THE DEPARTMENT OF ENVIRONMENTAL QUALITY

The Reduction of Toxics in State Waters

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.state.va.us/watermonitoring/.



COMMONWEALTH OF VIRGINIA RICHMOND JANUARY 1, 2004

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Table of Contents

TABLE OF CONTENTS	4
LIST OF TABLES	6
LIST OF FIGURES: FOLDERS 3 THROUGH 6	6
LIST OF APPENDICES	7
TABLE OF ACRONYMS AND ABBREVIATIONS	8
EXECUTIVE SUMMARY	10
FOREWORD 2003	12
INTRODUCTION	
FUNCTIONAL DEFINITIONS AND LISTS OF TOXICS	
DEQ'S NEW AMBIENT WATER QUALITY MONITORING STRATEGY	
REVIEW OF TOXIC CHEMICAL PARAMETERS AND THEIR MONITORING METHODOLOGIES	17
MONITORING FOR TOXICS IN STATE WATERS	
CHEMICAL MONITORING	
BIOLOGICAL MONITORING	
TOXICS MONITORING – SURFACE WATERS AND SEDIMENTS	
Toxics in the Water Column	
Clean Dissolved Metals in Surface Waters Clean Total Metals in Surface Waters	
Dissolved Pesticides and Other Organic Contaminants	
Toxics in the Sediment	
Sediment Metals	
Sediment Pesticides and Other Organic Toxics	
New Initiatives in the Ambient Monitoring of Toxics	
Probabilistic Sampling for the Statewide Characterization of Surface Waters Free Running Freshwaters	
Free Running Freshwaters Tidal Estuarine Waters – The Coastal 2000 / National Coastal Assessment Program	
Monitoring Dissolved Toxic Organics with SPMDs.	
Expanded Organic Toxics Monitoring in the Sediment	
Specialized Fish Tissue and Sediment Analyses	
PERMITTED DISCHARGES AND TOXICS MONITORING OF PERMITTED FACILITIES	
SPECIAL STUDIES CONCERNING TOXICS:	
Benthic TMDL Special Studies Involving Toxicity Tests	
THE MY2004 WATER QUALITY MONITORING PLAN Evaluation of Trends in Toxics Concentrations in State Waters	
THE 2004 305(B) / 303(D) REPORTS TO THE U.S. EPA AND CONGRESS	
MORE RECENT VIRGINIA DEPARTMENT OF HEALTH FISHING RESTRICTIONS AND HEALTH ADVISORIES	
THE CHESAPEAKE BAY PROGRAM	
Toxics Reduction and Prevention Strategy	
Toxics 2000 Strategy	
Mixing Zone Elimination	
Region of Concern Restoration Toxics Characterization	
Recent Chemical Contaminant Monitoring in Areas of Insufficient Data	
THE ELIZABETH RIVER PROGRAM	

T is a Tissue This optimology	
Fish Tissue Histopathology TBT Monitoring	
Benthic Index of Biotic Integrity (BIBI) monitoring	
Benthic Index of Biotic Integrity (BIBI) monitoring Low Level Contaminants	
Elizabeth River Monitoring Reports: 2002-2003	
VIRGINIA TOXICS RELEASE INVENTORY	
REDUCTION OF TOXICS BY POLLUTION PREVENTION	
REDUCTION OF TOXICS BY POLLUTION PREVENTION	53

All tables, folders, figures and appendices referred to in the text are available as "Read Only" files on DEO's WebPages (http://www.deq.state.va.us/watermonitoring/). Users may download them as they are and then rename them if editing or reformatting is desired.

List of Tables

Table 1.	DCLS Toxics Groups and Costs (MY2003)
Table 2.	Numbers of Ambient Toxics Samples and Costs (MY2003)
Table 3.	Clean Dissolved Metals in the Water Column - All Basins - MY2003
Table 4.	Clean Total Metals in the Water Column - All Basins - MY2003
Table 5.	Sediment Metals - All Basins - MY2003
Table 6.	Sediment Pesticides - All Basins - MY2003
Table 7a.	Fish Tissue Sample Results - WQS MY2002 (Rec'd 2003)
Table 7b.	Sediment Analysis Results - WQS MY2002 (Rec'd 2003)

List of Figures: Folders 3 through 6

The numbering of figure-containing Folders corresponds to the numbers of the associated Tables 3 through 6, which contain the complete results for the monitoring of toxic materials from the past monitoring year. The Microsoft Excel® notebooks that contain the graphs of historical toxics concentrations also include worksheets with descriptive statistical summaries of historical data arranged as follows:

- (1) Historical data arranged by monitoring year for all toxic parameters in the class, and
- (2) Historical data arranged by toxic parameter for monitoring years 1997 through 2003.

Folder 3 - Metals, Dissolved, Historical

Historical Dissolved Metals - (1) Potomac-Shenandoah (2003) Historical Dissolved Metals - (2) James (2003) Historical Dissolved Metals – (3) Rappahannock (2003) Historical Dissolved Metals – (4) Roanoke (2003) Historical Dissolved Metals – (5) Chowan-Albemarle Sound (2003) Historical Dissolved Metals – (6) Tennessee-Big Sandy (2003) Historical Dissolved Metals -(7) Chesapeake Bay and Coastal (2003) Historical Dissolved Metals – (8) York (2003) Historical Dissolved Metals – (9) New (2003) Shenandoah Basin Dissolved Mercury Special Study - 2003

Folder 4 – Metals, Total in Water, Historical

Historical Total Metals in Water Column - (1-) Potomac-Shenandoah Basin (2003) Historical Total Metals in Water Column - (2-) Elizabeth River - James River Basin (2003) Historical Total Metals in Water Column - (2-) James River Basin, excl. Elizabeth R. (2003) Historical Total Metals in Water Column - (3-) Rappahannock River Basin (2003) Historical Total Metals in Water Column - (4A) Roanoke River Basin (2003) Historical Total Metals in Water Column - (5A) Chowan River Basin (2003) Historical Total Metals in Water Column - (5B) Dismal Swamp - Albemarle Sound (2003) Historical Total Metals in Water Column - (6-) Tennessee - Big Sandy Basin (2003) Historical Total Metals in Water Column (7-) Chesapeake Bay & Coastal Basins (2003) Historical Total Metals in Water Column - (8-) York River Basin (2003)

Historical Total Metals in Water Column - (9-) New River Basin (2003) Shenandoah Basin Total Mercury Special Study - 2003

Folder 5 – Metals, Sediment, Historical

Historical Sediment Metals – (1) Potomac-Shenandoah (2003) Historical Sediment Metals – (2) James (2003) Historical Sediment Metals – (3) Rappahannock (2003) Historical Sediment Metals – (4) Roanoke (2003) Historical Sediment Metals – (5) Chowan-Albemarle Sound (2003) Historical Sediment Metals – (6) Tennessee-Big Sandy (2003) Historical Sediment Metals – (7) Chesapeake Bay and Coastal (2003) Historical Sediment Metals – (8) York (2003) Historical Sediment Metals – (9) New (2003)

Folder 6 – Pesticides, Sediment, Historical

Historical Sediment Pesticides – (1) Potomac-Shenandoah (2003) Historical Sediment Pesticides – (2) James (2003) Historical Sediment Pesticides – (3) Rappahannock (2003) Historical Sediment Pesticides – (4) Roanoke (2003) Historical Sediment Pesticides – (5) Chowan-Albemarle Sound (2003) Historical Sediment Pesticides – (6) Tennessee-Big Sandy (2003) Historical Sediment Pesticides – (7) Chesapeake Bay and Coastal (2003) Historical Sediment Pesticides – (8) York (2003) Historical Sediment Pesticides – (9) New (2003)

List of Appendices

Appendix A. Appendix B. Appendix C1. Appendix C2. Appendix D. Appendix E.	Chesapeake Chemicals of Concern EPA Regulated Toxics List (Dec 92) DEQ Water Quality Standards (Aug 03) Summary of Chemical Parameters and Monitoring Strategies Summary Sediment Screening Values (MY2003) EPA Risk-Based Screening Values for Fish Tissues
Appendix F1.	Historical Toxics-Monitoring Station List (30Oct1970 – 18Oct2001)
Appendix F2	WQM Toxics-Monitoring Station List (1Jul2002 - 30Jun2003) - by
	Parameter Group Code
Appendix G1.	Potential Sediment and Fish Tissue Monitoring Stations 2004 - WQS
Appendix G2.	Coastal 2000 Program Stations - MY2000-2003
Appendix H1.	Biological Monitoring Sites Visited During MY2003
Appendix H2.	Prospective Probabilistic Monitoring Sites (MY2004-05)
Appendix I.	Special Studies Related to Toxics – MY2003
Appendix J.	Facilities with Toxics Parameter Limits (MY2003)
Appendix K.	List of Permits, Parameters, Parameter Limits and Units (MY2003)
Appendix L.	Permitted Facilities and their Compliance Status – MY2003
Appendix M.	List of Segments not Fully Supporting Designated Uses because of Toxics (303(d) Report 2002)
Appendix N1	Impaired Segments selected for Toxicity Testing 2002/2003
Appendix N2	Impaired Segments selected for Toxicity Testing 2003/2004

Table of Acronyms and Abbreviations

AMD	Acid Mine Drainage
BDE	Bromated biphenyl
BIBI	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 assess-ment of
	freshwater sediment)
DCLS	Division of Consolidated Laboratory Services
DEQ	Department of Environmental Quality
DMR	Discharge Monitoring Report
EDAS	Ecological Data Application System [database]
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
MGD	Millions of Gallons per Day
MonPlan	Annual Water Quality Monitoring Plan
MY	Monitoring year
NOAA	National Oceanic and Atmospheric Administration
NPS	Non-Point Source (pollution)
OCP	Organochlorine Chlorine Pesticide
OPP	Office of Pollution Prevention
РАН	Polycyclic Aromatic Hydrocarbon
PCB	Polychlorinated biphenyl
POTW	Publicly Owned Treatment Works
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 database]
SV	Screening Value
TBT	Tributyltin
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

VDH	Virginia Department of Health
VEEP	Virginia Environmental Excellence Program
VERC	Virginia Emergency Response Council
VIMS	Virginia Institute of Marine Science
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 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.

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 general population with objective, summarized information not readily available from other sources.

Monitoring: DEQ began the probabilistic monitoring (ProbMon) of freshwater streams and rivers in the spring of 2001. The agency produced a report on its first year of freshwater probabilistic monitoring results in January of 2003. "The Quality of Virginia Non-Tidal Streams: First Year Report" is currently available on the DEQ WebPages at <u>http://www.deq.state.va.us/water/probmon.pdf</u>. A similar report is currently being developed for the second year of ProbMon and should become available at the same Internet address in the spring of 2004.

The spring and summer of 2003 comprised the third year of DEQ's freshwater probabilistic monitoring. An EPA grant provided for fifty semi-permeable membrane devices that were utilized for monitoring dissolved toxic organic compounds at probabilistic sites across the state during 2003. The USGS is analyzing the samples and the results should be included in next year's TRISWat report.

DEQ is currently revising/updating/expanding its Water Quality Monitoring Strategy document to include adaptations and new EPA guidelines developed since 2000. Draft copies should be available for review by upper DEQ administration and to EPA by early spring 2004.

Permitting: DEQ's Toxics Management Program (TMP) currently includes 279 facilities that have active permit-defined toxics limits in their effluents, and 75 active applications in the CEDS database. The CEDS database now records Discharge Monitoring Reports (DMRs) on a monthly basis.

Toxics Release Inventory (TRI): The most recent Virginia Toxic Release Inventory Report (SARA Title III TRI, May 2003) indicated that 508 Virginia facilities reported to the TRI program for the 2001 activity year. Statewide toxic releases to the water totaled approximately 7.0 million pounds or 9.9% of the total onsite releases to all media during 2001. This represents a 14.6% decrease from 2000 releases, in spite of the lower reporting thresholds introduced for lead and lead compounds (persistent bioaccumulative toxins or PBTs).

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) increased from 122 to 152, an increase of 25% over 2002.

- Virginia DEQ actively participated with EPA's National Environmental Performance Track Program (NEPT), rewarding "high-performing" pollution prevention facilities with regulatory flexibility incentives.
- During the past two years, the Electronics Recycling & Stewardship Program, initiated in late 2001, stimulated local governments, businesses and consumers to recycle about 100 tons of obsolete computers and potentially hazardous components. A single day record of 28 tons of equipment collected for recycling took place in the Charlottesville area.
- DEQ's Pollution Prevention in Healthcare Program continues to be active in the reduction of medical wastes, to reduce toxicity by encouraging environmentally preferable purchasing, and to eliminate the use of mercury in the health care industry.
- Participants in the Businesses for the Bay (B4B) Program reported 16.7 million pounds of waste reduction, and cost savings of about \$664,000. As of October 2003 B4B has over 540 participants and approximately 120 mentors providing peer-to-peer assistance.
- The onsite Pollution Prevention Technical Assistance Program was eliminated in 2003 because of state budget reductions in the fall of 2002.

Foreword 2003

MY2003 Toxics Reduction in State Waters Report

(January 2004)

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, currently undergoing a revision for 2004
- Formal Quality Assurance Program and Project Plans (QAPPs),
- Established Standard Operating Procedures (SOP's), and
- Sampling Protocols.

The annual program plans (MonPlans) cover the period from 1 July of each year through 30 June of the following year. This period corresponds to the Commonwealth's fiscal year (FY), but is commonly referred to as the monitoring year (MY) in documents and reports related to water quality monitoring. The present document uses the terms monitoring year and fiscal year interchangeably.

The MY2003 Toxics Reduction in State Waters (TRISWat-04) Report is the seventh 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. 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 only on the DEQ website at http://www.deq.state.va.us/watermonitoring/, and are not provided in hardcopy form.

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 – 2003) 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. The incorporation of historical, STORET-stored data into the water quality module of DEQ's new Comprehensive Environmental Data System (CEDS) 2000 database in 2001 unified all previously collected ambient toxics data into a single source and format. This will facilitate the statistical summary of historical data in the same graphical format as that used here, and will allow for more sophisticated statistical procedures as well. Future TRISWat reports will consequently include longer-term summaries that will permit more meaningful interpretation.

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 keeps the governor, 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 Service 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 TRISWat Report (January 2004) contains tables of both raw data and statistical summaries of MY2003 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": Virginia legislation (Chapter 3.1, Title 62.1, § 62.1-44.17:2 of the Code of Virginia) 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 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. For example, as noted below, the government is currently revising downward the national drinking water criterion for arsenic.

Virginia Water Quality Standards: The Commonwealth of Virginia has established and has periodically revised and added to its own water quality standards (WQSs) (DEQ-WQS, Aug 2003, as summarized in Appendix C1), 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 WQSs have recently undergone their required triennial review. Summaries of several considerations related to toxics follow:

• The State Water Control Board updated existing criteria based on EPA's most recent 304(a) guidance and adopted numerical criteria for all 307(a) pollutants. Previously, only criteria for 307(a) pollutants known to be present in Virginia's waters were in the regulation. Adoption of this new proposal has resulted in revisions of 30 existing criteria and the addition of approximately 33 new criteria.

• Another item was the proposed adoption of EPA's newly revised drinking water criterion of 10 μ g/L for arsenic, to replace the existing drinking water criterion of 50 μ g/L.

These amendments, along with others not directly related to toxics, were reviewed by the Office of the Attorney General for agency statutory authority and were approved by the State Water Control Board in March 2003. The adopted triennial review amendments of Virginia's Water Quality Standards are available on the DEQ-WQS WebPage at <u>http://www.deq.state.va.us/wqs</u>. These amendments are awaiting EPA approval before they can be published with an effective date. 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 <u>http://www.deq.state.va.us/wqs/rule.html</u> 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. The high cost (approximately \$5000 / sample) of this methodology limited its use to fifty statewide probabilistic sites during this first deployment. Details of this sampling methodology and its results 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 and the data are only useful for locating and identifying the sources of dissolved toxics.

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 2004 305(d) Report can currently be found in the draft guidance for the report on DEQ's WebPages at <u>http://www.deg.state.va.us/wqa/305b2004.html</u>.

In the past, DEQ has 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 will use 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 the draft guidance for the 2004 305(b) Report on DEQ's WebPages at <u>http://www.deq.state.va.us/wqa/305b2004.html</u>.

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 1999 risk-based screening values DEQ used for fish tissue consumption appears in Appendix E of this report. These screening values are adjusted as necessary, following monthly updates in the EPA IRIS database, available at <u>http://www.epa.gov/iris</u>. An updated list of the Risk-Based Tissue Screening Values (TSVs) for fish tissue to be used for the 2004 305(d) Report can be found in Tables 6a and 6b on pages 39 through 41 of the Water Quality Assessment Guidance PDF document at <u>http://www.deq.state.va.us/pdf/water/wqassessguide.pdf</u>. Values for specific compounds can also be found listed in the tables of fish tissue analytical results posted on the DEQ WebPage at <u>http://www.deq.state.va.us/fishtissue/</u>.

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 results from 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. More details of this procedure, as well as a summary of its current status, are included later in this report in the section on DEQ's Water Quality Monitoring Strategy.

Federal Reporting Requirements: Federal law currently requires reporting procedures for the production, movement, storage, use, and release of many of these toxic substances. These procedures, as well as Virginia's annual Toxics Release Inventory (TRI) Report, are discussed more fully below.

DEQ's Ambient Water Quality Monitoring Strategy

The DEQ 2000 Ambient Water Quality Monitoring Strategy, developed during several years of intense work and deliberation by DEQ's former Water Quality Monitoring Task Force, received favorable reviews from the Academic Advisory Committee assembled by the task force, as well as from the U.S.EPA. Both groups approved and praised the contents of the new strategy, offering only minor suggestions to improve its form. In May 2001, National EPA water quality scientists and EPA Region III water quality monitoring coordinators met with DEQ water program managers and Water Quality Monitoring Program coordinators in Northern Virginia. Following the meeting, which included a four-hour presentation and informal discussion of the details of DEQ's monitoring strategy, EPA voiced the opinion that Virginia's Water Quality Monitoring Strategy would serve as a model for the development of similar strategies in other states. The WQM Strategy document subsequently underwent an independent review, completed by a DEQ-appointed "Scientific Advisory Committee" in 2002. This group also provided a favorable evaluation of the Strategy, offering a number of constructive comments to improve its comprehensiveness.

DEQ's staff continues to revise and improve its Water Quality Monitoring Program as well as the descriptive Strategy document. A revised edition of the Water Quality Monitoring Strategy document is currently under development. Draft copies of the revised document will be provided for review, directly to the US EPA and, via the DEQ Water Quality Monitoring Website, to the general public by the summer

2004. Under the continual planning process, the document will continue to adapt to new monitoring needs as they develop.

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. The annual plans cover the period from 1 July of each year through 30 June of the following year. This period corresponds to the Commonwealth's fiscal year (FY), but is commonly referred to as the monitoring year (MY) in documents and reports related to the subject. The present document uses the two terms "monitoring year" and "fiscal year" interchangeably.

The recently expired MY2003, which began on 1 July 2002 and ended on 30 June 2003, concluded the first two-year rotational phase of the six-year monitoring cycle described in the WQM Strategy 2000 document. The second two-year rotation, which was originally scheduled for 1 July 2003 through 30 June 2005, has been extended an additional year in order to synchronize the rotation of watershed stations with DEQ's 305(b) assessment cycle. By extending the second rotation for one year, and expanding the 305(b) assessment window to six years, the assessments will begin to include three two-year station rotations at the end of the 2006 monitoring year (30 June 2006). 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 both the watershed and the probabilistic monitoring networks.

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 target 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 resulted 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

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

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 freshwater probabilistic sites will provide annual summaries of the status of freshwaters on a statewide basis.

Since 1998 saltwater sampling in several areas of the state has indicated essentially the same results as those reported for freshwaters, with typical concentrations proving to be consistent with global concentrations. The probabilistic sampling of estuarine waters for dissolved metals was initiated in July of 2003, as part of the Coastal 2000 / National Coastal Assessment Program. The results from this first season of sampling (July - September 2003) will be summarized in next year's Toxics Reduction in State Waters Report.

The tables of dissolved metals parameters on the following pages present the target analyte list for freshwater (Text Table 1) and saltwater (Text Table 2).

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 to include more current use compounds and new analysis methods currently provide significantly lower detection limits for most substances on the list. Text Table 3 lists the toxic organic compounds presently being monitored as target analytes. Recommended changes suggested by DEQ's 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 World Wide Web at http://www.deg.state.va.us/wgs.

The concentration and distribution of dissolved trace organics in freshwater is being determined through a probabilistic sampling design as outlined in the strategy. In the spring of 2003, 50 semi-permeable membrane devices (SPMDs) were deployed in freshwater streams and rivers. The SPMD devices normally remain at the station 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 being 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. Additionally, the samples will be analyzed for endocrine disrupters and for mutagenic toxicity. The assessment of the results from these stations will be used to determine future study design for characterizing the extent and severity of key trace toxic analytes.

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 analyzing programs are as follows:

- The regional office field staff from WQMA 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.

- EPA-contracted laboratories analyze sediment samples (metals, organics, and toxicity) and whole fish tissue samples (metals and organics) collected from the probabilistic sites of the Coastal 2000 Program (EPA Assistance Agreement No. R-82854401-0: 2000-2004).
- 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 samples 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.

The **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 <u>potential causes</u> of 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 and salt waters. The current standards used for these comparisons are listed in each 305(b) Report Assessment Guidance document (<u>http://www.deq.state.va.us/wqa/</u>) as well as in Appendix C1 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 assess 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 305(b) Report Assessment Guidance document (http://www.deq.state.va.us/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.state.va.us/wqa/) as well as Appendix E – "EPA Risk-Based Screening Values for Fish Tissues" 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 <u>observed effects</u> 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 environmental impairment**. DEQ no longer possesses the facilities to perform its own toxicity testing although, when necessary for special studies, DEQ contracts with commercial or university laboratories to perform the desired tests. As mentioned elsewhere in this report, estuarine sediment samples collected in the Coastal 2000 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 toxics monitoring. In addition, it will use chemical monitoring to determine and evaluate the possible causes of observed biological impairment.

² The Water Quality Monitoring Program Strategy document, prepared by the DEQ Office of WQMA, underwent review by U.S. EPA Region III and by the Academic Advisory Committee and was released for public review and comment early in 2000. It has since received an additional review by an independent scientific advisory committee. A revised, reformatted edition will be submitted to EPA for evaluation by September of 2004.

Parameter Cod	Freshwater Metals
1106	ALUMINUM, DISSOLVED (UG/L AS AL)
1095	ANTIMONY, DISSOLVED (UG/L AS SB)
1000	ARSENIC, DISSOLVED (UG/L AS AS)
1005	BARIUM, DISSOLVED (UG/L AS BA)
1010	BERYLLIUM, DISSOLVED (UG/L AS BE)
1025	CADMIUM, DISSOLVED (UG/L AS CD)
915	CALCIUM, DISSOLVED (MG/L AS CA)
1030	CHROMIUM, DISSOLVED (UG/L AS CR)
1040	COPPER, DISSOLVED (UG/L AS CU)
1046	IRON, DISSOLVED (UG/L AS FE)
1049	LEAD, DISSOLVED (UG/L AS PB)
925	MAGNESIUM, DISSOLVED (MG/L AS MG)
1056	MANGANESE, DISSOLVED (UG/L AS MN)
50091	MERCURY-TL FILTERED, ULTRATRACE METHOD NO
1065	NICKEL, DISSOLVED (UG/L AS NI)
1145	SELENIUM, DISSOLVED (UG/L AS SE)
1075	SILVER, DISSOLVED (UG/L)
1057	THALLIUM, DISSOLVED (UG/L AS TL)
1090	ZINC, DISSOLVED (UG/L AS ZN)

Text Table 2. Clean, Dissolved Metals in Saltwater

Parameter Code	Saltwater Metals
1106	ALUMINUM, DISSOLVED (UG/L AS AL)
1095	ANTIMONY, DISSOLVED (UG/L AS SB)
1000	ARSENIC, DISSOLVED (UG/L AS AS)
1025	CADMIUM, DISSOLVED (UG/L AS CD)
915	CALCIUM, DISSOLVED (MG/L AS CA)
1040	COPPER, DISSOLVED (UG/L AS CU)
1046	IRON, DISSOLVED (UG/L AS FE)
1049	LEAD, DISSOLVED (UG/L AS PB)
925	MAGNESIUM, DISSOLVED (MG/L AS MG)
1056	MANGANESE, DISSOLVED (UG/L AS MN)
50091	MERCURY-TL FILTERED, ULTRATRACE METHOD NC
1065	NICKEL, DISSOLVED (UG/L AS NI)
935	POTASSIUM, DISSOLVED (MG/L AS K)
1145	SELENIUM, DISSOLVED (UG/L AS SE)
930	SODIUM, DISSOLVED (MG/L AS NA)
1090	ZINC, DISSOLVED (UG/L AS ZN)

Organochlorines	Herbs	PAHs	PCB Congeners	Organophosphates	
HCCP	3,5-DBCA	1,4-Dichlorobenzene	PCB-001	Dichlorvos	
-BHC & HCB & Diallate	Dicamba	Isophorone	PCB-005+008	Mevinphos	
-BHC & g-BHC	MCPA	Dibenzofuran	PCB-018	TEPP	
I-BHC	MCPP	Bis[2-ethylhexyl]phthalate	PCB-028+031	Thionazion	
Ieptachlor	Dichlorprop	Butylbenzylphthalate	PCB-52	Demeton	
Aldrin	2,4-D	Di-N-octylphthalate	PCB-44	Ethoprop	
sodrin	2,4-DB	Dimethyl phthalate	PCB-101	Tributylphosphate SS	
Heptachlor Epoxide	Pentachloroanisole	Di-N-butylphthalate	PCB-66	Naled	
-Chlordane	2,4,5-TP	Diethyl phthalate	PCB-81+77	Dicrotophos	
Endosulfan I & a-Chlordane	Chloramben	2-Methylnaphthalene	PCB-110	Sulfotep + Phorate	
Dieldrin	2,4,5-T	Acenaphthylene	PCB-87	Monocrotophos	
DDE	Bentazon	Acenaphthene	PCB-151	Dimethoate	
Endrin & Endosulfan II	Picloram	Anthracene	PCB-118	Terbufos	
Chlorbenzylate	DCPA	Fluorene	PCB-105	Monophos	
DDD	Acifluorfen	Naphthalene	PCB-153	Diazinon	
Endrin Aldehyde & Kepone		Phenanthrene	PCB-141	Disulfoton+Phosphamidon+Dichlorofenthion	
ndosulfan Sulfate	7	Total LM PAHs	PCB-126	Chlorpyrifos(methyl)	
DDT		Benzo[a]anthracene	PCB-138	Parathion(methyl)	
Endrin Ketone		Benzo[b]fluoranthene	PCB-187	Ronnel	
Iethoxychlor		Benzo[k]fluoranthene	PCB-183	Fenitrothion	
Kepone		Benzo[e]pyrene	PCB-128	Malithion	
•		Benzo[a]pyrene	PCB-156	Chlorpyrifos+Aspon	
		Benzo {g,h,i]perylene	PCB-169	Fenthion	
		Chrysene		Parathion	
		Dibenz[a,h]anthracene	1	Trichlornate	
		Fluoranthene	1	Chlorfenvinphos	
		Indeno[1,2,3-cd]pyrene	1	Crotoxyphos	
		Pervlene	1	Tetrachlorvinphos	
		Pyrene	1	Tokuthion	
			-4	Folex	
				Fensulfothion	
				Ethion	
				Carbophenothion	
				Bolstar	
				Famfur	
				Triphenylphosphate SS	
				Phosmet	
				EPN	
				Leptophos	
				Guthion(methyl)	
				Guthion	
				Coumaphos	
				Dioxathion	

Text Table 3. Toxic Organic Parameters in the Water Column

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 analytic costs, 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 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 severity, cause, and geographic extension of the contamination, or they may be included in the sampling plan of the Fish Tissue and Sediment Monitoring program carried out by the Special Research Unit of the WQS.

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 pesticides and other organics,
- Sediment pesticides and other organics, and
- Toxic metals and pesticides/organics in fish tissues.

Other toxic organic compounds, 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 specific parameters DCLS analyzed during the most recent monitoring year, their associated laboratory analysis group codes, 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.

Table 2 summarizes the number of samples, the analytical expenses, and the parameter group codes included in metal and pesticide analyses performed by the state laboratory (DCLS) during the 2002 monitoring year. This summary includes only those samples collected by the Ambient Water Quality Monitoring Program of the WQMA. (<u>Not included</u> are the numbers of samples, analytical costs, etc., of fish tissue and sediment samples collected by personnel from the WQS during various special studies or toxics samples collected in the Coastal 2000 Program.)

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, has 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.
- Cooperative efforts among Virginia, Maryland, the Interstate Chesapeake Bay Program, and EPA Region 3 during 2003 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.

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 *potential 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 RBP-II biological evaluations, biologists classify Virginia's waterbodies and waterbody segments as "*fully supporting*" of the aquatic life designated use, as "*fully supporting but having observed effects*" for aquatic life use, or as "*impaired*" for aquatic life use, in comparison with regional reference conditions which are considered to be of acceptable water quality. <u>Advantages of Biological Monitoring</u>: Although biological monitoring is 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 water bodies where more intensive studies are necessary. 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.

<u>Development of a Biological Monitoring Database</u>: In 1998, the EPA awarded a two-year research grant (1999-2000) for Tetra Tech Inc., a Maryland-based ecological consulting firm, to collaborate with DEQ in developing a relational biological database and determining efficient Indices of Biological Integrity (IBIs) for additional ecoregions in Virginia. The resultant EDAS database facilitates the integration of Virginia's biological data into a standardized format for the transferal of biological monitoring data from DEQ's various regional offices and, possibly, qualified data from citizens' monitoring groups to a unified statewide database at DEQ's central office in Richmond. The database also contains programs to automatically calculate a number of "metrics", numerical values used to measure and describe the community structure of the biological assemblage samples stored in the database. Eventually, the same database will be programmed to calculate an appropriate "Index of Biological Integrity" (IBI) to express the ecological health of the community for assessment purposes.

At the time the EDAS database was developed, the geographical distribution and number of sites in DEQ's biological monitoring database were not yet sufficient for determining optimal IBIs for each ecoregion in the state. The targeted and judgmental sites previously monitored, and the lack of strict definitions for the selection criteria for reference sites for regional streams, had created some bias in the results and had limited the database's utility for defining IBIs. The Biological Monitoring Program initiated probabilistic monitoring late in MY2001 (April-May, 2001) and has continued through MY2003. Plans to extend the ProbMon biological monitoring beyond the original five-year program are currently under consideration. The accumulated results from this completely randomized sampling are providing:

- 1. The data for an unbiased statewide characterization of freshwater benthic communities, and
- 2. The information required for designating regional reference streams.
- 3. Concurrently collected chemical monitoring data will help establish regional and eco-regional criteria and/or standards for nutrients and other water quality parameters.

Appendix H1of this report lists the biological monitoring stations visited during MY2003. Much of the information in this appendix 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 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 H2, "Prospective Probabilistic Monitoring Sites MY2004-05", provides a comprehensive list of the possible biological stations that may be included in the ambient program during calendar year 2004. The final list will become available only after regional biologists perform both map and field reconnaissance prior to their sampling in the spring of 2004.

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 pesticides 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.)

Text Box 1, below, presents the total number of ambient WQM samples collected during MY2003 for which analytical results are currently available (November 2003). 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 imposed during the past three years 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 a long-term special study on mercury [Hg] distribution and mobility in impaired segments of the Shenandoah River basin.)
- Metals and pesticides in the sediment are generally sampled simultaneously and 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. In addition, technical difficulties at DCLS during the spring resulted in the loss on a number of samples and/or results. The lost samples are being recollected during the fall of 2003 for subsequent analysis.

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 identification, 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. (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 2003.

Basin Code	River Basin Name	Clean Dissolved Metals	Clean Total Metals	Sediment Metals	Sediment Pesticides ²
		(water)	(water)		
1-	Potomac / Shenandoah	$22 (+113^{1})$	72^{1}	7	0
2-	James (excluding Elizabeth River)	27	1	15	2
2-	Elizabeth River	0	0	0	0
3-	Rappahannock	5	0	3	0
4A	Roanoke	8	0	7	0
5A	Chowan	6	0	24	0
5B	Dismal Swamp / Albemarle Sound	1	0	0	0
6-	Tennessee / Big Sandy	14	0	21	0
7-	Chesapeake Bay and Coastal	1	0	4	0
8-	York	2	0	0	0
9-	New	8	0	15	0
	Total	207	73	96	2
	Grand Total	378			

Text Box 1. Summary of Ambient Toxics Monitoring Samples from Virginia's Surface Waters for which data are available - MY2003. (Excludes SPMD sampling)

¹ In conjunction with the Shenandoah Basin Mercury Special Study.

² Sediment samples for organics analysis were collected at approximately 60 probabilistic sites during the spring of 2003. Due to technical difficulties, it was necessary to recollect them in the fall, and the results will not be available until next year's toxics report.

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 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 in the Water Column - All Basins - MY2003" presents the results of clean, dissolved toxic metals monitoring during MY2003 in their raw form and statistically summarized, river basin by river basin. Table 3a summarizes the results from a Shenandoah River Basin special study of dissolved mercury distribution. The program codes in the first column of the table identify the subdivisions of the overall ambient monitoring program for which each sample was collected: AQ = ambient monitoring; FP = freshwater probabilistic monitoring; RL = regional lakes monitoring; AT = AmTox 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 as being at the detection limit, a slight upward bias has been introduced into some statistical summaries. When the detection limits are near or above the standard for the metal in question, the apparent results may suggest that the standard was exceeded, when in fact the actual concentrations were considerably lower. Such cases can be identified by the Remark Code "U" (non-detect) in the tabulated raw data summaries of Tables 3 through 6 of this report.

The two statistics that have been determined for the annual summaries since 1997, the upper quartile (75^{th} percentile) and lower quartile (25^{th} 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):

Limits = 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 graphs of Folder 3 represent the 95 percent confidence intervals for the median concentrations observed in each year. 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.

Clean 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. The single ambient total metals sample collected from the water column during the year is presented in Table 4. During MY2003, however, DEO researchers again collected clean total metals samples from the Shenandoah River basin for the purpose of monitoring the transport of mercury (Hg) at many of the same sites where clean dissolved mercury samples were collected. The resultant data from these samples, along with their statistical and graphical summaries, appear in this report as Table 4a. 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 - MY2003, historical summaries of clean total metals results are presented in graphical format, by basin, along with year-by-year and metal-by-metal statistical summaries. As mentioned above, the vertical lines in the graphs represent the 95 percent confidence intervals for the median concentrations observed in each year. The small, horizontal black lines represent the medians (i.e., 50^{th} 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 available technology. 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 offered the promise of significantly improving the monitoring of dissolved organics. Consequently, with the aid of a \$250,000 EPA grant, DEQ deployed Semi-Permeable Membrane Devices (SPMDs) at 50 freshwater probabilistic monitoring sites during the spring and fall of 2003. This study is described in more detail below, but the results are not yet available.

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. In addition, the WQS

Program 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 discussion 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 - MY2003" presents tabular results and a statistical data summary of the MY2003 WQM sediment metals data, 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. Studies carried out by the WQS Program and the CBP are discussed elsewhere, in separate sections.

The Excel® workbooks of Folder 5 - "Metals, Sediment, Historical" 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 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).

Sediment Pesticides and Other Organic Toxics

DEQ also monitors organic toxics deposited in the sediments underlying the Commonwealth's waters. Table 6 - "Sediment Pesticides - All Basins - MY2003" presents the sediment pesticide data from MY2003 basin by basin, followed by their statistical summaries. The Excel® workbooks of Folder 6 – "Pesticides, Sediment, Historical - MY2003" present historical sediment pesticide results in graphical and tabular form, basin by basin. The vertical lines in the 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). Interpretation of these tables and graphs can be carried out in the same manner as described previously.

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. Stewart and Smith are environmental specialists at the Richmond Central Office of DEQ's WQMP.

Additional monitoring for pesticides and other toxic organic chemicals, primarily in sediment, is carried out by DEQ's Chesapeake Bay Office in collaboration with EPA's interstate Chesapeake Bay Program, and by the field team from the DEQ Office of Water Quality Standards. These two programs are discussed in more detail later in this report.

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 new 2000 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 sampling programs described in the Probabilistic Monitoring Module of the DEQ WQM strategy include the chemical monitoring of toxic metals and organic compounds 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 includes 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.). The results from this first year of freshwater probabilistic sampling were summarized in a freshwater probabilistic monitoring report that was completed in January of 2003. That report, "The Quality of Virginia Non-Tidal Streams: First Year Report", is currently available on the DEQ WebPages at http://www.deq.state.va.us/water/probmon.pdf). A similar report, on the second year of freshwater probabilistic monitoring is currently being drafted and should be available by the spring of 2004. Appendix H2 provides a list of prospective probabilistic monitoring sites to be sampled during the spring and fall of 2004. This list will only be finalized after regional DEQ biologists have performed site reconnaissance and confirmed the suitability and accessibility of the sites.

Tidal Estuarine Waters – The Coastal 2000 / National Coastal Assessment Program

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 Program, later renamed the National Coastal Assessment (NCA) Program. This grant (EPA Assistance Agreement No. R-82854401-0) provides \$200,000 per year for a 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 generates 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. Most years, complementary probabilistic sampling of estuarine environments by EPA, NOAA, and the Chesapeake Bay Program help to complement the geographic extension of DEQ's efforts.

DEQ initiated its five-year NCA tidal tributary probabilistic sampling program (tidal freshwater and saltwater) in July 2000, with sampling from sites in the Chesapeake Bay mainstem and its major tidal

tributaries. Sampling in 2001 and successive years has been concentrated in minor tidal tributaries to the Bay, the Atlantic Ocean and Back Bay/Albemarle Sound. Each year, DEQ contracts the Fisheries Science Laboratory of the Virginia Institute of Marine Science (VIMS) to trawl fish samples from these sites. The results of these analyses, as well as of water column and sediment studies, will be summarized in an additional five-year probabilistic monitoring report on estuarine waters. Fish community structure, the occurrence of fish pathologies, and general habitat characteristics will also be evaluated, based on the results of the VIMS sampling campaign.

Analyses of water column parameters (nutrients, chlorophyll and suspended solids) and of total organic carbon and particle size in the sediment are analyzed at the Division of Consolidated Laboratory Services (DCLS) of the Virginia Department of General Services and become available within a few weeks. All other sediment analyses (chemical, toxicological, and taxonomy of benthos) and fish pathology / tissue chemistry analyses are performed by EPA-contracted laboratories, and it is generally a year or more before they are available to DEQ.

DEQ's Coastal 2000 sampling during the first summer (2000) concentrated on the Chesapeake Bay and its major tidal tributaries. Sampling during subsequent years has concentrated on minor tidal tributaries to the Bay, to Atlantic coastal waters of the Delmarva Peninsula, the southern Virginia coastline, and Back Bay/North Landing River. The selection of an additional 50 sites for the summer 2004 sampling campaign will follow the same guidelines as utilized for the past three years; concentrated on minor tidal tributaries with a 70% - 30% distribution within the Chesapeake Bay watershed and coastal drainages, respectively.

Appendix G-2 provides complete lists of the DEQ Coastal 2000 / NCA probabilistic stations sampled in 2000, those sampled by NOAA in September 2001, and the 50 stations added annually during the summers of 2001 through 2003. EPA has not yet provided the list of prospective stations for the summer of 2004.

Monitoring Dissolved Toxic Organics with SPMDs

The newly developed probabilistic monitoring design and new methodologies for the sampling and analysis of dissolved metals have greatly enhanced statistical evaluations of the differences among watersheds and drainage basins, as well as providing a mechanism for improving the understanding of regional trends in the concentrations of toxic metals.

Traditional monitoring for toxic organic compounds has been confined to fish tissue and sediment samples in recent years. State statutes require the monitoring of fish tissue, and such monitoring will continue as described below. 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.

- 1. 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.
- 2. 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 ultrapurified 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 mounted in protective cages and exposed to sample water by direct deployment in the field for periods of up to 30 days. They consequently provide an integrated average of toxics concentrations over the whole sampling period.

SPMDs have several advantages over traditional sampling methods:

- 1. The results are representative of the waters at a specific site.
- 2. There is no loss of target analyte through metabolism or depuration.
- 3. Unlike grab samples or short-duration filtered samples, they are integrative because they are deployed for up to a month at a time.
- 4. Their 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. They represent the dissolved phase of the contaminants, which is considered to be the toxic component and for which water quality standards exist.
- 6. Their extracts 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.

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

In 2002 EPA awarded a two-year, \$250,000 probabilistic monitoring grant to DEQ. This grant money was consolidated into a single one-year study and used to provide SPMD sampling at 50 of Virginia's probabilistic monitoring sites in free-running fresh waters during the spring of 2003. These SPMDs were deployed during April or May and were recovered approximately 30 days later. Because of the

uncharacteristically abundant rainfall and flooding during the period, a number of the SPMDs were lost or destroyed. Consequently, during the fall (September-October) of 2003 sixteen replacement SPMDs were deployed at the sites where the originals were lost during the spring. All SPMDs were recovered after approximately 30 days of deployment and the samples were sent to the USGS's Columbia Environmental Research Center Laboratory in Columbia, Missouri for extraction and analysis.

Because of the laborious and time-consuming processes of extraction and precision analyses of the trace organic compounds, the results from the sampling in the spring and fall of 2003 will not be available until 2004, and will consequently be discussed in the January 2005 Toxics Reduction in State Waters Report. The toxic organic parameter list from the SPMDs will contain essentially the same suite of analytes as was analyzed for during the SPMD estuarine pilot study in the Elizabeth River (USGS, 2001), and is comparable to the new suite of organic analytes that DCLS is now analyzing in sediment samples.

Researchers worldwide continue to determine calibration curves for the uptake rates of numerous additional toxic organic substances and, resources permitting, DEQ will continue with SPMD sampling in Virginia's waters in the future. The long-term analysis of water column trace organics using SPMDs will permit the agency to determination whether significant trends in the concentrations of dissolved toxic organics, exist in Virginia's freshwater streams. Many of these trace organics enter the watersheds via atmospheric deposition, and determining their geographic distribution within the state's waters will facilitate locating and identifying the various sources of organic input into our streams. The extent of both spatial and temporal variations of these compounds in the water column, on a statewide scale, will be the most extensive study of organic contaminants yet conducted in Virginia.

Expanded Organic Toxics Monitoring in the Sediment

Beginning with freshwater probabilistic monitoring sites in the spring of 2003, the Ambient Water Quality Monitoring Program has employed 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 methodologies, with significantly lower detection limits. Rather than using the "PES1S" parameter group code employed in the past, DEQ has started utilizing a new group code, "AMB_TOX", as summarized below. This will expand the number of organic compounds monitored from 13 to 115. The current parameter group code and its analyte list has been included in Table 1 - "DCLS Toxics Group Codes and Costs (MY2002 – MY2003)" of this report, but may still be modified prior to taking its final form.

<u>Group Code</u>	Description
AMB_TOX	OC & OP pesticides; PCBs; Semi-Volatiles; Herbicides in sediment Price: \$1335.49 Turn-around Time: 45 days

The cost of this organics analysis is currently estimated to be approximately \$1335 per monitoring site, although it may change with the addition or removal of analytes, and increasing the total number of samples analyzed may reduce the costs for individual analyses.

The relocation of the DCLS laboratories to their new building during the spring and summer of 2003, and technical difficulties with their analytical equipment and LIMS database resulted in the loss of samples and/or analytical results from the spring sample collection. Sediment samples are consequently being

recollected during the fall visits to DEQ's freshwater probabilistic monitoring stations, and the resultant data will be included in the January 2005 Toxics Reduction n State Waters Report.

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 periodically samples all nine of Virginia's significant river basins (14 sub-basins) on a five-year, rotating schedule, as well as carrying out other relevant special studies. Sediment samples from the same sites are routinely collected at the same time.

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.

Appendix G-1 lists and identifies the stations and dates where the WQS field team sampled fish tissues and sediments during the summer of 2003. (The normal summer sampling season spans parts of two consecutive monitoring years.) The results from these sediment and tissue samples are subsequently compared with the screening values listed in Appendices D and E, respectively. Table 7-1 - "Fish Tissue Metal Analysis Results - WQS MY2002 (Rec'd 2003)", Table 7-2 - "Fish Tissue PCB Analysis Results - WQS MY2002 (Rec'd 2003)", Table 7-2 - "Fish Tissue PCB Analysis Results - WQS MY2002 (Rec'd 2003)", and Table 7-3 - "Fish Tissue PAH Analysis Results - WQS MY2002 (Rec'd 2003)" summarize the most recent results from fish tissue samples in relation to the EPA-IRIS screening values. Table 7-4 - "Sediment Analysis Results - WQS MY2002 (Rec'd 2003)" summarizes the results of sediment samples from the same period, in relation to the NOAA ER-M screening values. The analyses of some samples collected in the summer of 2002 may not yet be complete. The majority of the results from sampling during the summer of 2003 should be available for next year's Toxics Reduction Report.

Additional information on the fish-tissue/sediment monitoring program is available from Alex M. Barron, Office of WQS, (804) 698-4119. Several reports on fish tissue and sediment monitoring by the Office of WQS can be found on the DEQ WebPages at <u>www.deq.state.va.us/rivers/ fishsed.html</u>.

A few 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 (MY2003)".

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 <u>numerical effluent limits</u> 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 (MY2003)" 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 – "List of Permits, Parameters, Parameter Limits and Units" along with the effective dates of each permit. The compliance record of each permitted facility during the 2003 monitoring year is reported in Appendix L – "Permitted Facilities and their Compliance Status – MY2003".

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 Facilities and their Compliance Status – MY2003" lists the most recently reported data (1 Jul 2002 – 30 Jun 2003) 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 or, if necessary, the associated Deputy Regional Director (see list below). Deputy Regional Directors have assumed the role and responsibilities of Compliance Enforcement Managers at the regional level.
Regional Office Compliance Auditors and Deputy Regional Directors

Regional Office	Compliance Auditor	<u>Deputy Regional Director</u>
Northern Virginia	Christine Monroe (703) 583-3844	John Bowden (703) 583-3880
Piedmont	Patrick Bishop (804) 527-5127	James Golden (804) 527-5052
Southwest	Ruby Scott (276) 676-4882	Dallas Sizemore (276) 676-4842
South Central	Nonna Heagy (434) 582-5120 Ext. 342	David Miles (434) 582-5345 Ext. 345
Tidewater	Debbie Kay (757) 518-2127	Harold Winer (757) 518-2153
Valley	Brennon Wion (540) 574-7826	Larry Simmons (540) 574-7810
West Central	Tammy Rogers (540) 562-6776	Norm Auldridge (540) 562-6870

Special Studies Concerning Toxics:

Special studies that dealt with toxics during MY2003 are listed in Text Box 2 below. In the past, such special studies often were initiated independently at the Regional Office level in response to locally recognized problems. Consequently, it was often 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 - MY2003" describes several of these studies in more detail, and interim or final reports on some are also available on the DEQ Website at <u>www.deq.state.va.us/water/reports.html</u>. The names and contact information for the responsible individuals at the Regional and/or Central Office levels are provided in the text box.

An additional special study, that includes the toxicological characterization of sediment, is described below in the section on the Chesapeake Bay Program (CBP). The primary objective of the study is to characterize tidal waters where earlier evaluation by the CBP had been inconclusive because of insufficient data. In

brief, this study utilizes the standard triad of benthic community diversity and structure, sediment toxicity, and sediment chemistry, at randomly selected sites, to evaluate the ecological condition of the sediments in the region.

DEQ's CEDS 2000 database now includes a module that registers and tracks the progress of all special studies as they evolve. All special studies receive 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 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 will be electronically linked to it in the CEDS database to facilitate the complete retrieval of all related information.

Benthic TMDL Special Studies Involving Toxicity Tests

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. Consequently, beginning in November of 2002, water samples have been collected and shipped to contracted laboratories for toxicity testing related to TMDL studies of a number of stream segments impaired for benthic organisms. Appendix N1, "Impaired Segments Selected for Toxicity Testing 2002-2003", presents a summary of those TMLS studies where toxicity testing was carried out during the fall of 2002 and the spring of 2003. Of twenty-seven site sampled between November of 2002 and July 2003, no results have yet revealed significant acute or chronic toxicity. Four results did, however, reveal "sub chronic" toxics effects, i.e. some indication of toxicity exists, but the results of standardized test for chronic toxicity were not significant.

Appendix N2, "Impaired Segments Selected for Toxicity Testing 2003-2004", lists those benthic-impaired segments where toxicity tests have been, or will be performed during the indicated period. No results are yet available from those tests initiated in October of this year.

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

Northern Virginia Regional Office

There were no active special studies involving toxics carried out in the Northern Virginia Region during MY 2003.

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. PCB Source Assessment in the James River, Richmond, VA, to Windmill Point, VA – 2002 A tiered study was begun in 2002 to localize the sources and determine the geographic distribution and severity of Carp and Blue catfish contamination by PCBs in the lower James River. This study continues on schedule as described in the work plan in Appendix I.

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

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

South Central Regional Office

There were no active special studies specifically directed at toxics carried out in the South Central Region during MY2003. Several bioassay (toxicity testing) studies related to benthic TMDL development are listed in Appendix I.

For further information concerning projects in the South Central Region, contact:

Kyle I. Winter DEQ – Lynchburg Regional Office (804) 582-5120, ext. 229

Southwestern Regional Office

There were no active special studies involving toxics carried out in the Southwestern Virginia Region during MY 2003.

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

Frederick W. Kaurish DEQ – Southwestern Regional Office (540) 676-4840

Text Box 2. Toxics Related Special Studies Active during MY 2003.

Tidewater Regional Office

No new Special Studies specifically related to toxics were carried out in TRO during Monitoring Year 2003. The Red Bank Creek study of agrochemical runoff, as described last year, is currently being summarized and a report on its findings should be available prior to next year's TRISWat Report. 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 2002. This monitoring project is the continuation of an ongoing mercury-monitoring program being directed by DEQ. 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 This is part of an ongoing study of fish, water, and sediments. Monitoring began in the late 1970s and is expected to continue well into the future. See Appendix I for further details.
- 2. Water Sample Collection and Analysis for Determining Mercury Content in a Portion of the South River, Waynesboro, VA. This monitoring project is also the continuation of an ongoing mercury-monitoring program being directed by DEQ. 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. See Appendix I for further details.
- **3.** Phase II of an ongoing intensive survey of local mercury distribution in the South River was initiated in August of 2003 and results will be summarized in next year's TRISWat Report.

More details are available on the DEQ website: http://www.deq.state.va.us/rivers/mercury.html, or contact:

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

Text Box 2. (cont.) Toxics Related Special Studies Active during MY 2003.

West Central Regional Office

1. A new "Special Study of PCB Source Assessment in the New River, Radford, VA to the VA/WVA State Line - 2003" was initiated from the West Central Office in 2003. An inventory of facilities considered possible sources of PCBs was conducted from January through May 2003, and some site inspections and terrestrial sampling were conducted from June through September. Further activities will depend upon the results of the sampling, which are not yet available.

For further information on the status of the project, results, reports, etc., contact: Kip Foster DEQ – West Central Regional Office (540) 562-6782

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.

For further information on the status of the project, results, reports, etc., contact: Roger K. Everton, DEQ - Tidewater Regional Office (757) 518-2150

Text Box 2. (cont.) Toxics Related Special Studies Active during MY 2003.

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715160	Contrary Creek	Detail	
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795101	Pagan River	Detail	
795105	Nottoway River	Detail	
795106	Chowan River	Detail	
<mark>795110</mark>	Lynnhaven River	Detail	
815102	James River	Detail	
825101	Roanoke River	Detail	
825102	Blackwater Sp. DO Study	Detail	
835101	Nansemond River	Detail	
835102	Chuckatuck River	Detail	
815101	Chickahominy River	Detail	
835103	Philpott Reservoir	Detail 👻	

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

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

The MY2004 Water Quality Monitoring Plan

The Annual Water Quality Monitoring Plan (or MonPlan) is generally elaborated in the first quarter of each calendar year and is usually finalized by early April. The MonPlan provides a complete list of the ambient WQM stations that will be actively sampled during the following monitoring year (1 July - 30 June). The MonPlan identifies specific programs associated with each site, the parameters that will be measured there, the number of samples that will be collected, and the frequency of sampling. The MonPlan also provides the information necessary to estimate the resources required for the following year's monitoring efforts and to advise the state's Division of Consolidated Laboratory Services in advance of the human, technical, and chemical resources that will be necessary for analytical purposes. In addition, it provides a convenient overview for the monitoring coordination group at DEQ's Central Office to evaluate the consistency of site and parameter selection among the agency's seven regional offices.

The annual Monitoring Plan for MY2004, which began on July 1 2003, 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. Annual MonPlans will soon be posted on the DEQ Website at http://www.deq.state.va.us/watermonitoring/. The new plan for MY2005 will be finalized during the winter/spring of 2003/2004, and should be available at the DEQ Website address by mid-April.

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 into 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. Periodic 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 midterm 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 water quality parameters within drainage basins (1997 through 2003) can be evaluated from these figures. As indicated earlier in the discussion of pesticide results, however, graphical comparisons can be misleading unless all pertinent information is considered.

The figures are presented as an example of how trends can be evaluated graphically when sufficient data are available. The six (or fewer) years of data included in the figures represent only a single five- to six-year cycle of toxics 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 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 305(b) / 303(d) Reports to the U.S. EPA and Congress

The 2004 305(b) / 303(d) report is currently in preparation. The draft guidance for this report has been public noticed once, then edited and replaced, for further EPA and public comment, on the DEQ Website at <u>http://www.deq.state.va.us/wqa/305b2004.html</u>. A draft 305(d)/303(d) Report should be available for EPA and public comment by February or March and the target date for the final report is still April 2004. Preparation of the 2004 report has been somewhat delayed due to EPA's requirement for the inclusion of a newly developed Benthic Index of Biotic Integrity (B-IBI) for assessment of Chesapeake Bay probabilistic benthic monitoring results. Consultations among EPA Region 3, the Interstate Chesapeake Bay Program, the states of Maryland and Virginia, and VERSAR Consulting (Columbia, MD), from January through October 2003, resulted in consensus on a standardized benthic assessment protocol that will be utilized by both states in their 2004 305(b) Reports.

The discussion that follows relates to the 2002 305(b)/303(d) Reports, and is unchanged from last year's TRISWat Report, except for the addition of several Virginia Department of Health fishing advisories in Text Box 3.

The most recent 305(b) Report on Virginia Water Quality Assessment (DEQ-WQA, 2002) is still available at the DEQ Website as http://www.deq.state.va.us/water/305b.html. As previously mentioned, this 305(b) report is based on consideration of the five-year period between 1 January 1996 and 31 December 2000. The <u>Text Table</u> on the following page summarizes the quantity of waters assessed as "impaired" for various categories of toxics in the new 305(b) Report. DEQ has classified a number of water bodies, primarily free-running streams, as suffering minor, moderate, or major impact to benthic community structure. Most of these impairments, including portions of the Chesapeake Bay mainstem, result from low oxygen concentration and are not directly related to toxics in the water. Because of the possibility of toxics-related benthic impairments, those that remain with "cause unknown" classifications have been included here. Any observed impairment, however, stimulates more intensive monitoring and chemical analyses to identify its cause. Once DEQ has identified specific causes, it can take appropriate measures to resolve the problems.

Chapter 2.5, "Public Health / Aquatic Life Concerns," of the same report provides listings and detailed descriptions of all waters that have fishing advisories or restrictions due to the presence of toxic substances in fish tissues or the environment. An additional 220 square miles of the estuarine (tidal) James and its tidal tributaries had been under a VDH fish advisory because of Kepone in the sediments (7/1/88). VDH has removed the Kepone derived limits on fish consumption from this region, but a more recent restriction (July 2002 – see Text Box 3, below) has been announced for essentially the same area because of PCBs in the tissues of carp and blue catfish. (Note that new [October 2003] VDH Fish Advisories have been added to the Text Box below.)

Appendix M - "List of Segments not Fully Supporting Designated Uses because of Toxics (2002)" of the current Report presents a comprehensive list and description of all water-body segments that were assessed as impaired because of toxics for the 2002 305(b)/303(d) Report. Appendix M will be updated for the January 2005 Toxics Reduction in State Waters Report, once the 305(b)/303(d) Report for 2004 has been completed and approved.

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

Cause	Waterbody Type	Quantity Impaired
General Standards (Benthics) Note: Cause unknown!	River (mi.) Lakes (acres) Estuary (sq. mi.)	649.96 0 382.50
Un <u>-</u> ionized Ammonia	River (mi.) Lakes (acres) Estuary (sq. mi.)	1.46 0 1.95
Cause Unknown	River (mi.) Lakes (acres) Estuary (sq. mi.)	4.27 0 0
Priority Organics	River (mi.) Lakes (acres) Estuary (sq. mi.)	10.44 0 0.05
PCBs	River (mi.) Lakes (acres) Estuary (sq. mi.)	370.58 29,040.24 82.53
Metals	River (mi.) Lakes (acres) Estuary (sq. mi.)	234.33 0 0
Non-Priority Organics	River (mi.) Lakes (acres) Estuary (sq. mi.)	90.44 20,300.00 24.77
Fish Tissue	River (mi.) Lakes (acres) Estuary (sq. mi.)	452.74 8,836.24 65.09

Quantity of Virginia Waters Impaired, by Various Categories of Toxics (TABLE 3.3-4 from the 2002 305(b) Report)

More Recent Virginia Department of Health Fishing Restrictions and Health Advisories

A number of additions to VDH fishing advisories occurred during MY2003, several of which were added as recently as October 2003 (MY2004). Text Box 3, on the next two pages, summarizes the rivers and affected boundaries, contaminants of concern, and the specific advisory/restriction for these changes. The complete VDH fishing restrictions and health advisories currently in effect can be found on the VDH Website at www.vdh.state.va.us/HHControl/fishing advisories.htm.

River and Affected Boundaries	Contaminant	Health Advisory / Restriction
Dragon Run Swamp/Piankatank River (Counties of Middlesex, King and Queen, and Gloucester) from State Route 603 near Mascot downstream (~19 miles) to Deep Point Boat Landing (State Route 606) on the Piankatank River, across from Piankatank Shores	Mercury	Largemouth bass caught in these waters may contain mercury. Eat no more than two eight-ounce meals per month of largemouth bass taken from the advisory area. Women who are pregnant or may become pregnant, nursing mothers, and young children should not eat any fish contaminated with mercury from these waters. (10/29/03)
Blackwater River (Counties of Southampton and Isle of Wight and Cities of Franklin and Suffolk) from State Route 460 in Zuni downstream (~40 miles) to the Virginia-North Carolina state line	Mercury	Largemouth bass and redear sunfish caught in these waters may contain mercury. Eat no more than two eight-ounce meals per month of any largemouth bass or redear sunfish taken from the advisory area. Women who are pregnant or may become pregnant, nursing mothers, and young children should not eat any fish contaminated with mercury from these waters. (10/29/2003)
Great Dismal Swamp Canal (Chesapeake) from Deep Creek Locks south to the Virginia-North Carolina state line including the feeder ditch to Lake Drummond	Mercury	Bowfin and chain pickerel caught in these waters may contain mercury. Eat no more than two eight-ounce meals per month of bowfin or chain pickerel taken from the advisory area. Fishing in this area is primarily for consumption. It is advisable that people limit consumption of all species from these waters until additional data are collected. Women who are pregnant or may become pregnant, nursing mothers, and young children should not eat any fish contaminated with mercury from these waters. (10/29/2003)
James River at the Interstate 95 James River Bridge crossing in Richmond downstream (~43 miles) to Flowerdew Hundred where the power lines cross the river about seven miles from the Benjamin Harrison Bridge	PCBs	Blue catfish and carp caught in these waters may contain PCBs. VDH recommends people do not eat any blue catfish and only two eight-ounce meals per month of carp from the advisory area. Women who are pregnant or may become pregnant, nursing mothers, and young children should not eat blue catfish or carp from these waters. (7/1/02)
Knox Creek in Buchanan County from the Virginia/Kentucky state line upstream (~17miles) to its headwaters near the Virginia/West Virginia state line	PCBs	Fish taken from these waters may contain PCBs. Eat no more than two meals per month of any fish taken from the advisory area. Women who are pregnant or may become pregnant, nursing mothers, and young children should not eat any fish taken from these waters. (5/15/03)

Beaver Creek in Washington County from the Beaver Creek Lake Dam downstream to the Virginia/Tennessee state line within the City of Bristol	PCBs	Fish taken from these waters may contain PCBs. Eat no more than one meal per month of any fish taken from the advisory area. Women who are pregnant or may become pregnant, nursing mothers, and young children should not eat any fish taken from these waters. (5/15/03)
Roanoke River/Smith Mountain Lake (Counties of Roanoke, Franklin, and Bedford) from the Niagara Dam downstream (~9.5 miles) to channel marker R78 on Smith Mountain Lake (~2 miles down the lake from Hardy Ford Bridge on County Route 634	PCBs	Flathead catfish caught in these waters may contain PCBs. Eat no more than one eight-ounce meal per month of flathead catfish from the advisory area. These fish can travel far distances. It is also advisable that people limit consumption of flathead catfish caught from the entire lake including upstream to the County Route 634 Bridge on the Blackwater River arm of the lake until additional data are collected. Women who are pregnant or may become pregnant, nursing mothers, and young children should not eat any fish contaminated with PCBs from these waters. (10/20/03)
Text Box 3 – Additions and Update Advisories during the Past Year	es to Departmen	t of Health Fishing Restrictions and Health

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. Relative to point sources, the Bay signatories committed to the eventual elimination of mixing zones. 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.

Mixing Zone Elimination

In accordance with the Chesapeake 2000 Agreement and the Toxics 2000 Strategy, initial steps to eliminate mixing zones through pollution prevention and other voluntary means were taken. First, a list of thirteen (13) persistent or bioaccumulative contaminants (PBTs) was developed. Using the list of PBTs, it was then possible to identify perspective dischargers that are allowed mixing zones for the chemical contaminants of interest. That is, the PBTs can be discharged at levels that exceed water quality criteria at the end of their outfalls, whereby dilution is allowed in the stream. The third step in the process is to determine which facilities actually discharge in excess of the water quality criteria at the end of their pipes, and then target those dischargers for pollution prevention activity. The initial target areas in Virginia were the Elizabeth River and the Lower Tidal James River, an Area of Emphasis.

Region of Concern Restoration

A revised Watershed Action Plan was developed in 2002 by many stakeholders (ERP - Elizabeth River Project) as a means to help restore the Elizabeth River. The plan contains fourteen action items known as the "clean fourteen". Some of the highest priority actions consist of cleaning up the Elizabeth River sediments (remove toxic pollutants), restoring wetlands, monitoring river trends, reducing toxics and nutrients in stormwater runoff, and educating school children and the public.

More recently, the stakeholder effort has broadened with the creation of the Elizabeth River Project Sediment Remediation Partnership. The new effort encompasses several federal agencies including EPA, NOAA, and the Fish and Wildlife Service, along with local stakeholders comprised of the Navy, Army Corps of Engineers, local businesses, governments, and citizens. The development of this group should lead to enhanced restoration of the Elizabeth River through a gain of resources including improved data management, increased diversity in expertise and greater availability for potential funding opportunities.

Toxics Characterization

In 1999 the Chesapeake Bay Program's Toxics Subcommittee completed a toxics characterization of the tidal tributaries of the Chesapeake Bay, which includes 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 characterizes each pre-defined regional area into one of four categories based on chemical contaminant exposure and biological affects. *Regions of Concern* (e.g., Elizabeth River) are highly impacted areas, *Areas of Low Probability for Adverse Effects* are regional areas that are not impacted by chemical contaminants, and *Areas of Emphasis* have the potential for serious chemical contaminant-related impacts. A fourth category included *Areas of Insufficient or Inconclusive Data* where the data were not sufficient to place the area into one of the three categories above. An example of a management action could include ambient toxics monitoring in those regional areas characterized as *Areas of Insufficient Data*.

Recent Chemical Contaminant Monitoring in Areas of Insufficient Data

Lower Mobjack Bay, York River Segment of the Chesapeake Bay

Similar to the 2000 and 2001 Tidal James River studies (Roberts *et al.*, 2002a, Roberts *et al.*, 2002b), in the fall of 2002 DEQ toxicologically characterized the Chesapeake Bay near the mouth of the York River, which also includes the Back and Poquoson Rivers (Roberts *et al.*, 2003. [Draft]). The approach consisted of a sediment quality triad study that utilizes sediment toxicity tests, chemical contaminant analysis, and a benthic community assessment.

The study area was subdivided into three distinct strata: Back River, Poquoson River, and the Chesapeake Bay near the mouth of the York River. Four (4) random stations were sampled within each of the aforementioned strata. The results indicate there was no measurable toxicity and at most sites the chemical contaminant concentrations were below levels of perceived toxicological concern. At one station the pesticide DDT was present at a level that exceeded its Effects Range-Median sediment toxicological benchmark. Additionally, two PCB compounds were detected at different stations, but the concentrations were not analytically confirmed with Mass Spectrometry. The condition of the benthic community at all four stations in the Back River and three of four stations in the Poquoson River proved to be either degraded or severely degraded. A single station in the Poquoson met the Chesapeake Bay Restoration Goal, while all four stations in the Chesapeake Bay stratum met or exceeded the Restoration Goals. It was concluded that the stressed benthic communities are likely impacted by eutrophication derived from adjacent residential land use.

While these studies were designed to make statements about the entire segment relative to chemical contaminants, conclusions from this study cannot rule out the possibility for localized impacted areas.

Further information on the Chesapeake Bay Program's toxics studies is available from Mark Richards, Environmental Program Planner, DEQ Chesapeake Bay Office in Richmond, at (804) 698-4392. 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: <u>http://www.chesapeakebay.net/</u>.

Citation

Roberts, M.H., Jr., M.A. Richards, and P.F. De Lisle. 2003. Chemical and Toxicological Characterization of Lower Mobjack Bay, York River, Virginia Segment of the Chesapeake Bay. Draft Final Report to VA Department of Environmental Quality. 47 pp.

The Elizabeth River Program

Historically speaking, while significant research has been conducted in the Elizabeth River, it has been sporadic in nature and severely lacking in coordination among various research efforts. With Virginia's commitment to implement the Elizabeth River Watershed Action Plan as our toxics reduction strategy in this troubled river, a massive effort to restore this river is underway. 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 in contracting the consulting firm URS Greiner, Inc. to produce a comprehensive WQM 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. Unfortunately, recent economic crises have restricted financial resources for the Elizabeth River Program, and the intensity of monitoring and research has been reduced.

Several specific 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

Dissolved Metals

Upon review the available water column metals data from the River, the Elizabeth River Monitoring Committee has recommended that the monitoring of dissolved metals be suspended until adequate funding is restored to the monitoring program.

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 Vogelbien 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 Zwerner, 2000).

A final draft report on the 2001 fish histopathology monitoring, including an evaluation of sediment PAH values, is currently under review. The revision was not concluded prior to mid-December. Consequently, a summary of the findings will be included in next year's TRISWat Report.

TBT Monitoring

Tributyltin (TBT) data have been collected 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 <u>trillion</u>) 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 exceeding 20 ng/L and 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 <u>http://www.vims.edu/env/projects/tbt_deq/</u>.

Benthic Index of Biotic Integrity (BIBI) 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 around estimates of condition of the benthic communities and allows estimates of the areal extent of degradation of the benthic communities. Based upon probability-based sampling the estimate of benthic bottom not meeting the benthic restoration goals was 76 % in 2002, 52 % in 2001, 72 % in 2000, and 64 % in 1999. Dr. Dauer submitted the most recent report on the Benthic Biological Monitoring Program in the Elizabeth River in November 2003 (Dauer, 2003). His report is cited below and in the references. 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 <u>http://www.chesapeakebay.odu.edu/Reports/reports.htm</u>.

Low Level Contaminants

No new SPMD monitoring activities were carried out during MY2003.

Elizabeth River Monitoring Reports: 2002-2003

Dauer, D.M. 2003. Benthic Biological Monitoring Program of the Elizabeth River Watershed (2002) with a Study of Paradise Creek. Daniel M. Dauer, Old Dominion University, Department of Biological Sciences, November 2003.

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

Virginia Toxics Release Inventory

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

The most recent Virginia Toxic Release Inventory Report (SARA Title III TRI, May 2003) indicated that 508 Virginia facilities reported to the TRI program for the 2001 activity year. Statewide toxic releases to the water totaled approximately 7.0 million pounds or 9.9% of the total onsite releases to all media during 2001. This represents a 14.6% decrease from 2000 releases, in spite of the lower reporting thresholds introduced for lead and lead compounds (persistent bioaccumulative toxins or PBTs).

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 (DEQ-SARA Title III, 2002). The May 2003 Virginia TRI Summary Report, summarizing data from CY2001 industry reports, is available on the DEQ Website at <u>http://www.deq.state.va.us/sara3/3132000.html</u>.

For further information on the Virginia TRI, contact Dona Huang, Environmental Program Manager, SARA Title III, at (804) 698-4489.

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: <u>http://www.epa.gov/tri/</u>. 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 2001, should be available by March 2004.

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 focusing 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 2003 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 original report presents detailed summaries of the major components of VIP2 activities during 2003, several of which are briefly summarized here.

1. The total number of facilities in the <u>Virginia Environmental Excellence Program (VEEP)</u> increased from 122 to 152, an increase of approximately 25% in 2003. Virginia has continued to promote coordination and cooperation with EPA's National Environmental Performance Track Program, which rewards "high-performing" facilities with regulatory flexibility incentives.

2. During its first two years, the <u>Electronics Recycling & Stewardship Program</u>, initiated in late 2001, stimulated local governments, businesses and consumers to divert about 100 tons of obsolete computers and potentially hazardous components from Virginia landfills to recycling alternatives. A record one-day recycling collection of 28 tons of equipment was accomplished in Charlottesville during 2003.

3. DEQ's <u>Pollution Prevention in Healthcare Program</u> (Hospitals for a Health 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.

4. Participants in the <u>Businesses for the Bay (B4B) Program</u> reported 16.7 million pounds of waste reduction and cost savings of \$664,000. As of October 2003, the program had over 540 participants and about 120 mentors providing peer-to-peer assistance.

5. The Office of Pollution Prevention (OPP), which carries out DEQ's p2 program, was greatly impacted by state budget reductions in the fall of 2002. Seven of the program's ten positions were reassigned to other non-state funded areas of the agency. Some aspects of the program were eliminated in 2003, including onsite P2 technical assistance, and some others were significantly reduced in scope.

6. In 2004, the Office of Pollution Prevention will be focusing on a few primary areas, including:

- Full implementation of the Virginia Hospitals for a Health Environment initiative;
- Co-hosting of a "green lodging" conference;
- Expanded efforts to reduce hazardous waste generation by promotion of the National Waste Minimization Plan;
- Continued outreach in the areas of renewable energy and regulatory incentives for environmental performance.

The entire Pollution Prevention Annual Report (2003) is available on the OPP (P2) page of the DEQ Website: www.deq.state.va.us/p2/pdf/2002p2rept.pdf. Additional information about the activities of the OPP during the past year is available from the P2 Website (www.deq.state.va.us/p2), and from Sharon Baxter, environmental program manager, at (804) 698-4344.

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

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Note: *The EPA online website at <u>http://www.epa.gov/iris/</u> is updated periodically with new chemical substances and the results of new toxicological studies. This listing, as of 15*

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Glossary of Terms Used in the Toxics Management Program

Acute Toxicity - An adverse effect, that usually occurs shortly after exposure to a toxic substance. Lethality is one commonly used "end-point" for the evaluation of acute toxicity to an organism. When death is not easily verified, immobilization of an organism may be used as an alternative criterion.

Applicability Criteria - The basic criteria used to determine whether a facility must participate in the Toxics Management Program and conduct toxicity tests in order to assess the need for toxicity reduction evaluations and the development of Whole Effluent Toxicity (WET) limits. The criteria include the following:

1. A discharge that has demonstrated actual or potential toxicity or contains toxic pollutants;

2. Any industrial discharge that falls into one of the standard industrial classification (SIC) codes listed as a primary industry for the Toxics Management Program;

3. Any industry with a daily maximum wastewater flow greater than or equal to 50,000 gallons per day;

4. Publicly owned treatment works (POTWs) with flows greater than or equal to one million gallons per day (MGD);

5. Any POTW with a pretreatment program; and

6. Any other discharge that the Water Board deems has the potential for toxicity or in-stream impact based on an evaluation of manufacturing processes, indirect discharges, treatment processes, effluent or receiving stream data, or other relevant information.

Chronic Toxicity - An adverse effect that is irreversible or progressive or occurs because the rate of injury is greater than the rate of repair during prolonged exposure to a toxic pollutant. This includes low-level, long-term effects such as reduction in growth or reproduction.

Effluent Limitation Guidelines (ELGs) - ELGs are established by the EPA and are often used when more stringent water-quality-based effluent limitations (WQBELs) are not required to maintain water quality standards adopted by Virginia.

Toxics Management Plan - All facilities applying for Virginia Pollutant discharge Elimination System (VPDES) permits are assessed for the need for a toxics management plan. This plan is the process through which the facility assesses the toxicity of its discharge, evaluates potential toxicity reductions if the discharge fails toxicity tests, and develops the information that is the basis for a WET limit, if required.

Toxicity – The inherent potential or capacity of [an excess of] a material to cause adverse effects in a living organism, including acute or chronic effects to aquatic life, detrimental effects to human health or other adverse (biological) environmental effects.

Toxics Reduction Evaluation (TRE) – The process through which a facility determines what is causing the toxicity of its discharge and evaluates alternatives for reducing the toxicity.

Water-Quality-Based Effluent Limitations (WQBELs) – WQBELs for Whole Effluent Toxicity (WET) are established whenever necessary to ensure that effluents meet the toxicity decision criteria or to protect all reasonable and beneficial uses of the state's waters. WQBELs are developed for specific toxic pollutants if data developed during effluent monitoring indicate that violations of the standards or criteria would occur in the receiving waters and that compliance with technology-based effluent limits would not prevent the violation.

WET Limits - WQBELs for aquatic tests. Whole Effluent Toxicity (WET) limits are developed and incorporated into a VPDES permit after testing discharges for impact on fish or other aquatic organisms reveals the potential for toxic discharge.