probabilistic monitoring station. The list of organic compounds to be monitored has been updated and expanded since then, to include more current use compounds, and new analysis methods currently provide significantly lower detection limits for most substances on the list. Table 1, “DCLS Toxic Parameter Group Codes and Prices - MY2006”, lists the toxic organic compounds monitored as target analytes in sediment during MY2006 using the Parameter Group Code AMBTOX2. Recommended changes suggested by DEQ’s most recent triennial review of Water Quality Standards have been approved at the state level and the updated status of this review process is available on the DEQ WebPages at <http://www.deq.virginia.gov/wqs/>.

The high cost of sampling for toxic organics, in conjunction with the low concentrations observed for most contaminants at most locations, has prompted the agency to restrict ambient toxic organics sampling surveys primarily to probabilistic sites under the 2005 Water Quality Monitoring and Assessment Strategy. More intensive localized special studies are carried out to define the severity, extent and probable source of contamination problems once they have been identified.

The concentration and distribution of dissolved trace organics in freshwater was determined through a probabilistic sampling design as outlined in the 2005 strategy. Semi-permeable membrane devices (SPMDs) were first deployed in the spring of 2003, in freshwater streams and rivers. Since that time, SPMDs have been employed in a number of localized special studies, primarily related to the distribution of polychlorinated biphenyls (PCBs). These special studies are discussed elsewhere in this report. The SPMD devices normally remain deployed in the field for one month (~30 days), during which time they selectively absorb hydrophobic contaminants by a mechanism identical to the uptake by fishes and other aquatic organisms via epithelial cell contact. Three classes of contaminants are normally identified from these samples: (1) organochlorine and organophosphorus pesticides and herbicides, (2) polynuclear

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<sup>1</sup> Biennial 303(d) Total Maximum Daily Load Priority List and Report, Virginia Department of Environmental Quality and Department of Conservation and Recreation.



aromatic hydrocarbons (PAHs), and (3) polychlorinated biphenyls (PCBs), the concentrations of which indicate the potential for adverse impacts from environmental contaminants. Selected samples in the original study were also analyzed for endocrine disrupters and for mutagenic toxicity. The assessment of the results from these previous studies has been used to determine future study design for characterizing the statewide extent and severity of key trace organic toxic analytes. Several special studies using SPMDs, directed specifically toward the distribution and concentration of PCBs, were initiated in 2004 in response to concentrations detected in tissues of fish collected in Lake Anna, the Bluestone River and Bull Run (tributary to the Occoquan Reservoir). Additional details about these and additional studies are described elsewhere in this report. Some of the final results of earlier SPMD analyses performed by the USGS laboratory in Columbia, Missouri, are now available on the DEQ WebPages: <http://www.deq.virginia.gov/water/reports.html>.

### **Monitoring for Toxics in State Waters**

The Commonwealth of Virginia monitors toxics and their effects in the state's surface waters by both chemical and biological methods, in the water column and sediment, and by chemical methods in fish tissues. The specific monitoring activities and analytical programs related to toxics are as follows:

- The regional office WQMA field staff carries out most chemical sampling for toxic substances in the water column and associated sediments at probabilistic, fixed-site, and/or rotating ambient monitoring stations.
- The Division of Consolidated Laboratory Services (DCLS) of the Virginia Department of General Services in Richmond analyzes most of the resulting samples, statewide.
- In the past, the U.S. Geological Survey laboratory in Columbia, Missouri, has produced SPMDs and has performed the extraction and broad-spectrum analysis of organic compounds collected using the SPMD technology. An authorized private laboratory, Environmental Sampling and Technologies (ES&T) Laboratory of St. Joseph, MO, now produces SPMDs, extracts the chemical concentrates following field deployment, and provides ampulated extracts for analyses elsewhere. More restricted subsets of organic compounds can be selected for analysis, reducing analytical costs. EPA laboratories have performed PCB analyses for one recent study. The Virginia state laboratory (DCLS) is still working to improve its accuracy and precision in the analysis of SPMD extracts. Once their results attain the desired Quality Assurance goals, analyses there may further reduce costs and allow the expansion of SPMD sampling in the future.)
- EPA-contracted laboratories currently analyze sediment samples (metals, organics, and toxicity) and whole fish tissue samples (metals and organics) collected from the probabilistic sites of the Estuarine Probabilistic Monitoring Program (EPA Assistance Agreement No. CR-83270801-0: 2005-2006).
- The field team from DEQ's Central Office of Water Quality Standards (WQS) performs additional chemical monitoring of toxics in sediments and fish tissues at selected sampling sites.
- The Virginia Institute of Marine Science (VIMS – Gloucester Point) and College of William and Mary (Williamsburg) laboratories usually analyze tissue and sediment samples, respectively, collected within the WQS Fish Tissue and Sediment Monitoring Program.
- DEQ's seven regional offices and, as required, permitted facilities whose discharge permits contain specified limits for toxics quantities or concentrations in their liquid effluents, carry out additional compliance monitoring and pollution complaint response monitoring for toxic substances.

More complete discussions of each of these monitoring programs are included later in this report.

**Chemical monitoring** of toxics consists of the direct, quantitative measurement of the concentrations of specific chemical elements and compounds in effluents, in the water column of the receiving water body, in the underlying sediments, and/or in animal tissues. Chemical monitoring is considered to be monitoring of the **potential causes of ecological stress and environmental impairment**.

**Toxics in the Water Column:** DEQ compares the results from water column analyses with water quality criteria and standards based on the acute and chronic toxicity of specific substances dissolved in fresh, brackish, and salt waters. The current standards used for these comparisons are listed in the Assessment Guidance document (<http://www.deq.state.va.us/wqa/>) for each Integrated 305(b)/303(d) Report, as well as in Appendix C of this Toxics Reduction Report.

**Toxics in Sediment:** In most cases, there are as yet no specific standards for toxics present in the sediment. Consequently, ecological risk assessments have generally compared toxics concentrations in sediment to Effects Range - Moderate (ER-M) concentration screening values (SVs). NOAA (NOAA, 1991), the EPA (U.S. EPA, 1992), and others (e.g., Long et al. 1995) have provided these sediment SVs to evaluate the potential effects of sediment contamination on aquatic life in estuarine and marine waters. Newly published “Consensus-Based” screening values are now used for freshwater sediments. A summary of current ER-M and Consensus screening values can be found in each Integrated 305(b)/303(d) Report Assessment Guidance document (<http://www.deq.virginia.gov/wqa/>), as well as in Appendix D of this Toxics Reduction Report.

**Toxics in Fish Tissues:** To assess the human health risk from edible fish tissues, the analytical results from fish tissue analyses are compared to human health contaminant Screening Values (SVs). The calculation of these SVs uses risk assessment techniques published by the EPA for chronic toxicity and for both carcinogenic and non-carcinogenic effects (U.S. EPA, 1994). The current 305(b) Report Assessment Guidance document (<http://www.deq.virginia.gov/wqa/>), as well as Appendix E – “EPA Risk-Based Screening Values for Fish Tissues – MY06” of this Toxics Reduction Report, provide summaries of current SVs. More specific details on the sampling and assessment of fish tissues and sediment appear in the Quality Assurance/Quality Control Project Plan for the Fish Tissue and Sediment Monitoring Program (DEQ-SRU, 1998).

**Biological monitoring** consists of evaluating the survival, growth and reproduction of living organisms, or of assessing the structure and function of aquatic communities in comparison with those existing under known reference conditions. Such monitoring may be carried out in the field or in the laboratory. When carried out in the field, it is considered monitoring for the **observed effects of environmental impairment**. **When impairment of biological communities occurs, it does not necessarily indicate toxic effects.** Intensive follow-up monitoring is necessary to determine the specific cause(s) of biological impairment. Ecological or biological toxicity tests performed in the laboratory generally expose living organisms, belonging either to endemic (native) species or to nationally or internationally standardized species, to water and/or sediment samples collected in the field.

Under laboratory conditions, the results of toxicity testing can only be considered the measurement of the **potential effects of toxicological stress on environmental impairment**. DEQ no longer possesses the facilities to perform its own toxicity testing although, when necessary for special studies, DEQ does contract commercial or university laboratories to perform the desired tests when deemed necessary. As mentioned elsewhere in this report, estuarine sediment samples collected in the National Coastal Assessment Program undergo toxicity testing at an EPA-contracted laboratory and other contracted toxicity



testing is currently being performed in conjunction with a number of freshwater benthic-related TMDL studies.

Many permitted facilities that have Whole Effluent Toxicity (WET) Limits described in their discharge permits must maintain laboratories for the programmed biological testing of toxicity of their own effluents and must report the results to DEQ. DEQ continually reviews these results and periodically collects effluent samples and sends them to independent laboratories to confirm the toxicity levels and the quality assurance/quality control procedures the permitted facilities are using.

DEQ's Water Quality Monitoring Program Strategy discusses more fully the relative merits of chemical versus biological monitoring and of field versus laboratory evaluations of environmental impact.<sup>2</sup> In summary, the costs of chemical sampling and analyses for toxics are high in comparison with the field evaluation of biological communities. Budgetary considerations limit the number of monitoring stations that can be sampled for chemical analyses as well as the frequency of sampling at each station. One specific objective of the Water Quality Monitoring Program is to increase the use of biological monitoring statewide, as an early warning system to detect toxic effects and to supplement chemical toxics monitoring. To this end, additional biologist's were authorized and hired in most DEQ regions in the fall of 2006. In addition, the agency will continue to use chemical monitoring to help determine and evaluate the possible causes of observed biological impairment.

## **Chemical Monitoring**

DEQ chemically monitors the state's surface waters, fish tissues, and associated sediments for toxics on a regular basis. Because of the high costs of analysis, however, the monitoring of toxic chemicals is normally carried out only at specified stations and on a periodic basis. The sites selected, as well as the frequencies sampled and parameters analyzed, depend upon several factors, including resource availability.

The Office of Water Quality Standards' Fish Tissue and Sediment Monitoring Program also considers:

- The past history of the water body,
- Known sources of toxics input, and
- The geographic typicality of specific sites.

In the recent past, the Ambient Water Quality Monitoring Program stations used for toxics monitoring have been divided into the following three distinct types:

1. Monitoring sites designated as "watershed mouth stations" or "trend stations" are considered representative of the quality of water moving from one geographically defined local drainage basin to another. Following the original WQM strategy, DEQ planned to sample such sites for toxics in the sediment and in the water column once during each six-year monitoring cycle. (Recent limitations on monitoring resources no longer permit toxics monitoring at such a large number of sites. DEQ has consequently suspended the monitoring of toxics at these sites and restricts its ambient monitoring for toxics to probabilistic stations, as described below.)

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<sup>2</sup> The Water Quality Monitoring Strategy document, prepared by the DEQ Water Quality Monitoring and Assessment Program, was submitted to EPA and accepted in the fall of 2004 and was officially implemented in MY2005. A minor revision of the original document, incorporating recent modifications of the monitoring program, is currently in preparation and will be submitted to EPA in the spring of 2007.

2. Additional sites, randomly selected each year from free-running freshwaters and from tidal estuarine waters, constitute the probabilistic monitoring module of the WQM strategy and are as a rule sampled only once, unless the first sampling event identifies a specific water quality problem. The results from chemical analyses of sediment and water and from benthic community analyses at these probabilistic sites provide unbiased characterizations of Virginia's ambient surface waters for a specific resource class, or on a regional, basin-wide, and/or statewide basis.
3. Sites identified as having unacceptably high concentrations of one or more toxic substances (based on analyses of previous samples from type 1 or type 2 sites), that have a known history of contamination by toxics, or that have a high risk of contamination, may be designated as "targeted stations." They may become part of a specific special study to document the geographic extension, severity, and cause of the contamination, or they may be included in the sampling plan of the Fish Tissue and Sediment Monitoring program carried out by the Special Research Unit of the Office of Water Quality Standards.

More complete descriptions of specific toxics monitoring activities appear below.

Toxic elements and chemical compounds are generally categorized into several primary groups, each of which has a specific chemical analysis code to identify the procedures necessary for its complete analysis by DCLS. The primary groups normally are:

- Clean dissolved and total toxic metals in the water column,
- Toxic metals in the sediment,
- Dissolved organic contaminants,
- Organic contaminants in the sediment, and
- Toxic metals and organics in fish tissues.

Various other toxic organic compounds (*e.g.*, PAHs and PCBs), for which water quality standards have been established and which appear on toxics lists published by the U.S. EPA and the Chesapeake Bay Commission, are generally evaluated together with pesticides.

Table 1 of this report summarizes the toxics-related Parameter Group Codes and the specifically associated analytes in the current DCLS laboratory catalogue within the DEQ CEDS database, including their associated reportable limits, costs, and turnaround times. The exact reportable limits may vary from day to day, depending on the stability of the analytical apparatus, the purity of reference materials and blanks, and possible interference from other substances present in the samples collected in the field. It should be understood that various Parameter Group Codes included in this list are seldom utilized within the Ambient Water Quality Monitoring (AWQM) Program. Some are specific to other matrices, such as fish tissues, soil, etc., or are utilized specifically for industrial facilities. Other group codes have already been updated and replaced with new codes because of concern with new chemical products, the availability of newer analytical methods and/or the availability of lower detection limits for the analytes of interest. Those parameter group codes actually employed by the AWQM Program during Monitoring Year 2006 are listed in Table 2.

Table 2 summarizes the number of samples, the analytical expenses, and the parameter group codes included in ambient toxics-related analyses performed by the state laboratory (DCLS) during the 2006 state fiscal year. This summary includes only those samples collected by the Ambient Water Quality Monitoring Program of the WQMA. (The numbers of samples, analytical costs, etc., of fish tissue and sediment samples collected by personnel from the WQS, or collected during various special studies or in the Estuarine Probabilistic Monitoring Program and analyzed elsewhere are not included here.)

## Biological Monitoring

*Benthic Community Evaluation:* Field sampling and evaluation of benthic communities has proven to be an invaluable tool in the assessment of water and sediment quality in Virginia as well as in numerous other states. Highlights of the biological assessment program include the following:

- Biological assessments in free-flowing freshwater streams have traditionally been carried out using standardized Rapid Bioassessment Protocols (RBPs) published by the EPA (U.S. EPA, 1989, 2000) and other federal and state organs.
- The Mid-Atlantic Coastal Streams Workgroup has produced a supplementary EPA manual for the evaluation of benthic communities in low-gradient, non-tidal coastal streams (U.S. EPA, 1997).
- Tetra Tech Inc., a Maryland-based ecological consulting firm, utilized the results of DEQ studies of benthic macroinvertebrate communities in Virginia streams to develop an efficient Stream Condition Index (SCI) for non-coastal streams in the Commonwealth. A final report on this study was delivered to DEQ in the spring of 2003. A copy of this report is available on the DEQ Website at <http://www.deq.virginia.gov/watermonitoring/pdf/vastrmcon.pdf>. Comments and responses from public review of the SCI document have been posted on the Website with the SCI Report. DEQ has taken considerable time and effort to address public comments and concerns regarding this report with assistance from the Academic Advisory Committee's (AAC) subcommittee on biological monitoring. DEQ personnel have conducted further data collection and analyses in order to verify and calibrate the SCI (DEQ-WQMA, 2006). The results of these efforts have also been posted on the Website. Pending approval of the final calibration, it is anticipated that biological assessments using the refined SCI will be included in the 2008 Integrated 305(b)/303(d) Report.
- Cooperative efforts from 2003 through 2005 among Virginia, Maryland, the federal Interstate Chesapeake Bay Program, and EPA Region 3 resulted in a standardized, interstate methodology for analyzing and assessing the results of probabilistic benthic invertebrate monitoring in tidal areas of the Chesapeake Bay watershed for the 2004, 2006 and subsequent Integrated 305(B)/303(D) Reports of both states. An additional product of this process was a benthic community Stressor Diagnostic Tool developed by Dr. Dan Dauer and Dr. Michael Lane of Old Dominion University. For benthic samples that receive degraded or severely degraded B-IBI scores, the Diagnostic Tool applies a discriminant function, based on the evaluation of individual benthic metrics, which estimates the probability that the benthic community was degraded by contamination. The results of Diagnostic Tool analyses were included in Chapter 6.7 of Virginia's 2006 Integrated 305(b)/303(d) Assessment Report.

Because communities of benthic invertebrates and algae, as well as certain fish species, are permanent residents within the waterbodies of interest, they are able to integrate the various causes of impairment over time, rather than representing a single temporal point-sample from the water column or sediment. The status of the biological community as a whole also presents an integrated measure of the ***ecological effects*** of numerous physical conditions and chemical substances, incorporating any antagonistic and/or synergistic biological-chemical interactions into the overall evaluation of ecological impact. In this respect, biological monitoring for toxic effects is much more informative than chemical monitoring.

In the past, based on the results of RBP2 biological evaluations, biologists classified Virginia's waterbodies and water-body segments as "*fully supporting*" of the aquatic life designated use, as "*slightly impaired*", "*moderately impaired*", or as "*severely impaired*" for aquatic life use, in comparison with regional reference conditions which were considered to be of acceptable water quality. The following text table

identifies four assessment classifications based on scores of the newly refined SCI: Excellent, Good, Stressed and Severely Stressed. Once the proposed classification procedure has been approved by agency management and EPA, the procedure will be described in detail in the Biological Monitoring SOP and in the Assessment Guidance Manuals for subsequent 305(b)/303(d) Integrated Reports.

<b>VSCI Score</b>	<b>ALU Tiers</b>
<42	Severe Stress
>42-<60	Stress
>60-<73	Good
>73	Excellent

**Virginia SCI scores and associated aquatic life use (ALU) tiers**

Similarly, following the partnership consensus for the Chesapeake Bay Program’s Benthic IBI described above, sample benthic IBI scores, when compared with those of reference populations, will be used to assess benthic communities as impaired or not impaired for the aquatic life use assessment of tidal water segments.

*Advantages of Biological Monitoring:* Although biological monitoring is generally incapable of identifying or accurately quantifying the exact cause of environmental impairment, it is rapid and relatively inexpensive in comparison with comprehensive chemical analyses and is able to identify waterbodies where more intensive studies are necessary. It has the added advantage that the organisms in an aquatic community are able to integrate the effects of various interacting stressors over an extended period of time. It permits the ambient monitoring of a larger geographic area with a minimum of additional cost, thus reserving limited financial and human resources for more intensive biological and chemical studies of areas where impacts have been confirmed.

Appendix H1 of this report lists the biological monitoring stations visited during MY2006. This list includes many of the probabilistic sites that are also described in Appendix H2a. Much additional habitat-related information from these stations is recorded in individual databases at each regional office and later consolidated at DEQ’s central office in Richmond. The EDAS database developed by the Tetra Tech Inc. consulting firm is being utilized to satisfy regional needs and formalize formats for data entry and transfer by regional biologists. At the present time, the Comprehensive Ecological Data System (CEDS) database at DEQ’s Central Office records only physical and chemical data from biological stations where researchers collect field parameter data (temperature, dissolved oxygen, pH, and conductivity) and water or sediment samples that are shipped to DCLS for chemical analysis.

Appendix H2a, “Freshwater Probabilistic Monitoring Sites MY2006-07”, provides a comprehensive list of the probabilistic monitoring stations that were included in the ambient program during fiscal year 2006. Many of these (wadeable sites) were also sampled for benthic invertebrate populations and are also included in Appendix H1.

Appendix H2b, “Prospective Freshwater Probabilistic Monitoring Sites MY2006-10”, provides a comprehensive list of the possible probabilistic/biological stations that may be included in the ambient program during the next five years. The final annual lists will become available only after regional biologists perform both map and field reconnaissance prior to their sampling in the spring of each year.

### **Toxics Monitoring – Surface Waters and Sediments**

Appendix F1– “Historical Toxics-Monitoring Station List Oct1970-Oct2001” contains a complete list of all WQM stations where ambient toxics samples had been collected prior to October 18 of 2001. The list spans the period from October 1970 through October 2001 and includes all the sites from which analytical results of sediment metals samples were available in DEQ’s CEDS 2000 database at that time. Researchers normally collect sediment pesticide samples simultaneously at the same sites. The list includes 2359 sites, which were visited a total of 26,783 times (average of 11.4 visits per site). A single visit may include the collection of multiple samples (e.g., sediment metals, sediment pesticides, dissolved and/or total metals in the water column, and dissolved pesticides), so the total number of samples collected during this period probably exceeds 50,000. (Not included are the recent samplings of clean dissolved and total metals during several special studies.) Samples collected since monitoring year 2001 are summarized in individual Toxics Reduction in State Waters Reports.

Text Box 1, below, presents the total number of ambient WQM toxics samples collected during MY2006 for which analytical results are currently available (November 2006). They include clean dissolved and clean total metals in the water column and metals and pesticide/organics analyses of sediment. Limitations to the analyses for the current year include the following:

- Budgetary restrictions experienced during the past several years have significantly reduced the number of toxics samples collected and analyzed during the period.
- There are no water quality criteria or standards for total metals in the water column. Consequently, the number of samples for total metals is generally much lower than for dissolved metals. (This year’s sampling was restricted primarily to special studies on mercury [Hg] distribution and mobility in impaired segments of the Shenandoah River basin and in Dragon Run (Piankatank River basin - Chesapeake Bay tributary).)
- Metals and pesticides in the sediment are generally sampled simultaneously at the same stations, but their chemical analyses and the availability of results are independent. The number of results reported for organic toxics is often less than that reported for metals because the organic analyses are more complex and take longer to perform.
- Additional parameter group codes that include incidental water column metals are not included in Text Box 1.

As mentioned above, Appendix F1 of this report consists of a list of the ambient monitoring stations with a history of sampling metals or pesticides and other organics. These listings provide station identifications, complete location descriptions including geographic coordinates, stream and basin names, hydrologic unit codes, and local watershed identifications, dates for the first and the most recent samplings prior to the query (October 2001), and the total number of visits to the site for toxics samples during the period queried. (A single visit to a site may result in multiple samples for toxics analyses, e.g., metals and/or pesticides in water and/or sediment.) Appendix F2 lists the ambient monitoring stations that were sampled for each toxics parameter group code during Monitoring Year 2006. Similar annual summary tables can be found in previous Toxics Reduction Reports (Jan1999-Jan2006).

Basin Code	River Basin Name	Clean Dissolved Metals	Clean Total Metals	Sediment Metals	Sediment Organics <sup>3</sup>
		(water)	(water)		
1-	Potomac / Shenandoah	7+89 <sup>1</sup>	19+82 <sup>2+</sup> 99 <sup>1</sup>	5+9 <sup>5</sup>	5+4 <sup>5</sup>
2-	James	31	0	17	17
3-	Rappahannock	11	0	3	3
4-	Roanoke	10	0	10	10
5-	Chowan	7	0	5	5
6-	Tennessee / Big Sandy	7	0	7+8 <sup>5</sup>	7+10 <sup>5</sup>
7-	Small Chesapeake Bay and Coastal	12+11 <sup>4</sup>	66 <sup>4</sup>	1	1
8-	York	7	0	4	4
9-	New	8	0	7	7
		-----	-----	-----	-----
	<b>Total</b>	<b>200</b>	<b>266</b>	<b>76</b>	<b>73</b>
	<b>Grand Total</b>	<b>615</b>			

**Text Box 1. Summary of Ambient Toxics Monitoring Samples from Virginia’s Surface Waters for which data are available - FY2006.** (Excludes SPMD and National Coastal Assessment sediment sampling)

<sup>1</sup> Mercury only, in conjunction with the Shenandoah Basin Mercury Special Study.

<sup>2</sup> Modeling Special Study for Potomac River Commission & Federal Interstate Chesapeake Bay Program.

<sup>3</sup> Sediment samples for organics analysis were collected at 59 freshwater probabilistic sites during the spring of 2006. The remaining were TMDL studies. Samples reported were collected and analyzed under the new AMBTOX2 parameter group code.

<sup>4</sup> Mercury only, in conjunction with Dragon Run Mercury Special Study.

<sup>5</sup> TMDL Special Studies

### Toxics in the Water Column

At the present time, science defines all existing water quality criteria and standards for toxic substances in terms of dissolved concentrations. In many cases, the defined standards are extremely low concentrations, near or below the detection limits of common analytical equipment and methodologies. Often, it has been necessary to collect and concentrate large volumes of water samples to produce meaningful results. Sampling of waters with such low concentrations of toxics also commonly presents severe problems in terms of sample contamination. Consequently, careful planning and specific SOPs are necessary to ensure the quality control of sample collection and transport and of the subsequent chemical analyses, and to guarantee the accuracy and defensibility of the results. A number of newly developed sampling and analytic technologies (discussed below) are now in use for improving the representativeness, accuracy, and precision of measuring dissolved toxics in the water column.

### Clean Dissolved Metals in Surface Waters

From June 1995 through July 1996, DEQ carried out a pilot project (Project No. 50205) for the sampling and analysis of trace metals in the Pigg River Basin of Franklin County, Virginia. The purpose of the study

was to gather the necessary background data and experience for formulating SOPs for the collection and analysis of freshwater and wastewater treatment plant effluents for trace metals. The final report from this project (DEQ-WQA, 1996) documents the precision requirements and the limits to recovery and detection of trace metals when applying the newly developed methodology. More recently, additional studies were carried out to validate this methodology for clean dissolved and total metals sampling and analyses in brackish and saltwater, primarily in the Elizabeth River.

The resultant sampling SOP (DEQ-WQA, 1998) is currently being applied in the collection and analysis of 19 dissolved trace metals in freshwater: aluminum (Al), antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), cadmium (Cd), calcium (Ca), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), mercury (Hg), nickel (Ni), selenium (Se), silver (Ag), thallium (Tl), and zinc (Zn). The suite of 16 metals analyzed from brackish and saltwater samples differs slightly from those included above: aluminum (Al), antimony (Sb), arsenic (As), cadmium (Cd), calcium (Ca), copper (Cu), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), mercury (Hg), nickel (Ni), potassium (K), selenium (Se), sodium (Na), and zinc (Zn).

Table 3 - "Clean Dissolved Metals - All Basins - MY2006" presents the results of clean, dissolved toxic metals monitoring during MY2006 in their raw form and statistically summarized, river basin by river basin. Additional spreadsheets in Table 3 summarize the results from Shenandoah River Basin and Dragon Run - Piankatank River special studies of dissolved mercury distributions. The program codes in the first column of the tables identify the subdivisions of the overall ambient monitoring program for which each sample was collected: AQ = ambient monitoring; C2 = Coastal 2000 - Estuarine Probabilistic Monitoring, FP = freshwater probabilistic monitoring; RL = regional lakes monitoring; RB = regional biological monitoring; SS = Special Study; TM = TMDL Special Study; HG = Shenandoah Mercury Special Study. Basin-by-basin historical summaries of clean dissolved metals results appear in graphical format in the Excel® workbooks in Folder 3 - "Metals, Dissolved, Historical, ..." along with year-by-year and metal-by-metal statistical summaries.

The most meaningful single statistic in these tables is the "median" concentration. This is the concentration that exactly half of the samples exceeded and half fell below. It can be used as an "average" value to compare the basin with the appropriate water quality standard. The "90<sup>th</sup> percentile" value is the concentration that only ten percent of the samples exceeded. Similarly, the 75<sup>th</sup>, 25<sup>th</sup>, and 10<sup>th</sup> percentiles are the respective concentrations that 25%, 75%, and 90% of the samples exceeded.

Where the results from multiple samples reveal the same (or very similar) values for the 90<sup>th</sup> (and/or 75<sup>th</sup>) percentile, the median, the 25<sup>th</sup> and 10<sup>th</sup> percentiles, and the minimum, the environmental concentration in the majority of the samples was at or below the detection limit for the methods used. That limit is generally quite similar to the value that is repeated in the table, although it may vary significantly from one sample to the next. Because samples with concentrations below the detection limits for a specific metal were reported at the detection limit, an upward bias has been introduced into many statistical summaries. When the detection limits are near or above the standard for the metal in question, the apparent results may suggest that the standard was exceeded, when in fact the actual concentrations were considerably lower. Such cases can be identified by the Remark Code "U" (non-detect) in the tabulated raw data summaries of Tables 3 through 6 of this report.

The two statistics that have been determined for the annual summaries since 1997, the upper quartile (75<sup>th</sup> percentile) and lower quartile (25<sup>th</sup> percentile) values, allow the estimation of 95 percent confidence intervals for the median values. They permit visual statistical comparisons among river basins (geographic variations within the same monitoring year), as well as among years in the same river basin (for analysis of

temporal trends). When sample numbers were sufficient, the upper and lower 95 percent confidence limits on the median were calculated using a formula published by the EPA for the evaluation of trends in lake water quality (Reckhow, et al., 1993). The upper and lower limits are, respectively, the value of the median plus or minus the value of 1.57 times the interquartile interval (I) divided by the square root of the sample size (number of samples = n):

$$\text{Limits} = \text{Median} \pm (1.57 [I / \sqrt{n}])$$

Allowing for variation among the samples, it is possible to have a confidence of 95% that the true median concentration of the toxic metal is between the upper and lower limits. If the confidence intervals for two years (or for two basins) do not overlap, it is possible to conclude with 95 percent confidence that the medians of the two basins differ significantly. The vertical lines in the first series of graphs of Folder 3 represent the 95 percent confidence intervals for the median concentrations observed in each year (see Text Figure 1a, below). The small black horizontal lines represent the medians (i.e., 50<sup>th</sup> percentile). When all observations are near the detection limits for the parameter of interest, the interquartile interval and the resultant confidence interval may become zero. In such cases, comparisons among the groups of samples are not trustworthy. In any case, the presence of numerous ‘non-detect’ values (>25% with ‘U’ remark codes) will bias the median and its confidence interval upward.

### **Total Metals in Surface Waters**

As mentioned above, all water quality criteria for toxic metals that the EPA provides, and that subsequently become the basis for the Commonwealth’s Water Quality Standards, are based on dissolved concentrations. The majority of the metals in the water column are bound to the surface of suspended mineral and organic particulate matter. For the most part, particle-bound metals are not considered to be biologically available to most aquatic organisms. Because there are no Water Quality Standards for total metals in the water column, the sampling of total metals is not normally included in ambient water quality monitoring. Incidental metals such as copper, iron and manganese are included in other parameter group codes, and calcium is often included to facilitate the calculation of ‘hardness’. During MY2006, however, DEQ researchers again collected clean total metals samples from the Shenandoah River basin and in Dragon Run (Piankatank drainage) for the purpose of monitoring the transport of mercury (Hg) at many of the same sites where clean dissolved mercury samples were collected. Additional total metals samples were collected for Potomac River / Chesapeake Bay modeling efforts. The resultant data from these samples, along with their statistical summaries, are included in separate spreadsheets of Table 4. The statistical summaries in this table can be interpreted in the same manner as described above, for Table 3. In the Excel® workbooks of Folder 4 - Metals, Total in Water, Historical - MY2006, historical summaries of clean total metals results are presented in graphical format, by basin, along with year-by-year and metal-by-metal statistical summaries. As mentioned above, the vertical lines in the graphs represent the 95 percent confidence intervals for the median concentrations observed in each year. The small, horizontal black lines represent the medians (i.e., 50<sup>th</sup> percentile).

### **Dissolved Pesticides and Other Organic Contaminants**

*The concentrations of dissolved organic compounds in the water column are generally extremely low, often at or below the detection limits of generally available analytical methods. For this reason, DEQ has suspended most ambient monitoring of dissolved pesticides using traditional methods during the past several years. The results of several pilot studies employing newly developed sampling technologies (Semi-*



*Permeable Membrane Devices – SPMDs) offer the promise of significantly improving the monitoring of dissolved organics. SPMDs were employed in several special studies on the distribution of polychlorinated biphenyls (PCBs) during MY2004 through MY2006. Several of these studies and some preliminary results are briefly described elsewhere in this report.*

## **Toxics in the Sediment**

Two separate groups within DEQ monitor sediments in Virginia’s surface waters. DEQ’s WQM Program has normally evaluated metals from selected permanent and/or rotating ambient WQM stations on a periodic, cyclic basis. More recently, DEQ has added the collection and analysis of sediment samples from each of its approximately 60 freshwater probabilistic monitoring stations each year. Sediment samples for chemical analyses of metals and organics have routinely been collected at 50 probabilistic sites of the Coastal 2000 / National Coastal Assessment (NCA) Program each summer since 2000, but these samples are shipped to EPA-contracted laboratories for analysis. In the past, results from these laboratories have not been received until one or more years following sample collection. Beginning with the 2006 Integrated 305(b)/303(d) Report, chemistry, toxicity and benthic results from the NCA sediment sampling were used for a toxics-related “Weight-of-Evidence” assessment of aquatic life use in estuarine waters.

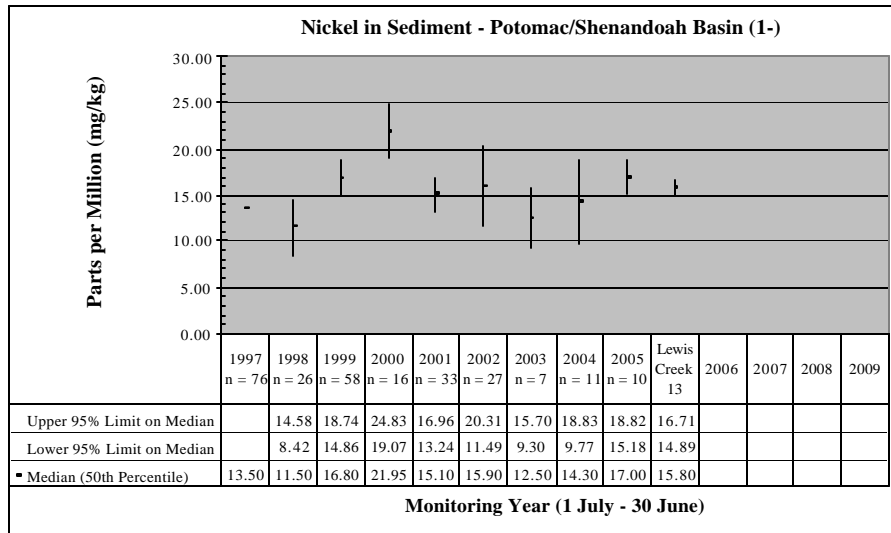
The WQS Fish Tissue and Sediment Monitoring Program also routinely analyzes sediment samples collected at or near the same sites where fish tissue samples are collected. DEQ also collaborates with NOAA and the EPA’s Chesapeake Bay Program and Coastal 2000 / National Coastal Assessment Program (see discussions above and below), as well as with various universities, in characterizing the sediments of Chesapeake Bay and tidal tributaries to the Bay and the Atlantic Ocean. DEQ collects sediment data from both tidal and non-tidal Chesapeake Bay tributaries, and DEQ data contribute directly to the CBP Information Management System (CIMS) database. In addition to DEQ’s own data, assessment of the Commonwealth’s waters uses sediment data collected by various universities and government organizations, once they have passed quality assurance and quality control checks.

## **Sediment Metals**

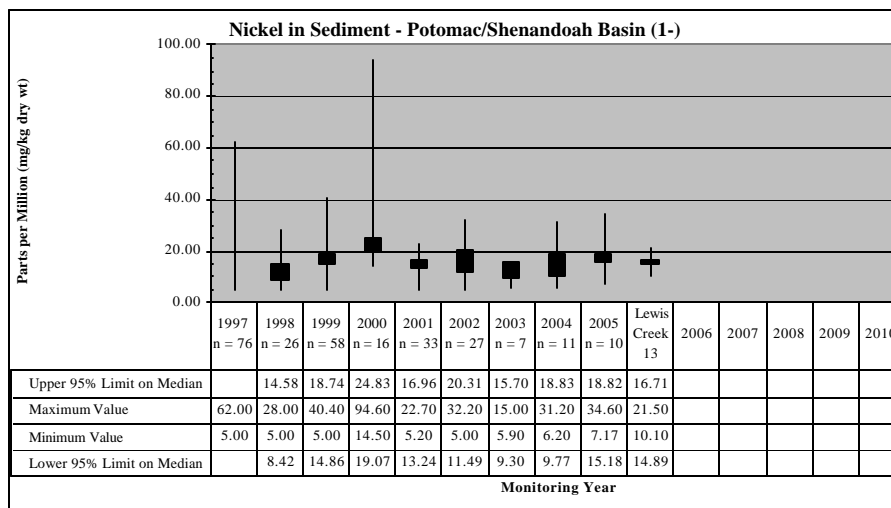
Table 5, “Sediment Metals - All Basins - MY2006” presents tabular results and a statistical data summary of the MY2006 WQM sediment metals data stored in CEDS, arranged by major drainage basin. The statistical summaries in this table can be interpreted in the same manner as described above for Tables 3 and 4. Sediment results from studies carried out by the WQS Program are discussed elsewhere, in a separate section.

The Excel® workbooks of Folder 5 - “Metals, Sediment, Historical MY06” present graphical summaries of the concentrations of selected metals observed in sediment samples, basin by basin, along with year-by-year and metal-by-metal statistical summaries. The vertical lines in the original graphs of Folder 5 represent the 95 percent confidence intervals for the median concentrations observed in each basin. The small, horizontal black lines represent the medians (i.e., 50<sup>th</sup> percentile). Additional graphical summaries were initiated in the January 2005 report that present the maximum and minimum (total range) of values for each metal analyte, in addition to the confidence interval for the median value. This facilitates identification of basins where occasional unusually high concentrations of analytes are observed in the sediment. For example, in Text Figure 1a (below) it can be seen that in the Potomac/Shenandoah Basin sediment nickel concentrations have generally varied symmetrically about the 95% confidence interval for the median concentration. This has been particularly true since most of the sampling became probabilistic (random) in

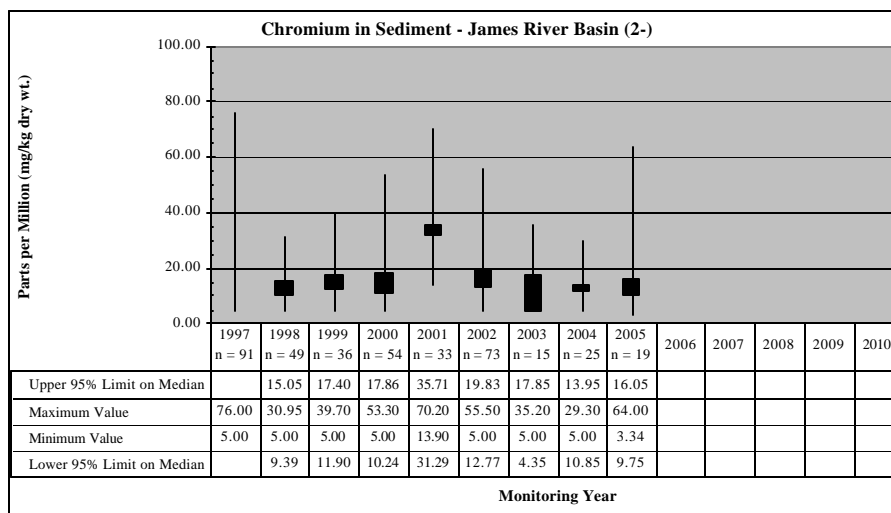
2001. Prior to 2001 sampling was often targeted on suspect areas, and asymmetric high spike concentrations were observed more frequently, as in MY1997 and MY2000 of the figure.



**Text Figure 1a. Statistical summary of nickel concentrations in sediment samples from the Potomac/Shenandoah Basin, 1997 – 2005.**



**Text Figure 1b. Statistical summary of nickel concentrations in sediment samples from the Potomac/Shenandoah Basin, 1997 – 2005.**



**Text Figure 1c. Statistical summary of Chromium concentrations in sediment samples from the James River Basin, 1997 – 2005.**

The graphs of the first series (see Text Figure 1a, above), which illustrate only the annual median concentrations and the 95% confidence interval for the medians for each basin/year, are useful primarily for the characterization of, and comparison among, monitoring years within basins and among basins for each year of the summary. The second series of graphs (Text Figure 1b & 1c, above), which includes maximum and minimum values in addition to the confidence interval for the median, provides a measure of the variation (total range in values) among monitoring sites within an individual basin, and identifies those basins and/or years where exceptionally high values were observed. When exceptionally high values of a specific analyte are observed, the specific sites and streams involved can be identified by referring to the corresponding table from the Toxics Reduction Report for the same year. For example, in MY2005 of [Text Figure 1c](#) (above), the maximum sediment chromium concentration of 64  $\mu\text{g}/\text{km}$  in the James River Basin is considerably above the maximum concentrations observed in MY2003 and MY2004. Examination of the James River Basin summary in “Table 5 - Sediment Metals All Basins MY2005” reveals that this value comes from a reservoir sediment sample collected near the dam of Lake Amelia, on the Appomattox River in Amelia County. The second highest sediment chromium concentration (47  $\mu\text{g}/\text{km}$ ) in the James Basin also came from a reservoir sample, collected near a dam on Lees Creek in Nottoway County. Both samples came from deep water (~7.0 meters), where residual sediment deposits had different characteristics from those of samples from the free-flowing stream samples that were collected at the probabilistic sites. The third highest sediment chromium value, of only 25.1  $\mu\text{g}/\text{km}$ , was from a probabilistic site and was well within the variation observed in the James Basin during recent years.

### Sediment Pesticides and Other Organic Toxics

DEQ also monitors organic toxics deposited in the sediments underlying the Commonwealth’s waters. In recent years, DEQ’s ambient monitoring program has expanded the suite of toxic sediment organics that it monitors from 13 compounds (with the old parameter group code PES1S) to more than 200 compounds (with the newly established parameter group code AMBTOX2). Consequently, it has become necessary to modify the format of statistical and graphical summaries of toxic organics monitoring results. What used to consist simply of Table 6 and Folder 6, each summarizing ‘Sediment Pesticides’, has now evolved into Tables and Folders:

- 6a - Sediment Organochlorine Pesticides (25 compounds)
- 6b - Sediment Organophosphorus Pesticides (41 compounds in two files)
- 6c - Sediment Herbicides (17 compounds)

- 6d - Sediment PAHs (31 compounds in two files)
- 6e - Sediment Semi-Volatiles (7 compounds)
- 6f - Sediment PCBs (in excess of 100 congeners in four files)

Table 6a - “Sediment OC Pesticides - All Basins - MY2006” summarizes the ambient freshwater sediment pesticide data from the most recent monitoring year, basin by basin, followed by their statistical summaries. The Excel® workbooks of Folder 6a – “OC Pesticides, Sediment, Historical MY06” present historical sediment organochlorine pesticide results in graphical and tabular form, basin by basin. The vertical lines in the first set of graphs of Folder 6 represent the 95 percent confidence intervals for the median concentrations observed in each year. Again, the small, horizontal black lines represent the medians (i.e., 50<sup>th</sup> percentile). As with sediment metals, a second series of graphs has now been added that illustrates the total range of results observed, along with the confidence interval for the median value. Even though occasional values greatly exceed the median, for the most part they did not represent an exceedance of the available sediment screening values. Interpretation of these tables and graphs can be carried out in the same manner as described previously for sediment metals.

Tables and Folders 6b, 6c, 6d and 6e are presented in essentially the same format as Table and Folder 6a. The results for sediment PCBs are so irregular that they were summarized only in tabular for the 102 individual congeners in Tables 6f-1 through 6f-4. Statistics for total PCBs (the sum of 102 congeners) are summarized in the first worksheet of Table 6f-4, and basin-by-basin graphical comparisons are on the second worksheet of the same table. No separate basin-by-basin summary folder has been developed. Statewide, detectable levels of PCBs were identified at 44 (74.6%) of 59 sites. Of the 102 congeners analyzed, less than half appeared in detectable concentrations at one or more sites. (See “Table 6f-4 – Grp4 – Sediment PCBs All Basins MY2006” for tabular and graphic summaries.)

Further information about the statewide Ambient Water Quality Monitoring Program is available from Roger E. Stewart at (804) 698-4449 or from Donald H. Smith at (804) 698-4429 at DEQ’s Richmond Central Office.

### **New Initiatives in the Ambient Monitoring of Toxics**

During 1998 and 1999, a DEQ Water Quality Monitoring Task Force defined the strategies to be applied in the monitoring of the Commonwealth’s ambient surface waters during the coming years. Two innovations integrated into the updated 2005 Water Quality Monitoring Strategy have significantly improved DEQ’s toxics monitoring program. They involve the probabilistic sampling of surface waters and the monitoring of dissolved toxic organics with SPMDs.

### **Probabilistic Sampling for the Statewide Characterization of Surface Waters**

The freshwater and estuarine sampling programs described in the Probabilistic Monitoring Module of the DEQ WQM strategy include the chemical monitoring of toxic metals and organic compounds in the sediment and the biological monitoring of benthic communities, in addition to the monitoring of conventional water quality variables such as pH, temperature, dissolved oxygen, conductivity or salinity, and nutrients. These probabilistic sampling programs ensure representative monitoring of all of the state’s continental surface water resources.

### **Free Running Freshwaters**

In 1999, EPA's ecological laboratory in Corvallis, Oregon, generated and provided DEQ with a list of 700 sites randomly selected from the state's non-tidal, freshwater streams and rivers. This list included 70 random sites and a similar number of backup sites for each of the first five years of probabilistic freshwater sampling. The sampling of such sites is normally carried out only once, unless the first sampling event identifies a potential water quality problem. In such a case, a special study would be initiated to confirm, and to investigate the severity and geographic extension problem. For an adequate assessment of freshwater benthic communities, however, it was felt that each site should be evaluated in both the spring and in the fall. Biologists from DEQ's regional offices began sampling benthic invertebrates at the first group of these sites in the spring (April - May) and fall (October - November) of 2001. Such probabilistic sampling has continued on an annual basis. During the spring visits to each site, the biologists collect sediment samples for both metals and pesticides analyses, as well as water samples for other traditional water quality parameters (temperature, pH, dissolved oxygen, conductivity, nutrients, chlorophyll, bacteria, etc.). Recent reports, summaries and presentations related to freshwater probabilistic monitoring are currently available on the DEQ WebPages at <http://www.deq.virginia.gov/probmon/#reports>. Appendix H2a provides a list of the freshwater probabilistic monitoring sites sampled during the spring and fall of 2006. Appendix H2b provides a list of prospective freshwater probabilistic sites for the years 2006-2010. Annual lists will only be finalized after regional DEQ biologists have performed site reconnaissance and confirmed the suitability and accessibility of the sites, year-by-year.

## **Tidal Estuarine Waters –**

### **The National Coastal Assessment Program and continued Estuarine Probabilistic Monitoring**

In the spring of 2000, DEQ received a grant from EPA for the purpose of conducting probabilistic sampling of estuarine waters as part of the Coastal 2000 Initiative, later renamed the National Coastal Assessment (NCA) Program. This grant (EPA Assistance Agreement No. R-82854401-0) provided \$200,000 per year for the planned five-year (summer 2000 - summer 2004) monitoring program. In support of this program, EPA's Office of Research and Development, Gulf Ecology Division (EPA/ORD/GED - Gulf Breeze, Florida) annually generated a list of 50 primary (plus a number of alternate) probabilistic sampling sites within Virginia's portion of the Chesapeake Bay and tidal tributaries to the bay and to the Atlantic coastline. Sediment chemistry and toxicity samples and benthic community samples were collected and analyzed from each probabilistic site in this program.

In the spring of 2004 EPA announced that the probabilistic survey methodology of the National Coastal Assessment Program had been elevated from an experimental to an established, permanent program and was being transferred from the EPA Office of Research and Development (ORD) to its Office of Water (OW). In the spring of 2005 a request for proposals (RFP) was issued for two-year transitional grants to continue support of the program during the transfer process. Participating states, including Virginia, were subsequently awarded two-year grants, at reduced funding levels of \$100,000 per year, to facilitate the transition. Federal requirements dictate that the majority of these resources be dedicated to sampling at 25 sites within the mainstem Chesapeake Bay and its major tidal tributaries during the transition. Matching state funds have providing for the continued probabilistic sampling of minor tidal tributaries during the two-year transitional period (summers of 2005 and 2006). In December of 2005 EPA released a mid-term schedule of National Probabilistic Surveys. In the future, the national surveys will rotate among five resource classes each five years: streams, large rivers, lakes, coastal waters and wetlands. Additional federal resources will be provided for state participation in this program. The currently scheduled field seasons for the national probabilistic survey of coastal waters will occur during the summer of 2009 and every five years thereafter. In the interim, DEQ plans to continue the Estuarine Probabilistic Monitoring

Program with the same sampling design (50 sites per year) by combining resources from general funds with those of the Chesapeake Bay Program.

Appendix G-2 provides complete lists of the DEQ Coastal 2000 / NCA probabilistic stations (and alternate sites) sampled during July - September 2005.

### **Passive Integrative Monitoring of Bioavailable Toxic Organics using Semi Permeable Membrane Devices (SPMDs)**

In recent years, traditional monitoring for toxic organic compounds has been confined to fish tissue and sediment samples. State statutes require the monitoring of fish tissue, and such monitoring will continue as described elsewhere in this document. Fish tissue monitoring is an important program, as its purpose is to protect human health by preventing the consumption of contaminated fish. Sediment monitoring is useful to determine the movement and redistribution of toxics within and between the water column and the sediment, as well as for locating and identifying the sources of contamination. Both fish tissue and sediment monitoring are important tools for the detection of toxic compounds, but both approaches have limitations. Because fish are mobile, fish tissue analyses often may not accurately reflect spatial or temporal variations in water concentrations from a specific site. Furthermore, different fish species uptake, metabolize and depurate the toxic organic compounds at different rates. Some of these losses are significant enough to yield non-detectable concentrations of target compounds in their tissues.

Sediment may suffer loss of analytes because of their chemical reduction and/or oxidation. Sediment erosion and deposition rates are often highly variable, thereby creating confusing temporal and microgeographic variations. An additional factor that weakens the use of sediment toxics data is that sediment standards based on national criteria are not yet available.

Historically, the analysis of toxic organic compounds directly from ambient water has seldom been used because of the typically ultra-low concentrations present (picograms or billionths of a gram per liter - pg/L) and the inability of routine analytical instrumentation to detect contaminants within these low ranges. However, over the past 10 years, the U.S. Geological Survey (USGS) has developed a cost-effective sampling technique for trace organics in the water column using Semi-Permeable Membrane Devices (SPMDs) that can efficiently sample low concentrations of a large number of toxic organic compounds, including pesticides.

Purified lipids within semipermeable membranes are capable of absorbing and concentrating numerous dissolved organic substances from the water column, analogous to the uptake of such chemicals by animal tissues. SPMDs are specially prepared, thin-walled, high-density polyethylene tubes containing the ultra-purified fish oil triolein. Using the same mechanism through which fish uptake dissolved organic compounds by interchange at the epithelial cell layer, SPMDs uptake dissolved contaminants through the thin, porous plastic and into the triolein 'keeper' solvent. SPMDs are subsequently mounted in protective cages and exposed to ambient water by direct deployment in the field for periods of up to 60 days. They consequently provide an integrated average of toxics concentrations over the whole sampling period.

SPMDs have several advantages over traditional sampling methods:

1. SPDM results are representative of the waters at a specific site.
2. There is no loss of target analyte from SPMDs through metabolism or depuration.
3. Unlike grab samples or short-duration filtered samples, SPMD samples are integrative because the devices are deployed for up to a month at a time.

4. SPMD use is considered a trace enrichment procedure because of the long duration of deployment. At typical background concentrations, trace organics are taken up in large enough quantities to be well above analytical detection limits by the time deployment is suspended.
5. SPMD samples represent the bioavailable phase of the contaminants, which is considered to be the toxic component and for which water quality standards exist.
6. SPMD extracts also can be used in estrogen assay studies to determine a relative endocrine disruption factor. Endocrine disruptors comprise a group of compounds not yet identified by national criteria. A number of studies have identified severe impairment in native fish species due to anthropogenic compounds that exhibit endocrine functions.
7. Matrix interferences, which may increase detection limits and decrease percent recovery of analytes, are typically present in fish tissue and sediments but are nonexistent in SPMD extracts

By means of a two-year pilot program conducted by the Office of Water Quality Monitoring and Assessment, DEQ has recently developed methods for applying this SPMD technology in both fresh- and saltwater environments. The integrative sampling technology applied to the Department's freshwater probabilistic monitoring program has been used to develop SOPs, followed by training of field personnel in the deployment and recovery of SPMDs for use in the probabilistic module of the DEQ Surface Water Monitoring Strategy and, when appropriate, in additional special studies. At the present time, the high costs of material, labor and analyses (~\$5,000 per site for complete analyte analyses) limit their use in widespread monitoring programs such as the watershed monitoring network.

The Code of Virginia, § 62.1-44.19:5, Water Quality Monitoring and Reporting, directs the Virginia Department of Environmental Quality to expand the percentage of river and stream miles monitored so as ultimately to be representative of all river and stream miles in the state according to a developed plan and schedule. In addition, the Code of Virginia directs the Department to expand its water quality monitoring program to include toxic contaminant assessment for those compounds for which the state has water quality standards (9 VAC 25-260-5 et seq.), those compounds that are of concern to the Chesapeake Bay Program Office of USEPA, and any other compounds which may be indicators of adverse water quality. In order to comply with this legislative requirement the Department's Water Quality Monitoring Strategy incorporated a probabilistic monitoring program targeted towards two different geographic strata, free flowing freshwater streams and estuarine waters (initially funded by the EPA Coastal 2000 project).

As new hydrophobic compounds with extremely low solubilities are introduced into our watersheds, there is an increasing need to detect these substances at the low concentrations at which they become biologically active. There is also a need to monitor our waters for these compounds at background concentrations to provide trend data and to predict any possible potential future threats to the ecosystem.

Since 2001 the Virginia Department of Environmental Quality (VADEQ) has operated a Probabilistic Monitoring (referred to as ProbMon) Program within the state's non-tidal, free-flowing streams. ProbMon sampling is carried out at randomly sited stations that are appropriate for making statistically based assessments of a subset of Virginia's streams. This approach differs from traditional monitoring programs in that stations are selected randomly, rather than with potential biases resulting from ease of access or targeting specific data needs. Data from randomly selected stations can statistically characterize the true distribution of conditions for a pre-defined subset of streams and provides confidence intervals for estimates of resource characteristics. Because the stations are randomly chosen, statistical tests can be performed to identify differences and/or similarities among types of streams, or among geographic or ecological regions of the state. This method provides statistical representativeness in water quality assessments and allows better communication of conditions and potential environmental needs to policy

makers. For a detailed explanation of the design of the ProbMon Program please refer to <http://www.deq.virginia.gov/probmon/>.

The objective of the SPMD project was to determine the background concentrations of ultra low-level dissolved hydrophobic organic chemicals in relation to Virginia's Water Quality Standards, and what percentages of Virginia's streams are supporting, threatened, partially supporting or not supporting fishable, swimmable, and aquatic life uses. The results of this initial study provide first-time estimates of the distribution and background concentrations of trace organic compounds over widespread geographic regions of Virginia. Because of the study design, additional conclusions about the prevalence and distribution of these contaminants were possible and will be discussed further below.

SPMD-derived estimates of water column concentrations (in picograms per liter) revealed detectable target analytes at a significant number of sites; see "Table 1 - Numbers of Sites where Target Analytes were Detected," below.



NUMBER OF DETECTS ABOVE METHOD DETECTION LIMIT			
Fluoranthene	42	Heptachlor	9
Pentachloroanisole	42	Trans-Permethrin	9
Pyrene	40	d-Benzenehexachloride	8
Trans-Nonachlor	37	Methoxychlor	8
Hexachlorobenzene	33	Oxychlordane	8
Dieldrin	32	Benzo[a]pyrene	7
Perylene	32	Trans-Chlordane	7
cis-Chlordane	30	1,2-dimethylnaphthalene	6
Endosulfan	26	Chrysene	6
2-methylphenanthrene	25	Biphenyl	5
Chlorpyrifos	23	cis-Nonachlor	5
p,p'-DDE	23	Dacthal	5
Endosulfan-II	22	Endosulfan Sulfate	4
o,p'-DDD	22	Indeno[1,2,3-c,d]pyrene	4
p,p'-DDD	22	1-ethylnaphthalene	3
2,3,5-trimethylnaphthalene	20	2-methylnaphthalene	3
Benzo[b]fluoranthene	20	Benzo[g,h,i]perylene	3
Diazinon	20	cis-Permethrin	3
o,p'-DDT	20	Lindane	3
Phenanthrene	20	a-Benzenehexachloride	2
1-methylfluorene	17	PCB, TOTAL	2
Benzo[k]fluoranthene	16	b-Benzenehexachloride	1
Endrin	16	Mirex	1
p,p'-DDT	16	3-methylcholanthrene	0
Benz[a]anthracene	15	4-methylbiphenyl	0
Fluorene	15	9-methylanthracene	0
Anthracene	14	Acenaphthylene	0
1-methylnaphthalene	13	Benzo[b]thiophene	0
Benzo[e]pyrene	13	Dibenz[a,h]anthracene	0
Dibenzothiophene	13	Naphthalene	0
Heptachlor Epoxide	13	o,p'-DDE	0
Trifluralin	13		
3,6-dimethylphenanthrene	12		
Acenaphthene	11		
2-methylfluoranthene	10		
Benzo[b]naphtho[2,1-d]thiophene	10		

**Table 1 – Numbers of Sites where Target Analytes were Detected**

Analytes are listed in the order of their statewide prevalence in free-flowing, non-tidal streams.  
(Total N = 42 sites)

Residue concentrations of several chlorinated pesticides (OCPs) and polynuclear aromatic hydrocarbons (PAHs) in SPMDs were found to be above the method detection limit at all or nearly all sites. Only the concentrations of the OCP pentachloroanisole (PCA), however, were at or above the method quantitation limit in SPMDs from every site sampled. Although PCA is classified as an OCP, it is a product of microbial methylation of the wood-preservative pentachlorophenol (PCP). The PCA concentrations detected were well below the water quality standard; however, it is important to note the widespread occurrence. Approximately 80% of the PCP used in the U.S. was for the treatment of wood utility poles. In 1987, 28 million pounds of PCP were used in the U.S. The use of PCP was banned at that time. Because of the large production volumes, the widespread use of treated utility poles, and the water solubility of PCP, it's not surprising to detect widespread PCP contamination in our rivers and streams. A number of the sites had quantifiable levels of some of the other OCPs, including the chlordanes, the nonachlors, hexachlorobenzene (HCB), dieldrin and endrin. At one site (ID 9-SNK019.59), the concentration of methoxychlor was significantly higher (i.e., eight-fold) than levels found from the next highest site. The highest concentrations of individual PAHs in SPMDs were of phenanthrene, fluoranthene and pyrene, which are three of the sixteen PAHs listed by the U.S. Environmental Protection Agency as priority pollutants. This finding is characteristic of the pattern of PAHs emitted from pyrogenic sources. Fluoranthene was present at detectable levels at every site. In several samples, methylated PAHs were also observed. This observation is characteristic of the pattern of PAHs emitted from petrogenic sources. More than half of the study sites also had detectable levels of at least one of the current-use pesticides. Endosulfans were the most ubiquitous of the current-use pesticides, with detectable levels found at 33 of the 42 sites sampled. Considering the concentrations of pesticides statewide, all of the pesticides classified as current-use were detectable at one site or another.

Summary statistics for the SPMD results are presented in "Table 2 - Summary Statistics," on the next page. The comparison of water column concentrations with Virginia Water Quality Standards revealed that, of all the compounds detected, only the concentrations of total PCBs were in the same order of magnitude as the corresponding standard. All other analytes were well below current standards; see "Table 3 - Comparison to Water Quality Standards," below.

The initial findings of this project are of great importance to DEQ's water quality monitoring program and to the understanding of the distribution and concentrations of anthropogenic contaminants among Virginia's watersheds. For the first time in the United States, the actual concentrations of toxic organic contaminants in free-flowing, non-tidal streams have been statistically characterized at the state level using a probabilistic sampling design coupled with a very sensitive integrative passive sampler. Using the statistically based design, DEQ has determined that, with the exception of PCBs, Virginia's free-flowing streams contain very low levels of most of the toxic organics for which the state has established Water Quality Standards, or that are Toxics of Concern or Potentially of Concern. We have established statistical correlations between the magnitude and occurrence of various contaminants and land use. The results of this study will help focus future projects for determining the occurrence, magnitude, and spatial distribution of other anthropogenic organics (such as antibiotics, personal care products, pharmaceuticals, etc.) that currently have no water quality criteria but are expected to occur in our watersheds.

COMPOUNDS WITH WATER QUALITY STANDARDS, pg/L						
COMPOUND	Observed MAX	Observed MIN	Observed MEDIAN	MEDIAN from CDF	Observed MEAN	MEAN from CDF
a-Benzenehexachloride	122.5	29.3	50.3	52.8	53.7	67.2
Acenaphthene	1401.5	197.5	317.3	332.5	415.0	522.9
Anthracene	260.3	20.1	35.4	59.2	60.7	72.1
Benzanthracene	954.6	14.8	41.8	48.5	91.2	85.5
BenzApyrene	218.0	12.4	32.0	33.1	42.1	52.0
BenzoBfluoranthene	1654.0	15.7	54.1	55.8	137.0	113.2
BenzoKfluoranthene	781.0	13.3	37.5	43.8	76.1	72.7
Chlorpyrifos	75.6	2.9	8.9	11.4	17.7	18.5
Chrysene	4226.8	231.3	547.7	632.0	762.2	970.4
Diazinon	2626.7	308.2	403.3	749.5	907.2	943.4
Dibenzanthracene	151.5	16.2	33.4	42.4	48.1	66.3
Dieldrin	308.2	6.5	29.9	36.5	57.7	52.8
Endrin	202.8	9.7	14.8	15.6	26.8	39.4
Fluoranthene	15349.0	8.2	312.3	445.1	1114.5	796.4
Fluorene	1369.2	138.2	223.4	261.8	382.6	543.0
Heptachlor	20.0	0.2	0.9	1.0	1.7	1.5
Heptachlor Epoxide	115.4	13.7	24.1	24.5	35.4	43.5
Hexachlorobenzene	45.9	3.9	13.3	13.9	17.2	18.6
Indenopyrene	223.2	12.7	30.0	34.7	40.8	52.8
Lindane	177.3	51.1	84.0	87.8	89.5	106.3
Methoxychlor	328.7	0.6	1.0	1.1	14.9	9.1
Mirex	8.3	0.3	0.7	0.8	1.1	1.5
<b>PCBS</b>	<b>2112.3</b>	<b>37.4</b>	<b>84.1</b>	<b>98.0</b>	<b>155.8</b>	<b>194.2</b>
Pentachloroanisole	416.1	7.2	77.2	98.4	115.2	142.9
Pyrene	9853.1	6.8	211.5	266.3	758.0	540.5
CHLORDANE	1388.1	49.9	125.4	145.6	206.0	207.2
DDE	166.2	7.0	22.8	26.5	33.2	44.1
DDD	270.2	9.7	38.9	40.0	58.2	67.3
DDT	188.6	7.6	35.8	44.4	46.6	73.3
PAHLOW	9886.8	998.9	6565.5	6769.1	5864.7	6056.8
PAHHIGH	29662.1	172.5	958.0	1069.1	2457.3	1985.7
PAHS	39548.9	1718.5	7240.7	7338.3	8322.0	8042.5

**Table 2 - Summary Statistics**

All units are in picograms (pg) per liter. (1 pg = 10<sup>-12</sup> g = 0.000,000,000,001 g)  
(Total N = 42 sites)

COMPARISON TO VIRGINIA'S WATER QUALITY STANDARDS, pg/L									
	SPMD RESULTS			AQUATIC LIFE				HUMAN HEALTH	
	MIN	MAX	AVG	FRESHWATER		SALTWATER		PUBLIC WATER	ALL OTHER
				ACUTE	CHRONIC	ACUTE	CHRONIC	SUPPLY	SURFACE WATERS
a-Benzenehexachloride	29	122	53					39,000	130,000
Acenaphthene	197	1,402	408					1,200,000,000	2,700,000,000
Anthracene	20	260	62					9,600,000	110,000,000
Benzo[a]anthracene	15	955	87					44,000	490,000
Benzo[a]pyrene	12	218	41					44,000	490,000
Benzo[b]fluoranthene	16	1,654	130					44,000	490,000
Benzo[k]fluoranthene	13	781	73					44,000	490,000
Chlorpyrifos	3	76	17	83,000	41,000	11,000	6		
Chrysene	231	4,227	745					44,000	490,000
Dibenz[a,h]anthracene	16	151	47					44,000	490,000
Dieldrin	7	308	55	240,000	56,000	710,000	1,900	1,400	1,400
Endrin	10	203	26	86,000	36,000	37,000	2,300	760,000	810,000
Fluoranthene	8	15,349	1,049					300,000,000	370,000,000
Fluorene	138	1,369	370					1,300,000,000	14,000,000,000
Heptachlor	0	20	2	520,000	3,800	53,000	3,600	2,100	2,100
Heptachlor Epoxide	14	115	34	520,000	3,800	53,000	3,600	1,000	1,100
Hexachlorobenzene	4	46	17					7,500	7,700
Indeno[1,2,3-c,d]pyrene	13	223	40					44,000	490,000
Lindane	51	177	89	950,000		160,000		190,000	630,000
Methoxychlor	1	329	14		30,000		30,000	100,000,000	
Mirex	0	8	1		0		0		
PCBS	37	2,112	150		14,000		30,000	1,700	1,700
Pentachloroanisole	7	416	110	8,700,000	6,700,000	13,000,000	7,900,000	2,800,000	82,000,000
Pyrene	7	9,853	713					960,000,000	11,000,000,000
CHLORDANE	50	1,388	196	2,400,000	4,300	90,000	4,000	21,000	22,000
DDE	7	166	32					5,900	5,900
DDD	10	270	56					8,300	8,400
DDT	8	189	46	1,100,000	1,000	130,000	1,000	5,900	5,900

**Table 3 - Comparisons of SPMD Results to Virginia's Water Quality Standards**

All units are in picograms (pg) per liter. (1 pg = 10<sup>-12</sup> g = 0.000,000,000,001 g)  
 (Total N = 42 sites)

## Expanded Organic Toxics Monitoring in the Sediment

As mentioned earlier in this report, beginning with freshwater probabilistic monitoring sites in the spring of 2003, the Ambient Water Quality Monitoring Program began employing a new parameter group code for the determination of organic contaminant concentrations in the sediment. The Division of Consolidated Laboratory Services (DCLS) of the Virginia Department of General Services has adopted new technologies and methodologies, with significantly lower detection limits. Rather than using the “PES1S” parameter group code employed in the past, DEQ started utilizing a new group code, “AMB\_TOX”. This expanded the number of organic compounds monitored from 13 to 133. The more recently developed group code of AMBTOX2 now provides for the analysis of 229 compounds, including 106 PCB congeners. Currently used parameter group codes and their analyte lists have been included in Table 1 - “DCLS Toxics Group Codes and Prices MY2006” with this report. With AMBTOX2 the per sample cost of sediment organic toxics analysis is now \$1,690.

## Statewide PCB Strategy

In 2004 the Virginia Department of Health (VDH) changed the trigger level at which they issue fish consumption advisories for polychlorinated biphenyls (PCBs) from 600 ppb to 50 ppb in edible fish tissues. On a statewide basis, this significantly increased the quantity of VDH fish consumption restrictions and advisories in effect for Virginia waterways. DEQ had already used a 54 ppb screening value to assess fish tissues for its 2002 and 2004 303(b)/305(d) Water Quality Assessment Reports, so the VDH expansion in fish consumption advisories included many of those waters previously assessed as impaired for PCB contamination in fish. The most recent data available from the DEQ Fish Tissue and Sediment Monitoring Program has resulted in a few new fishing advisories (see the Virginia Department of Health WebPages at: <http://www.vdh.virginia.gov/epi/publichealthtoxicology/fishingadvisories.asp>). All of these waters were listed in DEQ’s 2006 Integrated 305(b)/303(d) Report and are included in Appendix M of this Toxics Reduction Report.

Over the past several years, DEQ staff has initiated a number of studies under its Toxics Contamination ‘Source Assessment Policy’ to determine the sources of PCBs found in fish tissue. In following that Policy, as well as the agency’s ‘Guidelines for Use of the Virginia Environmental Emergency Response Fund’ (VEERF), these studies were approved for funding through VEERF. Since 1999, the Department has also been using the Total Maximum Daily Load (TMDL) program to address water quality impairments in state waters.

The Agency has completed several TMDL studies for PCB impairments that have already been approved by EPA ([http://gisweb.deq.virginia.gov/tmdlapp/tmdl\\_report\\_result.cfm](http://gisweb.deq.virginia.gov/tmdlapp/tmdl_report_result.cfm)), is in the process of developing draft reports for several others (<http://www.deq.virginia.gov/tmdl/2006.html>).

TMDL studies identify the sources of pollution and the reductions needed from the identified sources to attain water quality standards. Pollution from both point sources such as residential, municipal, or industrial discharges and non-point sources such as residential, urban, or agricultural runoff are included. TMDL studies are based on monitoring data, and require source identification as well as the quantification of each source’s contributions. Once the required pollutant reductions are identified, a cleanup plan is developed that identifies specific corrective actions, and their costs and benefits as well as timelines to restore water quality.

DEQ has anticipated that additional agency monitoring, as well as VDH's change to the PCB trigger value, will result in the identification of more PCB-impaired waters throughout the Commonwealth. These additional waters have already impacted the Agency's monitoring programs at a time when there are limitations in both financial and human resources. Consequently, DEQ elaborated a 'PCB Strategy for the Commonwealth of Virginia.' This strategy provides a framework for agency use in implementing the Toxic Source Assessment Policy protocols in surface waters identified as contaminated by PCBs and for applying environmental management programs such as the TMDL and Voluntary Remediation programs. This PCB Strategy and associated documents are now available to the public on DEQ's WebPages at:

<http://www.deq.state.va.us/fishtissue/documents/PCB-Statewide-Strategy-2005.pdf>, and  
<http://www.deq.state.va.us/fishtissue/pcbstrategy.html>

### **Specialized Fish Tissue and Sediment Analyses**

The collection of fish for fish tissue analyses is expensive and requires specialized sampling techniques, equipment, and training. A field team from DEQ's central Office of Water Quality Standards periodically samples all nine of Virginia's significant river basins (14 sub-basins) on a rotating schedule, as well as carrying out other relevant special studies. Sediment samples from the same sites are routinely collected at the same time. When sufficient resources are available, the basin rotation schedule is completed every three years; when resources are more limited, as is currently the case, a five-year rotation cycle is carried out.

Most samples, both fish and sediment, from this program are frozen until the end of the sampling season and sent to scientists at the Virginia Institute of Marine Science (VIMS – Gloucester Point) and the College of William and Mary (Williamsburg) for chemical analyses. Accumulating large numbers of samples prior to initiating analysis is convenient for the responsible laboratory, which will perform a number of identical analyses at the same time. Periodically reorganizing laboratory procedures for intermittent analyses during the monitoring year would be inefficient and more conducive to procedural errors, and would reduce the comparability of analytical results among river basins. The current procedure, however, often results in significant delays between the time of sampling and the availability of the resultant data for assessment, as well as for the dissemination of the information.

### **Fish tissue and sediment sampling plan for 2006:**

Two river basins were selected for the 2006 routine sampling season: the Rappahannock River Basin (last sampled in rotation 2001), and the Roanoke River (last sampled in rotation in 2002). In addition to the "routine" sampling stations located in the Rappahannock and Roanoke River Basins, the sampling stations list includes 16 stations in the Blackwater River watershed and 9 stations in the Nottoway River Watershed of the Chowan River Basin to supplement mercury contamination in tissue data for that watershed. In addition, several citizen requested stations are located in the following watersheds: 1 in the Potomac River (Lake Montclair); 1 Atlantic Ocean Small Coastal (Raccoon Creek) and 5 in the York River (Lake Anna). A total of 101 fish tissue and sediment sampling stations have been selected. A copy of the complete 2006 sampling plan is available at <http://www.deq.state.va.us/fishtissue/> and as Appendix G-1 to this Report. A complete list of sites scheduled for sampling during summer 2006 can be found on pages 6-10 of the sampling plan. (The normal summer sampling season spans parts of two consecutive monitoring years.)

The results from these sediment and tissue samples will subsequently be compared with the screening values listed in Appendices D and E, respectively. Tables 7a-1 – "Fish Tissue Metals 2005 (Rec'd 2006)", Table 7a-2 - "Fish Tissue PCBs WQS MY2005" (Rec'd 2006)", and Table 7a-3 – "Fish PAHs WQS

MY2005 (Rec'd 2006)" summarize the most recent results from fish tissue samples in relation to the EPA-IRIS screening values.

Table 7b - "Sediment Results WQS MY2005" (Rec'd 2006) summarizes the results of sediment samples collected during the summer of 2005, in relation to the NOAA ER-M and/or consensus-based PEC screening values.

The increased number of fish consumption advisories and restrictions that resulted from the Virginia Department of Health's 2004 decision to lower the human health screening value for PCBs in fish tissues, as well as the cosmopolitan distribution of such PCB-based advisories throughout the state, prompted DEQ to initiate several special studies related to the problem and to develop a Statewide PCB Monitoring Strategy. This strategy was published in January 2005 and can be found, along with related documents pertaining to the agency's fish tissue monitoring strategy for PCBs, on the DEQ WebPages at:

<http://www.deq.state.va.us/fishtissue/documents/PCB-Statewide-Strategy-2005.pdf>, and  
<http://www.deq.state.va.us/fishtissue/pcbstrategy.html>.

Additional information on the fish-tissue/sediment monitoring program is available from Alex M. Barron, Office of WQS at (804) 698-4119. Several reports on fish tissue and sediment monitoring by the Office of WQS can be found on the DEQ WebPages at <http://www.deq.virginia.gov/fishtissue>.

Several additional special studies and reports related to toxics in the water column, in sediment, or in fish tissues are discussed elsewhere in this document and in Appendix I – "Special Studies Related to Toxics (MY2006)".

## **Permitted Discharges and Toxics Monitoring of Permitted Facilities**

Both private and public facilities that discharge effluents into the state's waters are required to obtain permits from the State Water Control Board. The Virginia Pollutant Discharge Elimination System (VPDES) requires the establishment of limitations for such permits to ensure that Virginia's water quality standards are not violated in the water bodies receiving such discharges. These standards require that the state's waters be free from toxic compounds in toxic amounts. The water board adopted a toxics management regulation (TMR) in 1988 and amended it in 1996 (VAC 250-31-220) to incorporate more recent federal terminology and to simplify the regulatory structure.

DEQ's Toxics Management Program (TMP) assesses all VPDES permit applicants for their potential to discharge specific toxic chemicals that could violate water quality standards. Facilities with the potential to discharge these substances are given numerical effluent limits in their permits and are required to monitor and report to DEQ on their compliance with these limits following permit-specified schedules. Based upon evaluations done by the TMP, some permits may include Whole Effluent Toxicity (WET) limits, which require additional biological testing of effluent toxicity. The specific requirements for testing effluent toxicity criteria (both chemical and biological), for compliance self-monitoring, and for toxics reduction evaluation (TRE) are included in the Water Permit Program's guidance documents.

DEQ chemically samples in-pipe concentrations of specified substances on both scheduled and surprise inspections at all permitted facilities. When permits include WET limits, the facilities themselves are also required to perform toxicity tests on their effluents until such time that complete compliance is well established and potential toxic effects of the effluent have been minimized or eliminated. DEQ reviews the

results of the self-ministered toxicity monitoring tests for consistency and compliance status and takes the appropriate measures, when necessary, to ensure complete compliance.

Appendix J - "Facilities with Toxics Parameter Limits MY06" of this report lists facilities that currently have or have applied for permits with limits on the quantity or concentration of discharged toxics in their effluents. The same spreadsheet includes their respective addresses, geographic locations, receiving streams, etc. The effective limits (when specified) and reporting frequencies for toxics may vary, depending upon the chemical parameters involved. In some cases, a permit may have been modified, reissued, or adjusted in terms of the current limits within the past year. The current toxics parameters included in each permit, along with their limits and required reporting frequencies, are listed in Appendix K - "Permitted Parameters Limits and Units MY05." The compliance record of each permitted facility during the 2006 monitoring year is reported in Appendix L - "Permitted Toxics Parameters & Compliance MY06."

Some facilities may hold permits requiring only that they report, without a limit-specified value with which they must comply. Since they do not have a numeric value limit, they cannot be used for compliance testing. In the CEDS database, the limit may be an actual numeric value, it can be blank, have "NL" for No Limit, or have "\*\*\*\*\*" for not required to report. Appendix L - "Permitted Toxics Parameters & Compliance MY06" lists the most recently reported data (1 Jul 2005 - 30 Jun 2006) for those facilities with limits and reporting requirements on the quantity or concentration of toxic parameters, as provided in their Discharge Monitoring Reports (DMRs).

Further information on the compliance of permitted facilities with toxic substances in their discharges can be obtained from the appropriate Regional Office Compliance Auditor, who reports to the Regional Water Compliance Manager. In most regional offices, Deputy Regional Directors (see list below) have assumed the role and responsibilities of what was formerly the Compliance Enforcement Manager. The position (and title) of Compliance Enforcement Manager has now been eliminated.

### **Special Studies Concerning Toxics:**

Regional Office coordinated special studies that dealt with toxics during MY2006 are listed below. Such special studies are often initiated independently at the Regional Office level in response to locally recognized problems. Consequently, it has often been necessary to canvas the planners, monitoring coordinators, and TMDL coordinators at all Regional Offices to construct a comprehensive, centralized list of special studies. Although each newly initiated special study should now be recorded in the CEDS database, a survey query to all Regional Office monitoring coordinators still serves to confirm that the list is complete, and to identify additional special studies that are still in the planning stages. The special studies summarized on the following pages were obtained in this way.

Appendix I - "Special Studies Related to Toxics - MY2006" describes several of these studies in more detail, and interim or final reports on some studies are also available on the DEQ Website at <http://www.deq.virginia.gov/water/reports.html>. The names and contact information for the responsible individuals at the Regional and/or Central Office levels are provided in the sections below, as well as in the Appendix.

DEQ's CEDS 2000 database now includes a module intended to register and track the progress of all special studies as they evolve. Each registered special study receives a unique, system-generated identification code that is maintained in a table along with a short title for the study. A Special Study Codes Screen (Text Figure 1 below) is linked to a Key Words Search function to identify all special studies



related to a desired topic (e.g., toxics, metals, pesticides, etc.). The resultant Query lists the codes and short titles of all studies cross-referenced under the key words in the query, together with a “Detail” option that facilitates calling up further information about the study. The Special Study Detail Screen (Text Figure 2) provides the complete descriptive title of the study, a complete list of associated key words, links to the study’s project plan and other documents (such as interim and/or final reports), and up-to-date lists of monitoring stations, parameter group codes, numbers of samples, and total analytical costs of the project.

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### **Regional Office Compliance Auditors and Deputy Regional Directors**

<b><u>Regional Office</u></b>	<b><u>Compliance Auditor</u></b>	<b><u>Deputy Regional Director</u></b>
<b>Northern Virginia</b>	<b>Becky Vice</b> (703) 583-3922	<b>John Bowden</b> (703) 583-3880
<b>Piedmont</b>	<b>Kelly Harris</b> (804) 527-5029	<b>Robert Weld</b> (804) 527-5052
<b>South Central</b>	<b>Peggy Barbour</b> (434) 582-6203	<b>David Miles</b> (434) 582-6228
<b>Southwest</b>	<b>Ruby Scott</b> (276) 676-4882	<b>Dallas Sizemore</b> (276) 676-4842
<b>Tidewater</b>	<b>Debbie Kay</b> (757) 518-2127	<b>Maria Nold</b> (757) 518-2173
<b>Valley</b>	<b>(Vacant)</b> Interviews in progress	<b>Larry Simmons</b> (540) 574-7810
<b>West Central</b>	<b>Tammy Rogers</b> (540) 562-6776	<b>Norm Auldridge</b> (540) 562-6870

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Now that final adjustments have been made to the formatting, the final installation of this module into the production database has been carried out. Its use is now required for the formal proposal, approval, and execution of all future special studies. All intermediate and final reports, sampling and analysis protocols, quality assurance plans, responsible personnel, and so on, that are associated with the study are to be electronically linked to it in the CEDS database to facilitate the complete retrieval of all related information.

## Northern Virginia Regional Office

1. In cooperation with the U.S. Army Corps of Engineers, Norfolk District, the Lake Anna Civic Association and other partners, NVRO has conducted monitoring to investigate sources of PCB's and characterize potential metals contamination in Lake Anna. Metals sampling focused on the Contrary Creek arm of the lake while low-detection level PCB sampling has considered the entire reservoir. Sediment sampling and water column sampling through the use of semi-permeable membrane devices (SPMDs) was conducted throughout the lake and selected stream tributaries in the summer and fall of 2004. This effort, in conjunction with fish tissue data, was designed to identify regions of the lake exhibiting elevated PCB levels. The highest PCB levels were found to be in the Pamunkey Creek and Terrys Run arms of the lake. Extensive sediment sampling was conducted in the summer of 2005 as a follow-up to the initial sampling event. The extensive grid sampling approach in 2005 focused on the Pamunkey Creek and Terrys Run arms of the lake. In general, the highest PCB concentrations in sediment were discovered near bridge crossings. Monitoring activities in the summer of 2006 included limited sediment sampling on the Terrys Run arm of the lake and water column grab sampling during a storm event in September 2006. The water column sampling during the storm event seeks to understand relative PCB concentrations during high flow events versus normal lake pool levels. Data from the storm event sampling has not yet been analyzed.
2. Potomac River and Va. Tributary PCB TMDL (includes portions of the Piedmont Region): An interstate TMDL project involving Maryland, the District of Columbia, Virginia and the U.S. EPA was initiated in 2004 to investigate the severity, extent and probable sources of PCB contamination in the tidal Potomac River Basin. During the past year, water column grab sampling using low detection level analytical methods was conducted during base flow and storm flow events at selected tributaries to the Potomac River. Additionally, effluent sampling from identified significant wastewater treatment facilities was conducted using low detection level methods to evaluate PCB loadings from this source category. Effluent sampling was conducted using automated samplers to collect 24-hour composite samples from each of 11 facilities. The ambient stream and point source effluent samples were analyzed using EPA Method 1668, Revision A to determine congener specific PCB concentrations. The TMDL is scheduled for completion in September 2007. TMDL information can be found at the following website:  
<http://www.deq.virginia.gov/tmdl/mtgppt.html>
3. The acid mine drainage resulting from historical mining activities along Contrary Creek in Louisa County, Virginia has long been recognized as severely impairing the aquatic life of the stream. The stream is currently identified in the Clean Water Act §303(d) list for an aquatic life use impairment due to low pH. During the past year, clean metals testing was performed in the Contrary Creek watershed to understand the concentration of dissolved constituents in the water column. Three sampling events were performed during the course of the year. Sampling was performed along the entire length of the stream. This included testing of the Contrary Creek headwaters to measure background concentrations as well as testing into the inundated waters of Lake Anna to understand the extent of the zone exhibiting elevated levels of dissolved metals.
4. The Accotink Creek and Difficult Run watersheds are both located in Fairfax County, Virginia. Both streams are identified in the Clean Water Act §303(d) list for aquatic life use impairments due to impaired benthic macroinvertebrate communities. Benthic TMDLs for these streams are both scheduled to be completed in spring 2008. In preparation of TMDL development and evaluation of potential stressors to the benthic community, toxicity monitoring was performed in fall 2005. A

chronic toxicity study using fathead minnows (*Pimephales promelas*) and *Ceriodaphnia dubia* was conducted on ambient water samples collected from both streams. The tests were performed to determine if water column toxicity is stressing the benthic community. The results of the testing were indeterminate for Accotink Creek. However, Difficult Run was found to be toxic to the *Ceriodaphnia*. DEQ is now formulating monitoring plans to further investigate potential water column toxicity in these streams, in addition to evaluating other potential stressors to the benthic community.

For further information on toxics monitoring in the Northern Virginia Region, contact:

Bryant Thomas  
DEQ – Northern Virginia Regional Office  
(703) 583-3843

### **Piedmont Regional Office**

1. Dragon Swamp / Piankatank River Mercury Source Assessment Study – For the second year of this study, thirteen stream stations were sampled for total mercury on the same day during both high flow and low flow regimes, and the ‘Mercury Deposition Network’ station was continued in Harcum, VA, for atmospheric deposition data. To date, ambient water results continue to be far below water quality standards, and there appear to be no ambient point source hotspots in the basin. Atmospheric data for 2005 is undergoing interpretation at this time. This study will continue at least through June 2007 pending the availability of funding.
2. Potomac River and Va. Tributary PCB TMDL (includes portions of the Northern Region) – PRO collected ambient PCB water samples from three Potomac River tributaries under base flow and high flow conditions. In addition, a single PCB effluent sample was collected from the Town of Colonial Beach STP. All samples were analyzed using EPA’s high resolution, low detection method (1668A). These samples were in addition to SPMD and sediment samples collected early in 2005 for this project. The TMDL is due by September 2007.
3. Spring Branch Benthic TMDL – The TMDL was approved by EPA and the SWCB in 2006, with total phosphorus reductions as the TMDL endpoint. Post TMDL monitoring continues for nutrients, including ammonia.

For further information on the status, results, reports, etc., of projects in the Piedmont Region contact:

Mark S. Alling  
DEQ – Piedmont Regional Office  
(804) 527-5021

## South Central Regional Office

**Staunton (Roanoke) River TMDL** (includes portions of West Central Region): A PCB TMDL study was initiated in 2005 to identify potential sources and determine the geographic distribution and severity of contamination from the upper reaches of the Roanoke River to Smith Mountain Lake, to the lower reaches from Leesville dam to the backwaters of Kerr Reservoir. The TMDL, which is scheduled for completion in 2008, is in response to PCB fish consumption advisories in the river. PCB sampling has included the use of semi-permeable membrane devices (SPMDs) deployed in areas that will help delineate sources of contamination. Ambient water samples were also collected at five stations, some co-located with USGS flow gages, during base and elevated flow conditions. These samples were analyzed using EPA Method 1668A which has high resolution-low detection level capabilities. Effluents from selected facility outfalls were also assessed for potential PCB loadings to the watershed using the low detection method. The PCB results are currently being reviewed.

A descriptive sampling and analysis plan for this study, submitted by Tetra Tech, Inc. (Tetra Tech, 2005) is available on the DEQ WebPages at <http://www.deq.virginia.gov/tmdl/pptpdf/roansap1.pdf>. The results of this study, which will be available in spring 2007, will provide information for future PCB sampling.

For additional information on toxics monitoring in the South Central Region, contact:

Kelly Wills  
DEQ – South Central Regional Office  
(434) 582-6242

## Southwestern Regional Office

Additional information on several of the studies listed below is provided in Appendix I.

1. **Bluestone River, PCB's (TMDL)**: During low flow conditions semi-permeable membrane devices (SPMDs) were deployed in the fall of 2005 to further identify the extent of the PCB contamination problem. SPMD sampling devices were sent to the USGS laboratory for analysis. Results have not yet been received.
2. **North Fork Holston River, Mercury TMDL**: Olin Corporation continues to collect samples for USF&WS's Natural Resources Damage Assessment. This data will be used in the development of the North Fork TMDL.
3. **Levisa Fork PCBs (TMDL)**: A work plan has been developed to identify potential sources of PCBs and TMDL development. The study design shall include SPMDs and ambient water and effluent collection using a low level detection method (EPA 1668A). The study is planned for spring 2007.
4. **Benthic Impairment TMDLs sampled during FY 2006**:
  - a. Lick Creek
  - b. Bull Creek
  - c. Garden Creek
  - d. South Fork Pound River
  - e. North Fork Pound River
  - f. North Fork Powell River
  - g. Powell River
  - h. Indian Creek

For additional information on toxics monitoring in the Southwest Region, contact:

Stewart Phipps  
DEQ – Southwest Regional Office  
(276) 676-4839

## Tidewater Regional Office

- 1. Tyson Foods Metal Translator Study:** In 2005 a special study was conducted by Tyson Foods Incorporated, Temperanceville Facility (Tyson) Accomack County, Virginia, Virginia Pollutant Discharge Elimination System (VDES) Permit #VA0004049. The purpose of the study was determine the ratio of total copper to dissolved copper in the wastewater treatment plant's final effluent. By determining the contribution of bioavailable copper (dissolved portion) the facility was seeking modification of its final effluent limit for copper.

Previous data collected by the facility and by the monitoring and assessment staff of VADEQ indicated that copper in the facilities effluent and in the receiving stream exceeded regulatory limits.

The facility discharges stormwater and treated wastewater via outfall 001 to an unnamed tributary to Sandy Bottom Branch. The unnamed tributary and Sandy Bottom Branch were listed as impaired for Aquatic Life Use due to exceedance of the freshwater acute criteria for copper and exhibits Observed Effects based on slightly impaired results from stream benthic biological monitoring. The Wildlife Use is impaired due to exceedance of the freshwater acute criteria for copper.

The special study was conducted in accordance with the Department of Environmental Quality (DEQ) Guidance Memorandum No. 96-009 Obtaining Dissolved Metals Data – Amendment #1 and with the Environmental Protection Agency (EPA) Office of Water document 823-B-96-007 The Metals Translator: Guidance for Calculating a Total Recoverable Permit Limit from a Dissolved Criterion. The final report for this study was submitted in December 2005. The study demonstrated that 76% of the copper in the final effluent was bioavailable resulting in an adjustment to the permitted monthly and weekly average concentration.

- 2. City of Franklin Waste Water Treatment Plant – Effects Ratio of Toxic Bioavailable Copper:** In 2006 a special study was initiated by the City of Franklin, Virginia, Virginia Pollutant Discharge Elimination System (VDES) Permit #VA0023922. The purpose of the study is to determine a water effects ratio for copper in the wastewater treatment plant's final effluent. By determining the effects ratio of toxic bioavailable copper (dissolved portion) the facility is seeking modification of its final effluent limit for copper. The water effects ratio is being developed in accordance with EPA 823-B-94-001, "Interim Guidance on Determination and Use of Water-Effect Ratios for Metals.

Previous data collected by the facility indicates that copper in the final effluent are exceeding regulatory limits. The study is still ongoing – results from sampling and analysis completed in the summer of 2006 are still not available.

Toxics-related studies in the Elizabeth River Basin are summarized in the body of this year's TRISWat Report.

For further information on the status of these projects, results, reports, etc., contact:

Roger K. Everton  
DEQ – Tidewater Regional Office  
(757) 518-2150

## Valley Regional Office

- 1. Collection and Analysis of Fish Tissue for Mercury Content - South River and South Fork Shenandoah River.** The South River and the South Fork of the Shenandoah River have been under fish consumption advisories since the 1970s, due to historic releases from the former DuPont manufacturing plant along the South River in Waynesboro, VA. Mercury was used at the plant from 1929 - 1950, and resulted in a legacy contamination problem that continues today. As part of DEQ's ongoing monitoring of fish tissue, samples were collected from a number of sites in 2005, with analyses completed in early 2006. Details can be found at <http://www.deq.virginia.gov/fishtissue/mercury.html>. Results from the 2005 fish collections were evaluated by the Virginia Department of Health and were the basis for continuing the existing consumption advisories. Details on these advisories can be found at <http://www.vdh.virginia.gov/epi/publichealthtoxicology/ShenandoahRiver.asp>. DEQ will be collecting fish tissue samples from these rivers again in 2007.
- 2. Water Sample Collection and Analysis for Mercury in the South River and South Fork Shenandoah River, Virginia.** This monitoring project is also the continuation of an ongoing DEQ mercury-monitoring program. Mercury was released to the environment in the South River in Waynesboro during the first half of this century from a manufacturing process at the E.I. DuPont plant. In a 1982 settlement between DuPont and the State Water Control Board, a fund was established to support monitoring of water, sediments, and fish tissue in the river system for a projected 100-year period. Monitoring through the 1990s rarely detected measurable amounts of mercury in water, due to analytical constraints. With the development of more sensitive techniques ("clean" metals sampling and analyses), quantifiable levels are now routinely recorded. Since 2001, DEQ staff collects total and dissolved mercury samples from sites on the South River and South Fork Shenandoah River bimonthly.
- 3. South River Science Team.** DEQ staff members are coordinating with members of the South River Science Team on a number of surveys in which data are gathered for water, sediments, floodplain soils, and biota in and along the South River. The South River Science team is comprised of representatives from industry, academic institutions, state and federal agencies, environmental groups and independent researchers. This group meets quarterly to coordinate efforts, collaborate on future work, and communicate results. Ongoing studies address mercury source identification, fate and transport, methylation processes, and ecological processes.
- 4. South River Mercury TMDL.** DEQ has teamed with the United States Geological Survey (USGS) and Environmental Protection Agency (EPA) to conduct a Total Maximum Daily Load (TMDL) study of mercury in the South River. The project began in 2005 and will continue through 2008. The goals of the study are to quantify mercury sources in the watershed and to estimate the reductions from those sources that will be needed to decrease fish mercury levels to below the advisory level. As part of this study, USGS has established three continuous water quality monitoring stations, equipped for continuous monitoring of flow, temperature, dissolved oxygen, pH, turbidity, and conductivity. Routine base flow and storm flow water quality monitoring of total and dissolved mercury and methyl mercury also accompanies the continuous monitoring at these stations. This information will be used to establish loads and fluxes of mercury in the South River. With the help of the South River Science Team, USGS has also begun to quantify mercury sources in the watershed including base flow, storm flow, and groundwater loads from the former DuPont plant site, loads from other point sources, atmospheric loads, groundwater loads, and floodplain soil loads.

**5. North and South Forks of Shenandoah River - Fish Kill Investigations.** For the past 3 springs (2004-2006), extensive fish kills have occurred in the Shenandoah River drainage. In 2004, the fish kills affected nearly the entire length of the North Fork of the Shenandoah River. In 2005, over 100 miles of the South Fork Shenandoah River were impacted. In 2006, the fish kills returned to the North Fork Shenandoah, a portion of the South River, and the mainstem Shenandoah River. The Shenandoah fish kill events were preceded by a nearly identical fish kill in 2002 in WV's South Branch of the Potomac River. The fish kills in the North and South Forks of the Shenandoah River resulted in an estimated loss of 80% of the adult smallmouth bass and redbreast sunfish, both highly sought sport fish.

These fish kills are mysteries. Fish pathologists at USGS, Virginia Tech and the U.S. Fish & Wildlife Service determined that these fish were being stressed by undetermined factors and that the external bacterial lesions were apparently a secondary effect caused by stress. Review of historic water quality data has not indicated any notable changes in water quality in recent years or the presence of any chemicals at toxic levels. Traditional water quality sampling occurs only once per month and is insufficient to capture short-term environmental stresses that may occur, however. Much of the concern from citizens has focused on perceived impacts from agricultural, construction, and urban runoff.

To ensure a collaborative investigative and communication process, DEQ and the Virginia Department of Game & Inland Fisheries formed the Shenandoah River Fish Kill Task Force in July, 2005. The Task Force includes representatives of state and federal agencies, agriculture, industry, riparian landowners, anglers, academia, and citizen environmental groups from the Shenandoah Watershed. The Task Force has been meeting regularly since July 2005. The group has identified a number of hypotheses for the fish kills, along with strategies for investigating and validating possible causes. Recent collaborative efforts include participation with WV officials and USEPA in a CADDIS stressor identification workshop. DEQ is also contracting with regional fisheries experts to establish investigative priorities during 2007.

For additional information on Valley Region toxics studies Contact:

South River Mercury and  
Shenandoah fish kills:

Don Kain  
DEQ - Valley Regional Office  
(540) 574-7815

Lewis Creek and South River TMDLs:

Robert Brent  
DEQ - Valley Regional Office  
(540) 574-7848

## West Central Regional Office

1. **Smith River Biological TMDL:** WCRO performed toxicity testing in support of the Smith River biological TMDL in May 2006. All samples were sent to the U.S. EPA laboratory in Wheeling, West Virginia, but the results have not yet been received.
2. **Roanoke River TMDL (includes portions of South Central Region)** - A PCB TMDL study was initiated in 2005 to identify potential sources and determine the geographic distribution and severity of contamination from the upper reaches of the Roanoke River to Smith Mountain Lake, to the lower reaches from Leesville dam to the backwaters of Kerr Reservoir. The TMDL, which is scheduled for completion in 2008, is in response to PCB fish consumption advisories in the river. PCB sampling has included the use of semi-permeable membrane devices (SPMDs) deployed to help delineate sources of contamination. Ambient water samples were also collected at five stations, some co-located with USGS flow gages, during base and elevated flow conditions. These samples were analyzed using EPA Method 1668A which has high resolution-low detection level capabilities. Effluents from selected facility outfalls were also assessed for potential PCB loadings to the watershed using the low detection method. The PCB results are currently being reviewed. Another critical part of this source investigation entailed DEQ interviewing over 50 facilities in the upper Roanoke River basin from June to August 2005.

A descriptive sampling and analysis plan for this study, submitted by Tetra Tech, Inc. (Tetra Tech, 2005) is available on the DEQ WebPages at <http://www.deq.virginia.gov/tmdl/pptpdf/roansap1.pdf>. The results of this study, which will be available in spring 2007, shall provide information for future PCB sampling.

3. **Jackson River Biological TMDL:** WCRO performed water column toxicity sampling for benthic TMDLs at two locations in the Jackson River in Allegany County in MY 2005. The Jackson River is a major tributary in the upper James River watershed. All samples were sent to the U.S. EPA laboratory in Wheeling, West Virginia. These samples showed potential toxicity concerns in the Jackson River, but the developing TMDL will focus on nutrient reduction rather than toxicity.

For additional information on toxics-related TMDLs contact:

Mary Dail  
DEQ – West Central Regional Office  
(540) 562-6715

## Additional Special Studies Involving Toxics

1. **Elizabeth River Project** - Multiple sampling efforts have been involved in this extensive project (dissolved and total clean metals, dissolved organics – SPMD sampling, tributyltin sampling, and others). DEQ carries out some efforts and contracts out others. This project is discussed in more detail elsewhere in this report. (See the section on the Elizabeth River Program – pp 66-67.) The most recently released reports from the project are listed there, as well as in the References section of this TRISWat Report.

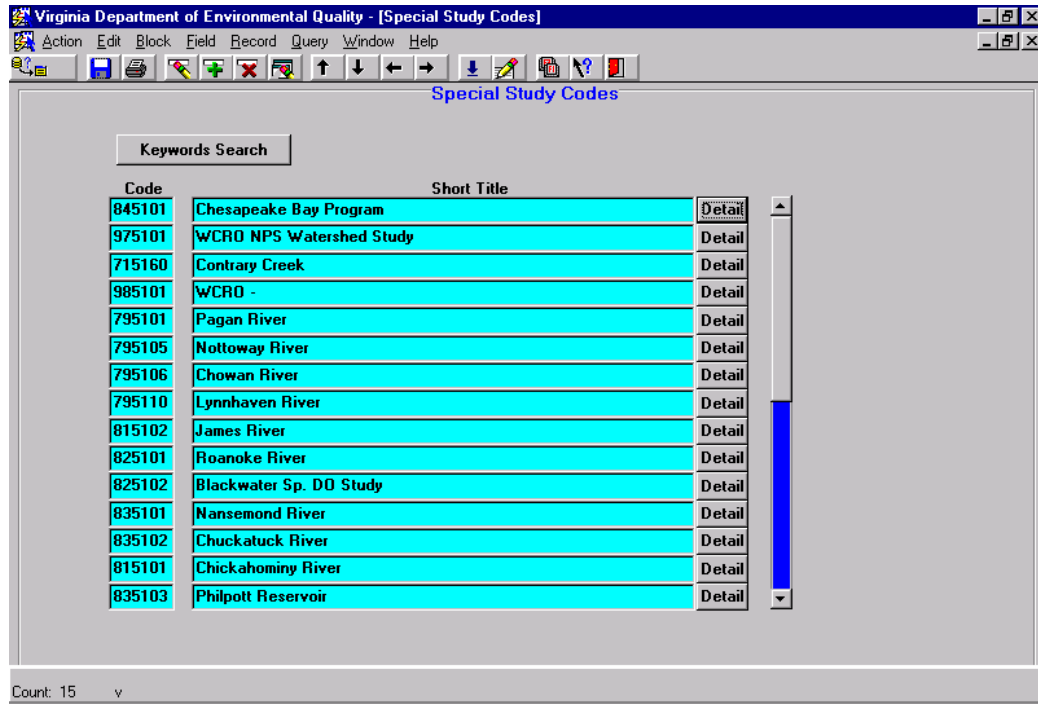


## **Benthic and other TMDL Special Studies Involving Toxics**

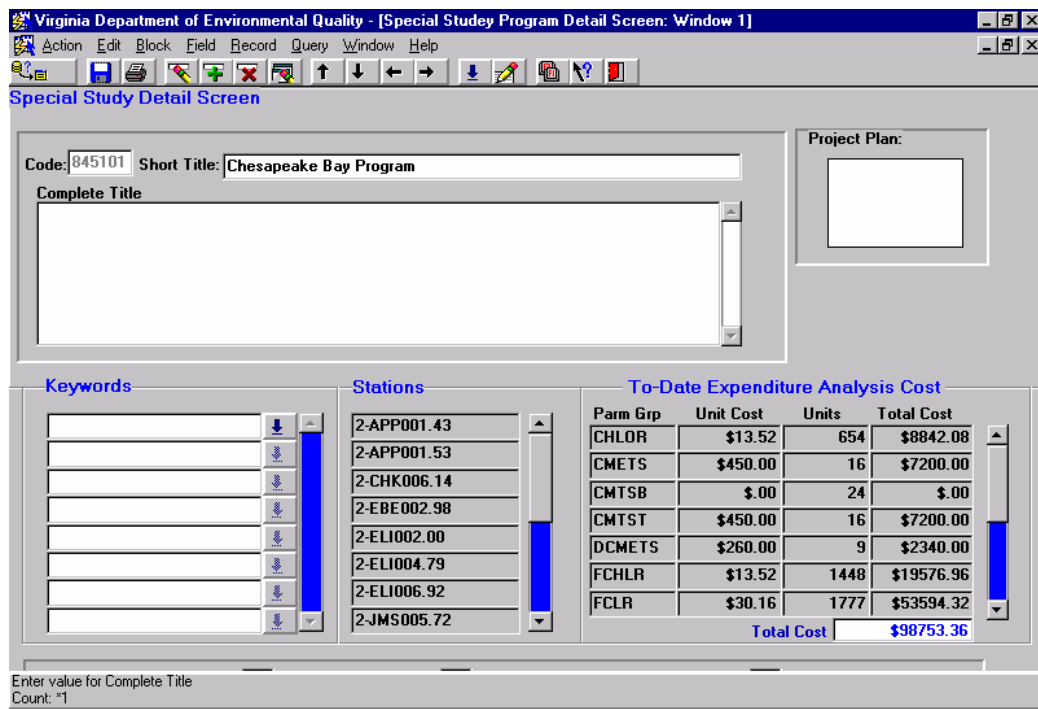
In many cases, determining the cause of benthic impairments can be quite difficult. A number of stressors, including toxicity, sedimentation, eutrophication, the introduction of non-native fish species, and other forms of habitat modification may be involved. Because toxics must be considered as one possible cause of benthic impairments, water samples have been collected and shipped to the EPA Laboratory in Cincinnati, Ohio, for toxicity testing related to TMDL studies of a number of stream segments impaired for benthic organisms since November of 2002.

Lists of benthic and other toxics-related TMDL studies scheduled for 2003 through 2008 can be found linked to DEQ's TMDL Homepage at <http://www.deq.virginia.gov/tmdl/homepage.html>. The type of impairment, whether benthic or for specific toxic parameters (e.g., PCBs), can be identified in the linked tables. The ten-year implementation plan for DEQ's TMDL Program can be accessed from the same web address.

For further information on the results of specific toxics-related TMDLs contact the individuals listed on the TMDL WebPages or, for more general information, contact Jutta Schneider at DEQ's Central Office in Richmond (804) 698-4099.



**Text Figure 1.** The Special Study Codes Screen Developed for the Special Studies Module of DEQ's CEDS 2000 Database.



**Text Figure 2.** The Special Study Detail Screen Developed for the Special Studies Module of DEQ's CEDS 2000 Database.

## **The Calendar Year 2007 Water Quality Monitoring Plan**

The Annual Water Quality Monitoring Plan (or MonPlan) has traditionally been elaborated in the first quarter of each calendar year and was usually finalized by early April. Such MonPlans provided a complete list of the ambient WQM stations that would be actively sampled during the following fiscal year (1 July - 30 June). Beginning in 2006, the DEQ Monitoring Year has corresponded to the calendar year, rather than the state fiscal year, in order to synchronize various ambient monitoring program schedules with one another, with the ecological and water year cycles, and with the traditional 305(b)/303(d) assessment and listing cycle. The lake monitoring program, the fish tissue and sediment monitoring program, and the newly established beach monitoring program (Virginia Department of Health), as examples, are based on summer or spring through fall sampling, and have traditionally bridged two monitoring/fiscal year periods. Under the old scheme, watershed and monitoring site rotations were carried out in mid-summer, which fragmented a single season's results into two separate monitoring year data sets. The new synchronization scheme is being described in detail in the 2007 revision of DEQ's Water Quality Monitoring and Assessment Strategy.

In addition to providing a complete list of the ambient WQM stations, the MonPlan identifies specific programs associated with each site, the parameters that will be measured there, the number of samples that will be collected, and the intended frequency of sampling. The MonPlan also provides the information necessary to estimate the resources required for the following year's monitoring efforts and to advise the state's Division of Consolidated Laboratory Services in advance of the human, technical, and chemical resources that will be necessary for analytical purposes. In addition, it provides a convenient overview for the monitoring coordination group at DEQ's Central Office to evaluate the consistency of site and parameter selection among the agency's seven regional offices.

In the past, Regional Monitoring Plans were produced by regional monitoring coordinators and were integrated into a single statewide plan at the DEQ Central Office in Richmond. The annual Monitoring Plan for MY2006, which began on 1 July 2005, was produced in a new format because the vast majority of the information that it contains could be queried directly from the CEDS database in the form of a report, rather than requiring independent monitoring plans from regional office monitoring personnel.

The new plan for calendar year 2007 is currently being developed and will be initiated in January of 2007. Once finalized, the annual Monitoring Plan will be summarized and posted on the DEQ Website at <http://www.deq.virginia.gov/watermonitoring/>. Those portions of the new plan that deal with long-term trend stations and two-year rotations of the watershed monitoring network will continue without significant modification until the end of December 2008. Other aspects of the Plan, which deal with TMDLs and other special studies or with shorter term rotations such as lake monitoring or citizen requests, will be updated and included by January 2008.

## **Evaluation of Trends in Toxics Concentrations in State Waters**

The distribution of toxic materials in ambient surface waters, and especially in sediments, is heterogeneous in both space and time. This is so for numerous reasons. The problem of extremely low concentrations of dissolved toxics in the water column and the inherent difficulties of sampling and analysis have already been mentioned. In addition, sampling of the water column has conventionally consisted of temporal "point-samples" in which a water sample is collected at a specific point in time for subsequent analysis. Daily, monthly, and yearly cycles and irregular fluctuations in input rates are often not documented,

especially at the low frequency at which toxics are normally sampled and analyzed, and the representativeness of the specific point in time that the sample was collected may be questioned. The effects of these factors have been noted in recent efforts to evaluate long-term trends in conventional water quality parameters and nutrients that were sampled on a much more frequent basis (e.g., Zipper et al., 1998, DEQ-WQM, 2006).

The 30-day integrated sampling of dissolved organic toxics using SPMDs may alleviate this problem within the water column. In addition, when united with the confidence estimates provided by probabilistic sampling, chemical characterizations of specific resource classes (stream types, drainage basins, ecoregions, etc.) can be formally compared statistically among themselves and between sampling periods. When resources become available, another probabilistic SPMD special study in the future will permit us to answer the question of whether contamination by specific dissolved organic compounds is decreasing, remaining stable, or increasing.

The concentrations of toxics within a specific unit of sediment may be more stable in terms of temporal variation, but concentrations may vary considerably even on a local spatial scale. Most toxic substances are readily bound chemically to organic material suspended in the water column or precipitated onto the surface of the sediment. This organic matter is generally lighter than the majority of suspended minerals, which may precipitate out of more rapidly moving waters, and the organics precipitate into the underlying sediments of more slowly moving waters, where they and the bound toxics may accumulate in relatively concentrated, localized deposits. However, any significant change in water velocity or flow pattern may spatially redistribute both the organic material and the associated toxics, and the age of contaminants and the date of such deposition is seldom known.

Even when spatially stable under calm waters, sediments tend to be temporally heterogeneous (stratified). The uppermost sediment layer is generally the most recent, the deeper layers often having been deposited days, weeks, months, or even years earlier. In the deeper, relatively undisturbed sediments, toxics may lie for years without reflecting more recent trends in concentrations. Very careful sampling, done by taking sediment cores and isolating the various strata of sediment for separate analyses, may reveal temporal trends in toxics concentrations. Determining the appropriate time scale, however, is very difficult, and the whole process is extremely costly.

In summary, the same factors that generate temporal and spatial variations in toxics distribution also create difficulties in achieving reliable and definitive statistical analyses. Consequently, much of the available historical database is not amenable to trend analyses. These factors can never be eliminated, but taking them into consideration can lead to more efficient sampling methods and better statistical evaluations that minimize their effects. DEQ's WQM staff is currently evaluating these factors. Continuing wide-scale probabilistic sampling of sediments, water, and biological communities will provide reliable statistical descriptions of regional conditions that can be compared from one sampling cycle to the next. Among the additional strategies being developed is the association of trend monitoring stations with USGS and DEQ gauging stations, to compensate for variations in flow rates and the consequent dilution of toxics in the water column.

The historical water and sediment quality Figures in Folders 3 through 6 present graphical summaries of the statistical descriptions presented in Tables 3 through 6, basin by basin. Historical variations of observed water quality parameters (especially metals) within drainage basins (1997 through 2006) can be evaluated from these figures. The annual summaries beginning in 2001 are generally more comparable and more informative than those from 2000 and earlier. Beginning in 2001, most ambient toxics monitoring (excluding special studies) has been carried out in association with the freshwater and estuarine

probabilistic monitoring programs and basin characterization are much more representative of actual ambient conditions. Prior to that time, toxics monitoring was often targeted on known or suspected problem areas, and the results were not appropriate for general basin-wide characterizations. As indicated earlier in the discussion of pesticide results, graphical comparisons can be misleading unless all pertinent information is considered. Especially pertinent are the numbers of ‘non-detect’ samples included in the summaries. When a specific analyte is not detected in a sample, its ‘Method Detection Limit’ (MDL) is generally reported, along with a quality control code of ‘U’. Because method detection levels have been substantially lowered during the past five years, apparent declines in toxics concentrations may only be an artifact of changing methodologies.

The figures are presented as examples of how trends can be evaluated graphically when sufficient representative data are available. The nine (or fewer) years of data included in the figures represent only a short historical segment for potential toxics trend monitoring. Although the time series is still too short to allow perception and evaluation of long-term temporal trends, it is possible to evaluate differences among groups of stations (consecutive years) within the same drainage basin. In many instances, the low concentrations of toxic substances, near or below the detection limits of the methodologies used for sampling and analysis, result in graphs with little or no perceived variation among samples. The formal evaluation of trends is impossible under these conditions. In other cases, however, variations are sufficient to suggest micro-geographical differences within the same basin.

### **The 2004 and 2006 305(b)/303(d) Water Quality Assessment Integrated Reports**

The complete 2004 Integrated 305(b)/303(d) Report, including interactive maps, is still available on the DEQ Water Quality Assessment WebPages at:

<http://www.deq.virginia.gov/wqa/ir2004.html>.

The 2006 Integrated Report was submitted in September of 2006 and the 303(d) list of impaired waters has already been approved by EPA. This report and the associated 2006 Assessment Guidance Manual are available at:

<http://www.deq.state.va.us/wqa/ir2006.html>.

The methodology for applying the newly developed Benthic Index of Biotic Integrity (B-IBI) for assessment of Chesapeake Bay probabilistic benthic monitoring results, which was initiated for the 2004 Integrated Report, has been modified for the 2006 assessment. Consultations among EPA Region 3, the Interstate Chesapeake Bay Program, the states of Maryland and Virginia, Dan Dauer (ODU) and VERSAR Consulting (Columbia, MD), since January of 2005, resulted in consensus on a new standardized benthic assessment protocol that was utilized by both states in their 2006 Integrated 305(b)/303(d) Reports. A new B-IBI stressor diagnostic tool also has been developed and was used in conjunction with the new B-IBI methodology to identify probable causes of benthic degradation. Among other toxics-related modifications that were included in the 2006 Report is the application of a “Weight of Evidence” assessment method for Aquatic Life Designated Use (ALU) in minor tidal tributaries, utilizing the sediment quality triad (SQT) of Benthic IBI score, sediment toxicity test results and sediment chemical analyses provided by DEQ’s Estuarine Probabilistic Monitoring Program.

Appendix M - “List of Segments not Fully Supporting Designated Uses because of Toxics (2006 303(d) Report)” of the current Toxics Report presents a comprehensive list and description of all water-body segments that were assessed as impaired because of toxics for the 2006 305(b)/303(d) Report. In the near future, detailed Fact Sheets related to each impaired segment in the 2006 Report will be accessible through the ‘Fact Sheet Search’ function on DEQ’s TMDL WebPages at:

<http://www.deq.virginia.gov/tmdl/develop.html>.

Use the ‘Water Body’ name in the fourth column (e.g., ‘Bailey Creek’) of Appendix M to facilitate the search for specific fact sheets. Text Box 3 (below) summarizes the total statewide impairments due to toxics, by pollutant, within specific water resource types. Appendix M will be updated, in agreement with the 2008 Integrated Report, prior to the January 2009 Toxics Reduction in State Waters Report.

Additional information on the Integrated 303(d) / 305(b) Report is available from Harry Augustine, Environmental Program Planner, at the Richmond Central Office of Water Quality Assessment and Planning, (804) 698-4037.

### Text Box 3 - Quantity of Virginia Waters Impaired, by Various Categories of Toxics

(Extracted from TABLE 3.16 – “Waters Impaired by Various Cause Categories” of the 2006 305(b)/303(d) Report)

Areas listed because of benthic community degradation are considered to be ‘potentially’ toxics impaired.

<i>Pollutant</i>	<i>Type</i>	<i>Impaired (Rounded to Nearest Whole Number)</i>	<i>Pollutant</i>	<i>Type</i>	<i>Impaired (Rounded to Nearest Whole Number)</i>
Aldrin	River (mi)	7	Heptachlor Epoxide	River (mi)	0
	Lakes (acres)	0		Lakes (acres)	0
	Estuary (mi <sup>2</sup> )	0		Estuary (mi <sup>2</sup> )	14
Ammonia	River (mi)	1	Mercury	River (mi)	0
	Lakes (acres)	0		Lakes (acres)	28
	Estuary (mi <sup>2</sup> )	0		Estuary (mi <sup>2</sup> )	0
Arsenic	River (mi)	3	Mercury in Fish Tissue	River (mi)	374
	Lakes (acres)	0		Lakes (acres)	3,401
	Estuary (mi <sup>2</sup> )	0		Estuary (mi <sup>2</sup> )	8
Benthic Assessment	River (mi)	1	Nitrates	River (mi)	2
	Lakes (acres)	0		Lakes (acres)	0
	Estuary (mi <sup>2</sup> )	639		Estuary (mi <sup>2</sup> )	0
Benzo(k)fluoranthene	River (mi)	35	PCB in Fish Tissue	River (mi)	973
	Lakes (acres)	0		Lakes (acres)	72,008
	Estuary (mi <sup>2</sup> )	0		Estuary (mi <sup>2</sup> )	2,110
Chlordane	River (mi)	2	PCB's	River (mi)	0
	Lakes (acres)	0		Lakes (acres)	28
	Estuary (mi <sup>2</sup> )	0		Estuary (mi <sup>2</sup> )	0
Chloride	River (mi)	50	Estuarine Sediment Bioassay	River (mi)	NA
	Lakes (acres)	0		Lakes (acres)	NA
	Estuary (mi <sup>2</sup> )	86		Estuary (mi <sup>2</sup> )	2
Copper	River (mi)	6	Tributyltin (TBT)	River (mi)	0
	Lakes (acres)	548		Lakes (acres)	0
	Estuary (mi <sup>2</sup> )	0		Estuary (mi <sup>2</sup> )	11
DDE/DDT	River (mi)	19	Zinc	River (mi)	4
	Lakes (acres)	0		Lakes (acres)	0
	Estuary (mi <sup>2</sup> )	0		Estuary (mi <sup>2</sup> )	0

## Most Recent Virginia Department of Health Fishing Restrictions and Health Advisories

The Virginia Department of Health regularly issues “Fish Consumption Advisories and Restrictions” for Virginia waterways based upon the results from the DEQ Fish Tissue and Sediment Monitoring Program and other sources. All waters subject to these restrictions and advisories are listed in DEQ’s biennial 305(d) Reports. The VDH Website always contains the most recently published updates to fishing restrictions and closures due to concerns related to human health and fish consumption. The complete VDH fishing restrictions and health advisories currently in effect for any waters in the state can be found summarized and mapped by basin at <http://www.vdh.virginia.gov/epi/publichealthtoxicology/fishingadvisories.asp>.

Current advisories/restrictions include:

### 1. Potomac/Shenandoah Basin

- Potomac
  - Various tidal and non-tidal Potomac River Basin PCB advisories – added or modified 12/13/04
  - Indian Run PCB advisory – added 7/27/05
  - Bull Run PCB advisory – modified 7/27/05
- Shenandoah
  - South River mercury advisory - modified 3/29/01
  - South Fork Shenandoah River, North Fork Shenandoah River, and Shenandoah River mercury advisory - 6/7/77; modified 3/29/01
  - Shenandoah River PCB advisory – modified 12/13/04
  - Lewis Creek PCB advisory – added 12/13/04

### 2. James River Basin

- Maury River PCB advisory – added 12/13/04
- Various James River and tributary advisories (primarily for PCBs) added or modified – 12/13/04 and 10/10/06
- Harrison Lake mercury advisory (entire lake, ~ 82 acres) - 7/20/06
- Chickahominy Lake mercury advisory (entire lake, ~1230 acres) - 7/20/06

### 3. Rappahannock River Basin

- Rappahannock PCB advisory – added 12/13/04
- Mountain Run PCB advisory – added 12/13/04

### 4. Roanoke River Basin

- Dan River PCB advisory – modified 12/13/04
- Upper Roanoke River PCB advisory – added 12/13/04
- Roanoke River/Smith Mountain Lake PCB advisory – modified 12/13/04 and 7/27/05
- Roanoke (Staunton) River PCB advisory – modified 12/13/04
- Kerr Reservoir PCB advisory – added 12/13/04

### 5. Chowan River / Dismal Swamp Basin

- Meherrin River PCB advisory – added 12/13/04
- Blackwater River mercury advisory – 12/29/03, modified 7/27/05
- Great Dismal Swamp Canal mercury advisory – 10/29/03, modified 7/27/05

### 6. Tennessee / Big Sandy Basin

- Knox Creek PCB advisory – 5/15/03, modified 6/15/04, 12/13/04 and 7/27/05
- Levisa Fork River PCB advisories (two) – modified or added 12/13/04

- Guest River PCB advisory – added 12/13/04
- Stock Creek PCB advisory – added 12/13/04
- Wolf Creek PCB advisory – added 12/13/04
- Beaver Creek PCB advisory – modified 12/13/04 and 7/27/05
- North Fork Holston River PCB advisory – added 12/13/04

**7. Chesapeake Bay and small Coastal Basins**

- Lake Trashmore mercury (9/30/04) and PCB (12/13/04) advisories added
- Lake Whitehurst mercury (9/30/04) and PCB (12/13/04) advisories added
- Little Creek PCB advisory – added 12/13/04
- Chesapeake Bay (mainstem) and its small coastal tidal tributaries PCB advisory – added 12/13/04
- Eastern Branch Lynnhaven River PCB advisory – added 12/13/04
- Mobjack Bay and tidal tributaries PCB advisory – added 12/13/04
- Tabb Creek PCB advisory – added 12/13/04
- Dragon Run Swamp (entire length)/ Piankatank River mercury advisory – modified 7/27/05

**8. York River Basin**

- York River PCB advisory – added 12/13/04
- Lake Anna PCB advisory – added 6/15/04; modified 12/13/04
- Mattaponi River PCB advisory – added 12/13/04
- Lake Gordonsville mercury advisory – added 9/30/04
- Pamunkey River mercury advisory – added 9/30/04
- Mattaponi River mercury advisory – added 9/30/04
- Herring Creek mercury advisory – added 9/30/04

**9. New River Basin**

- New River PCB advisory – modified 12/13/04
- New River / Claytor Lake PCB advisory – added 12/13/04
- Bluestone River PCB advisory – added 12/13/04

**The Chesapeake Bay Program**

**Toxics Reduction and Prevention Strategy**

The 1987 Chesapeake Bay Agreement committed the signatories to develop, adopt and begin implementation of a basin wide toxics strategy to achieve a reduction of toxics, consistent with the Clean Water Act of 1987, which would ensure protection of human health and living resources. Following the implementation of a multi-jurisdictional effort to define the nature, extent, and magnitude of toxics problems, the initial strategy was further strengthened with the adoption of the 1994 Basin Wide Toxics Reduction and Prevention Strategy. The primary goal of the 1994 strategy was to have a:

*“Bay free of toxics by reducing and eliminating the input of chemical contaminants from all controllable sources to levels that result in no toxic or bioaccumulative impact on living resources that inhabit the Bay or on human health.”*



## Toxics 2000 Strategy

Building upon progress achieved through the implementation of the 1994 Strategy, the Chesapeake Bay Program Executive Council adopted a revised strategy in December 2000 known as the “Toxics 2000 Strategy”. With the retention of the 1994 goal, new objectives and commitments were developed and incorporated into the document. An important strategy objective is to strive for zero release of chemical contaminants from point and non-point sources through pollution prevention and other voluntary means. For those areas with known chemical contaminant problems referenced as Regions of Concern, such as the Elizabeth River in Southeastern Virginia, the strategy includes commitments leading to their restoration. Finally, the strategy includes commitments that will provide the means to measure progress toward meeting the overall strategy goal. One approach consists of a toxics characterization where information derived from concurrent biological and chemical monitoring are synthesized within the context of toxicological impacts.

## Toxics Characterization

In 1999 the Chesapeake Bay Program’s Toxics Subcommittee completed a toxics characterization of the tidal tributaries of the Chesapeake Bay, which included all of Virginia’s tidal tributaries to the Bay (see EPA 903-R-99-010). The characterization served a dual purpose: (1) it was utilized as a guide in the development of the Toxics 2000 Strategy, and (2) it provided the basis from which management actions for chemical reductions could be targeted. The process characterized each pre-defined regional area into one of four categories based on chemical contaminant exposure and biological affects. *Regions of Concern* (e.g., Elizabeth River) are highly impacted areas, *Areas of Low Probability for Adverse Effects* are regional areas that are not impacted by chemical contaminants, and *Areas of Emphasis* have the potential for serious chemical contaminant-related impacts. A fourth category included *Areas of Insufficient or Inconclusive Data* where the data were not sufficient to place the area into one of the three categories above. An example of a management action could include additional ambient toxics monitoring in those regional areas characterized as *Areas of Insufficient Data*.

The Chesapeake Bay Program has a commitment to produce a new Bay-wide Toxics Characterization in 2007. A ‘Toxics Characterization Workgroup’ of the Toxics Subcommittee has actively worked to develop a new ‘toxics characterization matrix’ and standardized scoring system that can be used for evaluating toxics-related data from the entire estuarine region of Chesapeake Bay. The workgroup has identified six primary databases as sources of data for the new report and has issued a call to regional academic and private institutions for the identification of additional data sources. Complementary monitoring for toxics that has been carried out since 1999 should now have eliminated all of Virginia’s ‘Areas of Insufficient Data’ that were identified in the original report. The target date for the new comprehensive report is by December of 2007.

Additional information on the concentrations and trends of toxic substances and other water quality parameters, in the Chesapeake Bay and its tributaries, is currently available on the Chesapeake Bay Website at...

<http://www.chesapeakebay.net/toxics1.htm>, or the search engine at  
<http://www.chesapeakebay.net/search/pubs.htm>.

## **The Elizabeth River Program**

In 1997, in response to indications of toxic impairment of water quality in the Elizabeth River and its tributaries, DEQ and a group of Elizabeth River Project stakeholders collaborated to produce a comprehensive Water Quality Monitoring plan for the water bodies of concern. Under guidelines included in that plan, a baseline environmental study began in January 1998, with the goal of allowing the future assessment of trends in contaminant concentrations and their effects. Scientists from the Virginia Institute of Marine Science, Old Dominion University, and the Department of Environmental Quality are working with representatives from state, federal, and local authorities and other stakeholders to design and conduct this monitoring effort.

Several activities that have been continued under this initiative are described below.

### ***Conventional Pollutants / Nutrients***

DEQ and ODU continue to monitor for these parameters, which include such things as dissolved oxygen, nitrogen, phosphorus, pH, salinity and temperature. This monitoring, while done previously at a limited number of stations, was expanded to 14 stations in 1998 and now includes depth profiles and significantly more detailed nutrient analysis. Although the condition of nutrients and dissolved oxygen are still degraded, monitoring trends show significant improvements at many locations in the river (<http://sci.odu.edu/chesapeakebay/reports/trends/index.shtml>). Data can be viewed and downloaded from the Chesapeake Bay Information System (CIMS) at <http://www.chesapeakebay.net/wquality.htm>

### ***Fish Tissue Histopathology***

Recent academic studies indicate that a small, abundant and non-migratory fish, known as a mummichog, is an excellent indicator of adverse health effects attributable to pollutant exposure. An examination of internal organs has shown that numerous types of lesions, including cancer, can be observed and that the prevalence of these lesions may be directly related to the levels of certain pollutants in the environment. Working with Dr. Wolfgang Vogelbein of VIMS, DEQ has incorporated monitoring of this type into the Elizabeth River Monitoring Program at 12 stations in the Elizabeth River. Existing data generated by this DEQ histopathology monitoring show that, for certain types of liver lesion, prevalence can range from a low of 1.7% in fish collected in the Lafayette River and Western Branch to as high as 85% of the fish collected in the Southern Branch (Vogelbein and Unger, 2003).

A number of relevant research reports can be reviewed on the Internet at

<http://www.elizabethriver.org/Publications/ScientificStudies.asp>

### ***TBT Monitoring***

Dr. Mike Unger, from the Virginia Institute of Marine Science, has collected Tributyltin (TBT) data at 18 Stations in the Elizabeth River, Hampton Roads and the lower James River six times a year since August 1999. Only rarely have non-detectable (less than 1 part per trillion) levels of TBT shown up in these data. The highest measured concentrations occurred on September 20, 2001 with several stations near the confluence of the Eastern and Southern Branches of the Elizabeth River exceeding 20 ng/L; the highest measured concentration was greater than 70 ng/L at a station in the Southern Branch. However, no exceedences of the acute standard (360 ppb) have been observed. A summary of the monitoring results can be viewed at [http://www.vims.edu/env/projects/tbt\\_deq/](http://www.vims.edu/env/projects/tbt_deq/).

### ***Benthic Index of Biotic Integrity (B-IBI) monitoring***

Dr. Dan Dauer (Old Dominion University) initiated a study of the macrobenthic communities of the Elizabeth River watershed in summer 1999 as a means of characterizing the health of the benthic communities of the Elizabeth River watershed. A probability-based sampling design allows calculation of confidence intervals for estimates of condition of the benthic communities and allows estimates of the geographic extent of degradation of the benthic communities. Results for 1999 to 2005 are summarized in the table below.

Monitoring Year	Percent bottom substrate not meeting restoration goals	B-IBI values
1999	64 ± 10.1	2.7
2000	72 ± 17.6	2.6
2001	52 ± 19.6	2.7
2002	72 ± 17.6	2.4
2003	80 ± 15.7	2.3
2004	88 ± 12.7%	2.2
2005	84 ± 12.7%	2.2

In general for the Elizabeth River watershed, species diversity and biomass were below reference condition levels, while abundance was above reference condition levels. Community composition was unbalanced, with levels of pollution-indicative species above, and levels of pollution sensitive species below reference conditions.

Copies of relevant Elizabeth River Monitoring Reports by Dr. Dauer are available at the ODU WebPages on the Internet at <http://sci.odu.edu/chesapeakebay/reports/elizabeth.shtml>

#### Elizabeth River Monitoring Reports: 2003-2006

Dauer, D.M. 2006. Benthic Biological Monitoring Program of the Elizabeth River Watershed (2005). Old Dominion University, Department of Biological Sciences, August 2006.

Dauer, D.M. 2005. Benthic Biological Monitoring Program of the Elizabeth River Watershed (2004). Old Dominion University, Department of Biological Sciences, August 2005.

Dauer, D.M. 2004. Benthic Biological Monitoring Program of the Elizabeth River Watershed (2003). Old Dominion University, Department of Biological Sciences, October 2004.

Vogelbein, W.K. and M. Unger. 2003. The Elizabeth River Monitoring Program 2001 – 2002: Association between Mummichog Liver Histopathology and Sediment Chemical Contamination. Virginia Institute of Marine Science, November 2003

Additional information on the Elizabeth River Project is available from Roger K. Everton, Environmental Manager, DEQ Tidewater Regional Office, at (757) 518-2150.

## Virginia Toxics Release Inventory

Under the provisions of Section 313 of the Emergency Planning and Community Right-to-Know Act of 1986, also known as SARA Title III, Virginia manufacturing and federal government facilities that release certain chemicals into the air or water or onto the land, or that transfer these chemicals for off-site treatment, disposal, recycling, or energy recovery, are required to submit reports to the EPA. This information is reported on Form R–Toxic Chemical Release Inventory Reporting Form and is collectively referred to as the Toxic Release Inventory (TRI).

The most recent Virginia Toxic Release Inventory Report (SARA Title III TRI, March 2006) indicated that 477 Virginia facilities filed 1779 individual reports on the release, transfer, or management of TRI chemicals or chemical categories for the 2004 activity year. Statewide toxic releases to the water totaled approximately 9,146,470 pounds or 14.6 % of the total onsite releases to all media during 2004. This quantity (~9.15 million lbs.) represents an approximate 11.5 % increase from the 8,199,535 pounds released in 2003.

On-site releases to water include discharges to surface waters, such as rivers, lakes, ponds, and streams. On-site releases to the land (~5.6 million lbs.) refer to landfilling, surface impoundment, land treatment/application farming, or any other release of a TRI chemical to land within the boundaries of a facility. Some of these discharges may eventually find their way into the Commonwealth's surface waters as well. Virginia does not permit underground injection as a method of hazardous waste disposal, and no underground injection of TRI chemicals was reported in 2004.

Ten chemicals and chemical categories accounted for more than 99% of the on-site TRI chemical releases to the water. The top ten TRI chemicals released to water were: nitrate compounds (94.9% of total releases to water = 8.682 million lbs.), ammonia (1.93% = 0.177 million pounds), manganese and manganese compounds (1.45% = 0.133 million pounds), barium and barium compounds (0.30% = 0.028 million pounds), zinc and zinc compounds (0.27% = 0.024 million pounds), sodium nitrite (0.26% = 0.024 million pounds), chlorine (0.12% = 0.011 million pounds), ethylene glycol (0.097% = 0.009 million pounds), copper and copper compounds (0.087% = 0.008 million pounds) and dimethylamine (0.086% = 0.008 million pounds). Nitrate compounds are a common byproduct of industrial (and domestic) wastewater treatment processes and have consistently been reported as the major chemical released to the surface water. Nitrates can pose a nutrient problem to water bodies at lower than toxic concentrations.

A considerable amount of additional information on specific groups of chemicals and the quantities of their chemical releases is available in analyses within the original report (2004 VIRGINIA TOXICS RELEASE INVENTORY (TRI) REPORT - March 2006). The March 2006 Virginia TRI Summary Report, summarizing data from CY2004 industry reports, is available on the DEQ Website at: <http://www.deq.virginia.gov/sara3/3132004.html>.

For further information on the Virginia TRI, contact:

Primary Contact: Nichelle D. McDaniel  
Program Coordinator, SARA Title III  
(804) 698-4159

Alternate Contact: Sanjay Thirunagari  
Environmental Program Manager, SARA Title III  
(804) 698-4193.

Additional sources of information on the Toxic Release Inventory: Community Right-to-Know, including the access and use of TRI data and fact sheets for individual states, are available from the EPA's Internet site: <http://www.epa.gov/tri/>. A CD-ROM, containing all data from the 1987 through 1997 Toxic Release Inventory: Community Right-to-Know is also available from the EPA.

The next Virginia TRI report, summarizing toxic releases for calendar year 2005, should be available by March 2007.

### **Reduction of Toxics by Pollution Prevention**

The Office of Pollution Prevention (OPP) of DEQ contributes to the reduction of toxics in the state's waters through its multimedia (i.e., air, water, and waste) non-regulatory pollution prevention program. Although the P2 Program focuses primarily on the reduction of solid wastes, the reduction of waste also reduces the movement, use, and release of toxic materials. Such reductions occur not only within the consumer population but also among retail outlets and, perhaps most important of all, among industries using and/or producing toxic materials.

OPP's activities for each fiscal year are summarized in the Pollution Prevention Annual Report, submitted to the governor and the General Assembly in December of each year. The 2006 report summarizes the pollution prevention strategies developed and implemented by the Virginia Innovations in Pollution Prevention (VIP2) Program, which is coordinated with other DEQ activities as well as with those of the Department of Conservation and Recreation and of the Chesapeake Bay Local Assistance Department. The annual report presents detailed summaries of the major components of VIP2 activities during 2006, several of which are briefly summarized here.

- The total number of facilities in the Virginia Environmental Excellence Program (VEEP) has now reached almost 400, with 250 (75%) at the E2 level, 79 at the E3 level and 16 at the E4 level. A review of VEEP annual performance for 2005 reported elimination of the use of 53,000 lbs and the elimination or recycling of 7450 lbs of hazardous waste. In 2006 VEEP facilities earned over \$72,000 in permit fee discounts by implementing and performing their Environmental Management Plans.
- DEQ's Voluntary Mercury Reduction Initiatives have been successful. As a result of the "Virginia Switch Out" Pilot Project for the recycling of automotive mercury switches, initiated in 2005, legislation was enacted in 2006 requiring the removal of mercury switches from end-of-life motor vehicles prior to their demolition. End of Life Vehicle Solutions (ELVS), an organization created by automotive manufacturers, has distributed collection containers for mercury switches throughout the state and is already receiving recycled switches from automotive demolition facilities.
- DEQ's Pollution Prevention in Healthcare Program (Hospitals for a Healthy Environment) continued to promote the reduction of regulated medical wastes, to reduce toxic materials by encouraging environmentally preferable purchasing practices, and to eliminate mercury from health care purchases. The Program and its participants receive a number of awards and recognition from the national program. Participants reported the reduction of over 1000 lbs of mercury as well as 500 tons of solid waste. DEQ's Compliance Assistance Visitations, related to hazardous waste from hospitals has identified the management of pharmaceutical wastes as an additional issue.
- Of the 850 members (735 participants and 125 mentors) of the Businesses for the Bay (B4B) Program, forty percent are in Virginia. In 2006 they reported approximately 115 million pounds of

waste reduction and cost savings of \$3.8 million due to pollution prevention efforts. Virginia's participants earned eleven B4B Excellence Awards in 2006, more than half of the total awarded.

- DEQ administers Virginia's National Partnership for Environmental Priorities (NPEP) program, previously called the National Waste Minimization Program, which was renamed and re-energized in 2004. The NPEP program encourages public and private organizations to form voluntary partnerships, with states and the EPA, that reduce the use or release of any of the thirty-one substances that have been designated "Priority Chemicals". Milestones for 2006 included:
  1. Sentara-Williamsburg Community Hospital eliminated 32 lbs of mercury by replacing over 160 sphygmomanometers with electronic devices.
  2. Southern Graphic Systems, in Richmond, eliminated 4,800 lbs of lead through substitution with non-toxic alternative materials, and no longer uses lead in their manufacturing process.
  3. The Town of Blacksburg committed to the elimination of lead in the tires of their fleet of vehicles.

For additional information concerning the Pollution Prevention (P2) Program, visit the DEQ WebPages at <http://www.deq.virginia.gov/p2/> , or contact:

Sharon Baxter  
Director, Office of Pollution Prevention  
629 E. Main Street  
Richmond, VA 23219  
(804) 698-4344

## References

*Note: The list of references included here is cumulative, including citations from previous Toxics Reduction in State Waters Reports as well as those cited within the present report. The inclusion of past citations in the report has been maintained as a research tool for interested readers who wish to pursue deeper interests in toxics monitoring in the Commonwealth of Virginia.*

Chesapeake Bay Program. May 1999. Chesapeake Bay Basin Toxics Loading and Release Inventory. EPA 903-R-99-006, CBP/TRS 222-100.

Chesapeake Bay Program. June 1999. Targeting Toxics: A Characterization Report, A Report for Directing Management & Monitoring Actions in the Chesapeake Bay's Tidal Rivers. EPA 903-R-99-010, CBP/TRS 222/106.

W.L. Cranor, D.A. Alvarez, S. D. Perkins, G.A. Tegerdine, R.C. Clark, J.N. Huckins. 2005. Use Of Semipermeable Membrane Device (Spmd) Technology For A Probabilistic Assessment Of Hydrophobic Organic Contaminants In Selected Reaches Of Virginia Rivers. A Report to Virginia DEQ. U.S. Geological Survey, Columbia Environmental Research Center, June 10, 2005.

Dauer, D. M. 2000. Benthic Biological Monitoring Program of the Elizabeth River Watershed (1999). Old Dominion University, Department of Biological Sciences, July 2000.

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