COMMONWEALTH of VIRGINIA

DEPARTMENT OF ENVIRONMENTAL QUALITY

W. Tayloe Murphy, Jr.
Secretary of Natural Resources

Street address: 623 East Main Street, Richmond, Virginia 23219
Mailing address: P.O. Box 10009, Richmond, Virginia 23240
Fax (804) 698-4500 TDD (804) 698-4021
www.deq.state.va.us

Robert G. Burnley
Director

(804)698-4000
1-800-592-5482

December 30,2005

MEMORANDUM:

TO: The Honorable Mark R. Warner

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: Robert G. Burnley

SUBJECT: The Reduction of Toxics in State Waters Report 2005

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 the state's 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. 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

Monitoring Year 2005

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, 2006

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Report prepared by:

Donald H. Smith, Ph.D. Coordination Group – Ambient Water Quality Monitoring Program
DEQ Office of Water Quality Monitoring and Assessment
Central Office, Richmond
(804) 698-4429
dhsmith@deq.virginia.gov

With assistance and/or information from (alphabetical order)

Mark Alling	DEQ Piedmont Regional Office
Alex Barron	DEQ Office of Water Quality Standards
Sharon Baxter	DEQ Office of Pollution Prevention
Robert Brent	DEQ Valley Regional Office
Gabriel Darkwah	DEQ Office of Water Quality Standards
Eleanor Daub	DEQ Office of Water Quality Standards
Jason Hill	DEQ West Central Regional Office
Rick Hoffman	DEQ Chesapeake Bay Program Office
Donald Kain	DEQ Valley Regional Office
Stewart Phipps	DEQ Southwest Regional Office
Charles Morgan	DEQ Office of Water Quality Assessment
Roger Everton	DEQ Tidewater Regional Office
Mark Richards	DEQ Office of Water Quality Assessment – TMDL Program
Roger Stewart	DEQ Office of Water Quality Assessment – Ambient Monitoring
Jeff Talbott	DEQ Northern Virginia Regional Office
Sanjay Thirunagari	DEQ SARA Title III
Bryant Thomas	DEQ Northern Virginia Regional Office
Larry Willis	DEQ West Central Regional Office
Kelly Wills	DEQ South Central Regional Office

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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 Probable Effects Concentrations 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
VISE	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 1st 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 fall of 2006, to incorporate several minor modifications in monitoring schedules and additional water quality criteria and assessment procedures that have evolved in the interim. The revised Strategy is expected to be implemented in January 2007.

Summer (July-September) 2004 comprised the fifth year of DEQ's estuarine probabilistic monitoring and the spring and summer of 2005 comprised the fifth 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 2005 are included in this report. Results from summer (July-September) sampling in 2005 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, chemistry, toxicity and benthic taxonomic results from the probabilistic 'National Coastal Assessment Program' sediment sampling will be used for a toxics-related "Weight-of-Evidence" assessment of aquatic life use in estuarine waters. This will complement the newly developed Benthic Index of Biological Integrity (B-IBI) assessment performed within the Chesapeake Bay Program's benthic probabilistic monitoring program.

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 which are already the focus of TMDL-related special studies. Water column monitoring of toxic organic contaminants using Semipermeable Membrane Devices (SPMDs) reveals the same pattern, except in the case of human health criteria for polychlorinated biphenyls (PCBs) that reflects the cosmopolitan distribution already revealed by fish consumption advisories. Further analyses of freshwater probabilistic monitoring results have revealed that of 20 priority organics with established water quality standards, the concentrations of nine were significantly correlated with the degree of urban development in the associated watersheds, even at low concentrations. No such trends were identified for agricultural or forest land use patterns. More detailed, geographically specific conclusions about toxics-related water quality concerns will be presented in the 2006 Integrated 305(b)/303(d) Water Quality Assessment Report and will be summarized in the 2006 Toxics Reduction Report.

Permitting: DEQ's Toxics Management Program (TMP) currently includes 353 facilities/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 will begin accepting the electronic submission of DMRs (e-DMRs) late in 2005. This will improve 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 (2003 VIRGINIA TOXICS RELEASE INVENTORY (TRI) REPORT - March 2005) indicated that 501 Virginia facilities reported to the TRI program for the 2003 activity year. Statewide toxic releases to the water totaled approximately 8,199,535 pounds or 12.7 % of the total onsite releases to all media during 2003. This quantity (~8.2 million lbs.) represents a 1 % decrease from 2002 releases.

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

- The total number of facilities in the Virginia Environmental Excellence Program (VEEP) now exceeds 200, with 145 (almost ¾) at the E2 level, 52 at the E3 level and 8 at the E4 level.
- DEQ's Voluntary Mercury Reduction Initiatives included:
    1. Fluorescent Lamp Recycling Pilot Project – combined eventual recycling of the approximately 2,000,000 fluorescent lamps in use would be equivalent to 44 pounds of mercury.
    2. "Virginia Switch Out" Pilot Project for the recycling of automotive mercury switches – by the end of October 2005 more than 5,000 switches were collected, eliminating more than 15 pounds of mercury that could have been vaporized with the melting of auto bodies for recycled steel.
- 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. Participation in the program grew to 87 facilities.
- Participants in the Businesses for the Bay (B4B) Program reported 115 million pounds of waste reduction and cost savings of $3.8 million due to pollution prevention efforts. Virginia facilities make up over 40% of the participating facilities (302) and program mentors (54).
- 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 2005 included:

1. Significant reduction (400 gal/yr) in the use of Methyl Ethyl Ketone as a solvent (Flowserve Corp.),
2. Commitment to significant reduction in the use of other volatile organic compounds (25%) and hazardous waste generation (50% - Flowserve Corp.),
3. Significant reduction in lead waste (over 400,000 lbs), and reduction (50%) of the use of lead in solder (General Electric),
4. Replacement of mercury-containing sphygmomanometers (blood pressure meters) – elimination of 41 lbs of mercury (Sentara Williamsburg Community Hospital), and
5. Recycling of automotive mercury light switch assemblies (960 grams of mercury) and lead from battery terminals (240 lbs of lead – Virginia Auto Recyclers).

Foreword 2005

MY2005 Toxics Reduction in State Waters Report (January 2006)

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
- 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 still uses the terms monitoring year and fiscal year interchangeably.

The MY2005 Toxics Reduction in State Waters (TRISWat-06) Report is the ninth 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 to 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. 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 the following:

- 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 trends).

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 (MY1997 – 2005) 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, ninth TRISWat Report (January 2006) contains tables of both raw data and statistical summaries of MY2005 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 2007. A 'Toxics Characterization Workgroup' within the Subcommittee is currently (fall 2005) finalizing 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 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 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.**
- 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.

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 AUGUST 10, 2005), 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 will permit the expanded use of SPMDs in future 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 to be 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.

In the past, DEQ had used the same ER-M values for the assessment of sediments in freshwater, since there were no recommended criteria available for sediment toxics parameters in freshwater environments. Following recommendations by DEQ's Academic Advisory Committee, the use of these values for freshwater sediments has now been suspended. 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 (**http://www.deq.virginia.gov/waterguidance/ pdf/042006.pdf**).

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 to be 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, since 2000 DEQ has 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 - MY2005", summarizes the specific analytes included in these and other parameter groups. More details of this 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

A revised edition of DEQ's Water Quality Monitoring Strategy document was developed and provided for review by EPA Region 3 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 to the Strategy document, and the agency notified EPA Region 3 on September 27 that the document they received in August should be considered the final draft. DEQ was notified that EPA had found the final draft Strategy 'acceptable' in November of 2004. Under the continual planning process, the document will continue to adapt to new monitoring needs as they develop. The next (minor) revision is currently scheduled for completion by December of 2006, for implementation in 2007, followed by major revisions every six years thereafter.

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) will correspond to the calendar year, rather than to the Commonwealth's fiscal year (FY) as it has in the past. This modification will synchronize 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 the 305(b)/303(d) assessment window. The recently concluded FY2005, which began on 1 July 2004 and ended on 30 June 2005, terminated the second year of the second two-year rotational phase of the six-year watershed monitoring cycle described in the 2004 WQM Strategy document. FY2006, which is currently in progress, is the first year of the third rotation. In order to synchronize calendar year rotations, this third two-year rotation will be abbreviated to 18 months and will terminate 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 all major point source discharges and other targeted Standard Industrial Classifications (SICs) based on their permit status, 303(d)[1] 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.

The 2000 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 - MY2005", lists the toxic organic compounds monitored as target analytes in sediment during MY2005 using the Parameter Group Code AMB_TOX. This group code will be replaced by AMBTOX2, which contains additional organic analytes, in MY2006. 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 studied 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 is being 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: organochlorine pesticides, polynuclear aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs), the concentrations of which will indicate the potential of adverse impacts from environmental contaminants. Selected samples were also analyzed for endocrine disrupters and for mutagenic toxicity. The assessment of the results from these previous studies is being 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

[1] Biennial 303(d) Total Maximum Daily Load Priority List and Report, Virginia Department of Environmental Quality and Department of Conservation and Recreation.

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 state monitoring 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 ambulated 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 and the Virginia state laboratory (DCLS) may develop the ability to analyze SPMD extracts in the near future. (This will result in further cost reduction 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 – MY05" 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.[2] 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. In addition, it will continue to use chemical monitoring to 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 chemical toxics 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.)
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

[2] The Water Quality Monitoring Strategy document, prepared by the DEQ Office of Water Quality Monitoring and Assessment, underwent a second review by U.S. EPA Region III and was released for public review and comment in August 2004. A revised, reformatted edition was submitted to EPA for evaluation on September 27, 2004. EPA subsequently indicated it had no additional comments or suggestions and the Strategy was officially implemented in MY2005.

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 2005 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 2005 monitoring 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 <u>not</u> <u>included</u> here.)

Biological Monitoring

<u>*Benthic Community Evaluation*</u>: Field sampling and evaluation of benthic communities has proved 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:

- Assessments in free-flowing freshwater streams are 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 are conducting further data collection and analyses in an attempt to improve the SCI based on public comments and AAC recommendations. The results of these efforts will also be posted on the Website upon completion.
- Cooperative efforts among Virginia, Maryland, the federal Interstate Chesapeake Bay Program, and EPA Region 3 from 2003 through 2005 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 of Old Dominion University and Dr. Roberto Llansó of VERSAR Consulting (Columbia, MD). 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 will be included in Virginia's (and Maryland'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.

Based on the results of biological evaluations, biologists classify 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 are considered to be of acceptable water quality. This procedure is described in more detail in section 6.4.2.2 Free-Flowing Biological Assessment (pp 32-33) of the 2006 Assessment Guidance Manual. Similarly, following the partnership consensus described above, sample benthic IBI scores, when compared with those of reference populations, can 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 MY2005. This list includes many of the probabilistic sites that are also described in Appendix H2a. Much additional information from these stations was recorded in individual databases at each regional office and later consolidated at DEQ's central office in Richmond. 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 quality samples that are shipped to DCLS for chemical analysis. 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.

Appendix H2a, "Freshwater Probabilistic Monitoring Sites MY2005-06", provides a comprehensive list of the probabilistic monitoring stations that were included in the ambient program during calendar year 2005. Many of these (wadeable sites) were also sampled for benthic invertebrate populations.

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 MY2005 for which analytical results are currently available (November 2005). 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. The AMB_TOX parameter group code was modified during the period, and some parameters were not analyzed in all samples. The AMB_TOX parameter group code (134 analytes) will be replaced by AMBTOX2 (229 analytes) in MY2006.

- 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 2005. Similar annual summary tables can be found in previous Toxics Reduction Reports (Jan1999-Jan2005).

Basin Code	River Basin Name	Clean Dissolved Metals	Clean Total Metals	Sediment Metals	Sediment Organics [3]
		(water)	(water)		
1-	**Potomac / Shenandoah**	22+63 [1]	78 [2]+65 [1]	10+13 [5]	9
2-	**James**	16	0	19	17
3-	**Rappahannock**	6	0	6	6
4-	**Roanoke**	14	0	12	12
5-	**Chowan**	15	0	11	10
6-	**Tennessee / Big Sandy**	9	0	13	10
7-	**Small Chesapeake Bay and Coastal**	26	60 [4]	15	1
8-	**York**	4	0	3	3
9-	**New**	4	0	4	4
		---	---	---	---
	Total	**179**	**203**	**106**	**72**
	Grand Total	**560**			

Text Box 1. Summary of Ambient Toxics Monitoring Samples from Virginia's Surface Waters for which data are available - MY2005. (Excludes SPMD and National Coastal Assessment sampling)

[1] Mercury only, in conjunction with the Shenandoah Basin Mercury Special Study.
[2] Modeling Special Study for Potomac River Commission & Federal Interstate Chesapeake Bay Program.
[3] Sediment samples for organics analysis were collected at approximately 60 freshwater probabilistic sites during the spring of 2003. Due to technical difficulties, it was necessary to recollect them in the fall, and the results are included in this year's toxics report. Samples reported were collected and analyzed under the new AMB_TOX parameter group code rather than the previous PES1S group code.
[4] Mercury only, in conjunction with Dragon Run Mercury Special Study.
[5] Lewis Creek Benthic TMDL Special Study

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 - MY2005" presents the results of clean, dissolved toxic metals monitoring during MY2005 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; AT = AmbTox study (DEQ, Chesapeake Bay Program {CBP}, VIMS); ER = Elizabeth River Study; RB = regional biological monitoring; SS = 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 "90th percentile" value is the concentration that only ten percent of the samples exceeded. Similarly, the 75th, 25th, and 10th 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 90th (and/or 75th) percentile, the median, the 25th and 10th 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 (75th percentile) and lower quartile (25th 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., 50th 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 MY2005, 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 and for a benthic TMDL in Lewis Creek. 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 - MY2005, 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., 50th 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) offers the promise of significantly improving the monitoring of dissolved organics. SPMDs were employed in a several special studies on the distribution of

polychlorinated biphenyls (PCBs) during MY2004 and MY2005. Several of these studies and some preliminary results are briefly described elsewhere in this report.

Toxics in the Sediment

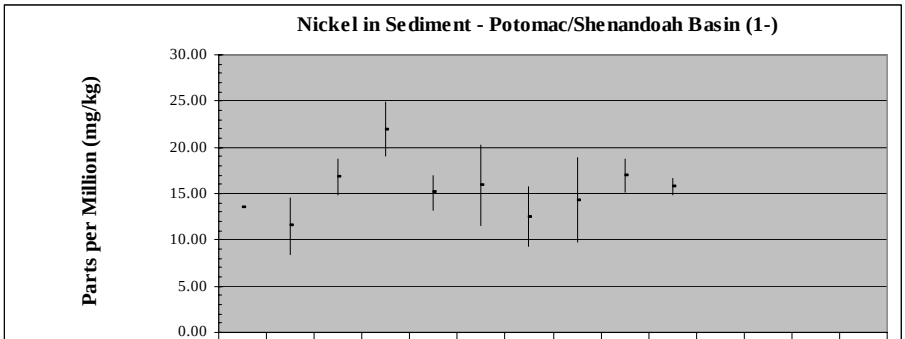
Two separate groups within DEQ monitor sediments in Virginia's surface waters. DEQ's WQM Program has normally evaluated metals from selected permanent and/or rotating ambient WQM stations on a periodic, cyclic basis. More recently, DEQ has added the collection and analysis of sediment samples from each 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 will be 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 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, assessment of the Commonwealth's waters uses sediment data collected by various universities and government organizations, once it has passed quality assurance and quality control checks, along with DEQ's own database.

Sediment Metals

Table 5, "Sediment Metals - All Basins - MY2005" presents tabular results and a statistical data summary of the MY2005 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.

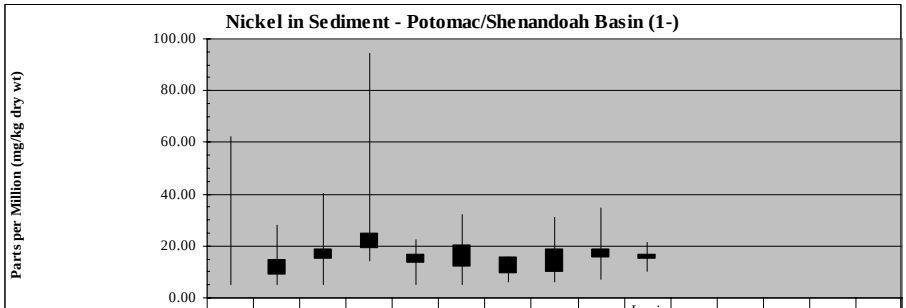
The Excel® workbooks of Folder 5 - "Metals, Sediment, Historical MY05" present graphical summaries of the concentrations of selected metals observed in sediment samples, basin by basin, along with year-by-year and metal-by-metal statistical summaries. The vertical lines in the original graphs of Folder 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., 50th percentile). Additional graphical summaries have been initiated in this 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.



	1997 n = 76	1998 n = 26	1999 n = 58	2000 n = 16	2001 n = 33	2002 n = 27	2003 n = 7	2004 n = 11	2005 n = 10	Lewis Creek 13	2006	2007	2008	2009
Upper 95% Limit on Median		14.58	18.74	24.83	16.96	20.31	15.70	18.83	18.82	16.71				
Lower 95% Limit on Median		8.42	14.86	19.07	13.24	11.49	9.30	9.77	15.18	14.89				
- Median (50th Percentile)	13.50	11.50	16.80	21.95	15.10	15.90	12.50	14.30	17.00	15.80				

Monitoring Year (1 July - 30 June)

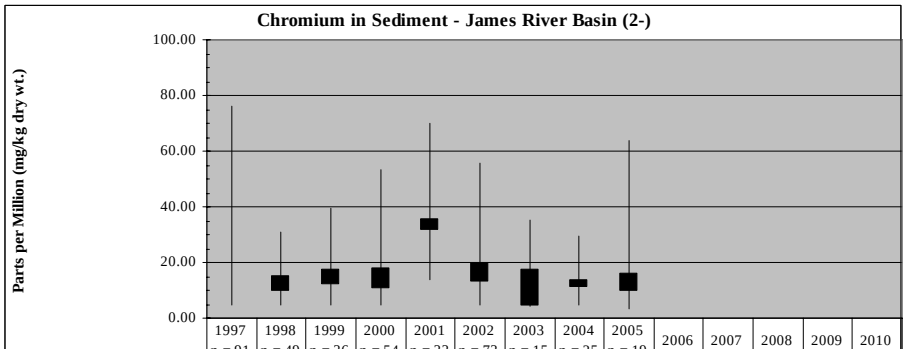
Text Figure 1a. Statistical summary of nickel concentrations in sediment samples from the Potomac/Shenandoah Basin, 1997 – 2005.



	1997 n = 76	1998 n = 26	1999 n = 58	2000 n = 16	2001 n = 33	2002 n = 27	2003 n = 7	2004 n = 11	2005 n = 10	Lewis Creek 13	2006	2007	2008	2009	2010
Upper 95% Limit on Median		14.58	18.74	24.83	16.96	20.31	15.70	18.83	18.82	16.71					
Maximum Value	62.00	28.00	40.40	94.60	22.70	32.20	15.00	31.20	34.60	21.50					
Minimum Value	5.00	5.00	5.00	14.50	5.20	5.00	5.90	6.20	7.17	10.10					
Lower 95% Limit on Median		8.42	14.86	19.07	13.24	11.49	9.30	9.77	15.18	14.89					

Monitoring Year

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



	1997 n = 91	1998 n = 49	1999 n = 36	2000 n = 54	2001 n = 33	2002 n = 73	2003 n = 15	2004 n = 25	2005 n = 19	2006	2007	2008	2009	2010
Upper 95% Limit on Median		15.05	17.40	17.86	35.71	19.83	17.85	13.95	16.05					
Maximum Value	76.00	30.95	39.70	53.30	70.20	55.50	35.20	29.30	64.00					
Minimum Value	5.00	5.00	5.00	5.00	13.90	5.00	5.00	5.00	3.34					
Lower 95% Limit on Median		9.39	11.90	10.24	31.29	12.77	4.35	10.85	9.75					

Monitoring Year

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 µg/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 µg/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 µg/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 (19 compounds)
- 6d - Sediment PAHs and Phalates (23 compounds)
- 6e - Sediment PCBs (in excess of 100 congeners)

Tables 6a-1 - "Sediment OC Pesticides - All Basins - MY2004" and 6a-2 - "Sediment OC Pesticides - All Basins - MY2005" summarize the ambient freshwater sediment pesticide data from the past two monitoring years, basin by basin, followed by their statistical summaries. The Excel® workbooks of Folder 6a – "OC Pesticides, Sediment, Historical MY05" 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., 50th 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 and 6d are presented in essentially the same format as Tables and Folder 6a. The results for sediment PCBs are so irregular that they were summarized in both tabular and graphic forms in

Table 6e, but no basin-by-basin summary folder has been developed as yet. The PCB results from the original AMB_TOX parameter group code were considered unsatisfactory, and an additional PCB group code (PCB_SIM_MS), utilizing mass spectrography, was utilized for PCB analyses. PCB_SIM_MS analyses of 103 PCB congeners were conducted at 51 probabilistic sites during MY2005. Detectable levels of PCBs were identified at 37 (72.5%) of the 51 sites. Of the 103 congeners analyzed, only 48 (46.6%) appeared in detectable concentrations at one or more sites. Only 16 (15.5%) of the 103 congeners were detectable at 10% or more of the sites sampled (see "Table 6e – Sediment PCBs All Basins MY2005" 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 2005. 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 are providing for the continued probabilistic sampling of minor tidal tributaries during the two-year transitional period (summers of 2005 and 2006). EPA has not yet committed to continued funding for the program, in its current form, after 2006.

Appendix G-2 provides complete lists of the DEQ Coastal 2000 / NCA probabilistic stations (and alternate sites) for the summers of 2005 and 2006.

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 disrupters 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 Water Quality Monitoring, Restoration, and Information Act of Virginia (§ 62.1-44.19:5.) directs the Department to expand geographic and parametric monitoring to include all waters of the state for all compounds which have water quality standards or are of special concern. Given limited financial resources

for laboratory analyses, this can only be done with probabilistic monitoring. Additionally, we can only reach detection limits that are sufficient to characterize actual concentrations in the water column and compare the results to our water quality standards with the integrative sampling method used in this type of study. The design of the study was modeled after the USEPA EMAP probabilistic program. The target population was all non-tidal perennial streams and rivers within Virginia. The sampling frame was the USEPA RF3 stream reach file, 1:100,000 map scale.

A random tessellation stratified (RTS) survey design[3] was used to select the stream sample sites. Stevens and Olsen[4] described the RTS design applied to streams. To ensure sampling would occur in the higher order streams, the sample design was weighted by stream order categories to achieve an expectation of approximately equal sample sizes across stream orders and across basins.

Categories for unequal Probability Selection: The sampling design used was developed to achieve approximately equal numbers of sample sites in 1st, 2nd, 3rd, 4th, and 5th or higher Strahler stream orders, each stratum with approximately 12 to 13 sites per year.

Sub-populations: Over time, the numbers of accumulated samples will be sufficient to characterize the water quality of specific smaller aquatic resource sub-populations. Examples of such sub-populations include: water quality classes, eco-regions, small watersheds (HUC designations), land use classes, and stream orders.

In 2002 EPA awarded DEQ Assistant Agreement No. CR-830796-01-3, a two-year $289,000 probabilistic monitoring grant. These resources were consolidated into a single one-year study and used to provide SPMD sampling at 41 of Virginia's probabilistic monitoring sites in free-running fresh waters during the spring and fall of 2003. This study was briefly described in previous Toxics Reduction Reports, but results are now available and are summarized here for the first time.

Summary of the findings:

Residue levels of several chlorinated organic pesticides (OCPs) and polynuclear aromatic hydrocarbons (PAHs) in SPMDs were found to be above the method detection limit at all sites. However, only the concentrations of the OCP pentachloroanisole (PCA) were at or above the method quantitation limit in SPMDs from every site analyzed. Although PCA is classified as an OCP, it is also a microbial methylation product of the wood-preservative pentachlorophenol[5]. PCA concentrations detected were well below the water quality standard; however it is important to note the widespread occurrence. 80% of the PCP used in the U.S. was for treatment of wood utility poles. In 1987, 28 million pounds of PCP were used in the U.S. PCP use was banned later the same year. Because of the large production volumes, the widespread application via utility poles, and the water solubility of PCP, it is 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, which include the chlordanes, the nonachlors, hexachlorobenzene (HCB), dieldrin and endrin. At one site (9-SNK019.59 - Sinking Creek in the New River basin) the concentration of methoxychlor was significantly higher (i.e., eight-fold) than

[3] Stevens, D.L., Jr. 1997. Variable density grid-based sampling designs for continuous spatial populations. Environmetrics, 167-95.
[4] Stevens, D.L., Jr. and Olsen, A.R. 1999. Spatially restricted surveys over time for aquatic resources. Journal of Agricultural, Biological, and Environmental Statistics, (submitted).
[5] W.L. Cranor, D.A. Alvarez, S. D. Perkins, G.A. Tegerdine, R.C. Clark, J.N. Huckins, Use Of Semipermeable Membrane Device (Spmd) Technology For A Probabilistic Assessment Of Hydrophobic Organic Contaminants In Selected Reaches Of Virginia Rivers, U.S. Geological Survey, Columbia Environmental Research Center, June 10, 2005.

levels found from the next highest site. The individual PAHs found in the highest concentrations in SPMDs were 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 (*i.e.*, combustion of fossil fuels). Fluoranthene was present at detectable levels at every site. In several samples, methylated PAHs, which are characteristic of the pattern of PAHs emitted from petrogenic sources (*i.e.*, non-combusted fossil fuels), were also observed. 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 sites. When considering the concentrations of pesticides across all sites, all of the pesticides classified as current-use were detected at at least one site.

As a result of this study's design, we were able to develop statewide cumulative distribution curves (CDF) which can be used to estimate the percentage of river miles characterized by specified concentrations of dissolved contaminants. Further use of the CDF curves permitted comparison of the results to our water quality standards. CDF graphs indicated that all hydrophobic organic compounds except for Polychlorinated Biphenyls (PCB) met state water quality standards. CDF results estimated that 2% of Virginia streams exceed the state water quality standard of 1700 pg/L for total PCBs. It should be noted that nearly 25% of streams are above the 170 pg/L criterion recommend by USEPA. When compared to the number of river miles impaired for PCB fish tissue consumption advisories, these findings are more supportive of a water quality standard in the range of EPA's recommended criterion.

Further analysis of the probability-based data, using the Spearman Rank correlation test, found that 9 of the 20 parameters for which Virginia has a water quality standard had a moderately significant tendency to increase in watersheds with higher urban components. There was no such trend for agricultural or forest land covers. Intuitively, from the large volume of data collected by environmental scientists, we have tentatively identified urban areas as the greatest source of anthropogenic toxic organics. The importance of this finding is significant because of the statistical power of the sampling design. We have demonstrated that the concentrations and distributions of several key compounds are correlated with population density.

SPMDs are currently being employed in several TMDL special studies related to the concentration, distribution and source identification of PCBs in ambient surface waters. In such studies, a reduced suite of analytes (only total PCBs and specific PCB congeners are quantified) has significantly reduced analytical costs per sample. More details on PCB special studies employing SPMDs can be found in the section on "Special Studies Concerning Toxics", later in this Report.

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. Both parameter group codes and their analyte lists have been included in Table 1 - "DCLS Toxics Group Codes and Prices MY2005" with this report. With AMBTOX2 the per sample cost of sediment organic toxics analysis will be $1690.

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 (http://www.vdh.virginia.gov/hhcontrol/fishing_advisories.htm). 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. In addition to reevaluating historical DEQ data, however, VDH also included the most recent data collected by the DEQ in generating its most recent listing of fishing advisories. These data were not available at the time of the 305(b) assessments and 303(d) listings for the 2004 Report, so the VDH fish consumption advisories issued in 2004 may include additional waters not currently on the DEQ list of impaired waters. Those additional waters will be included in the 2006 305(b) assessment and 303(d) listing process.

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 one TMDL study for PCBs and is in the process of developing several others.

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 anticipates 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, and that the additional advisories will impact the Agency's current programs at a time when there are limitations in both financial and human resources. Consequently, DEQ has 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 2005:

Two river basins were selected for the 2005 routine sampling season: the James River Basin (last sampled in rotation 2001), and the Potomac - Shenandoah River Sub-basin (last sampled in rotation in 2001). In addition to the "routine" sampling stations located in the James and Potomac River – Shenandoah River Basins, the sample station list included five special request stations. One special request station was located at Fort A.P. Hill in the York River Basin, one was located at Accotink Creek, Potomac Basin, and three were located in the Holston River Basin in Southwest Virginia. A total of 94 fish tissue and sediment sampling stations were selected. A copy of the complete 2005 sampling plan is available at http://www.deq.state.va.us/fishtissue/documents/2005sampleplan.pdf and as Appendix G-1 to this Report. A complete list of sites scheduled for sampling during summer 2005 can be found on pages 7-16 in 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 Metals WQS MY2004" (Rec'd 2005), Table 7a 2 - "Fish PCBs WQS MY2004" (Rec'd 2005), Table 7a 3 – "Fish Pesticides WQS MY2004" (Rec'd 2005), and Table 7a 4 - "Fish PAHs WQS MY2004" (Rec'd 2005) summarize the most recent results from fish tissue samples in relation to the EPA-IRIS screening values.

Table 7b-1 - "Sediment Chemistry Results WQS MY2003" (Rec'd 2004) summarizes the results of sediment samples collected during the summer of 2003, in relation to the NOAA ER-M and/or consensus-based PEC screening values. The reformatted 2003 results are for samples collected mainly in the York River Basin and Chesapeake Bay-Small Coastal-Atlantic Ocean Drainages, plus selected sites in the James River and Potomac River Basins. Special studies were conducted in the Tennessee-Big Sandy Basin (Guest River and Knox Creek) and Bluestone River Watershed.

Table 7b-2 - "Sediment Chemistry Results WQS MY2004" (Rec'd 2005) summarizes sediment chemistry results from samples collected during the summer of 2004, in relation to the NOAA ER-M and/or consensus-based PEC screening values. The 2004 results are for samples collected mainly in the Potomac River and New River Basins plus selected sites in the Shenandoah River, James River and Roanoke River Basins. Special studies were conducted in the Tennessee-Big Sandy Basin (Beaver Creek and Knox Creek) and Roanoke River Smith Mountain Lake Watershed for PCBs and in the Chowan River Basin (Blackwater River and Great Dismal Canal - Lake Drummond Watersheds) and Dragon Run Swamp, Piankatank River Watershed, for metals. The analyses of some samples collected in the summer of 2004 may not yet be complete. The majority of the results from sampling during the summer of 2005 should be available for next year's Toxics Reduction Report.

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 are listed in Appendix I – "Special Studies Related to Toxics (MY2004)".

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 MY05" 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," along with the effective dates of each permit. The compliance record of each permitted facility during the 2005 monitoring year is reported in Appendix L – "Permitted Toxics Parameters & Compliance MY05."

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 value, it can be blank, have "NL" for No Limit, or have "*********" for not required to report. Appendix L – "Permitted Toxics Parameters & Compliance MY05" lists the most recently reported data (1 Jul 2004 – 30 Jun 2005) 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.

Regional Office Compliance Auditors and Deputy Regional Directors

Regional Office	Compliance Auditor	Deputy Regional Director
Northern Virginia	**Becky Vice** (703) 583-3922	**John Bowden** (703) 583-3880
Piedmont	(Vacant - to be filled by Feb '06) Interim Contact – J.R. Bell (804) 527-5025	**James Golden** (804) 527-5052
Southwest	**Ruby Scott** (276) 676-4882	**Dallas Sizemore** (276) 676-4842
South Central	**Leah Reedy** (434) 582-5120 Ext. 6019	**David Miles** (434) 582-5120 Ext. 6028
Tidewater	**Debbie Kay** (757) 518-2127 **Maria Nold** (Enforcement Manager) (757) 518-2173	**Harold Winer** (757) 518-2153
Valley	**Nonna D. Good** (540) 574-7806	**Larry Simmons** (540) 574-7810
West Central	**Tammy Rogers** (540) 562-6776	**Norm Auldridge** (540) 562-6870

Special Studies Concerning Toxics:

Regional Office coordinated special studies that dealt with toxics during MY2005 are listed in Text Box 2 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 and monitoring coordinators at all Regional Offices to construct a comprehensive, centralized list of special studies. Although each newly initiated special study is now 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 contents of Text Box 2 were obtained in this way.

Appendix I - "Special Studies Related to Toxics - MY2005" describes several of these studies in more detail, and interim or final reports on some 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 Text Box 2 as well as in the Appendix.

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 developed a monitoring plan to investigate sources of PCB's and characterize potential metals contamination in Lake Anna. The monitoring plan was developed during monitoring year 2004, and was implemented August through October of 2004. The monitoring plan entails sediment sampling and water column sampling through the use of semi-permeable membrane devices (SPMDs) throughout the lake and selected stream tributaries. The available Phase I results of this study, including sediment and water column sampling for PCBs, are currently being compiled in a 'Summary Report on the Lake Anna PCB Study.' The target date for completion of the report is December 2005.

2. An interstate TMDL project involving Maryland, the District of Columbia, Virginia and the Chesapeake Bay Program was initiated in 2004 to investigate the severity, extend and probable sources of PCB contamination in the tidal Potomac River Basin. During the past year, integrated and comparative sampling has been carried out using SPMDs (Virginia) and bulk water sampling (Maryland). When available, the results will be utilized for modeling efforts by the Chesapeake Bay Program to facilitate recommendations for TMDL development and implementation. The current target date for completion of this TMDL project is September of 2007.

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 – 13 stream stations were sampled for dissolved and total mercury, plus a 'Mercury Deposition Network' station was established in Harcum, VA for atmospheric deposition data. To date, ambient water results have been far below water quality standards. No 'Point Source' hot spots were identified. Atmospheric data will be available in the spring of 2006. This study will continue into 2006 (MY2006 and 2007).

2. Potomac River and Va. Tributary PCB TMDL – PRO deployed and retrieved 8 SPMDs and obtained 5 sediment PCB samples in PRO Potomac tidal and non-tidal tributaries, the mainstem mouth of the Potomac and in Maryland's Wicomico River as a QAQC comparison with MD sample methods. The TMDL Project is now preparing to sample major point source dischargers. The only PRO discharger under consideration for sampling is the Town of Colonial Beach STP. This study will continue into 2006.

3. Spring Branch Benthic TMDL – Toxicity tests performed in November 2004 indicated significant toxicity in ambient water samples from Spring Branch. PRO performed VOC, semi-volatile organics, sediment organics, clean metals, and ammonia sampling, at a total cost of $16,500, attempting to confirm EPA bioassay toxicity results from Spring Branch and locate a source. A suspected source is the former Borden Chemical facility. However all organics results were below detection limits, clean metals were in normal ranges, and ammonia levels were not remarkable. Only occasional high levels of nitrate were found in a tributary to Spring Branch below the former Borden site. This study will continue into 2006.

Text Box 2. Toxics Related Special Studies Active during MY 2005.

South Central Regional Office

Roanoke (Staunton) River PCB TMDL Source Assessment, Leesville dam to backwaters of Kerr Reservoir – 2005: SCRO began development of a monitoring plan to investigate sources of PCBs in the Roanoke (Staunton) River in order to develop a Total Maximum Daily Load. Monitoring was scheduled for late summer/early fall 2005. Sampling has included the use of semi-permeable membrane devices (SPMDs) and a high resolution-low detection level analysis method (1668A) to assess water column PCB concentrations throughout the river and selected stream tributaries, as well as effluent concentrations at selected facility outfalls. The TMDL is scheduled for completion in July 2006. A final report on the study should be available at that time.

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.

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

Kelly Wills
DEQ – South Central Regional Office
(434) 582-5120

Southwestern Regional Office

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

1. **Bluestone River**; PCBs:
   a. 2004 - High flow SPMDs were employed, in collaboration with USGS, EPA, WVDEP, WVDHHR, VDH to evaluate PCB and Dioxin in the water column (the potential exists for future tests to include drinking water source assessment for both low level PCBs and ultra low level Dioxins); Low flow SPMDs were also deployed during Fall 2005. Results are not yet available.
   b. Spring & summer 2004 – Sediment was sampled for chemical analyses, in collaboration with EPA/WVDEP.
2. **Southwestern VA Fish Hatcheries Study** - PCBs. (Winter 2004)
   Study results did not indicate a problem. No report will be written.
3. **Knox Creek** - PCBs:
   Summer 2004 - Sediment and fish tissue sampling was performed; VDH request further information on water impaired for fish consumption.
4. **Levisa Fork** - PCBs in Sediment and Fish:
   Work plan has been submitted for additional monitoring for PCB source determinations and TMDL development. Goal is to eliminate active sources.
5. **Beaver Creek** – PCBs (2003):
   Summer 2004 - Sediment and Fish sampling
6. **New River** – Wythe County:
   PCBs in Sediment and Fish
7. **North Holston River** - Mercury TMDL (2005):
   Olin Corp. continues to collect samples for EPA's damage assessment. This data will be used in the TMDL development.
8. **Saltville** – Spring 2005:
   Chloride and conductivity sampling was conducted to investigate benthic impairment.
9. **Bioassays Chronic** - Benthic TMDL - MY 2005 (These were sampled in Fall 2004.)
   a. Knox Creek
   b. Pawpaw Creek
   c. Garden Creek
   d. Stock Creek
   e. Laurel Fork
   f. Chestnut Creek
   g. North Fork Holston River

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

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

Text Box 2. (cont.) Toxics Related Special Studies Active during MY 2005.

Tidewater Regional Office

1. A one-day metals sampling special study event (dissolved metals and sediment metals) was carried out at three sites in the Chowan Basin in order to provide data for the Atlantic Wood Industries discharge at their Newsoms, VA facility.

2. The Special Research Unit (SRU) fish tissue and sediment field team from DEQ's Office of Water Quality Standards in Richmond carried out additional follow-up sampling for mercury in the Blackwater River during the summer of 2005.

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 - Spring 2005.** This monitoring project is the continuation of an ongoing DEQ mercury-monitoring program. Results of this sampling effort are expected early in 2006. These data will be used to re-evaluate the existing consumption advisories on the South River (recommendation that no fish except stocked trout be eaten) and the South Fork Shenandoah River (recommendation of no more than 2 meals per month). These two rivers are sampled every 3 years under DEQ's long-term South River mercury monitoring program.

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 has met every two months for the past 5 years to coordinate efforts, collaborate on future work, and communicate results. Ongoing studies address mercury source identification, fate and transport, methylation processes, and ecological processes.

Text Box 2. (cont.) Toxics Related Special Studies Active during MY 2005.

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. This three-year 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, atmospheric loads, and floodplain soil loads.

5. **North and South Forks of Shenandoah River - Fish Kill Investigations**. During the spring of 2004 a fish kill of undetermined origin occurred in the North Fork of the Shenandoah River. The fish kill involved smallmouth bass and sunfish, almost exclusively, and seemed to target only adults of those species. Many of the dead fish were found to have skin lesions. Although fairly low numbers of dead fish were observed at any one place and time, the cumulative effect of the kill was severe, extending over the full length of the river for a period of about 2 months. DEQ and the VA Dept. of Game & Inland Fisheries (DGIF) investigated this fish kill and could not determine a cause. DEQ established a special study for monitoring water quality in the North Fork of the Shenandoah during the spring of 2005. This study focused on nutrients and ammonia. Results did not indicate any ambient concentrations that would result in toxicity to aquatic life, however. In the meantime, a very similar fish kill event occurred in the South Fork of the Shenandoah River in the spring of 2005. This kill involved the same species, same symptoms, and same time period. Again the effect was devastating for the two fish species. Once again, no clear cause was found. In response to these fish kills, the DEQ and DGIF formed the Shenandoah River Fish Kill Task Force, a diverse group of citizens, fishing guides, academia, citizen monitoring groups, and other state and federal agencies. This group has been meeting since July 2005 and is developing coordinated strategies for further investigations into these fish kills.

6. **Lewis Creek TMDL Toxics Study**. Lewis Creek in Staunton, Virginia, is on Virginia's 303d list of impaired waters for violation of the general aquatic life standard as assessed by benthic bioassessments. In previous sediment testing in Lewis Creek, mercury, chlordane, and five specific poly-aromatic hydrocarbon (PAH) compounds were found in concentrations above probable effect levels for aquatic organisms. As part of a Total Maximum Daily Load (TMDL) study to address the benthic impairment in Lewis Creek, DEQ has initiated additional testing of toxics in the water column and stream sediments. Base flow and storm flow samples from three monitoring locations were analyzed for toxic metals. Sediment from 13 monitoring stations on Lewis Creek and its tributaries were tested for mercury, PCBs, PAHs, organochlorine pesticides, and metals. Testing revealed PAH levels above probable effect levels for aquatic organisms at sites that have benthic impairments. Additional PAH testing at those sites was accompanied by sediment toxicity testing to determine if these sediments produce toxicity to benthic organisms. Following the conclusion of sediment testing, DEQ will conduct a stressor identification analysis and will develop a TMDL for the contaminant that is determined to be the most probable stressor.

Contacts:

South River Mercury:	Lewis Creek and South River TMDLs:
Don Kain	Robert Brent
DEQ - Valley Regional Office	DEQ - Valley Regional Office
(540) 574-7815	(540) 574-7848

Text Box 2. (cont.) Toxics Related Special Studies Active during MY 2005.

West Central Regional Office

1. WCRO performed water column toxicity sampling for benthic TMDLs at two locations in the Jackson River in Allegany County. 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 and the results will be used when developing the Jackson River TMDL.

2. **Roanoke (Staunton) River PCB TMDL Source Assessment:** (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 July 2006, is in response to PCB fish consumption advisories in the river. Sampling has included the use of twenty-five (25) semi-permeable membrane devices (SPMDs) deployed in areas that will help delineate sources of contamination. In addition, ambient water was collected at five USGS gauging stations during base flow conditions as well as elevated flows. These samples will be analyzed using EPA Method 1668a which has high resolution-low detection level capabilities. Effluents from selected facility outfalls shall also be assessed for potential PCB loadings to the watershed using the low detection method. 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 2006, will provide information for future PCB sampling.

For additional information on toxics-related TMDLs contact:

Jason Hill
DEQ – West Central Regional Office
(540) 562-6724

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. The most recently released reports from the project are listed there, as well as in the References section of this TRISWat Report

   The Elizabeth River Project has also suffered from recent reductions in the resources available for ambient monitoring. This has been especially true of expensive analytical costs associated with the chemical analyses of toxics, and several aspects of the program have been at least temporarily suspended.

Text Box 2. (cont.) Toxics Related Special Studies Active during MY 2004.

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.

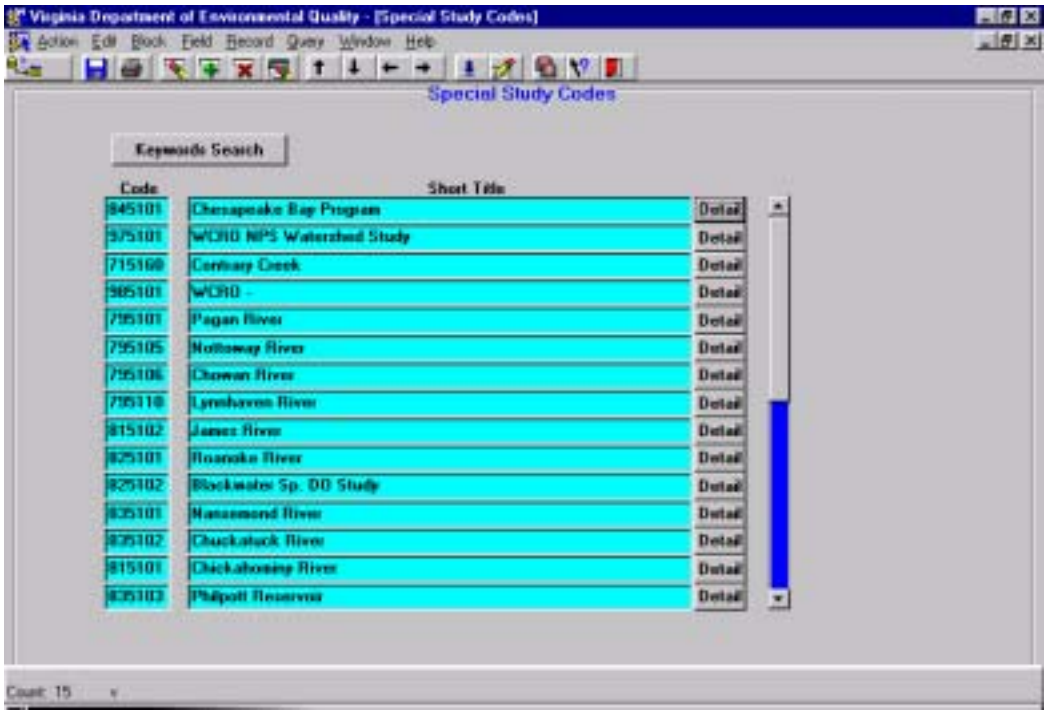
Now that final adjustments have been made to the formatting, the final installation of this module into the production database has been carried out. Its use is now required for the formal proposal, approval, and execution of all future special studies. All intermediate and final reports, sampling and 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.

Benthic and other TMDL Special Studies Involving Toxics

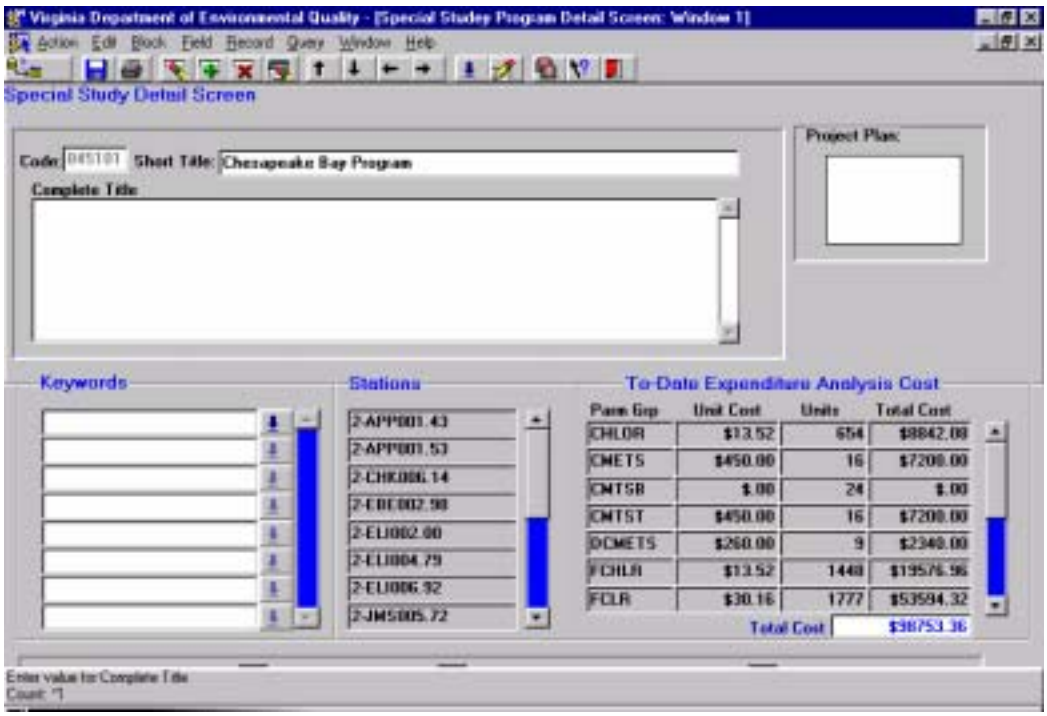
In many cases, determining the cause of benthic impairments can be quite difficult. A number of stressors, including toxicity, sedimentation, eutrophication, the introduction of non-native fish species, and other forms of habitat modification may be involved. Because toxics must be considered as one 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 MY2006 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 usually finalized by early April. The MonPlan provided a complete list of the ambient WQM stations that would be actively sampled during the following monitoring year (1 July - 30 June). The MonPlan also identified specific programs associated with each site, the parameters that would be measured there, the number of samples that would be collected, and the intended frequency of sampling. The MonPlan also provided 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 provided 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.

The annual Monitoring Plan for MY2006, which began on 1 July 2005, is in a new format, because the vast majority of the information that it contains is now queried directly from the CEDS database in the form of a report, rather than requiring independent manual entry of the information by Regional Office monitoring personnel. Beginning with 2006, the DEQ Monitoring Year will correspond 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 will be described in detail in the 2006 revision of DEQ's Water Quality Monitoring and Assessment Strategy.

Each year the annual Monitoring Plans are summarized and posted on the DEQ Website at http://www.deq.virginia.gov/watermonitoring/. The new plan for 2006 was elaborated during the winter/spring of 2004/2005, was initiated in July of 2005 and will continue without modification until the end of December 2006.

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).

The concentrations of toxics within a specific unit of sediment may be more stable in terms of time, 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 or 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 use of sampling devices such as the SPMDs mentioned above, which concentrate organic toxics and integrate concentrations over time (typically a 30-day period). 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, will also significantly improve sampling resolution. Once applied, these strategies will provide the data for more reliable mid-term and long-term trend analyses.

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 within drainage basins (1997 through 2005) 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.

Preparation of the 2006 report is currently in progress, with completion of draft report planned for April 2006, and the most recent edition of the 2006 Assessment Guidance Manual is 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 will be 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 will be used in conjunction with the new B-IBI methodology to identify probable causes of benthic degradation. Among other toxics-related modifications that are to be 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.

Appendix M - "List of Segments not Fully Supporting Designated Uses because of Toxics (2004)" 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 2004 305(b)/303(d) Report. More detailed Fact Sheets related to each impaired segment can be accessed through the 'Fact Sheet Search' function on DEQ's TMDL WebPages at:

http://www.deq.virginia.gov/tmdl/searchfs.html.

Use the 'Waterbody Id for Search Function' value in the first column 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 2006 Integrated Report, prior to the January 2007 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 3.1-6 of the 2004 305(b)/303(d) Report)

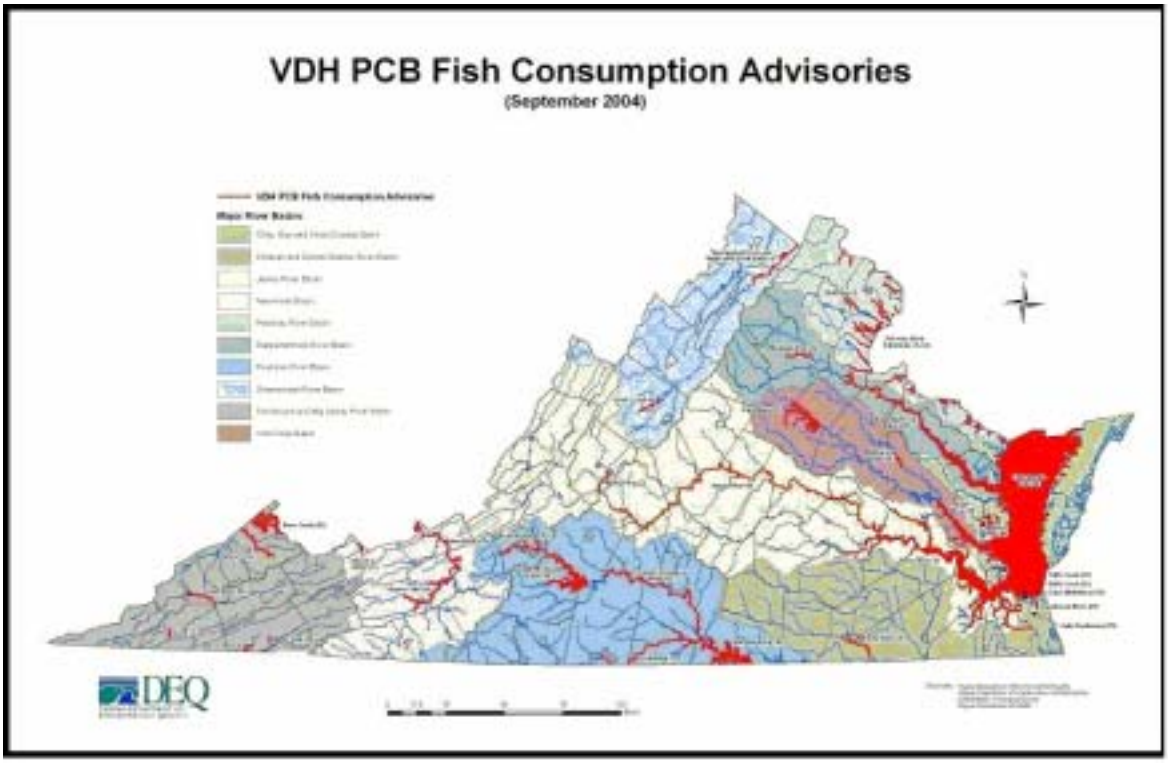
Areas listed because of benthic community degradation are considered to be 'potentially' toxics impaired. Chloride, iron, manganese, nitrates, phosphate and sulfates are not considered toxic at normal concentrations but were included because they occurred in the original table.

Pollutant	Resource Type	Area Impaired (Rounded to nearest whole number)
Aldrin	River (mi)	7
	Lakes (acres)	0
	Estuary (mi^2)	0
Ammonia	River (mi)	1
	Lakes (acres)	0
	Estuary (mi^2)	1
Arsenic	River (mi)	3
	Lakes (acres)	0
	Estuary (mi2)	0
Freshwater Benthic Assessment	River (mi)	1,183
	Lakes (acres)	0
	Estuary (mi^2)	0
Benzo(k)fluoranthene	River (mi)	19
	Lakes (acres)	0
	Estuary (mi^2)	0
Chlordane	River (mi)	1
	Lakes (acres)	0
	Estuary (mi^2)	0
Chloride	River (mi)	33
	Lakes (acres)	0
	Estuary (mi^2)	96
Copper	River (mi)	1
	Lakes (acres)	530
	Estuary (mi^2)	0
DDE/DDT	River (mi)	19
	Lakes (acres)	0
	Estuary (mi^2)	0
Estuarine Benthic Assessment	River (mi)	-
	Lakes (acres)	-
	Estuary (mi^2)	596

Pollutant	Resource Type	Area Impaired (Rounded to nearest whole number)
Iron	River (mi)	7
	Lakes (acres)	0
	Estuary (mi^2)	0
Lead	River (mi)	7
	Lakes (acres)	0
	Estuary (mi^2)	0
Manganese	River (mi)	7
	Lakes (acres)	0
	Estuary (mi^2)	0
Mercury	River (mi)	275
	Lakes (acres)	0
	Estuary (mi^2)	2
Nitrates	River (mi)	2
	Lakes (acres)	0
	Estuary (mi^2)	96
PCB's	River (mi)	421
	Lakes (acres)	45,905
	Estuary (mi^2)	96
Phosphate	River (mi)	0
	Lakes (acres)	0
	Estuary (mi^2)	96
Sulfates	River (mi)	10
	Lakes (acres)	0
	Estuary (mi^2)	0
Tributyltin (TBT)	River (mi)	0
	Lakes (acres)	0
	Estuary (mi^2)	15

Most Recent Virginia Department of Health Fishing Restrictions and Health Advisories

A number of additions to VDH fishing advisories occurred during or shortly after the close of MY2004. Most notable are those added as a result of the VDH's decision to lower the fish tissue PCB concentration that triggers fish consumption advisories from 600 ppb to 50 ppb. The general statewide distribution of PCB-based fish consumption advisories is summarized on the map below. The complete VDH fishing restrictions and health advisories currently in effect, summarized and mapped by basin for all contaminants, can be found on the VDH Website at http://www.vdh.virginia.gov/hhcontrol/fishing_advisories.htm. The VDH Website will always contain the most recently published updates to fishing restrictions and closures due to concerns related to human health and fish consumption.



Recent changes (additions and/or modifications) to the advisory/restriction list include:

6. **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
        - Shenandoah River PCB advisory – modified 12/13/04
        - Lewis Creek PCB advisory – added 12/13/04
7. **James River Basin**
    - Maury River PCB advisory – added 12/13/04
    - Various James River and tributary advisories added or modified – 12/13/04
8. **Rappahannock River Basin**
    - Rappahannock PCB advisory – added 12/13/04

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

9. 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
-

10. Chowan River / Dismal Swamp Basin

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

11. Tennessee / Big Sandy Basin

- Knox Creek PCB advisory – modified 6/15/04, 12/13/04 and 7/27/05
- Levisa Fork River 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

12. 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

13. 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

14. 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 <u>highly impacted</u> areas, *Areas of Low Probability for Adverse Effects* are regional areas that are <u>not impacted</u> by chemical contaminants, and *Areas of Emphasis* have the <u>potential</u> 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 is currently in the final stages of developing a 'toxics characterization matrix' and standardized scoring system that will 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 will issue a call to regional

academic and private institutions for the identification of additional data sources within the next two months. Complementary toxics monitoring that has been carried out since 1999 should now have eliminated all 'Areas of Insufficient Data' that were identified in the original report. The target date for the new comprehensive report is November of 2007.

Additional information on the concentrations and trends of toxic substances and other water quality parameters, in the Chesapeake Bay and it 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://www.chesapeakebay.odu.edu/Reports/ reports.htm). 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 pptr) have been observed. A summary of the monitoring results can be viewed at 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. Based upon probability-based sampling, the estimate of bottom substrate not meeting the benthic restoration goals was 64 ± 10.1% in 1999, 72 ± 17.6% in 2000, 52 ± 19.6% in 2001, 72 ± 17.6 % in 2002, 80 ± 15.7 % in2003, and 88 ± 12.7% in 2004. Average B-IBI values for the Elizabeth River watershed were 2.7, 2.6, 2.7, 2.4, 2.3 and 2.2, respectively, for the years 1999-2004. 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://www.chesapeakebay.odu.edu/Reports/reports.htm.

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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 2005) indicated that 501 Virginia facilities filed 1919 individual reports on the release, transfer, or management of TRI chemicals or chemical categories for the 2003 activity year. Statewide toxic releases to the water totaled approximately 8,199,535 pounds or 12.7 % of the total onsite releases to all media during 2003. This quantity (~8.2 million lbs.) represents an approximate 1 % decrease from 2002 releases.

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 2003.

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 (92.3% of total releases to water = 7.566 million lbs.), manganese and manganese compounds (2.94%), ammonia (2.04%), zinc and zinc compounds (0.70%), barium and barium compounds (0.31%), methyl ethyl ketone (0.30%), copper and copper compounds (0.27%), methyl tert-butyl ether (0.17%), chlorine (0.16%), and n-methyl-2-pyrrolidone (0.10%). 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.

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 (2003 VIRGINIA TOXICS RELEASE INVENTORY (TRI) REPORT - March 2005). The March 2005 Virginia TRI Summary Report, summarizing data from CY2003 industry reports, is available on the DEQ Website at: http://www.deq.virginia.gov/sara3/3132003.html.

For further information on the Virginia TRI, contact Sanjay Thirunagari, Environmental Program Manager, SARA Title III, at (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 2004, should be available by March 2006.

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 2005 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 2005, several of which are briefly summarized here.

- The total number of facilities in the Virginia Environmental Excellence Program (VEEP) now exceeds 200, with 145 (almost ¾) at the E2 level, 52 at the E3 level and 8 at the E4 level.
- DEQ's Voluntary Mercury Reduction Initiatives included:
    1. Fluorescent Lamp Recycling Pilot Project – combined eventual recycling of the approximately 2,000,000 fluorescent lamps in use would be equivalent to 44 pounds of mercury.
    2. "Virginia Switch Out" Pilot Project for the recycling of automotive mercury switches – by the end of October 2005 more than 5,000 switches were collected, eliminating more than 15 pounds of mercury that could have been vaporized with the melting of auto bodies for recycled steel.
- 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. Participation in the program grew to 87 facilities.
- Participants in the Businesses for the Bay (B4B) Program reported 115 million pounds of waste reduction and cost savings of $3.8 million due to pollution prevention efforts. Virginia facilities make up over 40% of the participating facilities (302) and program mentors (54).
- 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 2005 included:
    1. Significant reduction in the use of Methyl Ethyl Ketone as a solvent,
    2. Significant reduction in the use of other volatile organic solvents,
    3. Significant reduction in lead waste (over 400,000 lbs), and of the use of lead in solder (reduction of 50%),
    4. Replacement of mercury-containing sphygmomanometers (blood pressure meters) – elimination of 41 lbs of mercury, and
    5. Recycling of automotive mercury light switch assemblies (960 grams of mercury) and lead from battery terminals (240 lbs of lead).

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