

RESEARCH REPORT

Technologies and Techniques for Early Warning Systems to Monitor and Evaluate Drinking Water Quality: A State-of-the-Art Review

Office of Research and Development
National Homeland Security
Research Center



EPA/600/R-05/156

**Technologies and Techniques for Early Warning Systems to Monitor and
Evaluate Drinking Water Quality: A State-of-the-Art Review**

**U.S. Environmental Protection Agency
Office of Water
Office of Science and Technology
Health and Ecological Criteria Division**

August 25, 2005

[this page intentionally left blank]

DISCLAIMER

This document has been reviewed in accordance with U.S Environmental Protection Agency policy and approved for publication and distribution. The research described here was managed under EPA Contract 68-C-02-009 to ICF Consulting, Inc.

Mention of commercial products, trade names, or services in this document or in the references and/or endnotes cited in this document does not convey, and should not be interpreted as conveying official EPA approval, endorsement, or recommendation.

Questions concerning this document or its application should be addressed to:

Jafrul Hasan, Ph.D.
USEPA Headquarters
Office of Science and Technology, Office of Water
1200 Pennsylvania Avenue, NW
Mail Code: 4304T
Washington, DC 20460
Phone: 202-566-1322
Email: hasan.jafrul@epa.gov

[this page intentionally left blank]

ACKNOWLEDGMENTS

The research described here was funded by the National Homeland Security Research Center, Office of Research and Development, and managed by the Office of Science and Technology, Office of Water.

EPA gratefully acknowledges the contributions of the following persons and organizations to the development of the main Report *Technologies and Techniques for Early Warning Systems to Monitor and Evaluate Drinking Water Quality: A State-of-the-Art Review*.

EPA Work Assignment Manager: Jafrul Hasan

ICF Work Assignment Manager: David Goldbloom-Helzner

Co-Work Assignment Manager: Audrey Ichida

ICF staff: Tina Rouse and Mark Gibson

Subject matter experts consulted: Stanley States, Walter Grayman, and Rolf Deininger

Internal (EPA) Reviewers:

Jonathan Herrmann	Office of Research and Development/National Homeland Security Research Center
Irwin Silverstein	Office of Water/Water Security Division and Office of Research and Development/National Homeland Security Research Center
John Hall	Office of Research and Development/National Homeland Security Research Center
Roy Haught	Office of Research and Development/National Risk Management Research Laboratory
Robert Janke	Office of Research and Development/National Homeland Security Research Center
Alan Lindquist	Office of Research and Development/National Homeland Security Research Center
Matthew Magnuson	Office of Research and Development/National Homeland Security Research Center
Regan Murray	Office of Research and Development/National Homeland Security Research Center
Grace Robiou	Office of Water/Water Security Division
Cesar Cordero	Office of Water/Office of Science and Technology
Jafrul Hasan	Office of Water/Office of Science and Technology

External (non-EPA) Reviewers:

Ronald J. Baker	U.S. Geological Survey
Frank Blaha	American Water Works Association Research Foundation
Erica Brown	Association of Metropolitan Water Agencies
Bill Clark	Association of Metropolitan Water Agencies
Ricardo DeLeon	Metropolitan Water District of Southern California
Wayne Einfeld	Sandia National Laboratories
Lee Glascoe	Lawrence Livermore National Laboratory
Kevin Morley	American Water Works Association
My-Linch Nguyen	American Water Works Association Research Foundation
Irwin Pikus	University of Virginia
Connie Schreppel	Mohawk Valley Water Authority
Alan Roberson	American Water Works Association

TABLE OF CONTENTS

DISCLAIMER	i
ACKNOWLEDGMENTS	iii
LIST OF EXHIBITS	xi
ACRONYMS and ABBREVIATIONS	xiii
1. Report Highlights	1
1.1 Desired Characteristics of Integrated Early Warning Systems (EWSs)	2
1.2 Conclusions and Recommendations	3
1.2.1 General Conclusions and Recommendations	3
1.2.2 Specific Conclusions and Recommendations	4
2. Introduction	9
2.1 Concern for the Water Supply	9
2.2 Role of EPA in Water Security and Early Warning Systems	9
2.2.1 National Homeland Security Research Center Research	10
2.2.2 Environmental Technology Verification (ETV) Program	11
2.2.3 Technology Testing and Evaluation Program (TTEP)	11
2.2.4 American Society of Civil Engineers (ASCE) Guidelines for Designing an Online Contamination Monitoring System	11
2.2.5 Water Utility Users Group	11
2.2.6 Water Security Working Group (WSWG)	12
2.2.7 Water Contaminant Information Tool (WCIT)	12
2.2.8 Distribution System Research Consortium (DSRC)	12
2.2.9 EPA Resources/Guidance	12
2.3 Purpose of this State-of-the-Art Review	13
2.4 Approach for this State-of-the-Art Review	16
2.5 Sources of Information	16
2.5.1 Experts	16
2.5.2 Conferences and Seminars	17
2.5.3 Published Literature	17
2.5.4 Website Resources	17
2.5.5 Workgroup Efforts	17
2.6 Criteria for Selecting Products/Technologies	18
3. Desired Characteristics and Features of Integrated Early Warning Systems	19
3.1 Desired Characteristics for Integrated Early Warning Systems	19
3.1.1 Rapid Response Time	19
3.1.2 Range of Contaminants	20
3.1.3 Automation and Remote Operation	21
3.1.4 Affordable Cost	23
3.1.5 Low Skill and Training	23

3.1.6	Source of the Contaminant	23
3.1.7	Sensitivity	23
3.1.8	Minimal False-positives/False-negatives	24
3.1.9	Robustness and Continuous Functioning	25
3.1.10	Third Party Verification	25
3.2	Design Features of Integrated Early Warning Systems	25
3.2.1	Evaluate the Need for an Integrated EWS	28
3.2.2	Establish EWS Plan and Coordination	29
3.2.3	Determine Overall Approach to EWS Design	30
3.2.4	Develop Detailed Design of an Integrated Early Warning System	32
4.	Features of an EWS Related to Data Acquisition and Analysis; Contaminant Flow; Sensor Placement; Alerts; Data Security; and Communication, Response, and Decision Making	37
4.1	Real-Time Data Acquisition and Data Analysis	37
4.1.1	Basics	37
4.1.2	Demonstration Projects, Tests, and Products	40
4.2	Contaminant Flow Predictive Systems	41
4.2.1	State-of-the-Art Systems and Current Research and Development	42
4.3	Sensor Placement	45
4.3.1	Current Research and Development	45
4.3.2	State-of-the-Art Systems	46
4.4	Alert Management Systems	47
4.5	Integrating Water Distribution Modeling and Data Acquisition Systems	47
4.6	Data Security	48
4.7	Communications, Response, and Decision Making	49
5.	Multi-Parameter Water Quality Monitors as Candidates for Early Warning Systems	53
5.1	Descriptions of Various Multi-Parameter Water Quality Monitors	53
5.2	Efforts to Determine Performance of Multi-Parameter Water Quality Monitors and Establish Water Quality Baselines	56
5.2.1	Evaluate Sensor Performance	57
5.2.2	Investigate Baseline for Water Quality	57
5.2.3	Verify Sensor Performance	57
5.3	Efforts to Provide Red Flag EWS and to Identify Specific Contaminants via Signature Using Multi-Parameter Water Quality Monitors	57
5.3.1	Sensor Response to Contaminants	58
5.3.2	Multi-Parameter Response to Chemical or Biological Agent Simulants	58
5.3.3	Signature Development	58
5.3.4	Further Testing of Signature Concept	58
5.3.5	Multi-Parameter Response to Actual Chemical and Biological Agents	59
6.	Technologies that Detect Chemical Contaminants for Early Warning Systems	61
6.1	General Introduction to Assays and Sensors	61
6.2	Available Technology	61
6.2.1	Detection of Arsenic	61

6.2.2	Detection of Cyanide	62
6.2.3	Gas Chromatography	63
6.2.4	Enzyme-Based Detection	64
6.2.5	Biosensors	65
6.3	Potentially Adaptable Technology	69
6.3.1	Enzyme-Based Detection	69
6.3.2	Organism-Based Biosensors	70
6.3.3	Infrared Spectroscopy	72
6.3.4	X-ray Fluorescence	73
6.3.5	Ion Mobility Spectroscopy	73
6.3.6	Microchips for Portable Chemical Sensors	74
6.3.7	Microchip Surface Acoustic Wave (SAW) Technology	75
6.3.8	Microchip Chemiresistors	76
6.4	Emerging Technology	76
6.4.1	Organism-Based Biosensors	76
6.4.2	Eukaryotic Cell-Based Biosensors	77
6.4.3	Fiber Optic Cable-Based Sensors	77
6.4.4	Ion Mobility Spectroscopy (IMS)	78
6.4.5	Surface Acoustic Wave (SAW) Technology	78
6.4.6	Raman Spectroscopy	80
7.	Technologies that Detect Microbial Contaminants for Early Warning Systems	81
7.1	General Introduction to Assays and Sensors	81
7.2	Available Technologies	81
7.2.1	Immunoassays	81
7.2.2	Detection of Bacterial - ATP	84
7.2.3	Flow Cytometry- and Micro-Flow-Based Technology	85
7.2.4	Bioparticulate Monitors - Light Scattering Technology	86
7.3	Potentially Adaptable Technology	88
7.3.1	Fiber Optic-Based Biosensor	88
7.3.2	Dye-Loaded Microspheres	89
7.3.3	Detection of ATP	89
7.3.4	Cell-Based Biosensor	90
7.3.5	Polymerase Chain Reaction	90
7.3.6	Bio-Optoelectronic Sensor Systems (BOSS)	94
7.3.7	Surface Plasmon Resonance (SPR)	94
7.3.8	Electrochemiluminescence (ECL)	95
7.4	Emerging Technology	96
7.4.1	Lateral Flow Assay	96
7.4.2	Labels	97
7.4.3	Magnetic Beads	97
7.4.4	Flow-Through Columns	98
7.4.5	Raman Spectroscopy	98
7.4.6	Microelectrode Arrays	99
7.4.7	Microarray of Gel-Immobilized Compounds	99
7.4.8	Magnetic Microbeads	99
7.4.9	DNA Microarrays	100

7.4.10	Micro-Cantilever System	100
7.4.11	Photoluminescent Biochips	100
7.4.12	Polymer Microbeads - Taste Chip	101
7.4.13	Molecularly Imprinted Polymers	101
7.4.14	Magnetoelastic Sensors	102
7.5	Concentration Methods	102
7.5.1	Hollow Fiber Ultrafiltration	102
7.5.2	Hydroxyapatite Whole Cell Capture	103
7.5.3	Lectin and Carbohydrate Affinity	103
8.	Technologies that Detect Radiological Contaminants for Early Warning Systems	105
8.1	General Introduction to Methods of Detection	105
8.2	Available Technology	106
8.3	Potentially Adaptable Technology	107
8.4	Emerging Technology	108
9.	Technical Evaluation of Early Warning Systems	111
9.1	Approach for Technical Evaluation	111
9.1.1	Verification Studies	111
9.1.2	Degree of Government Involvement, Support, and Development for Technology	112
9.1.3	Field Experience and Case Studies	112
9.1.4	Other Studies	112
9.1.5	Expert Opinions	113
9.2	Evaluation of Various Operational Features of EWS	113
9.2.1	Issues and Gaps	113
9.2.2	Conclusions and Recommendations	114
9.3	Evaluation of Multi-Parameter Water Quality Monitors	115
9.3.1	Issue and Gaps	117
9.3.2	Conclusion and Recommendations	122
9.4	Evaluation of Chemical Sensors	124
9.4.1	Issues and Gaps	132
9.4.2	Conclusion and Recommendations	133
9.5	Evaluation of Microbial Sensors	135
9.5.1	Issues and Gaps	142
9.5.2	Conclusion and Recommendations	143
9.6	Evaluation of Radiological Sensors	144
9.6.1	Issues and Gaps	145
9.6.2	Conclusions and Recommendations	147
10.	Conclusions and Recommendations	149
10.1	General Conclusions and Recommendations	149
10.2	Specific Conclusions and Recommendations	151
10.2.1	Data Acquisition and Analysis	151
10.2.2	Flow Modeling	152
10.2.3	Sensor Placement	153
10.2.4	Alert Management	153

10.2.5 Decision Making and Response 154
10.2.6 Multi-Parameter Water Quality Technologies 154
10.2.7 Detection of Chemical Contaminants 155
10.2.8 Detection of Microbial Contaminants 156
10.2.9 Detection of Radiological Contaminants 158

REFERENCES 159

APPENDIX A A-1

APPENDIX B B-1

APPENDIX C C-1

APPENDIX D D-1

ENDNOTES E-1

[this page intentionally left blank]

LIST OF EXHIBITS

Exhibit 3-1. Drinking Water Contaminant Classes and Examples 22
Exhibit 3-2. Design Features of an Integrated Early Warning System 27
Exhibit 3-3. Conceptual Process for Designing an Early Warning System 28
Exhibit 3-4. Sample EWS Approach using First-Stage and Second-Stage Monitors 31

Exhibit 4-1. Examples of Water Distribution System Modeling Software 42

Exhibit 7-1. Lateral Flow Assay 83

Exhibit 9-1. Evaluation of Water Quality Parameter Monitors 118
Exhibit 9-2. Water Quality Monitors Comparison with Desired EWS Characteristics 120
Exhibit 9-3. Water Quality Monitors as EWS 123
Exhibit 9-4. Chemical Sensors Comparison with Desired EWS Characteristics 125
Exhibit 9-6. Microbial Sensors Comparison with Desired EWS Characteristics 136
Exhibit 9-7. Microbial Sensor Technologies and Techniques 144
Exhibit 9-8. Radiological Sensors Comparison with Desired EWS Characteristics 146
Exhibit 9-9. Radiation Sensor Technologies 147

[this page intentionally left blank]

ACRONYMS and ABBREVIATIONS

Å	Angstrom
AFD	Automated Food Device
AK	Adenylate Kinase
AMS	Advanced Monitoring Systems Center
AOAC	AOAC International (historically Association of Official Analytical Chemists)
APDS	Autonomous Pathogen Detection System
ASCE	American Society of Civil Engineers
ASTM	American Society for Testing and Materials
ASV	Anodic Stripping Voltammetry
ATP	Adenosine Triphosphate
ATR	Attenuated Total Reflection
AWWA	American Water Works Association
AwwaRF	American Water Works Association Research Foundation
BADD	BioWarfare Agent Detection Devices
BARC	Bead ARray Counter
BCIP	5-Bromo-4-Chloro-3-Indolyl Phosphate Disodium Salt Hydrate
BEADS	Biodetection Enabling Analyte Delivery System
BOSS	Bio-optoelectronic Sensor Systems
BTA	Bio Threat Alert®
CAD	Computer-Aided Drafting
CBR	Chemical, Biological, and Radiological
CBRTA	Chemical, Biological, and Radiological Technology Alliance
CBS	Case-Based Systems
CBW	Chemical Biological Warfare
CCD	Charge-Coupled Device
CDC	U.S. Centers for Disease Control and Prevention
CFD	Computational Fluid Dynamics
cfu	Colony Forming Unit
Ci	Curies
CIS	Customer Information Systems
COD	Chemical Oxygen Demand
cpm	Counts Per Minute
CRADA	Cooperative Research and Development Agreement
CWS	Contamination Warning System
DARPA	Defense Advanced Research Projects Agency
DHS	Department of Homeland Security
DNA	Deoxyribonucleic Acid
DO	Dissolved Oxygen
DOD	Department of Defense
DOE	Department of Energy
DSRC	Distribution System Research Consortium
DSS	Distribution System Simulator
ECBC	Edgewood Chemical Biological Center
ECD	Electrolytic Conductivity Detector
ECL	Electrochemiluminescence

EDS	Event Detection Software
ELFA	Enzyme-Linked Fluorescent Immunoassay
ELISA	Enzyme-linked Immunosorbent Assay
ELOD	Estimated Limit of Detection
EMPACT	Environmental Monitoring for Public Access and Community Tracking
EOC	Emergency Operations Center
EPA	U.S. Environmental Protection Agency
EPS	Extended-Period Simulation
ETV	Environmental Technology Verification
EWS	Early Warning System
FBI	Federal Bureau of Investigation
FDA	U.S. Food and Drug Administration
FID	Flame Ionization Detector
FPW	Flexural Plate Wave
FT-IR	Fourier Transform Infrared
GC	Gas Chromatography
GC-MS	Gas Chromatograph-Mass Spectrometer
GE	Genomic Equivalent
GIS	Geographic Information Systems
GMR	Giant Magnetoresistive
HA	Hydroxyapatite
HANAA	Hand-Held Nucleic Acid Analyzer
HRP	Horseshoe Peroxidase
HSPD	Homeland Security Presidential Directive
I-CORE	Integrated Cooling/Heating Optics Reaction
ICS	Incident Command System
ICWater	Incident Commanders Water Modeling Tool
IDSE	Initial Distribution System Evaluation
ILSI	International Life Sciences Institute
IMS	Ion Mobility Spectroscopy
INL	Idaho National Laboratory
ISAC	Information Sharing and Analysis Center
ISE	Ion Selective Electrode
JBAIDS	Joint Biological Agent Identification and Diagnostic System
LAN	Local Area Network
LEMS	Liquid Effluent Monitoring System
LIMS	Laboratory Information Management System
LLNL	Lawrence Livermore National Laboratory
LRAD	Long Range Alpha Detection
LRN	Laboratory Response Network
MAGIChip™	Micro Array of Gel-Immobilized Compounds
MALS	Multi-Angle Light Scattering
MALLS	Multi-Angle Laser Light Scattering
MCL	Maximum Contaminant Level
MEMS	Micro-Electro-Mechanical System
MIP	Molecularly Imprinted Polymers
MIT	Massachusetts Institute of Technology

MOEMS	Micro Optical Electro Mechanical Systems
MS	Mass Spectroscopy
MW	Molecular Weight
NaI	Sodium Iodide
NALOD	Nucleic Acid Limit of Detection
NASA	National Aeronautics and Space Administration
NDWAC	National Drinking Water Advisory Council
NHSRC	National Homeland Security Research Center
NNI	National Nanotechnology Initiative
NRMRL	National Risk Management Research Laboratory
NSF	NSF International (historically National Sanitation Foundation)
NTA	National Technology Alliance
OGWDW	Office of Ground Water and Drinking Water/U.S. EPA
OHS	Office of Homeland Security/U.S. EPA
OLM	On-Line Liquid Monitoring System
ORD	Office of Research and Development/U.S. EPA
ORNL	Oak Ridge National Laboratory
ORP	Oxidation-Reduction Potential
OW	Office of Water/U.S. EPA
PCR	Polymerase Chain Reaction
PDD	Presidential Decision Directive
PEC	Photosynthetic Enzyme Complex
pfu	Plaque Forming Unit
pfu-e	Plaque Forming Unit Equivalent
PID	Photo Ionization Detector
PNNL	Pacific Northwest National Laboratories
ppb	Parts Per Billion
ppm	Parts Per Million
ppt	Parts Per Trillion
psi	Pounds Per Square Inch
QA/QC	Quality Assurance and Quality Control
QLFA	Quantitative Lateral Flow Assay
R&D	Research and Development
RADACS	Radiological Assessment Display and Control Software
RAPID	Ruggedized Advanced Pathogen Identification Device
RBS	Rule-Based Systems
RLU	Relative Light Unit
RNA	Ribonucleic Acid
ROC	Receiver Operating Characteristic
SAIC	Science Applications International Corporation
SAW	Surface Acoustic Wave
SBIR	Small Business Innovation Research
SCADA	Supervisory Control and Data Acquisition
SDWA	Safe Drinking Water Act
SERS	Surface-Enhanced Raman Scattering
SIA	Sequential Injection Analysis
SMART™	Sensitive Membrane Antigen Rapid Test

SMP	Submitochondrial Particles
SNL	Sandia National Laboratories
SOPs	Standard Operating Procedures
SPCE	Surface Plasmon-Coupled Emission
SPME	Solid Phase Microextraction
SPR	Surface Plasmon Resonance
SSL	Secure Socket Layer
TAM	Thermo Alpha Monitor
TCD	Thermal Conductivity Detector
TCR	Total Coliform Rule
T&E	Test and Evaluation
TEVA	Threat Ensemble Vulnerability Assessment
TIGER	Triangulation Identification Genetic Evaluation of Risks
T&O	Taste and Odor
TOC	Total Organic Carbon
TRA	Technology Readiness Assessment
TTEP	Technology Testing and Evaluation Program
UC	Ultrafiltration Concentration
UHF	Ultra High Frequency
UPT	Upconverting Phosphor Technology™
URL	Uniform Resource Locator (also known as website address)
USACEHR	U.S. Army Center for Environmental Health Research
USAMRIID	U.S. Army Medical Research Institute of Infectious Diseases
USGS	U.S. Geological Survey
UV	Ultraviolet Light
VARA	Vulnerability and Risk Assessments
VHF	Very High Frequency
VOCs	Volatile Organic Compounds
WaterISAC	Water Information Sharing and Analysis Center
WATERS	Water Assessment Technology Evaluation Research and Security
WCIT	Water Contaminant Information Tool
WDM	Water Distribution Monitoring
WERF	Water Environment Research Foundation
WISE-SC	Water Infrastructure Security Enhancements-Standards Committee
WLA	Water Laboratory Alliance
WQS	Water Quality System
WS-CWS	WaterSentinel Contamination Warning System
WSD	Water Security Division
WSTB	Water Science and Technology Board
WSWG	Water Security Working Group
WUERM	Water Utility Emergency Response Manager

1. Report Highlights

Terrorist attacks have heightened concern about intentional threats to the U.S. water system, whether from physical destruction, computer interference, or chemical, microbial, or radioactive contamination. Such intentional contamination events can have a profound impact on public health and confidence in the nation's water infrastructure. An Early Warning System (EWS)^a can be an important tool to avoid or mitigate the impacts of an intentional contamination event in time to allow an effective local response that reduces or eliminates adverse impacts (ILSI, 1999). An integrated EWS includes sensors to detect the contaminant; systems to transmit, compile, and analyze data; links for communication and notification; and protocols for decision making and emergency response.

The goal of this EWS document is to review the state-of-the-art technologies and techniques for integrated EWSs for drinking water infrastructure, particularly for finished water supplies and distribution systems. The report summarizes and evaluates current and emerging EWS technologies for identifying general categories of chemical, microbial, and radiological contaminants. It also identifies future directions, technical issues, and research gaps. Information was gathered from a variety of sources, including company information, government information, verification studies, field case studies, and expert opinions.

The basis of this project is outlined in the Water Security Research and Technical Support Action Plan, Section 3.3e,¹ which recommends testing and evaluation of drinking water and other EWSs, focused on distribution systems. This study also supports the implementation of Homeland Security Presidential Directive (HSPD)-9² even though the study was started before HSPD-9 was issued. HSPD-9 directs the U.S. Environmental Protection Agency (EPA) to “develop robust, comprehensive, and fully coordinated surveillance and monitoring systems, ... that provide early detection and awareness of disease, pest, or poisonous agents.” To focus on the most promising products and technologies in this relatively new and rapidly progressing area, criteria were developed in this study to select technologies and products that are available now, are potentially adaptable to EWSs for drinking water systems, or have the potential to emerge as EWSs in the future.

^a Early Warning System or EWS is a term used throughout this document. The term is derived from the use of EWSs in monitoring source water. Detectors have been used to identify changes in source water quality upstream of a water intake (e.g., in rivers or streams for chemical spills). In its truest sense, an EWS would provide for an early warning of a contaminant prior to human exposures with public health impacts (e.g., “detect to warn”). Such may not be the case in the first generation of contaminant warning in drinking water distribution systems. An alternative term of art has evolved based on threat recognition, that being a “contamination warning system.” A contamination warning system involves the active deployment and use of monitoring technologies/strategies and enhanced surveillance activities to collect, integrate, analyze, and communicate information to provide a timely warning of potential water contamination incidents and initiate response actions to minimize public health and economic impacts. Based on currently available technologies, a contamination warning system is weighted toward “detect to treat.” However, with advances in technology and the ability to detect specific contaminants or specific contaminant categories in near real-time, it is anticipated that a contamination warning system will move toward “detect to warn.”

In response to HSPD-9, EPA is working with technical experts and stakeholders in the drinking water community to design a robust and comprehensive drinking water system monitoring program that would provide early indication of an attack and minimize public health consequences. An outcome of these efforts is WaterSentinel, which is a proposed demonstration project where EPA, in partnership with select utilities and laboratories, would design, deploy, and evaluate a model contamination warning system for drinking water security. A more detailed description of how the thinking behind the WaterSentinel concept has evolved is included in Appendix A.

This document is a state-of-the-art review and reflects knowledge and information gathered through May 2005. The fast pace of technology and technique development and the implementation of EWSs for drinking water indicate that this document should be viewed as a snapshot in time. It will be useful to utilities as they plan activities that provide early warning against potential threats and attacks to their water systems. As the state-of-the-art advances, periodic updates of this document will be necessary.

1.1 Desired Characteristics of Integrated Early Warning Systems (EWSs)

An EWS is an integrated system for monitoring, analyzing, interpreting, and communicating monitoring data, which can then be used to make decisions that are protective of public health and minimize unnecessary concern and inconvenience to the public. To become a widely used, effective, and reliable part of a water distribution security and quality monitoring system, an ideal integrated EWS should demonstrate a number of characteristics, such as the following:

- provide a rapid response
- include a sufficiently wide range of potential contaminants that can be detected
- exhibit a significant degree of automation, including automatic sample archiving
- allows acquisition, maintenance, and upgrades at an affordable cost
- require low skill and training
- identify the source of the contaminant and allows accurate prediction of the location and concentration downstream of the detection point
- demonstrate sufficient sensitivity to detect contaminants
- permit minimal false-positives/false-negatives
- exhibit robustness and ruggedness in continually operating in a water environment
- allow remote operation and adjustment
- function continuously
- allow for third party testing, evaluation, and verification

When a utility considers the development of an integrated EWS, especially for a distribution system, it should go through a structured process to determine the need for and approach to using an EWS. Some experts in the field of EWS design for drinking water distribution systems advocate a “tiered” approach with two stages. The first stage uses continuous real-time sensors that can provide a generic warning or trigger an alarm when a contaminant is detected in the water. Examples of this first stage include common multi-parameter online sensors typically used for monitoring water quality (e.g., pH, conductivity, chlorine residual, etc.). A warning would trigger a second stage using more specific and sensitive technology to confirm and identify the contaminant (ILSI, 1999; Hasan et al., 2004). A second-stage technology might be located in the field or could be brought to the site as a field portable unit. Another design could include first stage warnings in conjunction

with data from customer complaints and public health surveillance as triggers for confirmatory testing. Although real-time continuous monitoring may be the ultimate long-term goal, there may be intermediate EWS architectures that would be more effective until real-time monitors become available.

1.2 Conclusions and Recommendations

The conclusions and recommendations are based on a scientific and technical evaluation of EWS technologies. An expert review of qualitative, semi-qualitative, and quantitative information was conducted using various sources including verification studies, government research, and expert opinions.

The following are general conclusions and recommendations from this review of state-of-the-art technologies and techniques for EWSs. These are followed by specific conclusions and recommendations organized by the features of the EWS: data acquisition and analysis; flow modeling; sensor placement; alert management; decision making and response; multi-parameter water quality technologies; and detection of chemical, microbial, and radiological contaminants. The recommendations include a list of near term and long-term knowledge and research gaps.

1.2.1 General Conclusions and Recommendations

Viable integrated EWSs that meet the desired characteristics and can be routinely used are several years away. Some individual components are available currently; however, others need further development. Designs of EWSs for water distribution systems are largely theoretical or in preliminary stages. The systems that are in place do not have all the features of an integrated EWS, as described by this report. Most sensor and EWS components have not been third party tested or verified, and the types of contaminants and levels of exposure have not been well defined to support selection of sensor technologies. Utilities will need verification and demonstration studies to evaluate various manufacturer claims.

Short-Term Research Needs

- An in-depth review of EWS design and implementation should be conducted.
- Methods for vulnerability assessments should be adapted to focus on contamination scenarios.
- Research on international efforts on EWS is needed.
- Grab-sampling protocols and analysis technologies should be developed quickly.

Long-Term Research Needs

- Survey case studies and analyses should be performed on monitors/sensors/detectors used by utilities.
- EWS components need to undergo performance testing.
- Potential contaminants list should be reviewed on an ongoing basis.
- Concentrations that must be detected by a sensor should be reviewed on an ongoing basis.
- The fate and transport (including exposure levels, doses, and detectible concentrations) of contaminants, especially toxic byproducts, should be examined.

- Results from laboratory research by various agencies on EWSs should be replicated and the conclusions of EWS studies should be shared among government agencies and water utility stakeholders.

1.2.2 Specific Conclusions and Recommendations

- **Data Acquisition and Analysis**

Data collection by Supervisory Control and Data Acquisition (SCADA) or other automated systems is essential to handle the large volume of data from online sensors in an EWS. Much of the required data acquisition software and hardware already exists. However, software for security (e.g., encryption) of SCADA systems for EWSs is still under development and needs verification, but can probably be addressed by utilities simultaneously with general security issues.

Short-Term Research Needs

- Standardized methods/guidance for data analysis and interpretation are needed.
- Large-scale data storage and manipulation techniques are needed.

Long-Term Research Needs

- SCADA data security programs should be developed to link existing utility efforts with security characteristics necessary for EWSs.

- **Flow Modeling**

Predicting the movement and flow of contaminants in a water distribution system is important not only to prepare for a potential intentional contamination event, but also to improve the effectiveness of the EWS design. Distribution system modeling in general, and contaminant flow predictive systems in particular, are developing rapidly. Current contaminant flow models can also integrate data from geographic information systems. Calibration has been increasingly used in distribution systems. Consumption-of-water models are also being occasionally incorporated. Utility efforts to validate and develop predictive flow models would meet the dual purposes of general planning (expansion, upgrades, repairs, maintenance) and testing intentional contamination scenarios. These models also assist in the general management of water quality in the distribution system. Although there are currently no established calibration criteria in the U.S., static and dynamic calibration methods exist (EPA, 2005). Also, a committee of the American Water Works Association (AWWA) did propose a set of possible calibration guidelines in 1999 (ECAC, 1999). These possible calibration guidelines should serve as a catalyst or starting point to move forward on developing accepted calibration guidelines or standards. Utilities would need further education and guidance to make use of such predictive flow models, including a better understanding on how they are calibrated. EPA's Threat Ensemble Vulnerability Assessment (TEVA) program incorporates flow modeling (e.g., EPANET) in a probabilistic framework to evaluate contamination events.

Short-Term Research Need

- Improved contaminant flow models are needed.

Long-Term Research Need

- Flow models need to be verified and then used to improve EWS design.

- **Sensor Placement**

Because of both budgetary and technical constraints, utilities can make only a modest initial investment in sensors within their distribution system, and therefore often want to determine the most appropriate locations. Without resorting to sophisticated experimental optimization techniques, the limited numbers of utilities that are beginning to design EWSs and put sensors in place, usually determine sensor placement based first on logistical constraints (e.g., available power source, access to communications) and second on larger pipes that serve the most customers. Current research combining flow models and sensor technology is beginning to be developed, but such models must be verified before difficult and costly decisions are made by the utilities.

Short-Term Research Need

- Hardware and materials to protect remote sensors are needed.

Long-Term Research Need

- Research into sensor placement parameters is recommended.

- **Alert Management**

Alert management systems typically consist of two general areas: (1) establishing parameters for alert triggers and (2) reducing false alarms. Any anomalies in the comparison of sensor data to the baseline trigger alert the operator. Establishing reliable baseline data is key especially when water quality fluctuates. Alert management systems usually rely on strict data validation protocols or specialized software to reduce false alarms. Several companies are working on alert management, but are in preliminary stages of research, with often proprietary trigger algorithms.

Long-Term Research Need

- Alert management approaches/technologies should be examined and sensitivity to false-positives and false-negatives should be quantified.

- **Decision Making and Response**

The process linking the analysis of contamination data with decision making and response is outlined in EPA's Response Protocol Toolbox; however, additional tools to effectively implement the process are needed for water utilities. Tools to assist decision making and response, such as the Water Contaminant Information Tool (WCIT), are being developed and will help fill a current void.

Long-Term Research Need

- Technology to support and implement decision making and response strategies are needed.

- **Multi-Parameter Water Quality Technologies**

There is ongoing research on the use of the multi-parameter water quality monitors as part of an EWS for distribution systems. Multi-parameter water quality technology includes readily available water quality sensors that when analyzed together may be able to identify a physical or chemical change in water quality. Such a change may suggest that a contaminant has been accidentally or

intentionally added. Standard water quality parameters include chloride, specific conductance, turbidity, free chlorine, oxidation-reduction potential (ORP), pH, dissolved oxygen (DO), temperature, and sometimes total organic carbon (TOC). Parameters that appear, from EPA's preliminary tests, to be useful for monitoring in distribution systems include chloride (ion selective electrode, ISE), specific conductance (electrode), turbidity (nephelometric), free chlorine, and ORP (EPA, 2004). TOC is also helpful, but may be too expensive to be widely used. The multi-parameter approach has not been sufficiently evaluated to recommend widespread use. For example, no tests have been performed on chloraminated systems. Also, there is concern about false-positives. However, full-scale testing by the U.S. Geological Survey (USGS), EPA, and a participating water utility company over the next 12 to 18 months may help shed light on false-positives and whether a system can work with the fluctuations of normal water quality.

Several equipment manufacturing companies are attempting to identify contaminants or classes of contaminants through water quality parameter signatures. It is difficult to independently validate or replicate the activities of these companies because their methods and algorithms are proprietary, which indicates that caution should be used regarding these methods at this juncture. Also, the examination of water quality parameters in detecting and identifying contaminants is still being evaluated by EPA, USGS, the Army, and other organizations. There has yet to be a field-scale test of an EWS with these water-parameter components.

Short-Term Research Needs

- Verified baseline data to calibrate EWS alarm triggers are needed.
- Contaminant specific signatures are needed.
- Validation of event detection algorithms is needed.

Long-Term Research Needs

- Costs and benefits of using TOC sensors should be determined. More affordable and reliable TOC sensors should be developed.

• Detection of Chemical Contaminants

Portable field kits and devices are available for conducting analyses of grab samples for onsite detection of many possible chemical contaminants. In contrast to portable field technology, online detection technologies for specific chemical contaminants are not reasonably available or are not cost-effective. In the next several years, the field should show further development in terms of cost-effective and reliable devices. A few new technologies (e.g., microchip-based technology) could revolutionize the chemical detection field for drinking water. Disinfectant residuals normally present in treated drinking water (in the U.S.) may present a problem for many of the technologies (e.g., biomonitors) that detect toxins. A few technologies are mature enough to be recommended as good candidates for EPA Environmental Technology Verification (ETV) studies.

Short Research Need

- The impact and removal of disinfectant residuals on accuracy of detection should be examined.

Long-Term Research Needs

- Reliable field kits should be developed.

- Existing state-of-the-art detection technologies should be adapted for use in EWSs.

- **Detection of Microbial Contaminants**

Development of an online microbial detection technology appears to be years away. The light-scattering methodology shows some promise, but most methods are not suited for continuous online monitoring or for differentiating among microbes. However, to confirm the presence, viability, and concentration of a contaminant using a portable field unit with grab samples, there are several potentially adaptable methods from which to choose, including immunoassay, polymerase chain reaction (PCR), and adenosine triphosphate (ATP). These methods have not yet been exploited to their full potential, so will likely continue to be incorporated into new monitoring devices and systems. Grab sampling could include sampling at scheduled intervals or taking composite samples (e.g., collecting small volumes of sample continuously over time). In any sampling, the microbial integrity must be ensured. For drinking water, the challenge for most methods is the issue of concentrating the sample. A few methods of concentration show promise including the hollow fiber and the micropump. In general, concentration does not seem to be an insurmountable obstacle for some methods. One recommended approach was to screen a sample with a generic detector (e.g., multi-parameter probe or perhaps light scatter), then use an immunoassay device in tandem with another method for identification. ATP detection kits are promising for detecting microbial contamination, but current products have not been verified for treated drinking water. In the future, microchips have great potential for advancing online measurement of contaminants, but presently the field is not sufficiently mature to provide devices that would meet the needs of drinking water utilities.

Short-Term Research Needs

- Extraction and concentration technologies need improvement.
- Methods to distinguish concentrated interferants from target contaminants are needed.
- Further development of field-stable reagents is needed.
- ATP detection products should be third party evaluated for EWS application.

Long-Term Research Needs

- Antibodies for unique epitopes (present on threat agents) that show less cross-reactivity should be developed.
- Research on additional approaches and technologies that can detect emerging, evolving, and engineered microbes is needed.

- **Detection of Radiological Contaminants**

There are demonstrated technologies for examining radiation in wastewater, but the transfer or adaptation to drinking water has not yet taken place. Only a few products claim applicability to water, some on a grab-sample basis. More products are being developed by a few vendors, but it is still unclear whether the threat merits use of these expensive products on a real-time basis. The few items that are commercially available should be verified either by EPA or by a national laboratory that specializes in radiation. All of the radiological monitoring devices mentioned in this study usually require specialized expertise for installation, set-up, and routine calibration—even if they are labeled maintenance-free. Thus, early warning for radiation detection is not currently

available for finished water or distribution systems, and the market forces for such development may not be strong.

Short-Term Research Need

- Beta- and gamma-radioactivity detectors should be developed and verified for drinking water monitoring applications.

Long-Term Research Needs

- Low-cost, online radioactivity monitors are needed.
- Monitors should be developed that are specifically intended for water distribution systems.

2. Introduction

This chapter first presents background on the general concern for the water supply including the threat of intentional contamination of the water supply and the potential benefits of an EWS. It then describes the EPA's role in water security and EPA's efforts on EWS. Further, it outlines the objective of this study, which is to review the current and emerging technologies and techniques for integrated EWSs for drinking water infrastructure, particularly for finished water supplies and distribution systems. The chapter identifies current capabilities, future directions, technical issues, and research gaps. Finally, it presents the approach used to conduct the review.

2.1 Concern for the Water Supply

Terrorist attacks have heightened concern about intentional threats to the U.S. water system, whether from physical destruction, computer interference, or chemical, microbial, or radioactive contamination. Such intentional contamination events can have a profound impact on public health and confidence in the nation's water infrastructure. An EWS can be an important tool to avoid or mitigate the impacts of an intentional contamination event, reliably identifying a high impact contamination event in source or finished drinking water in time to allow an effective local response that reduces or eliminates adverse impacts (ILSI, 1999).

2.2 Role of EPA in Water Security and Early Warning Systems

EPA has a lead role in protecting the water supply and specifically to support efforts to develop EWSs. This role is outlined in several regulations, national strategies, and presidential directives, including the following:

- Presidential Decision Directive (PDD) 63, signed May 22, 1998, designates EPA as the lead for security of the national water infrastructure.
- The National Strategy for Homeland Security (July, 2002),³ designates EPA as responsible for protecting our national water supply.
- The Public Health Security and Bioterrorism Preparedness and Response Act of 2002 (the Bioterrorism Act), requires that community water systems serving > 3,300 people conduct vulnerability assessments and prepare emergency response plans. Also, the Act charges EPA with reviewing current and future methods to prevent, detect, and respond to the intentional introduction of chemical, biological or radiological contaminants into community water systems.
- HSPD-7 on Critical Infrastructure Identification, Prioritization, and Protection (HSPD-7), signed December 17, 2003, also reinforces EPA's role as the sector specific agency for the water infrastructure.
- HSPD-9, signed on February 4, 2004,⁴ instructs the federal agencies responsible for agriculture, food, and water security to "develop robust, comprehensive, and fully coordinated surveillance and monitoring systems ... that provide early detection and awareness of disease, pest, or poisonous agents." This study, although initiated before implementation of HSPD-9, supports the efforts of HSPD-9.

In response to HSPD-9, EPA is working with technical experts and stakeholders in the drinking water community to design a robust and comprehensive drinking water system monitoring program

that would provide early indication of an attack and minimize public health consequences. An outcome built upon existing efforts is WaterSentinel, which is a demonstration project proposed in the Fiscal Year 2006 budget where EPA, in partnership with select utilities and laboratories, would design, deploy, and evaluate a model contamination warning system for drinking water security. A contamination warning system involves the active deployment and use of monitoring technologies/strategies and enhanced surveillance activities to collect, integrate, analyze, and communicate information to provide a timely warning of potential water contamination incidents and initiate response actions to minimize public health and economic impacts.

Although EPA is continually refining its conceptual design for the program, WaterSentinel would adopt a four-fold approach to detecting contamination involving, first, the monitoring of water quality parameters; second, the direct monitoring and laboratory analysis of high priority chemical, biological, and radiological contaminants; third, the integration of water system data with existing public health surveillance systems; and fourth, active surveillance of customer complaints. In addition to other critical sources of information, such as intelligence threat analysis and reports from local law enforcement, WaterSentinel would harness and leverage an array of data streams in supporting a robust contamination warning system. A more detailed description of how the thinking behind the WaterSentinel concept has evolved is included in Appendix A.

Since 2001, EPA has formed the Water Security Division (WSD) in the Office of Water (OW) and the Office of Homeland Security (OHS). EPA has published the Strategic Plan for Homeland Security. To spearhead the research efforts on homeland security, EPA formed the National Homeland Security Research Center (NHSRC) in the Office of Research and Development (ORD⁵). The Water Security Research and Technical Support Action Plan (Action Plan), prepared by NHSRC and WSD, emphasizes the need for improving analytical monitoring and detection of biological, chemical, and radiological threats in drinking water systems as part of securing drinking water supplies and systems. The NHSRC has been working with the Department of Homeland Security (DHS), other government agencies, national laboratories, water stakeholders, and the utility industry to coordinate and conduct research on various issues including EWSs (Appendix B). EPA has initiated many efforts related to EWSs; they are included below.

2.2.1 National Homeland Security Research Center Research

EPA/ORD's National Risk Management Research Laboratory (NRMRL) has multiple above-ground distribution system simulator (DSS) units, located at the Test and Evaluation (T&E) Facility in Cincinnati, Ohio. The Water Assessment Technology Evaluation Research and Security (WATERS) Center is located at the T&E Facility and has access to NRMRL's DSS units. EPA has six different DSS units in operation at the facility. The DSS units are designed and fabricated to evaluate and understand the dynamics that influence water quality within water distribution infrastructure systems in the U.S. and abroad. All DSS units are designed and fabricated above ground to permit easy access to the entire pipe distribution system. The DSS units consist of six individual pipe-loop circulating units, three single-pass dead-end units, and two decontamination research loops. EPA is currently conducting research at the WATERS Center to evaluate various sensor and monitoring technologies, distribution system modeling, disinfection and decontamination, and data acquisition systems. The sensors and monitoring technologies are currently being evaluated to see how they respond to accidental and intentional contamination events and threats in a distribution system (Haught and Goodrich, EPA, personal communication).

2.2.2 Environmental Technology Verification (ETV) Program

The ETV Program operates as a public/private partnership through agreements between EPA and private testing and evaluation organizations. The goal of ETV is to provide credible performance data for commercial-ready environmental technologies to speed their implementation for the benefit of vendors, purchasers, permittees, and the public. Of the six ETV centers, three are working in water security relevant areas: ETV Advanced Monitoring Systems Center (AMS - Battelle), ETV Drinking Water Systems Center (NSF International), and ETV Water Quality Protection Center (NSF International⁶). Some testing areas formerly performed by ETV are being transferred to NHSRC's Homeland Security Technology Testing and Evaluation Program⁷ (TTEP).

2.2.3 Technology Testing and Evaluation Program (TTEP)

The TTEP was developed by NHSRC in 2004 to rigorously test technologies against a wide range of performance characteristics. TTEP's mission is to service the needs of water utility operators, building and facility managers, emergency responders, consequence managers, and regulators by providing reliable performance information from a trusted source. The technology categories of interest include detection, monitoring, treatment, decontamination, computer modeling, and design tools for protecting water and wastewater infrastructures and the outdoor environment. When possible, technologies will be tested for their ability to detect chemical, biological, radiological (CBR), and warfare agents. As an outgrowth of the ETV, many aspects of TTEP are similar to ETV. However, TTEP does not offer verification statements or endorsements to the vendors and it may test technologies with or without the involvement of the vendor.

2.2.4 American Society of Civil Engineers (ASCE) Guidelines for Designing an Online Contamination Monitoring System

Under a cooperative agreement with EPA, the American Society of Civil Engineers/Water Infrastructure Security Enhancements-Standards Committee (ASCE/WISE-SC) has developed interim voluntary security guidance that covers the design of online contamination monitoring systems to detect intentional contamination events (Phase I of the project⁸). Phase II of the project was to develop appropriate training materials for use in the water sector. Phase III of the project is to develop community consensus voluntary best practice standards for designing an EWS.

2.2.5 Water Utility Users Group

The AWWA has convened a group (formerly known as the Water Contaminant Detection Working Group) of water utilities to offer their opinions and experiences in contaminant detection. This group has met on several occasions in the past year (2004 to 2005) and representatives from EPA have been invited to participate in those meetings. Of particular interest to the Users Group is EPA's TEVA Research Program for Drinking Water Distribution System Security. The TEVA Research Program is developing software tools, methodologies, and strategies for assessing the public health consequences of chemical and biological attacks on drinking water, and for designing and evaluating mitigation and response strategies. Partnering with a small group of AWWA water utilities, the TEVA Research Program will use network models and water quality data gathered from the utilities to validate and improve TEVA. An interdisciplinary team of researchers from EPA, several Department of Energy (DOE) National Laboratories, and universities are collaborating to

develop these tools. Ultimately, the products of the TEVA Program will be useful for designing EWSs specific to an individual utility. This information will be aimed at evaluating strategies for sensor locations in drinking water distribution systems, and for optimizing response and recovery activities in the aftermath of a contamination event (Murray et al., 2004).

2.2.6 Water Security Working Group (WSWG)

The National Drinking Water Advisory Council (NDWAC) is comprised of members of the general public, state and local agencies, and private groups concerned with safe drinking water. The NDWAC advises EPA on the Agency's programs related to drinking water. NDWAC has several working groups that make recommendations to the full council, which in turn advises EPA on individual regulations, guidances, and policy matters. One group, the WSWG, has been charged by EPA to (1) identify, compile, and characterize active and effective security practices and policies for drinking water and wastewater utilities and provide an approach for considering and adopting these practices and policies at a utility level; (2) consider mechanisms to provide recognition and incentives that facilitate a broad and receptive response within the water sector to implement these active and effective security practices and policies, and make recommendations as appropriate; and (3) consider mechanisms to measure the extent of implementation of these active and effective security practices and policies, identify the impediments to their implementation, and make recommendations as appropriate. The WSWG began meeting in July 2004, and delivered a draft report on these issues to the NDWAC in June 2005. In June 2005, the NDWAC unanimously approved and adopted the WSWG's findings unchanged and elevated these findings to the status of recommendations to the EPA.

2.2.7 Water Contaminant Information Tool (WCIT)

EPA's 2004 *Homeland Security Strategy* calls for the deployment of WCIT to provide easy access to key information on priority contaminants, and to develop components of the Tool, including data on treatability and toxicity levels. In this program, detailed information is to be made available to utilities during a confirmed contamination event when the utility calls EPA's National Response Center. The information is then faxed to the utility. The *Strategy* recommends that the WCIT should be revised periodically, as new information becomes available.

2.2.8 Distribution System Research Consortium (DSRC)

Formed in June 2003, the DSRC is led by the EPA's NHSRC. The DSRC includes federal employees from a number of agencies with experience in water infrastructure, the water industry, EPA Program Offices and Regions, and other interested organizations. The DSRC provides a forum for information exchange on a diverse set of water distribution system security topics. Topics have included EWS research (e.g., sensors, field studies, sensor placement) and treatment and decontamination research.

2.2.9 EPA Resources/Guidance

EPA/OW/Office of Ground Water and Drinking Water (OGWDW) maintains a Water Infrastructure Security website that includes various guides including the Response Protocol Toolbox (e.g., Site Characterization and Sampling Guide, Analytical Guide), a Security Product Guide,⁹ Standardized

Analytical Methods for Use During Homeland Security Events (on NHSRC website), and a list of Sensors for Monitoring CBR Contamination.

2.3 Purpose of this State-of-the-Art Review

EWSs are needed for drinking water distribution systems because contamination of drinking water, especially in distribution systems, is an important concern. Research and development of technologies applicable to EWSs are rapidly progressing, making up-to-date reviews of the EWS field challenging.

The basis of this project is outlined in the Water Security Research and Technical Support Action Plan, Section 3.3e,¹⁰ which recommends testing and evaluation of drinking water EWSs and, if applicable, EWSs from other sectors amenable to application in the water environment, focused on distribution systems. More specifically, Action Plan Section 3.3e has the following four sequential, yet interdependent tasks:

1. Conduct a survey to gain improved understanding of EWSs that could be employed in protecting finished water supplies and distribution systems;
2. Perform pilot-scale testing and evaluation of EWSs that could be used by water utilities to give an early warning of a contaminant threat or accidental contaminant event;
3. Perform field-scale testing and evaluation of EWSs that could be used by water utilities to give an early warning of a contaminant threat or accidental contaminant event; and
4. Prepare a handbook on the application of EWSs for drinking water supply and system protection.

This report is intended to fulfill Task 1 of the Action Plan. It includes a comprehensive review of current and emerging EWS technologies and techniques, and evaluates their state-of-the-art so as to identify future directions, research gaps, and technical issues. An EWS for finished water presents a special set of challenges, compared with an EWS for source water. Finished water includes various treatment chemicals, including chlorine residual. The finished water also flows through miles of distribution system pipes, which makes the placement of EWS components difficult. The other three tasks would be addressed by programs such as WaterSentinel. All four tasks above are being addressed as part of an overall integrated approach being managed by EPA/NHSRC. Additional information on technologies available for ground water monitoring can be found in *A Review of Emerging Sensor Technologies for Facilitating Long-Term Ground Water Monitoring of Volatile Organic Compounds* (EPA, 2003).

Information is needed on how specific contaminants (microbial, chemical, radiological) affect the water quality parameters measured by some currently used online monitoring systems, particularly with regard to which current technologies will best detect a contamination event. A number of monitoring technologies and products are available that could potentially serve as an EWS, and a number of suppliers of conventional monitoring systems have begun to advertise them as water security monitoring systems. However, in most cases, the performance of these systems has not been fully or independently evaluated. Without basic performance information (such as detection limits, sensitivity, selectivity, rates of false-positives and false-negatives), it will be difficult to interpret monitoring results and derive the information necessary to make appropriate public health decisions.

Implementation of a minimally evaluated monitoring technology or EWS may result in a false sense of security, since there is no assurance that it is capable of meeting EWS requirements. It could also result in false-positive alarms that undermine the effectiveness of any monitoring program, or false-negatives that would discredit an EWS. A significant amount of research is underway to adapt existing and develop new technologies that may be suitable as EWSs for water systems.

As promising technologies continue to be developed and brought into the commercial market, there is a need for a mechanism to evaluate and verify EWS performance that includes field evaluation and testing sites. Ideally, such testing should be conducted according to a standard protocol by an independent third party, and the subject technology should be evaluated against standardized methods. This would provide water utilities with the data necessary to make informed decisions regarding the implementation of a specific technology in an EWS. EPA's TTEP can provide this independent testing. The TTEP process follows strict quality assurance procedures to evaluate technology performance. Stakeholders are involved in identifying and selecting technologies for testing, and in developing testing plans and reviewing evaluation reports.¹¹

Design of an EWS for finished water in the drinking water distribution system is not simple, as there are many issues and water system characteristics that need to be considered. The issues that should be addressed in the effective design of an EWS include planning and communication, characterizing the system, determining the target contaminants for the EWS, selecting an appropriate EWS technology, establishing appropriate alarm levels and monitoring frequency, employing hydraulic models to optimize the number and placement of sensors, selecting parameters to be monitored, and conducting data management and analysis.

Three recent projects complement the scope of this report. In the first project, the ASCE-WISE-SC white papers and guidance, mentioned earlier in this report, seek to provide specific guidance to utilities about the design and implementation of an online contaminant monitoring system (ASCE, 2004). In contrast, this study reviews the state-of-the-art EWS technologies and techniques and provides recommendations (e.g., research needs) to further the development of an integrated EWS. In the second project, the National Technology Alliance (NTA), through the Chemical, Biological, and Radiological Technology Alliance (CBRTA) released a report entitled *Water Monitoring Equipment for Toxic Contaminants Technology Assessment* (Black & Veatch, 2004). The NTA leverages commercial investment in technology to meet U.S. security and defense needs. The NTA report focuses on monitoring technologies for both source and finished water. In contrast, this study focuses on the components of an integrated EWS (e.g., monitoring, data acquisition, flow modeling), and specifically addresses finished water monitoring for distribution systems. An article by the AWWA entitled "Contamination Warning Systems for Water: An Approach for Providing Actionable Information to Decision-Makers" provides an easy to read summary of monitoring technologies, monitoring locations, data transmission, alarms, and response (Roberson and Morley, 2005).

The purpose of this study was to provide a current state-of-the-art review (i.e., snapshot in time). In the process, it also identifies areas of research needed in the short-term and long-term to develop workable EWSs. This study, however, was not able to address all of the issues associated with EWSs. The following are limitations in the scope of the study. This study does not discuss in detail the specific types of drinking water contaminants, and instead focuses on three categories of contaminants: chemical, microbial, and radiological. These categories are useful on a broad level

to evaluate monitoring technologies. Specific information, such as the concentrations at which a contaminant is detectable or effective in impacting human health, is important in evaluating a specific instrument or set of instruments. However, much of the detailed information and research efforts on the types and concentrations of contaminants is either not publically available or is undergoing collection and review. Detection limits for the different technologies are provided when available from the vendor, government agency, or testing/verification entity. Limits of detection may not be provided for emerging technology because of the newness of the technology.

The design of an EWS is a complex issue, and the design and development of EWSs for water distribution systems are still at an early stage and continue to evolve. This study summarizes the basic design and features of an EWS, but does not cover the topic in detail. For example, the study does not provide detailed criteria for selecting instruments, locating instruments, setting alarm levels, and integrating other independent data streams such as public health surveillance and consumer complaints monitoring. This document is not a guidance document, but instead a state-of-the-art review. As mentioned above, the ASCE has provided some guidance, including a ranking of the desired characteristics of the EWS (Carlson et al., 2004). Reviewers of early drafts of this study suggested that a more detailed treatment of design and implementation of an EWS is needed. To accomplish this, another multi-stage project would be necessary to further develop an adequate treatment of design possibilities and issues. Such a project should engage the water sector stakeholders, including utilities, equipment designers and manufacturers, researchers, and policy officials.

There are many technologies and products covered in this report. **EPA does not recommend or endorse the specific products mentioned in this report.** In addition, much of the information provided on specific technologies are from vendors and have not been independently verified unless otherwise indicated. Efforts were made to use more than one source to verify the information; however, EPA is not responsible for errors in company-provided information. The status of the technology (e.g., pilot, concept), as well as estimates for field implementation are based on vendor or government authorities, as indicated. It is particularly difficult to accurately predict when emerging technologies will evolve into reliable and marketable products.

This project's objective is to conduct a comprehensive review of the state-of-the-art technologies and techniques for integrated EWSs for drinking water infrastructure, particularly for finished water supplies and distribution systems. It seeks to identify the status of current and emerging EWS technologies and future directions, research gaps, and technical issues. Chapter 1 provides report highlights. Chapter 2 introduces the concept of an integrated EWS and discusses the approach used to conduct this state-of-the-art review. Chapter 3 presents a description of desired characteristics and component features that define EWSs. Chapter 4 addresses overall design and operation of EWSs, including data management and analysis, predictive flow modeling, sensor placement, alarm management, data security, and response communications. Chapter 5 presents the concept of using general water quality parameters as indicators for contamination events. Details of efforts being undertaken to develop multi-parameter water quality signatures for specific contaminants are also presented in Chapter 5. Chapters 6, 7, and 8 cover chemical, microbial, and radiological detection methods and technologies, respectively. These chapters are organized in a similar format, with a general description of a technology followed by specific example products that are available or could be adapted for drinking water, followed by emerging technologies that are more in the developmental stage. Chapter 9 addresses the evaluation of the technologies discussed in Chapters

5 through 8. Chapter 10 explains the conclusions and recommendations from the evaluation of EWS state-of-the-art. Tables are presented as Exhibits and are labeled by chapter number followed in chronological number as they appear in the text.

2.4 Approach for this State-of-the-Art Review

This review document on EWSs covers technologies and techniques that may be applicable for many different water monitoring needs, as well as specific EWS needs. The stepwise approach for reviewing and evaluating EWS components includes several forms of information gathering and critical review. Information was gathered from published literature, conferences, seminars, workgroups, and consultation with experts in the field. The review and evaluation protocol consisted of the following six steps:

- Step 1:* Identify experts on contamination issues for distributions systems to assist with the technical writing of this background document, with emphasis on intentional contamination events.
- Step 2:* Summarize characteristics and features for EWSs and the justifications for those criteria and features.
- Step 3:* Develop an inventory, and descriptions of function and status, of rapid detection technologies that might be appropriate components of an EWS. Methods are described in general terms, then specific products are presented. Technologies include water quality parameter monitors, and detectors for chemical, biological, or radioactive contaminants.
- Step 4:* Develop an inventory and report on the status of integrated EWS design and operation. General water quality monitors and specific detection assays combined with data relay, analysis, and display technologies are all part of EWS design. Where these technologies are located, how they interact, and how they are made secure and reliable are also integral parts of EWS design and operation.
- Step 5:* Identify and discuss research, gaps, information, and technical advancements needed to build future EWSs.
- Step 6:* Evaluate technologies for their capabilities and issues.

For the EWS commercial products identified in Steps 3 and 4, information collected includes a general description of the product, the extent to which it is a comprehensive EWS for real-time monitoring in a distribution system (e.g., detector only, not notification), method of detection, contaminants detected, limits of detection, level of verification, potential for piloting, current use, and other critiques. Complete information was not available for all the technologies and products discussed. See Appendix C for a list of products and manufacturers mentioned in this report.

2.5 Sources of Information

2.5.1 Experts

Government, industry, academia, and water utility experts in the field were consulted at various conferences, seminars, workshops, and by telephone and e-mail. Subject matter experts provided their experience and knowledge on the subject of EWSs (See Acknowledgments). In many cases, company representatives were contacted directly via e-mail and/or telephone for information regarding products and the application of their products. In general, information about products or

programs that was obtained through e-mail or telephone is cited as personal communication. All correspondence took place between July 2004 and July 2005.

2.5.2 Conferences and Seminars

EWS design and its component technologies are part of the emerging field of water security. As with all fields experiencing rapid growth, much valuable information is available from conferences and seminars. Materials from several conferences were compiled and reviewed for building the content of this state-of-the-art review. Conferences and seminars attended by the primary authors for the purpose of gathering information for this review, are listed below:

- Water Security Congress, AWWA (April 2004, April 2005)¹²
- AWWA-sponsored seminar on Contamination Monitoring Technologies (Richmond, Virginia; May 2004)¹³
- Water Infrastructure Security Enhancement Workshops Guidelines for Designing an Online Contaminant Monitoring System for Water Utilities (May 19, 2004)¹⁴
- Rapid Detection Technologies for Water Supply Safety and Security (Washington, DC; June 2004)¹⁵

2.5.3 Published Literature

Information from peer-reviewed published literature, government agency publications, vendor literature, and results of verification tests was gathered and critically reviewed for inclusion in this report. The information sources include the following:

- articles, publications (e.g., Water Environment and Technology)
- reference texts such as *Design of Early Warning and Predictive Source Water Monitoring Systems* (e.g., the American Water Works Research Foundation (AwwaRF))
- EPA Performance Verification Testing of commercially available rapid toxicity monitoring systems
- Studies from other federal agencies working in this area (e.g., Department of Defense (DOD), National Aeronautics and Space Administration [NASA])

2.5.4 Website Resources

Several hundred websites were evaluated for content applicable to this review. Electronic archives and hard copies of websites cited were collected for future reference because web content evolves so rapidly. The URLs are cited as endnotes throughout this report and were current as of April 2005.

2.5.5 Workgroup Efforts

Information from workgroups focused on EWSs was obtained, including EPA workgroups and the Water Contaminant Detection Working Group.

2.6 Criteria for Selecting Products/Technologies

The goal of this EWS document is to report on the state-of-the-art technologies and techniques for detecting contaminants, particularly chemical, microbial, and radiological contaminants in drinking water distribution systems. To focus on the most promising products and technologies in this relatively new area, criteria were developed for including technologies and products in this document. Most technologies and products that were either only conceptual or were not currently envisioned to apply to water were omitted. A complete discussion of the criteria used to select technologies, as well as a list of the products and technologies investigated, can be found in Appendix C.

Three categories of technology development were designated: (1) available now (being used, off-the-shelf technology, or could be used by water utilities) for use in EWSs; (2) potentially adaptable technology for use in EWSs (in use, but needs additional steps to address specific challenges for use with water distribution system); and (3) emerging technologies that may be applicable for use in EWSs.

In this report, technologies are classified based on the three categories above (e.g., available, potentially adaptable, emerging), and details are provided on the level of verification, if the information was available. For most products, except where noted, **manufacturer's claims have not been evaluated by independent sources and products mentioned are not endorsed by EPA.**

3. Desired Characteristics and Features of Integrated Early Warning Systems

An EWS is much more than a collection of monitoring technologies. It is an integrated system for deploying the monitoring technology; analyzing, interpreting, and communicating the results; and using the results in making decisions that are protective of public health while minimizing unnecessary concern and inconvenience within a community. EWSs should be viewed as a critical part of the operation of a water system in general. EWSs can be used to identify intentional contamination events and other non-intentional situations where water quality is impaired. To become a widely used, effective, and reliable part of a water distribution security (and water quality monitoring) system, there are characteristics that integrated EWSs should exhibit.

3.1 Desired Characteristics for Integrated Early Warning Systems

To become a widely used, effective, and reliable part of a water distribution security and quality monitoring system, an ideal integrated EWS should demonstrate a number of characteristics, such as the following (adapted from ILSI, 1999; Grayman, 2004a; Hasan, 2004):

- provide a rapid response
- include a sufficiently wide range of potential contaminants that can be detected
- exhibit a significant degree of automation, including automatic sample archiving
- allow acquisition, maintenance, and upgrades at an affordable cost
- require low skill and training
- identify the source of the contaminant and allows accurate prediction of the location and concentration downstream of the detection point
- demonstrate sufficient sensitivity to detect contaminants
- permit minimal false-positives/false-negatives
- exhibit robustness and ruggedness to continually operate in a water environment
- allow remote operation and adjustment
- function continuously
- allow for third party testing, evaluation, and verification

Currently, an EWS with all of the above characteristics does not exist. However, there are parts of an EWS that can meet certain core characteristics: (1) provide rapid response, (2) screen for a number of contaminants while maintaining sufficient sensitivity, and (3) operate as an automated system that allows for remote monitoring. Any EWS system that does not demonstrate these three core characteristics could not be considered an effective EWS. Although emphasis is placed on these three core characteristics, the other characteristics presented below cannot be ignored in the design of an EWS. For example, consideration should be given to the rate of false-positive/false-negative results and method sensitivity when interpreting the results. System operation and maintenance costs, sampling rate, and reliability should be considered in the design of an EWS. Furthermore, utilities are reluctant to invest in technologies that have not been third party verified.

3.1.1 Rapid Response Time

Response time for an EWS is typically from the time when the contaminant contacts the sensor to when a result is reported and a response is initiated (Mays, 2004). An ideal EWS would detect, interpret, and communicate the warning in sufficient time to take mitigation response actions before

human health is jeopardized (ILSI, 1999). It is especially desirable that the EWS is rapid between contamination occurrence and detection and identification of the contaminant. This time may be influenced both by the technologies used and the overall approach to identification of the contaminant. For example, an approach could involve an initial warning by one technology followed by a confirmation by another technology. In most of the current literature, the speed of a rapid detection technology refers mainly to the time between sample collection and final interpretation of the results. The ILSI report *Early Warning Monitoring to Detect Hazardous Events in Water Supplies* considers results in two hours or less to be rapid (ILSI, 1999). Some manufacturers call their field portable grab sample kits (or devices) rapid detection technologies. In these cases it is important to note that even if a technology boasts a 2-minute assay time, if the equipment is in storage and requires 30 minutes of set-up time before the sample is tested, then the effective time is really 32 minutes. In addition, the time it takes for the sample to be collected from the field will affect the overall response time.

Response time can also include the time to inform the decision makers of the results of the contaminant analysis, initiate the response decision making process, and initiate the implementation of the response plan. Since the definition of sufficiently rapid EWSs includes “sufficient time for action,” the desired outcome of the action should be defined. For example, the desired outcome could require actions as demanding as prevention of the contaminant reaching taps by mitigation measures or pump shut down or a more simple response of issuing a boil-water notice.

Although detection, data analysis, decision making, and response implementation all factor into the EWS’s overall response time, it seems reasonable that the detection technology should not be the bottleneck in the response process. Rapid detection technology should ideally have high throughput (collecting data or samples every few minutes or less), rapid assay, and brief analysis time. In a best-case scenario, a contaminant is detected, a decision is made, and a response is implemented before the contaminant has time to reach consumer taps. In this sense, an EWS should strive to “detect to protect” (incident detected and exposure prevented; may be instant) and “detect to warn” (incident detected before significant exposure or manifestation of public health indicators; may take hours). Systems that can only “detect to treat” (incident detected after exposure occurs or manifestation of public health indicators, may take hours to days) qualify as contamination warning systems but may not meet the rapid criteria of an EWS (Roberson and Morley, 2005). However, with improvements in technology and the ability to detect specific contaminants or specific contaminant categories in near real-time, it is anticipated that a contamination warning system will move toward “detect to warn.”

3.1.2 Range of Contaminants

It is impractical and probably unproductive to focus on specific drinking water contaminants when designing an EWS. In addition, long and exhaustive lists of agents can give a misleading impression of the extent of possible threats (WHO, 2004¹⁶). Because the potential lists of contaminants and potential threats are very large, it is unreasonable to expect to have a separate detection technology in place for each contaminant or threat. The unlimited range of existing and emerging contaminants would tax the resources and technical capacity of any water distribution system. Instead, there needs to be an ongoing process of grouping known contaminants by such properties as their physicochemical traits, source, public health impact, or the probability that they may be used to disrupt a water distribution system. Characteristics like these can be useful because they help

determine the appropriate type, placement, and cost of monitoring technologies. It is necessary, therefore, that a suite or panel of technologies be capable of detecting broad groups of contaminants and other threats, instead of separate detection technologies for each contaminant. Toxic chemicals, radiological contaminants, and microbial pathogens are broad categories that require particular detection and identification strategies. Additional subcategories with examples are provided in Exhibit 3-1 (EPA, 2003/2004).

3.1.3 Automation and Remote Operation

Automated systems have several advantages over manual sampling assays. Sampling intervals are easier to dictate and track with automated systems. Although human error and variability introduced due to different human operators remain factors for automated systems, they are much reduced compared to manual assays. With automated systems, remote monitoring is more feasible because personnel do not need to travel to the sampling site each time a sample is taken. Remote operation of the technology is also valuable. There are devices that are automated and can be placed remotely, but if parameters need to be adjusted, calibrated or validated, then personnel must travel to the devices. Performance optimization is cumbersome if traveling to each device is required to adjust parameters. Systems amenable to adjustment, calibration, or validation via a central command location are desirable but not available for many sensors used for detecting contaminants.

“Online” implies a certain degree of automation, remote control, and real-time capability. Online at a minimum refers to the capability of a device to be permanently installed. “Continuously online” can be used to emphasize real-time capability. This term should not be confused with “in-line” or “in-pipe” which refers to the placement of a device within a pipe, so distribution system water does not have to be re-routed out of the distribution system to be sampled. In-line or in-pipe technologies are also online.

Automatic sample archiving is necessary when confirmatory testing is desired. When an alarm is triggered, an automated sample collection device should store a grab sample so that the water sample that triggered the alarm can be analyzed either in the field with portable devices or in a laboratory for more sophisticated analysis. If automated sample collection is not in place, then it is problematic to determine if a monitor detected a transient spike in contamination or if there was a false alarm. Although flow rates vary throughout the distribution system, it is not unreasonable to predict that some contamination spikes of concern could pass by sensors before response teams could make it to the monitor location to perform a manual grab sample. Even if data from multiple sensors are integrated with flow models to predict downstream contamination location and concentration, it may still be desirable to have archived samples, particularly if a criminal investigation results from the event.

Exhibit 3-1. Drinking Water Contaminant Classes and Examples

Category	Examples
MICROBIOLOGICAL CONTAMINANTS	
Bacteria	<i>Bacillus anthracis</i> , <i>Brucella</i> spp., <i>Burkholderia</i> spp., <i>Campylobacter</i> spp., <i>Clostridium perfringens</i> , <i>E. coli</i> O157:H7, <i>Francisella tularensis</i> , <i>Salmonella typhi</i> , <i>Shigella</i> spp., <i>Vibrio cholerae</i> O1, <i>Yersinia pestis</i> , <i>Y. enterocolitica</i>
Viruses	Caliciviruses, Enteroviruses, Hepatitis A/E, Variola, Venezuelan equine encephalitis virus
Parasites	<i>Cryptosporidium parvum</i> , <i>Entamoeba histolytica</i> , <i>Toxoplasma gondii</i>
CHEMICAL CONTAMINANTS	
Corrosives and caustics	Toilet bowl cleaners (e.g., hydrochloric acid), tree-root dissolver (e.g., sulfuric acid), drain cleaner (e.g., sodium hydroxide)
Cyanide salts or cyanogenics	Sodium cyanide, potassium cyanide, amygdalin, cyanogen chloride, ferricyanide salts
Metals	Mercury, lead, osmium, their salts, organic compounds, and complexes (even those of iron, cobalt, copper are toxic at high doses)
Nonmetal oxyanions, organo-nonmetals	Arsenate, arsenite, selenite salts, organoarsenic, organoselenium compounds
Fluorinated organics	Sodium trifluoroacetate (a rodenticide), fluoroalcohols, fluorinated surfactants
Hydrocarbons and their oxygenated and/or halogenated derivatives	Paint thinners, gasoline, kerosene, ketones (e.g., methyl isobutyl ketone), alcohols (e.g., methanol), ethers (e.g., methyl <i>tert</i> -butyl ether or MTBE), haloalkanes (e.g., dichloromethane, tetrachloroethene)
Insecticides	Organophosphates (e.g., Malathion), chlorinated organics (e.g., DDT), carbamates (e.g., Aldicarb) some alkaloids (e.g., nicotine)
Malodorous, noxious, foul-tasting, and/or lachrymatory chemicals	Thiols (e.g., mercaptoacetic acid, mercaptoethanol), amines (e.g., cadaverine, putrescine), inorganic esters (e.g., trimethylphosphite, dimethylsulfate, acrolein)
Organics, water-miscible	Acetone, methanol, ethylene glycol (antifreeze), phenols, detergents
Pesticides other than insecticides	Herbicides (e.g., chlorophenoxy or atrazine derivatives), rodenticides (e.g., superwarfarins, zinc phosphide, α -naphthyl thiourea)
Pharmaceuticals	Cardiac glycosides, some alkaloids (e.g., vincristine), antineoplastic chemotherapies (e.g., aminopterin), anticoagulants (e.g., warfarin). Includes illicit drugs such as LSD, PCP, and heroin
Schedule 1 Chemical Weapons	Organophosphate nerve agents (e.g., sarin, tabun, VX), vesicants, [nitrogen and sulfur mustards (chlorinated alkyl amines and thioethers, respectively)], Lewisite
Biotoxins	Plant, animal, microbial, and fungal derived toxins (e.g. ricin, botulinum toxin, aflatoxins)
RADIOLOGICAL CONTAMINANTS	
Radionuclides	Does not refer to nuclear, thermonuclear, or neutron bombs. Radionuclides may be used in medical devices and industrial irradiators (e.g, Cesium-137, Iridium-192, Cobalt-60, Strontium-90). Class includes both the metals and salts.

3.1.4 Affordable Cost

Affordability is essential. Although what is considered affordable will vary for different water utilities, the desired characteristics and features of EWSs outlined in this chapter can serve as a checklist to compare systems to each other and to buyer requirements. In addition, other factors will likely be considered by potential users, such as how soon the equipment will become outdated, supply and maintenance costs, and budget demands from other high priority areas. A cost-effective EWS should allow for future growth and improvements. This might be accomplished by a modular design that could be upgraded stepwise on a planned schedule to incorporate new technologies as they become available. This type of spiral development should keep EWSs evolving, both in terms of performance and cost.¹⁷ Besides the capital costs, there are ongoing operation and maintenance costs.

3.1.5 Low Skill and Training

Skill level and training requirements will factor into the cost of the detection technologies and the EWS as a whole, and will impact the effective use of the system. Complicated technologies that require initial training along with further practice and hands-on experience for proper implementation will suffer from periods of shut down if personnel turnover is too rapid. In contrast, technologies that require a low skill level and minimal training to run effectively are more likely to yield results on a consistent basis. Skill and training required should be considered for both the actual sampling or assay technology, as well as the necessary software needed for analysis and interpretation.

3.1.6 Source of the Contaminant

It is desirable that the site of introduction of contamination be identified as quickly as possible. Although it is unlikely that an EWS will be able to pinpoint the point of entry, it should provide guidance for investigation of the event and narrow the possible locations. Where contamination is ongoing, this is valuable for halting contaminant entry. In the case of intentional contamination, the entry site would be subject to criminal investigation protocols. Sites of accidental transient entry would also need to be evaluated. Site locations for monitoring equipment throughout the system and special contaminant flow models will assist in tracing a contaminant to its point of entry. In addition, it is important to accurately predict the location and concentration of contaminants once they pass the detector site. This is valuable for knowing where an intervention, grab sample, or other response might be effective, for determining the particular users at risk, and for predicting exposures.

3.1.7 Sensitivity

Sensitivity of an assay or test impacts the utility and often the cost of the detection technology. Assays that can only reliably detect relatively high levels of contaminants would not be useful if lower levels need to be detected. Often assays that can detect very low levels of contaminants are swamped by high levels and may be more expensive than other appropriate options. An assay that can quantitate a broad range of concentrations, however, is likely to be prohibitively expensive. For regulated contaminants, an assay should be sensitive enough to detect concentration levels that

bound the regulatory levels. For potentially hazardous contaminants, such as CBW agents, the chosen thresholds of detection should be scientifically based and protective of public health.

3.1.8 Minimal False-positives/False-negatives

False-positives and false-negatives can make a system effectively useless. False-positive and false-negative rates can be defined for individual monitors within the integrated EWS and for the EWS as a whole. False-negatives lead to decreased protection because contaminants present at relevant levels escape detection. This could result in catastrophic public health consequences and/or loss of confidence in drinking water supplies. False-positives from devices or assays can slow down the effective response time, because each time a positive result is obtained, it must be confirmed by additional tests. If the consequences of a true positive are grave enough, then the initial presumptive positive result would trigger a response. Any response has an associated cost measured in labor time and direct costs. If the initial result is subsequently determined to be a false-positive, then money has been spent needlessly and in some cases public trust is eroded. Each contamination warning that the public finds inaccurate will increase the rate at which future warnings are ignored, which would increase the health impacts in a real contamination event. In many cases, the time needed to confirm a result is added before any response plan is initiated.

Appropriate data analysis and event correlation techniques can reduce the false alarm rate for the EWS. Only systems with either very low false-positive/negative rates or very rapid confirmation methods should be considered early warning. The Defense Advanced Research Projects Agency (DARPA) Chemical and Biological Sensors Standards Study presents methods for evaluating sensors by capturing the performance trade-offs between sensitivity, probability of correct detection, false-positive rate, and response time (DARPA, 2004). Hrudehy and Rizak (2004) have developed a statistical framework for hazard detection and judgment of the evidence to provide insight and mathematical justification to decisions regarding balancing false-positive and false-negative errors in the drinking water security context. In addition, Bravata et al. (2004) describe how sensitivity, specificity, and pre- and post-test probability are reported in receiver operating characteristic (ROC) curves to graphically communicate predicted false-positive and false-negative information. The authors also suggest that published guidance for evaluating clinical diagnostic tests can be adapted for evaluating detection systems because diagnostic test guidelines are well established and promote study designs that provide unbiased estimates of both sensitivity and specificity (or likelihood ratios) relative to an acceptable standard. Manufacturers and parties involved in third party verification should quantitate the false-positive and false-negative rates.

Sources of false-positives and false-negatives can be due to human error, such as inaccurate pipetting or mixing techniques. There are also common chemicals or conditions in the water distribution system that can interfere with some types of assays. For example, the chlorine residual can interfere with detection because chlorine itself may be measured as a toxin by some of the assays. Chlorine can also be toxic to biomonitors (e.g., fish, bacteria). Copper and other metals can affect the chemistry of some assays. Biofilms (microbial communities that coat the inside of pipes) commonly occur in the distribution system, and can naturally slough off, releasing microorganisms into the finished water. Microbial detection technologies could confuse this background level of microbial occurrence with an intentional contamination event. Such interferences are discussed in more detail in Chapter 9.

The rates of false-positives and false-negatives for individual devices and assays should be distinguished from the overall false rates of the EWS system. Although individual technologies may have false-positive and false-negative rates that can be compensated for by overall design of the EWS through the use of confirmatory and backup tests, the overall EWS should have a very low rate of false-positives and false-negatives. If a response plan includes calling in emergency responders from other community sources, utilities should consider that some local governments may have fines in place for organizations and individuals that exceed a certain number of false alarms in a given time period.

3.1.9 Robustness and Continuous Functioning

EWSs and the associated technologies should be resistant to damage or inaccuracies caused by human error or environmental conditions, such as continuous exposure to the water environment. This robustness decreases maintenance costs and provides increased reliability. These criteria apply to both the hardware and the software. Human error during maintenance should be easily detectable. Equipment that is highly sensitive to jarring, shaking, or falling has reduced utility and probably higher maintenance costs. Environmental conditions such as humidity and temperature will fluctuate, even in locations that are sheltered from direct sunlight and precipitation. Software that is prone to crashing or is overly complicated to master compromises the usefulness of the system. Battery life should be considered for hand-held units. For online units, automatic restart after a power interruption is desirable, particularly for remotely operated devices. Continuous, predictable, year-round functioning is a top priority for EWSs.

3.1.10 Third Party Verification

Third-party verification evaluation is desired to determine if specific devices and methods perform as they are intended and advertised. EPA's ETV Program and TTEP provide third-party verification evaluation reports for several products related to EWSs. Another organization that provides third party verification is the AOAC International,¹⁸ whose mission statement is to serve "the communities of analytical sciences by providing the tools and processes necessary for community stakeholders to collaborate and, through consensus building, develop fit-for-purpose methods and services for assuring quality measurements."

3.2 Design Features of Integrated Early Warning Systems

The design of an integrated EWS requires a conceptual framework of all its component parts. Exhibit 3-2 outlines the component features of an integrated EWS. An integrated EWS is more than just selecting sensors. It includes determining sensor locations, acquiring data, conducting data analysis, developing communication and notification links, establishing decision making procedures, and developing response protocols. Although public health surveillance, monitoring, consumer complaints, and consequence management are features of a more broadly defined contamination warning system (see Appendix A), this study focuses more on the use of contaminant sensors/detectors and the associated data and communication networks in the drinking water distribution system.

When considering an integrated EWS, especially for a distribution system, a utility should go through a structured decision making process. Exhibit 3-3 presents a conceptual process for

designing an EWS. The utility should (1) determine the need for an EWS, (2) conduct the proper and necessary planning and coordination, (3) prepare the overall EWS approach, and (4) develop the details of the EWS design. These steps are described in more detail below. Much of this information on the EWS design process has been reviewed by Hasan and colleagues in *Water Resources Update* (Hasan et al., 2004). In a related effort called the WaterSentinel Initiative (see Appendix A), EPA is designing a contamination warning system. Furthermore, EPA, in partnership with drinking water stakeholders, is developing a concept of operations which will be further designed and piloted for deployment by select water utilities.

Exhibit 3-2. Design Features of an Integrated Early Warning System

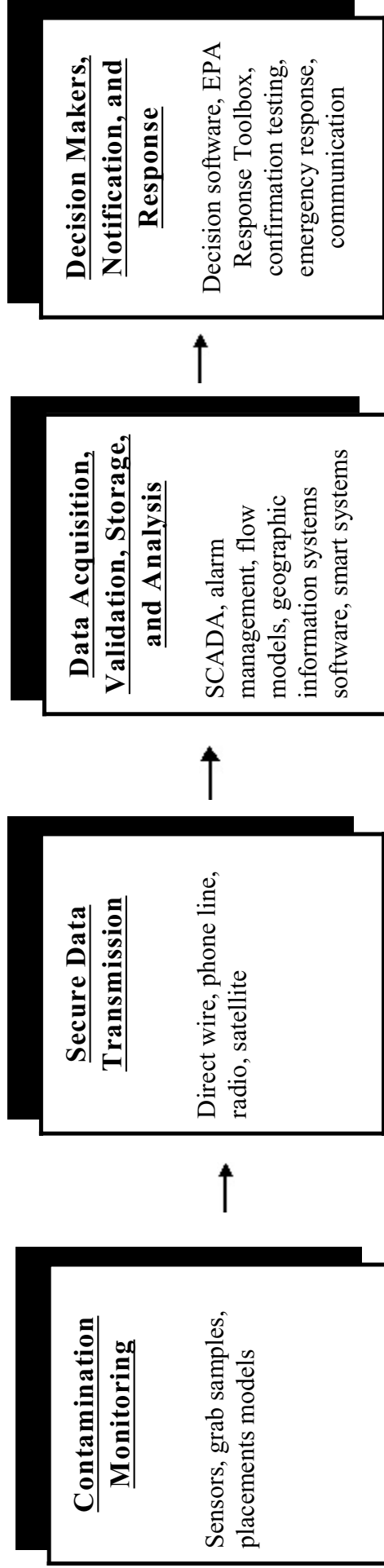
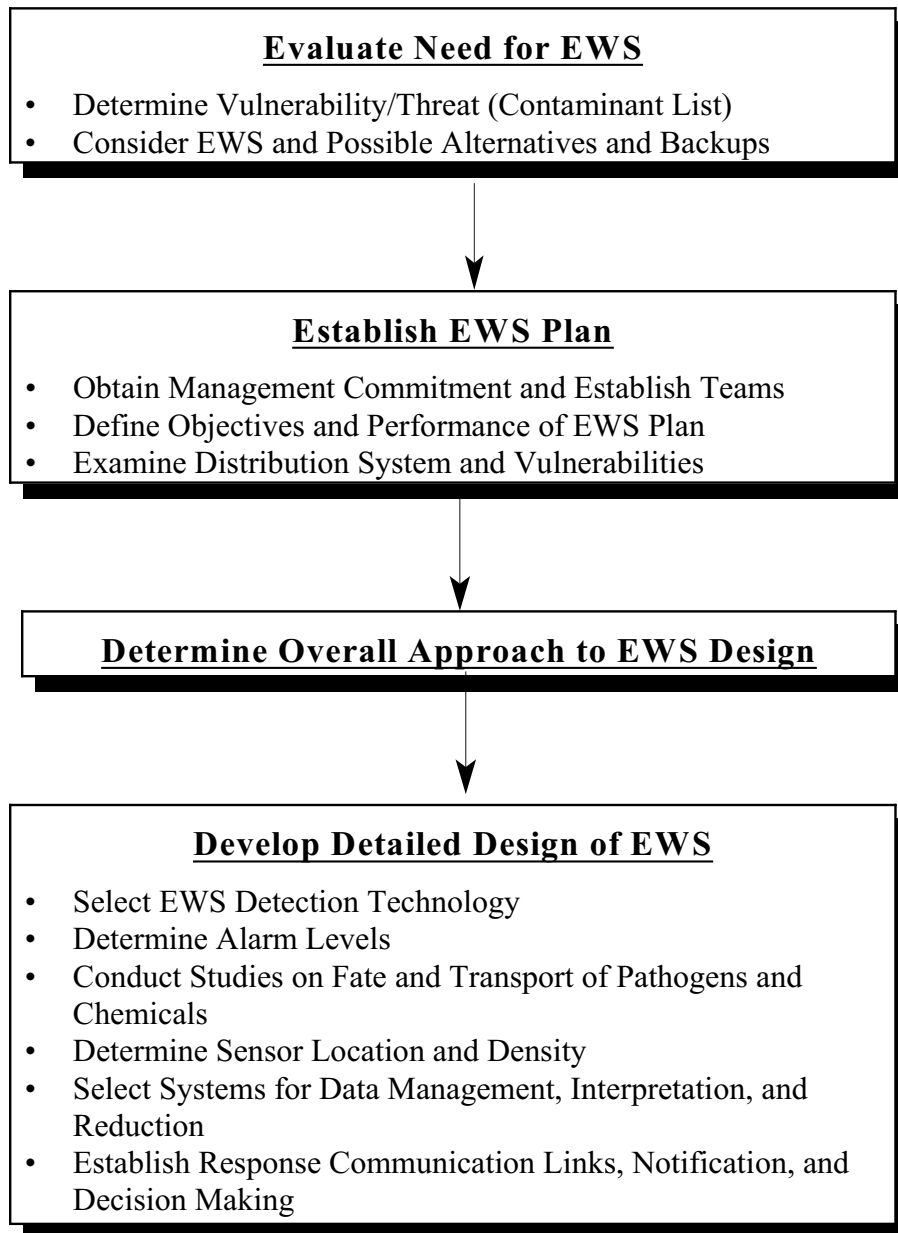


Exhibit 3-3. Conceptual Process for Designing an Early Warning System



3.2.1 Evaluate the Need for an Integrated EWS

In evaluating the need for an integrated EWS, the utility should perform or revisit its vulnerability assessment, especially with regard to the distribution system's vulnerability to intentional contamination events. The vulnerability assessment should consider the threat of such an event, the consequences of an event, and the status of the facility to prevent, identify, and respond to such an event. Additionally, the utility should characterize the distribution system to determine if there is a reasonable way for the utility to provide early warning to protect users. The utility's size, usage patterns, and vulnerability should be factors. The utility should also weigh the cost-benefits of integrating customer complaint monitoring and public health surveillance with contaminant sensors/detectors and the associated data and communication networks. The utility should consider

the cost and reliability of current EWS technologies. Although the protection of public health is the primary goal of an EWS, public perception of the effectiveness of the warning system should also be considered. Not only must the public actually be protected, the majority of the public should be made to feel protected to the extent possible. In this regard, utilities should consider the appropriate level of information to be released to the public. Although the level of information should be enough to allow confidence in the EWS and deter attacks, it should not compromise the effectiveness of the EWS. Utilities may choose to include additional design features that address the concerns of their customers.

The size of the water utility could greatly influence the appropriate design for an EWS. Large, medium, and small water utilities have significant differences that should be considered. For example, the number and strategic placement of sensors in a finished water system will depend on the size of the utility including the miles of pipeline in the distribution system, the populations served, and the flow dynamics. The types of contamination threats may also differ from large to medium to small systems so the EWS design should also reflect these differences. In addition, water utilities of differing size will have vastly different budgets to spend on integrated EWSs. For example, small or medium systems may need to rely mostly on lower cost screening techniques in conjunction with some water quality monitors and customer complaint data rather than investing in expensive online systems or confirmatory kits. Small systems may not have the more sophisticated data collection and analysis systems such as SCADA. Thus, other EWS designs may be needed with less automated or even manual data collection/analysis techniques.

3.2.2 Establish EWS Plan and Coordination

A decision to develop an EWS capability requires a commitment from management. The planning for an EWS usually requires the utility to assemble a team, which may include personnel from the water utility, the local and state health department, emergency response units, law enforcement agencies, and local political leadership. An EWS plan should be developed that outlines the objectives for the EWS which should be clearly defined. The plan should also include how the monitoring results or data will be interpreted, used, and reported. The plan can set performance criteria and some essential design elements. The team should consider legal and regulatory issues and the plan should define a budget and time line for the project. Note that the planning and coordination for an EWS for finished water may be a separate, but linked, effort with an EWS for source water contamination.

In developing the plan, the team should characterize the distribution system to be monitored. For example, a distribution system should be characterized in terms of flow, pressure, access points, water demand and usage patterns, extent of pipeline, and the locations of pipeline and pump stations. A hydraulic model may be useful in this characterization.

Additionally, the team should specifically examine the vulnerability of the distribution system to intentional contamination. Previously conducted vulnerability assessments, required by the Bioterrorism Act, can be extremely helpful in evaluating aspects of physical security. An expanded vulnerability assessment can help identify the contamination scenarios that could occur (e.g., pump to overcome pipe pressure), as well as the insertion location and method (e.g., dump over a short period; bleed, pump, or dissolving matrix over longer times). The duration of a contamination event is an important parameter for an EWS. Hydraulic modeling may be useful in identifying those

portions of the distribution system that, if compromised, would have the most time-sensitive consequences. The vulnerability assessment should also help to identify target contaminants.

System vulnerabilities and the ability of existing treatment barriers to remove or neutralize specific contaminants should be considered in choosing the contaminants of concern. The list could include groups of contaminants that cover a broad range of specific contaminants. Lists of contaminants are available from various agencies, including EPA. This step is important because different components of the EWS may be chosen to detect toxic, microbial, or radiological contaminants. During planning for an EWS, there should be a discussion of system maintenance requirements, housekeeping, system administration issues, human resource requirements including security and training, exercising the system and its human participants, and upgrading the system when improved technology is available.

3.2.3 Determine Overall Approach to EWS Design

There are many ways to approach development of an effective EWS design. While real-time continuous monitoring may be the ultimate long-term goal, there may be intermediate EWS architectures that would be more effective until real-time monitors are available. Under the proposed Fiscal Year 2006 budget, EPA will launch WaterSentinel, a proposed demonstration project by which EPA, in partnership with select utilities and laboratories, would design, deploy, and evaluate a model contamination warning system for drinking water security. EPA and its partners will thus gain operational and tactical experience that can assist in developing standardized and cost-effective approaches to coordinated surveillance and monitoring of drinking water. Until this program is implemented and lessons learned however, a few possible approaches to EWS design and some brief discussion on their capabilities and limitations are provided below.

- Some experts in the field of EWS design for drinking water distribution systems advocate a “tiered” approach with two stages. The first stage uses continuous real-time sensors that can provide a generic warning or trigger an alarm that a contaminant is in the water. Initial detection could occur within seconds, if first-stage monitoring is effective and located properly. This would trigger a second stage using more specific and sensitive technology to confirm and identify the contaminant (ILSI, 1999; Hasan et al., 2004). A second-stage technology might either be located in the field or be brought to the site as a field portable unit. Analysis could take minutes or hours depending on the method of detection and the location in the distribution system. This tiered approach addresses the current situation where limited or no technology exists that allows for affordable, online, real-time monitoring, and identification of hundreds of specific contaminants. The first screening stage alone of a monitoring system does not constitute an EWS. Thus, confirmatory analyses used to verify a positive result from a screening analysis should be integrated into the overall design of the EWS. A more complete discussion of a first-stage/second-stage approach to an EWS is provided in Exhibit 3-4. Other experts are concerned about the possibility of obtaining many false-positives for certain first-stage technologies that could be sensitive to normal fluctuations in water quality (Wayne Einfeld, Sandia National Laboratory, personal communication).

Exhibit 3-4. Sample EWS Approach using First-Stage and Second-Stage Monitors*First-Stage Monitoring*

A system that continuously monitors for general water quality parameters (e.g., turbidity, temperature, pH, ORP, conductivity) in the distribution system has the potential of providing first-stage monitoring for contamination events (intentional or accidental). Some, but not all, contamination events can cause detectable changes in water quality parameters that are sufficient level to provide an alarm. An intentional contamination event could even create changes in water quality parameters that present a more specific fingerprint/signature indicating a possible group of contaminants. In the laboratory, using confined distribution systems, online water quality monitoring, and controlled spiking of known contaminants and contaminant cocktails, data are being produced on how water quality parameters respond during contaminant influx. However, an important concern is that baseline fluctuations in water quality parameters would need to be determined before an anomaly in readings could be identified. This concern is the subject of current research by EPA and other agencies. Some patterns in fluctuations may be associated with storm events or certain operational conditions. It is likely that considerable experience with daily, seasonal, and event-related fluctuations will be required for a specific finished water distribution system before the monitoring system can be maximally useful for detecting contamination events. Thus, false-positives are a large concern of utilities. Chapter 5 reviews the specific technologies and research projects that are involved in developing first-stage monitoring capabilities. Note that first-stage monitoring is not limited to traditional water quality parameters; it could in the future also include biologically-based monitors.

Second-Stage Detection Confirmation

After routine first-stage monitoring has “raised a red flag,” second-stage confirmation can be used to verify detection and/or characterize specific contaminants. Second-stage confirmation differs from first-stage monitoring in that second-stage technologies are not as amenable to high throughput continuous sampling. For first-stage monitoring, speed is measured in seconds, while for second-stage confirmation speed is more appropriately measured in minutes (~10 to 120 minutes). Because second-stage confirmation is often not in continuous operation, set-up time (solution mixing, equipment warm-up), sample capture time (time to obtain an appropriate sample to be tested), and assay and analysis time should all be included in the estimate for how much time it will take from the initial “red flag” until second-stage confirmation is complete. The information gained from second-stage confirmation is more specific and should assist in choosing between more targeted response options. Rapid identification of the specific contaminant may also help mitigate adverse health outcomes for potentially exposed populations.

Note: “Stage” refers to levels of detection within the same EWS. It does not refer to near-term EWS design and long-term EWS design goals.

- Another approach, perhaps an intermediate EWS design, is to (1) use multiple water quality monitors to provide a red flag for contaminants, (2) perform frequent grab sample analysis by rapid contaminant-specific monitors (e.g., arsenic/cyanide), and (3) take automated weekly samples of water that can be analyzed for a suite of contaminants. The water samples could be screened by field methods or analyzed with laboratory instruments, which are more developed than online contaminant detectors. This approach has the advantage of monitoring for generic warnings while using some established technology that is now available (e.g., chemical monitors for continuous monitoring, automatic samplers, and established microbial tests). The approach provides some intermediate level of EWS monitoring.
- Another more advanced EWS design is to use multi-parameter water quality monitors and routine composite/grab sampling in conjunction with data collected from customer complaints and public health surveillance as triggers for confirmatory testing. This design provides a mechanism to identify potentially large scale events that are in the process of occurring.

Regardless of the approach, a properly designed EWS should include all other elements of a monitoring program necessary to inform decision officials responsible for public health protection. An EWS can be designed to be part of an overall water safety and security program for the utility. In addition to providing warning for intentional contamination, the EWS fills a dual role of providing water safety through routine and compliance monitoring. Other information sources such as customer complaints could be indicative of intentional as well as accidental contamination events. Utilities may want to consult with other utilities with additional experience, as well as keep informed on the latest research development and test results. Such discussions need to be part of the overall approach to EWS design.

3.2.4 Develop Detailed Design of an Integrated Early Warning System

This step is really a series of interrelated substeps, because the information from one may affect the other. For example, a decision about which EWS detection technology to choose may depend on the location and number of units to purchase. Whereas the alarm levels chosen may influence the selection of EWS technology (i.e., make and model). Thus, all of these substeps will be discussed together.

- **Select EWS Detector Technology**

Once target contaminants for the EWS have been identified, and the range of concentration necessary to detect them has been established, it is necessary to select a monitoring technology for the particular contaminant or class of contaminants. This assumes that a monitoring technology that meets the core requirements of an EWS currently exists. Furthermore, the monitoring technology should be capable of dealing with complex water matrices. This may require an extraction step to remove the material from the water matrix and/or a concentration step to enhance detection and quantification. Although techniques for isolating, concentrating, and purifying microbial and chemical substances have been developed for many laboratory methods, they may not necessarily be transferable to field deployable monitoring devices. The technology considered for use in an EWS should be evaluated to ensure that all steps of the methodology perform correctly and can detect the target contaminant(s) without excessive interference. Identifying a field-deployable technology with an acceptable methodology is only the first step. Performance of the monitoring

technology must also be adequate to meet the data quality objectives of the monitoring program. These data quality objectives should be defined during the design of the EWS and include specificity, sensitivity, accuracy, precision, and recovery, as well as rates of false-positives and negatives. If the monitoring technology cannot meet the data quality objectives, then another technology should be selected. If no technology can be identified that meets the objectives, then either the EWS should not be implemented, or the data quality objectives will need to be revised. If the later approach is taken, it will be necessary to modify the manner in which the results are used to be consistent with revised data quality objectives. There are a great variety of EWS detection technologies available (see Chapters 6 and 7). Certain technologies can be used online and provide more real-time capability.

- **Determine Alarm Levels**

The basis for setting alarm levels will depend on the previously determined levels at which contaminants need to be detected (based on human health risks) and on the type of EWS employed. The response that is initiated by an alarm must be established before the EWS is deployed. Automated systems with online monitoring especially should have alert capabilities. Operators should be able to set threshold values so the system automatically triggers an alarm if readings move outside of the range that has been defined as safe. Performance optimization of the system should allow for alarm trigger rates that minimize false alarms, but still detect contamination events that could pose a health risk. If a false alarm leads to a decision to issue a notice to the public to stop using the water, public health as well as public confidence could be impacted.

- **Conduct Studies on Fate and Transport Modeling of Pathogens and Chemicals**

Chemical and microbial contaminants can behave in a variety of ways as they migrate through a water system. Environmental conditions, the presence of oxidants or other treatment chemicals, and the hydraulic characteristics of the system will affect the concentration and characteristics of these contaminants. If information is available on contaminant characteristics that affect the contaminants' fate and transport, it should be factored into the design of an EWS. For example, if a target contaminant is known to chemically degrade at a certain rate in the presence of free chlorine, it may be possible to use a hydraulic/chemical model of the distribution system to predict the concentration profile through the system. This information in turn can be used to select optimal locations for sensors.

- **Determine Sensor Location and Density**

Choosing the location or site of sensor placement within a distribution system is a complex task. The location and density of sensors in an EWS is dictated by the results of the system characterization, vulnerability/threat assessment, usage considerations, risk minimization, and cost. Thus, the easiest site to place a sensor may not be a site that yields the most useful information. The size of the population downstream from the sensor may be a defensible criterion for choosing a site, but might not be the best site for system modeling. Due to the complexity and dynamic nature of distribution systems, it may be beneficial to develop a hydraulic model of the system to assist in the placement of sensors. Real-time integrated pressure and flow data can be used to build flow models that have well characterized predictive capabilities. Other factors to determine sensor location could be location of isolation valves, location of critical nodes (hospitals, emergency response), and

physical security of the location. Even if sensors can be optimally located within a distribution system, there may not be sufficient time to prevent exposure of a portion of the public to the contaminated water. At best, monitoring conducted within the distribution system will provide time to limit exposure, isolate the contaminated water, and initiate mitigation and remediation actions.

- **Select Systems for Data Management, Interpretation, and Reduction**

One of the challenges of a continuous, real-time monitoring system is management of the large amounts of data that are generated. Use of data acquisition software and a central data management center is critical. This will require that individual sensors deployed in the system be equipped with transmitters, modems, direct wire, or some other means to communicate the data to the acquisition and management systems. Furthermore, the data management system should be capable of performing some level of data analysis and trending in order to assess whether an alarm level has been exceeded. The use of “smart” systems that evaluate trends and can distinguish between genuine excursions and noise could minimize the rate of false alarms. A decision will also have to be made regarding the action that is taken when the data management system detects an excursion above the alarm level. At a minimum, the system should notify operators, public health agencies, and/or emergency response officials. If possible, redundant communication should be used (e.g., notifying multiple individuals through multiple routes such as telephone and fax). In some cases, it may be appropriate to program the data management system to initiate preliminary response actions, such as closing valves or collecting additional samples. However, these initial responses should be considered simple precautionary measures, and response decision makers should make decisions regarding decisive response actions. Integrated analysis of the data gathered on many different parameters and contaminant detectors is what makes an integrated EWS more than a collection of detection technologies and assays. Data validation helps ensure the integrity of data by requiring that appropriate quality assurance and quality control (QA/QC) procedures are followed, and that adequate documentation is included for all data generated. Data validation guidance may be different for different types of data and the stringency depends on the planned utilization of the data. Data security is also an essential part of the integrity of the system. It is important during the transmission of data and during the analysis and storage of information. For obvious reasons, it is important that data being transmitted from a remote sensor to a command center be free from tampering or accidental degradation. Because previously obtained data are accessed by the system to look for patterns, it is also important that old data be free from tampering or accidental degradation.

- **Establish Response Communication Links, Notification, and Decision Making**

An integrated EWS would also include network and communication links between command center operators and any people designated as response decision makers. The communications network should assist with the rapid relay of critical information to the utility decision makers who implement the response. The response may include the utility informing outside parties, such as public health officials, police force, or other emergency responders. Utilities can refer to local ordinances and laws to determine when they are required to inform outside parties. In general, threats should be deemed credible before other agencies are alerted. Many responses are possible when an early warning monitoring system triggers an alarm. Monitoring devices may report data to a command center that will relay information to utility decision makers. In turn, the response may use the same secure communications links to take actions in the distribution system (e.g., shut

isolation valves). Further actions may include monitoring and sampling for the contaminant at appropriate locations in the distribution system and monitoring for surrogate parameters that may indicate contamination (e.g., increased chlorine demand, changes in pH). The EPA Response Protocol Toolbox (EPA, 2003/2004) greatly assists with planning this part of the response.

After developing this comprehensive strategy for an integrated EWS, the utility is ready to develop an implementation strategy that includes buying and installing the equipment; providing maintenance and operation procedures; and providing training, testing, and exercises for systems and personnel.

[this page intentionally left blank]

4. Features of an EWS Related to Data Acquisition and Analysis; Contaminant Flow; Sensor Placement; Alerts; Data Security; and Communication, Response, and Decision Making

The purpose of this chapter is to characterize the state-of-the-art features of EWSs that are *not* related to sensors. These EWS features include real-time data acquisition and analysis; contaminant flow predictive systems; sensor placement; alert management; security enforcement; and communication, response, and decision making. These features of EWS design and operation should be part of an overall plan for the interpretation, use, and reporting of monitoring results (Hasan et al., 2004).

4.1 Real-Time Data Acquisition and Data Analysis

4.1.1 Basics

Continuous, real-time water quality monitoring systems for an EWS have the potential to generate large amounts of raw data, which can be unmanageable without the use of a data acquisition and management system. Water utilities are already familiar with collecting information on water quality and operating their drinking water treatment plant and distribution systems. Over 75 percent of drinking water utilities already operate online analyzers for water quality parameters such as chlorine and turbidity. However, not all of these utilities have monitors within the distribution system. The 75 percent figure includes utilities that have monitors only at the drinking water treatment plant (AwwaRF, 2002). Utilities often use the supervisory control and data acquisition system known as SCADA. A SCADA system links monitoring instruments, remote telemetry units, programmable logic controllers, and a host computer in order to integrate data collection and processing into a single system-wide control center that can be accessed from various locations (Carlson et al., 2004). Large utilities usually use a SCADA system for controls in the distribution system. Such a SCADA system can often incorporate data from online or remote sensors in a cost effective manner (Mays, 2004). The system triggers the collection of data. Remote locations could use microprocessor-based “smart” SCADA systems. Although slower and more expensive than programmable logic controller-based systems, the “smart” SCADA systems save on communication media costs, maintenance, and travel. The simplest SCADA systems only include three or four input/output channels for monitoring (Mays, 2004). SCADA systems that are already in operation for daily water quality monitoring purposes may not be configured so that they can serve all the locations where EWS detectors are needed (see Section 4.3 for discussion of sensor placement). Various approaches taken and systems used for data transmission, validation, and analysis are described below.

- **Data Transmission**

Data transmission to the central database occurs through either hardwired or wireless systems. Hardwired transmission requires the physical connection of cable or wire, and can utilize either coaxial or fiber optic technology. In some cases it may be difficult to hardwire remote locations. Wireless transmission can use a variety of methods, including microwave, UHF or VHF radio, basic telephone modems, cellular telephone modems, or satellite. Wireless transmission may require a direct line of sight between the transmitter and receiver, or the use of re-transmitters (also known as repeaters and amplifiers) (AWWA Workshop, 2004). The least expensive transmission systems

are typically phone lines or direct wire. A combination of data transmission approaches could be used throughout the distribution system, as long as the command center can achieve integration of the information. The data transmission method must be compatible with monitoring equipment and data acquisition equipment. In most cases, utilities would be expanding monitoring capabilities by adding to existing equipment and the existing SCADA system so newer upgrades need to be compatible with existing equipment and SCADA (AWWA Workshop, 2004). For water security applications, the existing monitoring system would need to be evaluated for its vulnerability to direct physical attack (e.g., wire cutting), and to cyber attack (e.g., tapping). Transmission of unencrypted data is a security risk, so hardware and software should have encryption capabilities. Traditionally, utilities have not seen a need to encrypt data from water quality monitors, however monitoring for security applications would require data encryption to reduce vulnerability.

The quantity of data that needs to be transmitted should be considered. Factors that influence data quantity are the number of instruments in the system, the number of data points each instrument generates in a given time frame (e.g., sampling rate of 1/second or 1/minute or 1/hour), and bits per sample. Some monitoring equipment may generate a relatively manageable quantity of data, whereas some equipment (e.g., video) may generate data that require considerably more transmission capability.

Currently, data transmission capacity, computer data storage capacity, and software support are adequate for online monitoring of contaminants. The water industry is not generally considered a large market force; thus, similarly developed systems in other markets may push development of technology for the water industry. For example, SCADA systems based on analog signals require special drivers to accept data from monitors (e.g., particle counters) with digital signals. Products for conversion between analog and digital formats are commercially available. Expected future developments will probably alleviate this concern (AwwaRF, 2002).

- **Data Verification**

Manual verification of sensor data will not usually be an option with a continuous, real-time monitoring system due to the large amount of raw data collected. Therefore, automated data validation processes are indispensable to ensure accurate results from data analysis. A simple yet effective protocol is to compare data received from monitoring sites with data stored at the sensor locations to ensure accuracy and completeness (Carlson et al., 2004). Traditional SCADA systems perform data validation processes such as range checking and data filtering (e.g., moving window averaging). Other approaches under development for data validation are simple outlier detection by commercial off-the-shelf data mining software and finding formal correlations among spatial and temporal data attributes (e.g., pH, temperature, DO, specific conductivity, turbidity, chlorophyll) (Mays, 2004). Data verification is part of an overall quality assurance plan which is a systematic procedure for determining that all aspects of the EWS are functioning as expected.

- **Data Analysis**

Once obtained, the data may go through quality assessment and validation, aggregation, transformation, and analysis (AwwaRF, 2002). Data analysis is performed by specialized software and can take the form of univariate and multivariate analysis, Rule-Based Systems (RBS), or Case-Based Systems (CBSs). Univariate analysis targets one parameter at a time, in order to note

changes in a specific parameter or instrument response in the event of a change in water quality. This separate monitoring of instrument response is useful in determining instrument sensitivity to different contaminants, and in confirming the validity of other similar instrument responses when considering potential false alarms (Carlson et al., 2004). Multivariate analysis uses inputs from all instruments simultaneously to detect data anomalies. The benefits of multivariate analysis are the potential to detect contamination events sooner and the means to learn more about the type of contaminant that generated the alarm. RBSs are characterized by IF-THEN rules, which provide real-time reasoning by looping through rules and polling for new data on a programmed schedule. CBSs operate by comparing a collection of current measurements to a database of historical measurements. Any deviations of the current state from past data will notify the operator, who can run a predictive WHAT-IF model to evaluate scenarios (Carlson et al., 2004). The development of logic systems (e.g., artificial neural networks and fuzzy logic) to interpret the data that are produced by an EWS may be an integral part of some EWS designs. As more and more information is collected by an array of instrumentation, there must be a dependable system developed to interpret all the data produced. One example of such a project was published by IHT Delft, entitled *Use of Artificial Neural Networks and Fuzzy Logic for Integrated Water Management: Review of Applications*.¹⁹

When online instruments provide a stream of data from which the utility will need to manage and potentially use for response decisions, the data quality has to be handled and analyzed carefully (AwwaRF, 2002). The utility should consider the performance characteristics of the instrument, so that the proper degree of validity of the online measurements can be determined. Online data aggregation and the handling of those data should be considered so that large amounts of data can be processed effectively.

For online data, a predictable percentage of the data will be dropped or lost, particularly for remote sites. For these cases some methods for data validation include gap filling, range checking (when data out of range, check along full working range of sensor), rate of change check (peaks/outliers usually a result of disturbance of the sensor), and variance check (check small variations in repeatability). Cross validation methods explore the connection between online measurements. This is particularly valuable for detectors with multi-parameters. Highly correlated parameter measures can be programmed into a model and used for determining confidence in measures.

An EWS may generate real-time data for quick analysis and decisions and action. There are various techniques for assisting in real-time reporting and decision support. They include data filtering, operational indexes (commonly used by operators to calculate measures that represent trends for routine operational performance), short-term prediction using software sensors, and classification and state description to reduce information overload. Predictive modeling can also be used for assisting with data validation (AwwaRF, 2002).

Short-term and long-term data storage and backup needs also must be assessed. For some parameters, baseline characterization may require a full year's worth of data. Data storage needs will depend on how the utility wishes to use the data. The monitors discussed in Chapter 5 potentially serve the dual purpose of general water quality monitoring for operations and of red flag alert for potential security threats. Although data analysis for the purpose of determining immediate security threats may not require long-term storage of data, there may be other secondary uses for the data that would warrant longer term storage. For example, older data could be released to the

utility's systems modeling contractors or to the research community to answer future research questions. A standard minimum storage of data for at least several years is not unreasonable to expect. Utilities should consider developing a policy that maximizes the usefulness of the gathered data, while also addressing the concerns of their legal counsel, and the budgetary constraints of data storage and access.

4.1.2 Demonstration Projects, Tests, and Products

EPA recently conducted a project to evaluate and demonstrate the usefulness of SCADA systems for real-time monitoring of water sensors within distribution systems (EPA, 2004). The test was conducted at the WATERS Center in Cincinnati, OH. Within the WATERS Center, there are two DSSs, which were designed and fabricated to evaluate and interpret the dynamics that influence water quality within water distribution infrastructure systems typical in the U.S. and abroad.²⁰ EPA concluded that a SCADA system is a critical feature for handling the data from online sensors in the distribution system. Analyzing the data from multiple sensors is too difficult and time-consuming without a centralized SCADA. If the data were collected separately from different sensors, the data would have to be downloaded, processed with a computer, and analyzed. This would not provide an effective real-time alert.

A centralized SCADA system also provides a time-stamp on the measurement for comparative analyses. The EPA report also addressed the frequency of sampling for multi-parameter water quality monitors. The EPA report suggested a frequency of between 2 and 10 minutes depending on the ability of the SCADA system to take the data (based on SCADA system setup and bandwidth), the location of the sensor, and the water flow rate. This sampling frequency would also help utilities to establish trends in water fluctuations so as to reduce false alarms. Also, during the test, a number of problems occurred in processing 4 to 20 milliamper signals through the SCADA system so the report recommends purchasing monitors with the option of RS232 outputs, as these are not subject to ground loop problems and other electrical interferences. Further challenges that were identified are the need for regular maintenance and calibration schedules for the sensors and that operator experience and expertise with the sensors and SCADA system are essential. It is important to note that there are technologies other than SCADA that are available for combining and integrating data.

Remote monitoring has applications to an EWS for finished water. An operation can monitor the water quality on line for intentional contamination. A demonstration project conducted by EPA a few years ago examined remote monitoring of drinking water treatment. The remote monitoring system consisted of the sampling units and an associated data acquisition unit. The SCADA units were programmed to monitor, record, and control water treatment and distribution system operation in three locations: Washington, DC; McDowell County, WV, and a distribution system simulator (DSS-1) at EPA's T&E Facility in Cincinnati. In Washington DC, online instruments measured temperature, turbidity, pH, and residual chlorine at locations within the distribution system. In West Virginia, EPA collaborated with the McDowell County Public Services Division to implement a smart SCADA in 1998. The smart SCADA unit observed trends in pressure, chlorine, turbidity, and flow at 15 minute intervals. The system also was programmed to provide an alert if certain conditions were met. The project showed that remote monitoring can be a practical option for small rural utilities (AwwaRF, 2002). Details on EPA's research in Cincinnati on online instruments are discussed in Sections 5.2 and 5.3.

There are several commercial products currently available on the market to help acquire and manage sensor data remotely to improve water security. One company, PDA Security Solutions (Greer, SC), is marketing the Hydra Remote Monitoring System. It captures data from sensing devices located remotely throughout the water distribution system. It includes trend analysis tools, and it continuously compares real-time water quality data against benchmark water profiles. Alarms are programmed to alert operations and security personnel. Biometric login and data encryption are part of the system. EPA has a Cooperative Research and Development Agreement (CRADA) with PDA to develop a nationwide water quality surveillance project. Under the Federal Technology Transfer Act, EPA can form CRADAs with the private sector in order to speed the development of technologies for various programs. Currently, EPA's NHSRC and NRMRL are developing CRADAs for the development of technologies specifically to accomplish the nation's homeland security initiatives.²¹

During the 2002 Olympic Games in Salt Lake City, UT, the Hach Company (Loveland, CO) demonstrated the remote transmission of data from a dozen continuously monitoring sensor platforms in the distribution system. The data were transmitted through unbroken cellular telephone data transfer or directly to the SCADA system. The data were monitored around the clock with provisions for triggering alarms.²²

An emerging technology project in Copenhagen, Denmark is integrating information from existing data sources for a water distribution network in a utility. In the pilot project, the data from real-time sensors are provided to a SCADA system. The sensor information is stored in a database allowing for analysis. Automated checks of the system compare against baseline measurement. Data are validated with standard modules that will flag potentially suspect or corrupt data. The project began in 2001 and is expected to be completed sometime in 2005.

One commercial vendor, PureSense Environmental Inc. (Moffet Field, CA), has a PureSense System which covers the full spectrum from data acquisition to alert and notification. The system includes four components. The PureSense iNode™ is a remote data communication device that uses cellular and Wi-Fi services to collect monitoring data and send commands to remote sensors. The PureSense iWatch™ is an internet data management system that enables the integration of disparate data sets, including data from remote online sensors. The PureSense iServe™ allows automated analysis of real-time data, while PureSense AlertNet™ provides automated alerts. EPA had entered into a CRADA with PureSense Environmental to test the system.

4.2 Contaminant Flow Predictive Systems

From the beginning of the planning phase, an EWS for water distribution systems should develop the capability to predict the movement of flow and contaminants in the system. This predictive ability is important not only to prepare for a potential contamination event, but also to determine the effectiveness of the monitoring system.

Contaminant flow predictive systems are used to predict how a contaminant would move through the distribution system. Such systems are built upon hydraulic and water quality modeling technology known as water distribution system models that are now in wide use within the water industry. This capability could be applied to accidental contamination events (e.g., backflow, cross-connections) or intentional contamination.

Hydraulic modeling dates back to the 1930s when Professor Hardy Cross of the University of Illinois developed an iterative procedure for predicting flow and head within a distribution system (Cross, 1936). This manual procedure was used throughout the water industry for almost 40 years. With the advent of computers, computer-based models using the Hardy Cross methodology and improved solution methods were developed and were in widespread use by the 1980s. These models have become ubiquitous within the water industry and are an integral part of most water system design, master planning, and fire flow analyses. In the 1980s and 1990s, hydraulic analysis was extended to include the ability to model water quality, water age, and source tracing in distribution systems. The usability of these models was greatly improved in the 1990s with the introduction of the public domain EPANET model (Rossman, 2000) and other Windows-based commercial water distribution system models (ASCE, 2004). Exhibit 4-1 provides examples of current water distribution system modeling software.

In order to apply a hydraulic/water quality model to reliably predict the movement of a contaminant in the distribution system, a calibrated, extended-period simulation (EPS) model is needed. An EPS model represents the normal temporal variation in demands and operation. Such a model can be used for planning purposes as part of vulnerability studies and emergency response plans, and as a real-time tool during an actual contamination event. Another challenge is the effort to incorporate pipe networks into the modeling framework, although geographic information systems (GIS) are assisting utilities with this effort

Exhibit 4-1. Examples of Water Distribution System Modeling Software

Network Modeling Software	Company	URL
AQUIS	Seven Technologies	http://www.7t.dk/company/default.asp
EPANET	U. S. EPA	http://www.epa.gov/ORD/NRMRL/wswrd/epanet.html
InfoWater/H2ONET/H2OMAP	MWHSoft	http://www.mwhsoft.com
InfoWorks WS	Wallingford Software	http://www.wallingfordsoftware.com/
MikeNet	DHI, Boss International	http://www.dhisoftware.com/mikenet/
Pipe2000	University of Kentucky	http://www.kypipe.com/
PipelineNet	SAIC, TSWG	http://www.tswg.gov/tswg/ip/PipelineNetTB.htm
SynerGEE Water	Advantica	http://www.advantica.biz/
WaterCAD/WaterGEMS	Haestad Methods	http://www.haestad.com

4.2.1 State-of-the-Art Systems and Current Research and Development

Distribution system modeling in general and contaminant flow predictive systems in particular are developing rapidly. Work is being sponsored by governmental agencies, professional organizations such as ASCE and AwwaRF, and private companies. Predictive modeling is more extensively integrated into European utilities than U.S. utilities. The state-of-the-art in contaminant flow predictive models and some current active areas of research include the following:

- Integration of models with GIS and computer-aided drafting (CAD) software packages has been and continues to be an active area of research and development. GIS and CAD were initially used to help build water distribution system models. Present research and development is directed towards complete integration of distribution system models into the GIS or CAD platform in order to facilitate modeling, display, and assessment. PipelineNet, an integration of EPANET and ArcView GIS, and commercial integration packages such as WaterGEMS and InfoWater provide direct capabilities to assess impacts of contamination events. Additional efforts by EPA are to expand EPANET to account for multiple interacting species and to better involve hydrologists and biologists (DSRC Meeting, 2004).
- Calibration of a model involves adjustments in model parameters so that the model reflects observed field behavior. Optimization techniques for calibrating hydraulic models based on genetic algorithms and other mathematical methods have recently become part of many commercial models (Walski et al., 2003). Continued research in this area is underway to expand the use of these tools to extended period simulation calibration and calibration of water quality parameters. Another area of development in the calibration field is the use of tracer studies in distribution systems. A conservative tracer substance such as sodium chloride is injected into the distribution system and monitored using online conductivity meters. The resulting dataset can be used to calibrate and validate hydraulic models. Although there are currently no established calibration criteria in the U.S., static and dynamic calibration methods exist (EPA, 2005). Also, a committee of the AWWA did propose a set of possible calibration guidelines (ECAC, 1999). These guidelines have not been officially accepted however, there is no active process underway to adopt them. Using these possible calibration guidelines as a catalyst or starting point, it would be recommended to move forward on developing accepted calibration guidelines or standards.
- Existing modeling software is being applied and advanced modeling-based tools are currently under development to assist in evaluating the vulnerability of a distribution system to contaminant events. Carlson et al. (2004) demonstrated the use of existing hydraulic models by creating three case studies of the movement of a contaminant through a distribution system. The capabilities of PipelineNet have been demonstrated through a series of applications in actual distribution systems (Bahadur et al., 2003a). It has been applied as a modeling tool for use in emergency response to contamination of a distribution system. TEVA, a probabilistic distribution system simulation model, is being developed by EPA to evaluate both vulnerability and sensor placement in distribution systems (Murray et al., 2004). Van Bloemen Waanders et al. (2003) have developed a nonlinear programming method for tracing an observed contamination event in a distribution system back to where it was introduced.
- Recent studies have recognized that there are both uncertainty and variability associated with distribution system modeling. Application of such models in a purely deterministic framework where all parameters are assumed to be known with certainty does not provide the information needed for decision making. Baxter and Lence (2003) present a general framework for the analysis of performance risk in a water supply. Kretzmann and van Zyl (2004) incorporated uncertainty through a stochastic analysis of water distribution systems. Grayman et al. (2004b) used Monte Carlo simulation in estimating contaminant exposures while reconstructing an unintentional contamination event. The aforementioned TEVA system incorporates a probabilistic framework for a large range of contamination scenarios.

- Consumption (demand) is an important factor in affecting movement of water and contaminants in a distribution system. Typically, monthly or quarterly meter readings and approximate diurnal water use patterns are used in estimating demands in models. This is recognized as inadequate for detailed contaminant flow models and is being addressed through ongoing research and development in demand models, demand metering, and customer information systems (CIS). Li and Buchberger (2004) have developed and applied models using a Poisson Rectangular Pulse method to simulate fine time scale demand patterns. Metering systems that will measure customer water use at fine time scales and transmit the information to central locations are on the market. CISs provide a mechanism for managing consumption data so that they can be used as a basis for providing better demand data for distribution system models.
- Real-time use of water distribution system models is an active area of development with applications in the improved operations of water systems leading to savings in energy usage and water quality, and as a response tool to contamination events (Jentgen et al., 2003). This is being accomplished through integration of models with SCADA systems that provide information on operation of a water system on a continuous and real-time basis. Commercial water distribution system software companies and companies offering SCADA systems are the primary developers of such systems (Fontenot et al., 2003).
- Tanks and reservoirs have been identified as key elements in water systems that are especially vulnerable to purposeful contamination. If a contaminant enters a tank in the inflow or through direct contamination of the tank contents, the manner in which it mixes with the ambient water in the tank and how it subsequently exits on the outflow affect how and when customers will be exposed to the contaminant. Various mathematical modeling techniques have been developed to assist in predicting the mixing within tanks. These include both detailed computational fluid dynamics (CFD) models and conceptual systems models (Grayman et al., 2004c).
- Water quality models have most commonly been used to represent conservative substances, chlorine residual, and trihalomethanes. Current research is directed towards improving the capability to model disinfectants and disinfectant by-products and expanding models to include bacteria and non-conservative substances that may be introduced in purposeful attacks (Powell et al., 2004). An upgrade to EPANET will allow the simultaneous simulation of multiple interacting chemicals in a distribution system (Uber et al., 2004b). For example, this will allow a simultaneous simulation of both chlorine and a contaminant whose concentration is affected by the chlorine residual.
- Incident Commanders Water Modeling Tool (ICWater)²³ extends the capability of a previously developed RiverSpill modeling tool to allow an incident commander to analyze and react quickly to chemical and/or biological contaminants introduced into surface water sources. ICWater will allow “plug-and-play” with existing incident commander and emergency response tools such as the Chemical Biological Response Aide, Consequence Assessment Tool Set, Natural Hazard Loss Estimation Methodology, and the EPA Emergency Response Analyzer.
- The hydraulic portion of flow contaminant models are still based largely on the methods and assumptions of Hardy Cross developed over 75 years ago. More sophisticated representations of the hydraulics may be required to adequately predict the behavior of water quality

contaminants in the distribution system. The research community is starting to re-examine some of the basic assumptions concerning hydraulic representation of phenomena such as dispersion, pipe mixing, and flow dynamics (Li et al., 2005).

4.3 Sensor Placement

Historically, monitors and sensors have been placed in distribution systems to meet regulatory requirements. Their locations have been determined based on ease of access and a general intuitive assessment of representative locations. Lee et al. (1991) proposed a method for locating monitors based on the concept of coverage, which is defined as the percentage of total demand that is sampled by a set of monitors. Various other researchers further addressed this issue using alternative mathematical methods (Kessler et al., 1998). Though widely cited, these methodologies have rarely been applied in actual practice. However, following the events of September 11, 2001, there has been a renewed interest in sensor placement primarily as a mechanism for detecting purposeful contamination of distribution systems.

4.3.1 Current Research and Development

Many current studies are applying optimization techniques to determine the optimal placement for monitors in distribution systems based on a defined objective function. Ostfeld (2004) and Ostfeld and Salomons (2004) provide reviews of past work in this area and present example mathematical formulations using genetic algorithm solution techniques. Their methodology finds an optimal layout of an early warning detection system comprised of a set of monitoring stations aimed at capturing deliberate external intrusions through sources, nodes, or tanks under an extended period of unsteady conditions. The optimization considers the maximum volume of contaminated water exposure at a concentration higher than a defined safe level. Berry et al. (2004) used an integer programming optimization technique to place a limited number of perfect sensors in the pipes or junctions of a water network so as to minimize the expected amount of damage to the public before detection, assuming the attack occurs on a typical day. Watson et al. (2004) used a mixed-integer linear programming model for the sensor placement problem over a range of design objectives. Using two case studies, they showed that optimal solutions with respect to one design objective (e.g., population exposed) are typically highly sub-optimal with respect to other design objectives (e.g., time to detection). The implication is that robust algorithms for the sensor placement problem must carefully and simultaneously consider multiple, disparate design objectives. Uber et al. (2004a) describe an iterative numerical solution methodology using the “greedy heuristic” algorithm for the sensor location problem.

In general, the optimization methods described above are experimental approaches that have been applied only to hypothetical or small water systems and are based on assumptions about the availability of monitoring technology, ability to define explicit objective functions, and limited incorporation of the variability of water system operation. Further research, development, and practical applications are needed before this technology is ready for routine use.

Research and development of formal methods for locating monitors in water distribution systems are likely to continue in parallel with the development of monitors that can be effectively placed in distribution systems. Though most of the cited research is related to monitors to be used to detect intentional contamination events, related research efforts on sensor location are likely in the future

to support future water quality regulations. For example, the Initial Distribution System Evaluation (IDSE) component of the Stage 2 Disinfectants and Disinfection Byproducts Rule that is approaching promulgation by EPA requires additional routine monitoring in distribution systems. Similarly, re-evaluation of the existing Total Coliform Rule (TCR) will also focus on sampling requirements. An AwwaRF sponsored study that is just commencing as this report neared completion, *Methodologies for Assessing and Improving Water Quality Sampling Programs in Drinking Water Distribution Systems*, will focus in part on sensor location in a probabilistic framework (see Appendix D, Project #3017).

Sandia National Laboratories (SNL) is conducting a project to develop algorithms to identify and quantify the threat to water systems, and thus determine optimum sensor placement locations. An additional purpose of the project is to determine the contaminant source location in real-time. The research team has identified the challenge of determining population density at any node and how it changes throughout the day. Under an interagency agreement with EPA, SNL is planning to develop a new set of mathematically based tools for designing an EWS. Scalability to very large networks and the general uncertainty in the input parameters may be other issues (DSRC Meeting, 2004).

EPA's TEVA program is developing software and tools to examine system vulnerability and help design response strategies. TEVA has developed a model to indicate sensor location, based on protecting the greatest number of people. The TEVA program is comparing its model to other models that have different sensor placement objectives, such as fastest warning or minimizing the number of attacks that would be missed (system coverage, not based on population served). The TEVA model uses a statistical approach, by simulating thousands of scenarios (different contaminant injection locations) and calculating average impact for the entire set of simulations. The comparative analysis should be completed in 2005.

There is a National Science Foundation project effort underway entitled Placement and Operation of an Environmental Sensor Network to Facilitate Decision Making Regarding Drinking Water Quality and Security. The objective of the project is to develop drinking water quality models for multiple potential chemical and biological threats. It should also improve spatial and temporal resolutions for sensor collection networks.²⁴

Online sensors are typically installed using special sample taps that require interruption of water flow through pipes. New installation techniques are being developed to enable installation without interrupting the water flow or requiring major excavation. Sensors also need to be able to withstand the harsh environment of different locations (AwwaRF, 2002).

4.3.2 State-of-the-Art Systems

With sophisticated models at their disposal, Bahadur et al. (2003b) pioneered a technique using PipelineNet in which GIS data and hydraulic model results guide the manual placement of monitors in order to fulfill certain general criteria. In a case study conducted with personnel at a water utility, 25 potential monitor sites were identified and subsequently reduced to the two best sites using the GIS/PipelineNet framework. This approach is more closely related to the traditional methods for locating monitors than are the optimization techniques currently in the research and development stage.

Due to budgetary and technical constraints, many water utilities will face a common situation—the utility wishes to make a modest initial investment in sensors within its existing distribution system and wants to pick the most appropriate locations. Without resorting to the sophisticated experimental optimization techniques that have been previously described, a two-stage procedure is typically followed. In the first stage, likely sites for sensors are determined based on technological constraints for available sensors. Most current sensors require an external power source, a secure location with protection from the elements, access to communications, and easy accessibility for maintenance. These constraints typically result in a limited number of potential sensor locations. In the second stage, the potential sites are evaluated in terms of the “information content” that will be provided if a sensor is placed at that location. This typically translates into placing sensors throughout the system on larger pipes that serve the most customers. This process can be done informally by operations personnel who know and understand the distribution system or more formally, using hydraulic models to identify high flow pipes. This procedure, in effect, emulates the methodology developed by Professor Deininger at the University of Michigan (Lee et al., 1991) based on the concept of coverage that is defined as the percentage of total demand that is sampled by a set of monitors.

4.4 Alert Management Systems

Alert management systems consist of two general areas: (1) establishing parameters for alert triggers and (2) reducing false alarms. During the data analysis phase, new data points are compared to baseline data values. The baseline should incorporate all potential variations due to seasonal water quality fluctuation and cover typical operational changes (Carlson et al., 2004). It may be necessary to incorporate up to a year’s worth of data into the baseline for it to adequately capture these variations. The baseline must also differentiate between single data versus multiple data streams (i.e., one physical/chemical parameter versus multiple parameters), but the amount of baseline data needed will vary according to the technology used and the statistical variance of the data (AWWA Workshop, 2004). Any anomalies in the comparison of new data to the baseline trigger alerts to the operator. For example, Hach Company (Loveland, CO) has developed a trigger algorithm to create an alarm when conditions in water depart from expected baseline parameter values. Because utilities regularly experience changes in water quality, there are always concerns regarding false-positives.

Alert management systems usually rely on strict data validation protocols or specialized software to reduce false alarms. PureSense Environmental, Inc. (Moffet Field, CA), for example, created a software product to reduce false-positive and negative readings in standard water quality sensors. EPA had entered into a CRADA with PureSense Environmental²⁵ to test the system to determine if the software can reduce false signals in EWS in water distribution networks. PureSense systems are currently in use in public water systems and in the U.S. military.

4.5 Integrating Water Distribution Modeling and Data Acquisition Systems

The following systems comprise the state-of-the-art in integrating water distribution modeling and data acquisition to support the goals of an EWS.

MIKE NET-SCADA unites EPA modeling software and SCADA systems in an effort to optimize system performance to recognize and respond to alarm conditions. The system’s online module performs real-time comparisons of the measured and calculated data, automatic data pre-processing

for the off-line module, and pressure/flow calculations at any point of the system. The model results are stored back into the SCADA database and the online viewer is used to display detailed model results (Fontenot et al., 2003). In addition, the online module features automatic data validation procedures, in which all measurements are automatically checked and validated with standard modules. These modules will tag questionable data and, if possible, fill in gaps in the time series. This ensures that only validated data will be transferred and used as boundary conditions in the strategic model, decreasing the potential for false alarms (Fontenot, 2003).

MIKE NET-SCADA's off-line module models IF-THEN scenarios, models system breakdowns, and predicts system behavior using demand and control rules prediction. It uses Microsoft Access to store and maintain model alternatives. Coupling the online and off-line results of MIKE NET-SCADA allows the operator to quickly detect abnormalities and help analyze ways in which the abnormality can be remedied or its impact minimized (Fontenot, 2003).

Clarion Sensing Systems' (Indianapolis, IN) Sentinal™ is a remote computing platform that features logical data processing at the monitoring sites and compatibility with various forms of wireless and wired data transmission. The system integrates sensor data into a single display that presents information through the Internet, a local area network, or a local terminal. The data are presented in a web page format with analytical and historical data storage capability. Each monitoring site has its own Internet Protocol address and serves its own web page to allow for specific site monitoring and remote configuration of the water quality profile of the site. The Sentinal™ system can be integrated into an existing system such as SCADA, and its software is compatible with spiral development approaches, since new sensor technologies can be integrated into the system (Martin Harmless, Clarion Sensing Systems, personal communication).

AQUIS is a water network management system designed for both on- and off-line, real-time monitoring. The software, produced by Seven Technologies (Denmark),²⁶ is used to create models to efficiently manage water resources. The models allow utility managers to minimize the impact of operational disruptions in order to maintain continuity and quality of service. The software also allows managers to explore strategies for responding to emergencies, including the introduction of contaminants and increased demands placed on the system by extensive fire-fighting or other surge demands. AQUIS is currently in use in 1,500 cities worldwide.

AQUIS offers a Contingency Management Software Package that has five modules designed to establish a point of entry for contaminants, determine a method for limiting the spread of the contaminant, and determine methods to mitigate any harmful effects. The modules include a model manager for GIS data management and a hydraulic module for modeling throughout the distribution system. A water quality module tracks the chemical composition of the water throughout the system, and a diagnostic module identifies the source of contaminants. Finally, a flushing module facilitates cleaning the distribution network.

4.6 Data Security

Utility management is provided routine characterization of water through daily, weekly, and monthly reports. Monitoring data are often collected by SCADA information and then analyzed. A major concern is that most data are not secure or encrypted by SCADA and could be subject to security breaches. Thus, security enforcement is a major issue for all EWSs to ensure the integrity

of the system. There are a number of security considerations related to the design of an EWS. Hardwired data transmission systems have the benefit of being more secure than wireless, because it is harder to obtain the physical connection to the cable required for data interception (AWWA Workshop, 2004). Hardwired systems also may be more robust during a crisis situation because there could potentially be issues with wireless network availability. A number of wireless transmission systems rely on an outside network, which makes it difficult to ensure their security. Similarly, Internet-based software applications like those in the Sentinal™ system are vulnerable to viruses and hackers. Ideally, the SCADA system should be isolated from other systems to avoid competition for bandwidth and prevent potential system crashes (Carlson et al., 2004).

In addition to a secure design, the water distribution facility should establish security policies to be followed by all personnel and develop a security module for the EWS. Policies should restrict data sharing and document access to the public, especially concerning sensitive information such as individual sensor locations. Need-to-know requirements and data quality and integrity objectives form the basis for these security policies (Mays, 2004).

The security module includes three areas of protection:

- *Authentication.* A password-based authentication mechanism should be employed for users to access the sensor data and document databases.
- *Access Control.* A fine-grained access control system is capable of specifying access control permissions based on the users' credentials, which are verified electronically.
- *Secure Data Transfer.* Encrypted communication using protocols such as SSL (Secure Socket Layer) helps ensure confidentiality and integrity of the sensor data and documents during their transit from the sensors to the system, as well as from the system to the users.

4.7 Communications, Response, and Decision Making

EPA's Response Protocol Toolbox (EPA, 2003/2004) provides guidance to utilities and response agencies for evaluating, communicating, and responding to threats to the water system. Managing the threat is based on the Incident Command System (ICS) in which the utility names a Water Utility Emergency Response Manager (WUERM) to be the initial Incident Commander. EPA's guidance specifically outlines a threat management system in which three main threat levels occur, "possible," "credible," and "confirmatory." At each level, there are evaluation, notification, and response suggestions. Although information from many sources (e.g., outside law enforcement) can elevate the threat from one level to another, the focus in this study is on how information on water contamination provided by EWSs or subsequent laboratory analysis elevates the threat level.

A "possible" threat exists with the first sign of unusual water quality that significantly differs from established baseline data. This information could be provided by multi-parameter water quality monitors. The data should be compared with other monitoring locations to determine if changes in source water could be the cause of the unusual data. Such possible classifications result in notifications within the utility. Response may include identifying sites and initiating a site characterization in order to rapidly test the water and collect samples for possible delivery to a laboratory. Other responses include investigating unusual consumer complaints and consulting with external information sources.

A “credible” threat exists when additional information collected during the site characterization, as well as other factors, corroborate the threat warning. Evaluation at this stage should determine if the unusual data are substantially different from other water quality episodes, if the unusual water quality is indicative of a specific contaminant, and if the unusual water quality is clustered in a specific area. “Credible” threats result in notification of the drinking water primacy agency, state and local public health agencies, local law enforcement, and the Federal Bureau of Investigation (FBI). At this stage, appropriate response should estimate the affected area and isolate it if possible, implement appropriate public health protection measures, and further analyze samples from the site characterization in a laboratory.

“Confirmation” represents the transition from a credible contamination threat to a confirmed contamination, based on definitive information that the water has been contaminated. Often at this stage, the contaminant information is available. Emergency response agencies, as well as the National Response Center, are notified. The WUERM is no longer responsible for incident command at this stage, but still plays a vital role in helping other agencies. An external source that may help determine the “confirmatory” stage is the WCIT, which is currently in development by EPA. At this point, the local Emergency Operations Center (EOC) may be fully activated in order to support an effective and coordinated response. All of the participating organizations will likely be coordinated under existing incident command structures designed to manage emergencies at the state or local level. One agency will be designated as a lead agency and will be responsible for incident command. Public health protective measures are revised as necessary and may include a “boil-water” notice, a “do not drink” notice, or a “do not use” notice, which involves consideration of an alternate water supply for consumption, sanitation, and other uses.

Water utilities and public health officials should develop specific criteria for making important notifications and to identify key contacts within each agency. These criteria will ensure that effective communications occur and appropriate public health response actions are taken in the event of a water-related public health incident. EPA recommends the use of the Water Information Sharing and Analysis Center (WaterISAC) for rapid information exchange.²⁷ The WaterISAC has secure portals and established protocols for handling information. A WaterISAC security analyst follows up on incident reports. When responding to the threat, three factors should be considered: (1) the credibility of the threat, (2) the potential consequences of the contamination incident, and (3) the impact of the response action on consumers.

AwwaRF, with its partner the Water Environment Research Foundation (WERF), is conducting research to assist utilities in efforts to communicate, respond, and make decisions during a disaster such as a terrorist attack. In one research effort, AwwaRF/WERF is developing written and oral message statements to be used by public agencies and elected officials to communicate with the public in the event of a water contamination threat (see Appendix D, Project #3046). They will also include an action plan for working with the public to increase public awareness of potential public health risks, and appropriate responses. Another research effort is to provide a decision support system for water distribution system security. The effort, involving Colorado State University and Advanced Data Mining, will provide a broad and substantial knowledge base for utilities about the impact of a toxicological attack on a distribution network and cost-effective approaches for detecting and mitigating such attacks (see Appendix D, Project #3086).

Summary reports containing monitoring data could assist in the response. Such reports are increasingly being developed in electronic format. To support the communications of contamination information, there are the beginnings of web-based communication of results to critical response agencies (AwwaRF, 2002). Data communication between online monitors is becoming part of a “knowledge-based” management environment (Rosen et al., 2003). Furthermore, water utilities serving more than 3,300 people have developed emergency response plans under the Public Health Security and Bioterrorism Preparedness and Response Act of 2002. These plans help in facilitating response and decision making.

[this page intentionally left blank]

5. Multi-Parameter Water Quality Monitors as Candidates for Early Warning Systems

As noted elsewhere in this report, a first-stage approach to online screening for contaminants has typically been the use of readily available online sensors that measure simple physicochemical parameters typical for monitoring water quality (e.g., temperature, pressure, pH, conductivity, chlorine residual). A second-stage is analysis that confirms and identifies the contaminant. Exhibit 3-3 provides a more complete discussion of the Stage One/Stage Two approach to an EWS. Technologies to continually measure basic water quality parameters have been commercially available and widely used by utilities for some time. They are used for process control and to ensure regulatory compliance. These technologies are rapid and relatively easy to use on a continuous basis via remote access to data and are available from a variety of manufacturers. Vendors have developed panels of sensors that monitor multiple water quality parameters. The most basic application for such sensors is to detect a physical and/or chemical change in water quality (e.g., change in state) that might suggest that a contaminant had been accidentally or intentionally added to the water. The goal is to use multi-parameter water quality monitors to provide an online early warning or red flag of an unspecified contaminant. This has been referenced by some in the field as a Stage One EWS (Hasan et al., 2004).

A more advanced application for the use of routine physicochemical sensors is the attempt to establish a characteristic pattern of changes in multiple parameters that might be used to actually presumptively identify the contaminant. Such a characteristic pattern is often termed a contaminant signature. This application is currently in the development and testing phase and is being actively pursued by several manufacturers and government research groups. Applications utilizing routine multi-parameter water quality monitors (e.g., simple detection of change of state as well as establishment of a contaminant signature) are described in this section.

5.1 Descriptions of Various Multi-Parameter Water Quality Monitors

Typical multi-parameter water quality sensors for finished water have the following types of water monitoring methods:

- colorimetric and membrane electrode for chlorine
- thermistor for temperature
- membrane electrode or optical sensors for DO
- potentiometric method for ORP
- glass bulb electrode for pH
- nephelometric method or optical sensor for turbidity
- conductivity cell method for specific conductance
- ion-selective electrodes for Cl^- , NO_3^- , and NH_4^+

In addition to basic screening of single parameters by individual sensors, some vendors are now offering preassembled packages consisting of several conventional water quality sensors. The following are a few example multi-parameter platforms of water quality sensors. All of these are considered available technologies except for STIP-Scan, which is designed for wastewater applications but is potentially adaptable for drinking water. **EPA does not endorse or recommend**

any of the following technologies. The summary information below was obtained from company websites, promotional literature, and personal communication with company representatives.

The Hach Corporation (Loveland, CO) is marketing the Water Distribution Monitoring Panel. This panel combines established instrumentation into a preconfigured system for more comprehensive monitoring. The basic model includes the following:

- Hach CL17 Chlorine Analyzer
- Hach 1720D Low Range Turbidimeter
- Hach/GLI pH Controller
- Hach/GLI Oxidation Reduction Potential Controller
- Hach/GLI Conductivity Controller
- GEMS Pressure Sensor

The expanded model also includes a Hach Astro UV TOC analyzer and an American Sigma 900 MAX auto sampler that can be activated to collect and archive samples when pre-specified setpoint values are exceeded for any of the parameters being measured. The Hach Distribution Monitoring Panel is designed to continually measure these six to seven physicochemical parameters from a side stream of water in a municipal distribution system, and the results can be reported directly to the utility SCADA system.²⁹

In addition to the system designed to continually sample a side stream of water, the Hach Corporation is also marketing a multi-parameter probe that is installed directly into a water distribution pipe. The Hach Water Distribution Monitoring PipeSonde In-Pipe Probe can be installed into any water pipe (at least eight inches in diameter), via a two-inch corporation stop



(ball valve), and is designed to withstand water pressures of up to 300 psi. The Pipe Sonde can measure the following parameters: pressure, temperature, conductivity, turbidity, ORP, DO, and chlorine concentration. A sample port is available for attachment of an autosampler and a TOC analyzer. As was the case with the Hach Water Distribution Monitoring Panel, the PipeSonde In-Pipe Probe can be configured to communicate directly with a utility's SCADA system. The Hach Event Monitor Trigger System allows for real-time analysis of data from the Water Distribution Monitoring Panel, PipeSonde In-Pipe Probe, and the online TOC analyzer. It triggers an alarm when water quality deviates from a baseline. It can thus profile and catalog events. The trigger signal and all parameter measurements can be viewed from the main touch screen interface³⁰. (Image reproduced with permission from Hach Company.)

Dascore, Inc. (Jacksonville, FL) markets a multiarray sensor called Six-Cense™. The Six-Cense™ system, like Hach's Pipe Sonde, is designed for permanent insertion into a pressurized water main. However, unlike the Hach products, Six-Cense™ consists of electrochemical sensors mounted on

a one square inch ceramic chip layered with gold. Measurement is accomplished via electrochemical methods, rather than through the use of reagents. The system can continuously monitor six parameters including chlorine or chloramine, DO, pH, ORP, conductivity, and temperature. The system can be operated remotely with data reported to the utility SCADA system.³¹

Emerson Process Management - Rosemont Analytical (Columbus, OH) is marketing a continuous-monitoring system for freshwater and water distribution networks. The Model WQS Multi-Parameter Electrochemical/Optical Water Quality System (Model 1055 Solu Comp II) continually analyzes a low flow (< 3 gal/hr) side stream of water. No reagents are utilized. Six parameters are analyzed by electrochemical methods (pH, conductivity, ORP, DO, free chlorine, and monochloramine). Two parameters are assayed via optical methods (turbidity and particle index). The particle monitor counts particles utilizing optical laser technology, and reports particle concentration as a particle index.³²

(Image reproduced with permission from Emerson Process.)



**Model 1055 Solu Comp Analyzer
(Emerson Process)**

YSI Environmental, Inc. (Yellow Springs, OH) produces standard equipment to monitor drinking water for ORP, DO, pH, specific conductance, and temperature. In addition, YSI systems measure turbidity, and levels of chloride, ammonia nitrogen, and nitrate nitrogen. YSI currently uses its technology in surface water applications. (Image reproduced with permission from YSI Environmental.)



(YSI Environmental)

Analytical Technology, Inc.'s, (Collegeville, PA) Series C15 Water Quality Monitoring system allows the user to choose those parameters for which monitoring is desired and to integrate those components into a monitoring package suitable for continuous monitoring, alarming, and data collection. System components are currently available for free chlorine, combined chlorine (for chloramine treated systems), dissolved ozone, pH, ORP, conductivity, and temperature. In addition,

DO and turbidity modules will be added to the system in the future.³³



Sentinal™ (Clarion Sensing Systems)

Clarion Sensing Systems' (Indianapolis, IN) Sentinal™ integrates sensor data into a single display which can be viewed remotely (e.g., over the Internet). Clarion sells the complete system including sensors, or can integrate a utility's existing sensors from a variety of manufacturers. The system is modular, so utilities can select to monitor various parameters including: chlorine,

pH, temperature, flow, pressure, conductance, turbidity, ORP, DO, radiation, TOC, VOCs, and certain chemical weapons. The Sentinel™ software is compatible with spiral development approaches, since new sensor technologies can be integrated into the system. The system can run off of AC current or solar power and automatically re-boots if power is interrupted. Data can be transmitted via LAN or satellite link (Martin Harmless, Clarion Sensing Systems, personal communication) (Image reproduced with permission from Clarion Sensing Systems.)³⁴

STIP-scan from STIP Isco GmbH (Germany) analyzes multiple wastewater parameters with a single device. Although designed for wastewater applications, the equipment is potentially adaptable for drinking water distribution systems. Designed to operate in municipal and industrial wastewater treatment plants at the inlet, in the aeration basin, and in treated effluent, the STIP-scan UV/Vis spectroscopic sensor is capable of simultaneous measurement of nitrate, chemical oxygen demand (COD), TOC, spectral absorption coefficient (SAC254), total solids, sludge volume, sludge volume index, and turbidity. It can also be used for river monitoring. In addition to these parameters, the STIP-scan measures absorption in any specified range within the wavelength spectrum from 190 to 720 nm for detection of other compounds. No sample filtration or preparation is required, and the wiping action of the piston seals cleans the measuring cell on each cycle. The controller is equipped with analog outputs and a bidirectional serial interface to transmit data. A color display presents the data as continuous daily graphs of nitrate, COD, TOC, or SAC254. Data intervals are two minutes and can be stored up to 14 days.³⁵

5.2 Efforts to Determine Performance of Multi-Parameter Water Quality Monitors and Establish Water Quality Baselines

During the process of developing a workable EWS based on multi-parameter water quality monitors, there are various validation steps that are occurring simultaneously. These include efforts to determine the performance of multi-parameter water quality monitors as well as establishing operating water quality baselines so that anomalies can be spotted. Several tests have and are being performed at EPA. Some efforts have occurred under CRADAs. Under the Federal Technology Transfer Act, EPA can form CRADAs with the private sector in order to speed the development of technologies for various programs. In forming these CRADAs, EPA is aiming to continue research into the detection and identification of contaminants, response and mitigation, and prevention and protection. Private industry, as well as state and local governments, can utilize CRADAs to access federal laboratory equipment, personnel, and services.³⁶

EPA has used its T&E Facility in Cincinnati, OH, for much of the past research. The specific center is called the WATERS. Within the WATERS Center, there are multiple DSSs, which were designed and fabricated by the NRMRL to evaluate and understand the dynamics that influence water quality within water distribution infrastructure systems typical in the U.S. and abroad.³⁷ EPA research investigators selected a platform array of real-time online sensors and instrumentation that represent the various types of technologies currently used by utilities to monitoring water quality. Experiments are underway to evaluate the selected online water monitoring sensors in the various DSS units for their ability to detect changes in water quality due to chemical, physical, and microbial contaminants at concentrations that would present a public risk in a distribution system. Water quality sensors utilized for the EPA WATERS Center studies can be classified in two groups—traditional sensors and continuous monitors. EPA is conducting studies to evaluate the sensitivity, response, limit of detection, reproducibility, potential for false-positives/false-negatives,

and other limitations of the selected sensors. The individual conclusions of these evaluations are discussed in Chapter 9.

5.2.1 Evaluate Sensor Performance

An important part of developing a first stage EWS is to evaluate whether the normal operation of water distribution systems can be documented in terms of sensor response. At the WATERS Center, EPA has conducted tests to understand which sensors can determine a baseline water quality and if sensor drifting takes place. A basic conclusion was that specific-conductance, TOC, and free chlorine monitors drift very little when properly calibrated and serviced, and therefore these sensors are ideal for characterizing normal or safe conditions (EPA, 2004).

5.2.2 Investigate Baseline for Water Quality

The USGS New Jersey District, EPA, and a local water utility, under an Interagency Agreement, will plan a study to implement and test an EWS in an actual water distribution system. The study will test sensors, optimize the sensor location, and develop a baseline water quality profile of the distribution system (DSRC Meeting, 2004). AwwaRF has two projects that analyze online water quality data to address normal fluctuations in water quality parameters and develop methods to differentiate them from contamination events (see Appendix D, Projects #3035 and #3086).

5.2.3 Verify Sensor Performance

Another series of tests is currently being conducted at the EPA WATERS DSS facility to verify the capability of multi-parameter water monitors for normal daily operation of distribution systems. The testing is being performed under the auspices of EPA through the ETV Program. The work is being performed by Battelle Laboratories (Columbus, OH), which is managing the ETV AMS Center through a cooperative agreement with EPA. Vendor representatives are installing, maintaining, and operating their respective technologies throughout the test (Ryan James, Battelle, personal communication³⁸) A CRADA with EPA will test YSI technology in water distribution systems to determine how applicable the technology is to online monitoring of water distribution. This project is separate from the research project described below, because the sensors are being verified for their ability to perform as basic water quality monitors, and their response to injected contaminants is not being tested.

5.3 Efforts to Provide Red Flag EWS and to Identify Specific Contaminants via Signature Using Multi-Parameter Water Quality Monitors

There is an increasing level of activity to examine the use of multi-parameter water quality monitors to provide a red flag EWS and to identify the actual contaminant using signatures. Historically, utilities have invested in multi-parameter water quality monitors to enhance the management capabilities of drinking water treatment plants' and distribution systems' daily operations. If these same monitors prove to be useful for detecting even a subset of intentional contamination events, then the monitors would serve dual purposes. If the same equipment can be used for both daily operations and for detecting system perturbations due to intentional contamination, then their value to utility companies would be enhanced. Further details of the evaluation are provided in Chapter 9.

5.3.1 Sensor Response to Contaminants

At the WATERS Center, EPA investigated whether various sensors could identify contaminants. The conclusion was that certain sensors can provide only a general indication of the contaminant class (such as inorganic, organic, or a reactive species producing chlorine demand) (EPA, 2004).

5.3.2 Multi-Parameter Response to Chemical or Biological Agent Simulants

Another study at EPA's WATERS Center investigated the response of a combination of off-the-shelf sensors to detect changes caused by the injection of wastewater, groundwater, a chemical mixture, and individual chemicals. The sensor system showed promise for providing quick detection of water quality changes caused by these contaminants. With additional optimization, a system of sensors may be used as an EWS (EPA, 2004). However, because the range of contaminants was narrow, additional types of contamination and scenarios should be examined to further test this conclusion.

5.3.3 Signature Development

An advanced application of conventional physicochemical sensors for security monitoring is the presumptive identification of a specific contaminant through interpretation of a characteristic pattern of changes (signature) in multiple parameters. Typically, the interpretation of such a pattern of changes is accomplished with the help of a computerized data system. Just as in the previously described effort to infer the occurrence of an unidentified contaminant by observing a physicochemical change, a reliable parameter baseline must first be established for successful interpretation of sample results. Furthermore, when attempting to actually identify a contaminant through observation of a characteristic pattern of changes in parameter values, it is also necessary to characterize the expected changes in multiple parameters ahead of time. The signature data for the characterization would need to be obtained empirically. Several manufacturers are exploring this signature approach for water contaminant monitoring. One company, Hach (Loveland, CO), has tested this signature approach.³⁹ The signatures being developed by Hach and others to identify contaminants or classes however, are difficult to independently validate because their methods and algorithms are not available to the public. Also, the examination of water quality parameters for use in detecting and identifying contaminants is still being evaluated by EPA, USGS, the Army, and other organizations, and there has yet to be implemented a field-scale test of a full EWS with these water parameter components. These add to the caution in currently recommending use of these water quality parameter-based EWSs.

5.3.4 Further Testing of Signature Concept

To quickly facilitate the development and use of multi-parameter water quality monitors as part of an integrated EWS for water distribution systems, EPA has entered into a CRADA with Hach Company. Hach Company currently produces a real-time water distribution monitoring panel that is composed of several different types of sensors. The CRADA will determine if this technology can be adapted to real-time monitoring of water distribution systems to detect contaminants such as pesticides, herbicides, industrial chemicals, and wastewater.

5.3.5 Multi-Parameter Response to Actual Chemical and Biological Agents

Working with EPA, the Edgewood Chemical Biological Center (ECBC) is planning to test multi-parameter water quality monitors using actual CBR Agents.

[this page intentionally left blank]

6. Technologies that Detect Chemical Contaminants for Early Warning Systems

6.1 General Introduction to Assays and Sensors

The technologies presented in this chapter are for the detection of chemical contaminants. However, several of the technologies are also capable of detecting microbial pathogens. For EWSs, second-stage confirmation technologies can come mostly in the form of portable field kits or hand-held sensor devices. Online and kit assay biomonitors that measure effects on biological organisms are also included even though they do not identify specific contaminants. Online gas chromatography and mass spectroscopy (GC-MS) is also included, and although it may be too expensive for continuous operation, it would be valuable for remote identification when triggered by a stage one alarm (e.g., red flag). Kits are generally portable versions of bench top assays that require pipetting, mixing, and reaction containers. They may also require a reader device for monitoring the assay reaction. Sensors and detection devices can be based on a variety of technology platforms, many of which are described in this chapter and Chapter 7, and can be of a suitcase, backpack, or hand-held size.

EPA does not endorse or recommend any of the following technologies. Much of the summary information below was obtained from company websites, promotional literature, personal communication with company representatives, and some government sources.

6.2 Available Technology

6.2.1 Detection of Arsenic

To evaluate the presence and concentration of arsenic in water there are two basic types of technologies that are used in commercially available tests, which have been third party verified by EPA's ETV Program (see Chapter 9 for verification results). Both types of technologies are used in portable devices designed for onsite rapid analysis of arsenic in water. The first type involves a color reaction kit in which a water sample is mixed with a series of reagents producing a color change in an indicator, which is then compared to a standard color gradient that corresponds to the concentration of arsenic in the water.

Industrial Test Systems, Inc. (Rock Hill, SC) offers five Quick™ test reaction kits that identify arsenic levels at varying concentrations, depending on which kit is used. For these products the indicator strip, in addition to being read visually, can be read with the hand-held instrument or with a portable scanner and laptop system. Both operate on the same principle as a colorimeter, provide a quantitative result, and are available separate from the test kits. All five Quick™ tests are easy to use and easily transportable to the field. The time to analyze one sample is approximately 15 minutes. Peters Engineering (Austria) offers the AS 75 arsenic test kit, another color reaction kit, which is also field portable. It measures the color change in a filter after reagent tablets are dropped into the sample by visual comparison to a color chart, or by the battery operated AS 75 tester. Another color reaction test kit is the As-Top Water test kit offered by Envitop, Ltd. (Oulu, Finland). The kit is easily transportable to the field and analysis takes 35 minutes (EPA-ETV, 2004).

A second type of test to evaluate arsenic concentrations employs anodic stripping voltammetry (ASV), which can be used to analyze various analyte metal ions. The measurement is performed

in an electrochemical cell. A reducing potential is applied to the working electrode. When the electrode potential exceeds the ionization potential of the analyte metal ion in solution (in this case, arsenic), it is reduced to the metal which plates on the working electrode surface. The analyte is then stripped (e.g., oxidized) off the electrode by an applied potential. The electrons released by this process form a current, which is measured and can be plotted as a function of applied potential to give a “voltammogram.” The current at the oxidation/stripping potential is read as a peak, and to determine analyte concentration the height or area of the peak can be measured and compared to that of a known standard solution (EPA-ETV, 2004).

Monitoring Technologies International Pty., Ltd. (Perth, Australia) offers the PDV 6000 portable analyzer which measures arsenic in water using ASV. For this device, the sample concentration result is provided as a digital readout on a hand-held controller, or can be measured using VAS Version 2.1 software. The PDV 6000 portable analyzer is easily transported from the field to a storage shed where samples are analyzed. Instrument setup and calibration takes about 30 minutes and analysis time per sample is about five minutes. Another device that employs ASV technology is the Nano-Band™ Explorer made by TraceDetect (Seattle, WA). This device has a three-electrode cell which combines a Nano-Band™ Explorer electrode with a reference and auxiliary electrode. The samples take one hour to prepare prior to analysis, then the concentration is detected within seconds and displayed in real-time using software run on a laptop computer. The Nano-Band™ Explorer is optimized for trace metal analysis and allows for detection of some metals as low as 0.1 parts per billion (ppb). The Nano-Band™ Explorer measurement system includes Explorer software, but not a laptop computer (EPA-ETV, 2004).

6.2.2 Detection of Cyanide

To evaluate the presence and concentration of cyanide in water there are two basic types of technologies in use by commercially available tests, both of which have been third party verified by EPA’s ETV program (see Chapter 9 for verification results). Both types of technologies are used in portable devices designed for onsite rapid analysis of cyanide in water. The first is a portable colorimeter in which a sample and reagent(s) are mixed producing a color whose intensity is proportional to the cyanide concentration. The color is measured photometrically to provide a quantitative determination of cyanide in the sample (EPA-ETV, 2004).

The VVR V-1000 multi-analyte photometer was used with the V-3803 cyanide module and self-filling reagent Vacu-vial® ampoules, all by CHEMetrics, Inc. (Calverton, VA) to test for cyanide concentrations. The CHEMetrics VVR operates on four AA batteries, was easy to operate, and was easily transported to the field. The 1919 SMART 2 Colorimeter with the 3660-SC Reagent System by LaMotte Company (Chesterton, MD) was also tested by ETV. The LaMotte SMART 2 operates at 120V/60Hz and was easy to use and transport to the field. Analysis for one sample takes approximately 22 minutes. The Mini-Analyst Model 942-032 by Orbeco-Hellige (Farmingdale, NY) also operates on four AA batteries. Analyzing one sample takes approximately 18 minutes. The AQUAfast® IV AQ4000 colorimeter by Thermo Orion (Beverly, MA) automatically identifies the species to be measured and selects the method, wavelength, and reaction time. It also operates on four AA batteries and can measure cyanide concentration when used with AQ4006 cyanide reagents. The AQ4000 was easily transported to the field and clear instructions assured easy operation. However, sample throughput for only one sample would take approximately 17 minutes (EPA-ETV, 2004).

The second basic technology type that is used to measure cyanide concentrations in water is found in a device that consists of a solid sensing element containing a mixture of inorganic silver compounds bonded to the tip of an epoxy electrode body. When the sensing element is in contact with a cyanide solution, silver ions dissolve from the membrane surface. Silver ions within the sensing element move to the surface to replace the dissolved ions, establishing a potential difference that is dependent on the cyanide concentration in the solution. Upon calibration with solutions of known cyanide concentrations, these potential differences are converted to concentrations and displayed on the digital readout at milligrams per liter (mg/L) (EPA-ETV, 2004).

One device that employs this technology is the Thermo Orion Model 9606 Cyanide Electrode with the Model 290A+ Ion Selective Electrode Meter, which operates on a 9-volt battery. The Thermo Orion ISE was easily transported to the field and the instruction manual for its use was clear and concise. Sample preparation takes 1-2 minutes per sample, calibration takes between 15 to 20 minutes and each sample took approximately 5 minutes to attain a reading. The Cyanide Electrode CN 501 with the Reference Electrode R503D and Ion Pocket Meter 340i (WTW ISE) by WTW Measurement Systems (Ft. Myers, FL) operates on four AA batteries and was easily transported and used in the field setting (EPA-ETV, 2004).

6.2.3 Gas Chromatography

GC can be used to analyze for a wide variety of organic chemicals such as industrial chemicals and components of fuel oils. Individual organic compounds are separated as the compounds are carried by a carrier gas (e.g., nitrogen, helium, argon, hydrogen) through a packed or coated column containing a stationary phase. The columns are coiled in an oven. At the beginning of the coil, the compound is vaporized into a gas. The compounds separate from each other within the column due to differing affinity among the sample compounds for the gas and liquid phases. As a result, the individual compounds travel through the column at different speeds. The time required to pass completely through the column and reach the detector varies from compound to compound. The components of a complex sample matrix can be separated, compared to known standards, and the concentrations then quantified. For smaller devices, photolithographic machining techniques are used to produce injection and detection systems on silicon microchips (see Section 6.3.5 for general description of microchips). GC alone can only provide tentative identification. For more definitive identification, traditional and microfabricated GC columns can be coupled to detectors such as thermal conductivity detector (TCD), surface acoustic wave (SAW) detector, electrolytic conductivity detector (ECD), electron capture detector, flame ionization detector (FID), photo ionization detector (PID), and mass spectrometer. Volatile organic compounds (VOCs) can be extracted and concentrated from water samples using purge and trap technology. The volatile compounds are initially purged from the water sample using a purge gas such as helium and are sorbed onto an organic resin trap. The compounds are subsequently desorbed from the trap by flash heating and enter the GC column. Purge and trap gas chromatography has been used for years to monitor raw waters such as the Ohio River and Rhine River for industrial spills (ILSI, 1999). In some cases analyses are conducted on grab samples one or more times each day. In other cases sample collection has been automated and occurs at regular intervals throughout a 24-hour period. The units require skilled operators and regular maintenance.

One commercially available automated gas chromatograph that is being used as a continuous online monitoring system for the analysis of VOCs is the Scentograph CMS500 manufactured by INFICON

(East Syracuse, NY). It can operate automatically and unattended providing real-time measurements. The system can measure concentrations ranging from parts per million (ppm) to parts per trillion (ppt) with sampling and reporting of results at programmable intervals. The Scentograph CMS500 analyzes VOCs in water using a modified EPA purge and trap protocol (the SituProbe). Since no pumps, valves, or cells are exposed to the water matrix, there is no need for sample pretreatment or filtration, allowing the analysis of even complex water samples. Currently, a medium-sized U.S. city is using an automated gas chromatograph (INFICON Scentograph CMS500) in its water distribution system to detect trihalomethanes and other chemicals.



HAPSITE® SituProbe Purge and Trap GC/MS System (Inficon)



CT-1128 Portable GC/MS (Constellation Technology Corporation)

Portable versions of GC instruments are also available. INFICON's Scentograph CMS200 is a portable version of the online instrument described above. INFICON's HAPSITE® GC/MS is used in 15 different countries for military and homeland security applications. It is backpack portable, can be operated by individual soldiers, and yields results in minutes.⁴⁰ Constellation Technology Corporation's (Largo, FL) CT-1128, is also a portable GC-MS, but weighing 70 pounds, is set up from the back of a truck⁴¹. (Images reproduced with permission from INFICON and Constellation Technology.)

6.2.4 Enzyme-Based Detection

- **Inhibition of Cholinesterase**

The Severn Trent Field Enzyme Test (distributed by Capital Controls a division of Severn Trent Services, Fort Washington, PA) was developed for qualitative detection of nerve agents in a field setting. The test is based on the inhibition of the enzyme cholinesterase. A membrane disk is saturated with cholinesterase and dipped into a water sample for one minute. If no pesticide/nerve agent is present in the water sample, the cholinesterase on the membrane disk hydrolyzes esters resulting in the formation of a blue color. If sufficient concentrations of pesticide/nerve agent are present, the cholinesterase on the membrane is inhibited, the ester is not hydrolyzed, and there is no change in color (i.e., remains white). The detection limits cited by the manufacturer for pesticides are: carbamates (0.1 to 5 mg/L); thiophosphates (0.5 to 5 mg/L); and organophosphates (1 to 5 mg/L). No data are available for detection limits for nerve agents.⁴²

- **Inhibition of Horseradish Peroxidase - Indicated by Decreased Chemiluminescence**

A chemiluminescence detection technique based on the reaction of luminol and an oxidant in the presence of the enzyme horseradish peroxidase (HRP) can be used to indicate the presence of toxins in a sample. The HRP mediated reaction produces light that is measured by a luminometer. Phenols, amines, heavy metals, or compounds that interact with the enzyme reduce light output and indicate contamination.



Eclox™ Water Test Kit
(Severn Trent Services)

Eclox™, developed by Severn Trent Services (Fort Washington, PA), is a broadband chemiluminescence test that qualitatively assesses a water sample to determine contamination by a variety of chemical and biological agents. The Eclox™ portable kit/luminometer is applicable for both laboratory and field use (EPA-ETV, 2004, photo from ETV Report 2003/2004).⁴³

Aquanox™, developed by Radox Laboratories (Co. Antrim, United Kingdom), is a hand-held water quality-monitoring instrument based on enhanced chemiluminescent technology. Aquanox™ offers onsite analysis of water and effluent waste testing in a range of industrial applications including chemical wastewater treatment plants.⁴⁴

6.2.5 Biosensors

Biosensors work to identify toxic substances in the water using whole-organism or cellular response approaches. Biosensors measure changes in physiology or behavior of living organisms resulting from stresses induced by toxins. This type of biosensor does not identify the specific toxin, but indicates that there is an unusual condition in the water. The overall rationale is that the organism can respond with sensitivity to all the factors that contribute to stress. Fast acting toxins associated with acute effects are most quickly detected. However, slower acting toxins or toxins with chronic effects would not be rapidly detected if they do not also have acute effects. It is important to note that the biosensors presented are not effective for detecting human pathogens because pathogens are often species- or tissue-specific and require incubation times (typically days or weeks) before disease symptoms are noticeable.

Biosensors have used bacteria (prokaryotic cells) and eukaryotic cells, as well as organisms such as daphnia, mussels, algae, and fish. Organisms or cells that have been genetically modified to contain specific response elements and reporter constructs such as bioluminescence can be designed to respond to specific contaminants. Because the living organisms are sensitive to chlorine and other water treatment chemicals, many biosensors are currently limited to raw water application. If such treatment chemicals are sufficiently removed from the sample, the biosensors have the potential to be used at critical points in the water distribution system. Portable sensors can be used to monitor grab samples.

- **Bacteria-Based Biosensors**

Biosensors using bacterial responses show promise for use in early warning screening because bacteria can rapidly react to toxins (biological or chemical). The metabolism of bacteria is disrupted as a result of exposure to toxins. Some detection techniques work by monitoring for reduction in bioluminescence. Some bacteria have natural or engineered bioluminescence, which emits light when the cells are healthy. This bacterial bioluminescence is closely tied to respiration, so that changes in the cellular metabolism or disruption of the cell structure decreases luminescence, which is measureable. Kits come with freeze-dried or customer-activated bioluminescent bacteria. The reconstituted or cultured bacteria are exposed to the water sample and the luminescence is compared to bacteria exposed to control water. A decrease in bioluminescence (light reduction) suggests the presence of toxins. Other detectors monitor bacterial metabolism based on color changes or on bacterial oxygen demand. Substances that interfere with such bacterial monitoring include chlorine, chloramine, and copper.

There are currently several commercially available bioluminescent bacterial monitoring systems that have been verified under EPA's ETV Program,⁴⁵ including Tox Screen II (Check Light, Ltd), BioTox™ (Hidex Oy), MicroTox®/DeltaTox® (Strategic Diagnostics Inc.), ToxTrak™ (Hach Company), and POLYTOX™ (InterLab Supply, Ltd.). Brief descriptions of these technologies are provided below.

ToxScreen-II

ToxScreen-II Rapid Toxicity Testing System was developed by CheckLight, LTD (Qiryat Tivon, Israel). The basis for this technology rests on bacterial metabolism as indicated by bioluminescence. This product uses the luminous bacteria *Photobacterium leiognathi* and special assay conditions to detect toxins in water samples. There are two assay buffers designed to discriminate between organic pollutants and metal toxins at sub-mg/L concentrations. Changes in bioluminescence indicate water toxicity. The system involves a series of steps including sample preparation and a 90-minute incubation period. Results are captured using a portable luminometer, which can be integrated with a personal computer for data acquisition, evaluation, and storage.⁴⁶ The ToxScreen-II test kit costs \$300 and luminometer costs \$2,895 (EPA-ETV, 2004, photo from EPA-ETV, 2004).⁴⁷



ToxScreen-II (CheckLight, Ltd.)

BioTox™

BioTox™ Rapid Toxicity Testing System was developed by Hidex Oy (Turku, Finland) and bases its technology on bacterial metabolism as indicated by bioluminescence. The test uses the photobacteria *Vibrio fischeri*, which reduce their bioluminescent output when exposed to toxic chemicals. The BioTox™ Flash Test is an improved *Vibrio*



Triathler™ Luminometer with Injector (Hidex Oy)

fischeri test for rapid screening of water and sediment samples. The detection process is the same as BioTox™, but BioTox Flash™ automatically corrects for color/turbidity interference and can screen the majority of the samples within a few seconds. The system uses freeze-dried BioTox™ reagent (\$128 for entire kit) together with the Hidex Oy Triathler™ (portable combination liquid scintillation counter, luminometer, gamma counter, totaling \$8,900 with injector)⁴⁸ Results take from 5 to 30 minutes. The product is small enough to be portable, but can only be operated on 110-volt AC electricity (EPA-ETV, 2004, photo from EPA-ETV, 2004).⁴⁹

DeltaTox®

DeltaTox®, developed by Strategic Diagnostics Inc (Newark, DE), is the portable, field-applicable version of MicroTox®, a laboratory testing system based on bacterial metabolism as indicated by bioluminescence.⁵⁰ Both products can detect multiple kinds of toxins by measuring the light output of the photobacteria *Vibrio fischeri*. The organisms'



Microtox® Model 500
(Strategic Diagnostics Inc.)



Deltatox®
(Strategic Diagnostics Inc.)

metabolism and thus light output are reduced in the presence of toxins, indicating sample contamination. Results are obtained in 5 to 15 minutes. DeltaTox® is a self-calibrating photometer that incorporates a photomultiplier tube, a data collection and reduction system, and software. The system costs \$5,900 and the test kit is \$370. MicroTox® Model 500 costs \$17,895 and the reagents are \$360. The DeltaTox® lacks the temperature control chambers of MicroTox® (EPA-ETV, 2004).⁵¹ Both MicroTox® and DeltaTox® are sensitive to chlorine, which makes them difficult for use in water distribution systems. The maker of MicroTox® is developing a commercial online system that can remove the chlorine residual. (Image reproduced with permission from Strategic Diagnostics Inc.)

ToxTrak™

ToxTrak™ Rapid Toxicity Testing System was developed by the Hach Company (Loveland, CO) as a colorimetric test based on resazurin dye chemistry. The basis for this technology is bacterial metabolism as indicated by a color change. The process uses resazurin reduction to measure respiration, a critical pathway for cell viability. Resazurin is a redox-active dye which, when reduced, changes color from blue to pink. Substances that are toxic to bacteria can inhibit their metabolism and thus, inhibit the rate of resazurin reduction. The test indicates the presence of a toxic substance if the color of the dye does not change; a colorimeter or spectrophotometer must be used to determine color changes (not included in the kit). ToxTrak™ costs \$280 for the kit, \$100 for the reagent set, and spectrophotometer cost approximately \$3,950 (EPA-ETV, 2004, photo from EPA-ETV, 2004⁵²).



ToxTrak™ (Hach)

The Hach Company supports the use of this system as a cost effective and wide scope monitoring method for use as an EWS by drinking water utilities.

POLYTOX™

POLYTOX™, developed by InterLab Supply™, Ltd (The Woodlands, TX) uses the respiration of microorganisms to indicate the toxicity of a water or wastewater stream, including the presence of chemical and biological contaminants.⁵³ When activated in water, the mixture of bacterial cultures in POLYTOX™ breathe in oxygen and respire carbon dioxide at a rate that can be monitored and measured as milligrams (mg) of oxygen consumed per liter per minute. A change in respiration rate is an indication of toxins in the sample. The portable dissolved oxygen probe and meter cost \$1,600 and the test kit costs \$147 (EPA-ETV, 2004, photo from EPA-ETV, 2004).⁵⁴



POLYTOX™ (InterLab Supply, Ltd.)

microMAX-TOX

None of the preceding technologies is designed for use in water distribution systems. However, a system called microMAX-TOX Screen is being adapted to distribution systems. Tox Screen is manufactured by SYSTEM Srl. (Italy) and is based on the measurement technology developed by an Israeli company (Check Light, Inc.). It is similar to MicroTox® but applied in continuous online mode. It has two online analyzers, one colorimetric and the other ion selective. The detection mechanism uses freeze-dried bioluminescent bacteria. It is fully automated to activate alarms and conducts the analysis every 30 to 60 minutes (grab samples). Every two weeks, the instrument is re-supplied with a new set of liquid buffers and a freshly hydrated suspension of bacteria. The interfering chlorine residual is continuously removed by sodium thiosulfate. It is expected to be commercially available in 2005 (Grayman et al., 2003).

- **Organism-Based Biosensors**

MosselMonitor®

Mussels will change their behavior in response to toxins, such as closing their shells to reduce exposure to the toxin. Thus, the frequency of valve opening and closing can be monitored to indicate toxin avoidance behaviors. Delta Consult (Netherlands) has a commercially available MosselMonitor® that can be used to monitor chlorinated drinking water by applying a thiosulphate pre-treatment to remove chlorine. Thiosulfate does not remove all disinfectants used in finished water, therefore systems that use chloramines would not be able to use this technology. For drinking water applications,



**MosselMonitor®
(Delta Consult)**

an Automated Food Device (AFD) is used to provide a continuous supply of nutrients. The MosselMonitor® can be run online continuously for up to two to three months before replacement of mussels is necessary. The data presentation software allows for near real-time graphical presentation at a remote location or on the Internet. Only eight mussels are required because each mussel's behavior is analyzed against its own previous behaviors, then the combined results from all eight mussels are analyzed. The MosselMonitor® has been used with five different bivalve species (three for freshwater and two for marine water⁵⁵). The MosselMonitor® has been used by Waterworks of Budapest, Hungary, to monitor chlorinated drinking water. Although the company recommends replacement of mussels every three months, in the Budapest installation the mussels survived 10 months before needing to be replaced (Jan de Maat, Delta Consult, personal communication). (Images reproduced with permission from Delta Consult.)

Fish Bio-sensor®

Biological Monitoring, Inc. (Blacksburg, VA) makes Bio-Sensor®, which monitors the bioelectric field of 8-12 fish to assess if abnormal behavior indicates the presence of a toxin.⁵⁶ Concurrent automated and continuous physicochemical monitoring enhances the reliability of the results. In an event when a toxin is indicated, an alarm is generated both locally and remotely, so as to inform the users. A water sample is also automatically collected should advanced (chemical) analytical verification be desired. A dechlorination module can be added if Bio-Sensor® is installed in the distribution system. An automated feeder reduces the maintenance interval to a recommended once monthly. Bio-Sensor® is currently installed in distribution systems in Singapore, Australia, and South Africa (Joe Rasnake, Biological Monitoring Inc., personal communication). (Image reproduced with permission from Biological Monitoring Inc.)



Bio-Sensor®
(Biological Monitoring Inc.)

6.3 Potentially Adaptable Technology

Several technologies that have been developed for other applications, such as monitoring in source water or air, may be adaptable for use in distribution systems.

6.3.1 Enzyme-Based Detection

- **Inhibition of Photosynthetic Enzyme Complexes (PEC)**

LuminoTox developed by Lab_Bell Inc. (Shawinigan, Canada) utilizes either photosynthetic enzymes isolated from plants, or detection of photosynthetic activity of algae, to detect toxic analytes. Photosynthetic enzyme complexes (PECs) isolated from plants are stabilized by vacuum evaporation for storage. The LuminoTox system using PECs can detect toxic molecules such as



LuminoTox2
(Lab_Bell Inc.)

herbicides, hydrocarbons, phenols, divalent cations, polycyclic aromatic hydrocarbons (PAHs), and aromatic hydrocarbons. LuminoTox used with photosynthetic algae allows for the specific detection for herbicides, organic solvents (e.g., gasoline, hydrocarbons), ammonia nitrogen and organic amines. In the urban and industrial effluents the company has tested, toxicity can be measured in 10 to 15 minutes, while sensitivity of detection can be increased by lengthening the incubation time. The hand-held portable luminometer allows the system to be field portable. In 2005, the company introduced an online version called Robot LuminoTox, which is self-cleaning, monitors pH and temperature, and records a toxicity measurement every 30 minutes. The data are stored in an Excel file. Robot LuminoTox is operated via Windows and can be processed via a SCADA system⁵⁷. (Images reproduced with permission from Lab_Bell Inc.)

Researchers from the Institute of Microbiology (Czech Republic) have demonstrated that Photosystem II complexes coupled to a screen-printed electrode can detect triazine and phenylurea herbicides. The biosensor is reusable with a half-life of 24 hours and limit of detection of approximately 10^{-9} M for diuron, atrazine, and simazine (Koblizek et al., 2002⁵⁸). However, this system is at the research stage.

- **Inhibition of Submitochondrial Particles**

Harvard BioScience, Inc. (Holliston, MA) produces a toxicity detection kit called MitoScan that uses fragmented inner mitochondrial membrane vesicles isolated from beef heart. The submitochondrial particles (SMPs, called “micelles”) contain complexes of enzymes responsible for electron transport and oxidative phosphorylation that are inverted from their *in vivo* orientation. The enzymes in the SMPs produce a hydrogen ion gradient which is used to produce ATP from adenosine diphosphate, and this process (oxidative phosphorylation) is coupled to electron transport as it occurs *in vivo*. Progress of this reaction is directly proportional to the redox state and can be monitored spectrophotometrically at 340 nm. When specific inhibitors or toxicants are added to the SMPs the reactions are slowed or inhibited. The SMP vials from the MitoScan kit need to be stored at -20°C and are viable for up to four weeks. For longer storage, SMPs should be stored at -80°C. The test kits include all necessary reagents and SMPs in 100µl or 500µl vials. MitoScan bioassays can be configured for microwell plate readers or for manual cuvette formats using single-beam spectrophotometers. Cuvettes with a portable spectrophotometer capable of running kinetic assays at 340 nm make the kit field portable. The assay also requires cuvettes, sample dilution tubes, pipettors, and pipettor tips. MitoScan tests can be formatted to provide results in less than 30 minutes.⁵⁹ The kit has not yet been third party verified.

6.3.2 Organism-Based Biosensors

Several biomonitors are available and used for monitoring surface water. They are not currently used in treated water distribution systems because the chlorine residual is toxic to the organisms. Thus these may be adaptable for use in distribution systems if chlorine can be removed, similar to what been done with MosselMonitor® and Bio-Sensor®.

- **Daphnia-Based Biosensors**

Daphnia (water fleas) are small free-swimming organisms that are very sensitive to toxins. A daphnia toximeter consists of daphnids contained in a glass chamber through which sample water

continuously flows. The swimming behavior is monitored by closed circuit TV and analyzed via integrated computer. Variations in speed, altitude, and frequency of turning can indicate a potential contaminant. Sometimes the method for measuring toxins is based on feeding the daphnids fluorogenic food, which when metabolized by healthy daphnids, generates a fluorescent glow. In either identification method, the setup requires high maintenance (e.g., changing daphnia periodically) and the daphnia are sensitive to changes in temperature. The method was extensively used in Europe and during the 2002 Salt Lake City Olympic Games. The method is primarily used to monitor raw water because the daphnids are sensitive to the chlorine in finished water. This makes the method more difficult for use in treated water distribution systems.

The IQ Toxicity Test™ kit for grab samples was developed by Aqua Survey, Inc. (Flemington, NJ) and detects various chemical and biological contaminants, including nerve agents and biotoxins, in potable water.⁶⁰ This method is based on fluorescent tagging and metabolism of live multicellular organisms. In the presence of toxins, the metabolism of *Daphnia magna* is reduced, blocking their normally visible light emittance. Test preparation includes growing and feeding *Daphnia magna* a fluorescent sugar reagent, while the test itself takes 75 minutes. Aqua Survey, Inc., has packaged the IQ Toxicity Test™ into a product called Threat Detection Kit™, which the company claims can detect 9 different toxins at levels 2 to 20 times below the human lethal threshold. Based on EPA's ETV study, IQ-Tox™ can detect both nerve agents and biotoxins (EPA-ETV, 2004). However, the results also may suggest that the test is too chlorine sensitive for use in finished water and distribution systems.⁶¹

The Daphnia Toximeter, developed by bbe moldaenke (Kiel-Kronshagen, Germany), is used on line with a measuring cycle of 30 minutes. Toxicity is assessed based on monitoring the behavioral parameters, swimming speed, swimming altitude, turns and circling movements, growth rate, and number of live daphnia. Allowable temperature range is between 0 to 30°C. The maintenance interval is greater than seven days.⁶²

- **Algae-Based Biosensors**

Algae can be used to detect the presence of toxic compounds by monitoring chlorophyll fluorescence. An Algae Toximeter (bbe moldaenke) cultures algae in a fermenter that regulates the concentration and activity of the algae. A water sample is automatically injected with standardized algae and monitored for changes in fluorescence. Activity of the algae is constant if no toxic substances are present. Monitor maintenance is required, at most, once every seven days.⁶³ The Algae Toximeter has not been adapted for use with finished drinking water. (Image reproduced with permission from bbe moldaenke.)

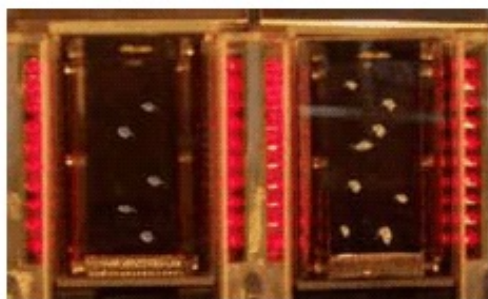


Algae Toximeter
(bbe moldaenke)

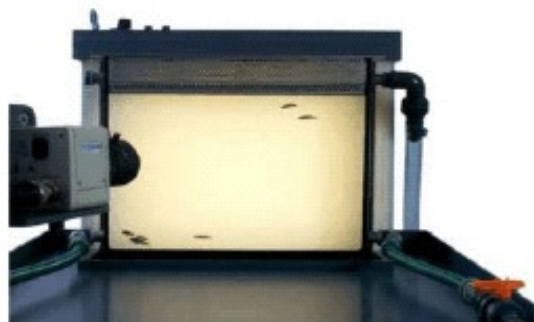
- **Fish-Based Biosensors**

The German company that manufactures daphnia and algal toximeters (bbe moldaenke) also makes a Fish Toximeter and a combined Fish and Daphnia Toximeter. The system uses zebrafish and daphnia which are both fed by an integrated algae fermenter. Both toximeters use visual monitoring for analysis of behaviors to assess organism health. Parameters measured are speed, altitude, turns, circling movements, growth, and number of living fish. The presence of toxins is indicated by

changes in behavioral parameters. The measuring cycle is 1 to 30 minutes and the maintenance interval is greater than seven days⁶⁴. (Images reproduced with permission from bbe moldaenke.)



Daphnia and Fish Toximeter
(bbe moldaenke)



Fish Toximeter Real Time Biomonitoring
(bbe moldaenke)

- **Dinoflagellate-Based Biosensor**

Because human cells are eukaryotic (contain a nucleus and organelles), eukaryotic cell responses could be better models for toxicity to humans than bacterial cell responses. The only eukaryotic cell-based biomonitor currently commercialized for use with water is the dinoflagellate-based Lumitox®. Lumitox® (Lumitox Gulf L.C., River Ridge, LA) uses bioluminescent dinoflagellate mutants to detect the presence of toxins in the ppb range. It is field portable and the company indicates it is unaffected by a broad range of pH, turbidity, and salinity. The American Society for Testing and Materials (ASTM) has published a guide (ASTM E1924-97) for using Lumitox®. It can test both marine and non-marine fluids, soils, and chemicals (either water-soluble or lipophilic). The patented TOX BOX® testing instrument is considered easy to operate, and no computer is required. Grab sample screening can be completed in two to four hours.⁶⁵

6.3.3 Infrared Spectroscopy

HazMatID™ is the newest product from SensIR Technologies (now merged with Smiths Detection, Edgewood, MD)⁶⁶ for identification of a variety of weapons of mass destruction, toxic industrial chemicals, narcotics, and explosives. This is a portable tool using Fourier transform infrared (FT-IR) attenuated total reflection (ATR) spectroscopy for field identification of analytes in the solid or liquid phase. HazMatID™ features an integrated computer system with wireless remote control capabilities to instantly compare the spectroscopy of the unknown contaminant against an onboard spectroscopy database of known substances. Its Bio-CheckIR software can alert the user when at least 10 percent of the sample is composed of proteins, indicating that a possible biological material is present (Mark Norman, Smiths Detection, personal communication). The sample interface is a diamond sensor with integrated video monitoring and is operational in extreme weather and temperatures. Since infrared analysis is limited in aqueous samples containing less than 10 percent product, SensIR has developed an accessory product to HazMatID™, called ExtractIR™. This portable tool physically removes nonvolatile organic chemicals from the interfering water



HazMat ID™
(Smiths Detection)

matrix. By doing this, chemical levels as low as 100 ppm in water can be identified. ExtractIR™ can be used in a hot zone by a responder in full Level A protective gear, and the entire process takes about 10 minutes.⁶⁷ The suitcase unit can be operated in extreme temperatures and can be totally immersed in water for decontamination.⁶⁸ (Image reproduced with permission from Smiths Detection.)

6.3.4 X-ray Fluorescence

ITN Energy Systems, Inc. (Littleton, CO)⁶⁹ has been given an EPA Small Business Innovation Research (SBIR) Phase I award for the period of March 1, 2005 to August 31, 2005.⁷⁰ The ultimate project goal is to adapt ITN's x-ray fluorescence technology to provide a smart, automatic early warning sensor for trace levels of toxic metals in water on a ppb scale. This technology has been proven in solar cell manufacturing where the sensor continuously monitors very small amounts of metal in products and automatically provides feedback to process control. The sensor is capable of simultaneously detecting multiple metals, including mercury, arsenic, and lead. In Phase I, the feasibility of this approach will be demonstrated by showing the sensor can detect 20 ppb of mercury in water without interferences from other metals, chemical state of the metals, or organic material.

6.3.5 Ion Mobility Spectroscopy

Ion Mobility Spectroscopy (IMS) is a technique for identifying and measuring volatile compounds. An ambient air or vapor sample is drawn over a semi-permeable membrane. Smaller volatile compounds pass through the membrane into the detection cell, where the sample is ionized by a weak plasma formed by a nickel-63 radioactive source. The ionized sample molecules drift through the cell under the influence of an electric field. An electronic shutter grid allows periodic introduction of the ions into a drift tube where they separate, based on charge, mass, and shape. Smaller ions move faster than larger ions through the drift tube and arrive at the detector sooner. The amplified current from the detector is measured as a function of time and a spectrum is generated. A microprocessor evaluates the spectrum for the target compound, and determines the concentration based on the peak height.⁷¹ IMS is used in explosives detection equipment at airport security check points.⁷² There are several portable IMS sensors for chemical detection but all have been designed for use with air/vapor samples.⁷³ One example is described below.

Smiths Detection produces a hand-held chemical vapor detector called the SABRE 4000, that utilizes IMS and can detect and identify over 40 threat substances (explosive, chemical warfare agent, toxic industrial chemical, or narcotic substances) in approximately 15 seconds. It takes 10 minutes to warm-up and weighs seven pounds including the four-hour battery.⁷⁴ The Sabre 4000 can be used in two modes, vapor mode or direct thermal desorption mode. In the latter mode, the Sabre 4000 can test liquid or solid samples. Either temperature controlled ramping to evaporate the sample or a fiber solid phase microextraction (SPME) probe are needed to measure aqueous samples. IMS technology can detect volatile organic and inorganic compounds (MW < 1,000) above about 5 to 10 ppb concentrations. The technology could be used to detect many different substances, but only about 40 to 50 profiles can be saved in



SABRE 4000 (Smiths Detection)

the current versions of the sensor devices (Rachel Kohn, Smiths Detection, personal communication). (Image reproduced with permission from Smiths Detection).

6.3.6 Microchips for Portable Chemical Sensors

Not all portable sensors are based on microchip technology, but many are. The name, microchip, is derived from the micrometer dimensions of the individual components that comprise microchips. Any technology that can be miniaturized to the micrometer scale could be mounted on a solid platform and form the basis of a microchip technology. Miniaturization is a key development for making small portable sensors. When semiconductor devices (e.g., transistors and resistors) were miniaturized into the form of microprocessors, the computer industry was revolutionized. Since the early 1990s, other technologies have been adapted to microchip dimensions and technologies that would not be feasible on a macro level have also been invented for microchip platforms. This newer class of microchips is often referred to as “lab-on-a-chip,” because the kinds of data generated by the microchips are comparable to data that would have previously required bench-top sized equipment to gather. “Lab-on-a-chip” generally refers to microetched chambers that can contain nanoliter volumes of liquid to carry out multiple, small-scale, side-by-side chemical and/or biological reactions. Microfluidics technology which allows minute quantities of liquids (reagents and sample) to be manipulated and delivered to microchip components is an essential part of any chip design that utilizes aqueous solutions.⁷⁵

“Microarray” refers to microchips that have zones of unique characteristics. Current technology can allow for as many as 100,000 distinctly unique zones or elements in a microarray. Each element within an array can be designed to react with or respond to a different sample component. For example, if the microarray has elements that recognize different DNA sequences, when a sample of mixed DNA sequences is delivered to the microarray elements, only a subset of the elements will respond to the sample. The response of the elements is detected or “read” by a chip reader device. For example, the chip transducer could be based on optical, piezoelectric, magnetic, electrochemical, or thermometric mechanisms. Although there are many different technologies for reading microchips, the microchip design and the microchip reader device are designed as a single system and in some cases are fully integrated. Microchips may or may not be reuseable. Several companies offer custom designed microchips, which means they will incorporate subsets of elements specific for the particular targets the customer wants to identify.

Micro-Electro-Mechanical System (MEMS) microchips have miniaturized mechanical and electrical components.⁷⁶ Microcantilevers and magnetoelastic sensors are examples of MEMS. Research and development of MEMS-based technologies is a large field covering many potential applications. As this field grew out of the integrated circuit field, much of the technology is built on silicon wafers.⁷⁷

Biochips, which often come in the form of microarrays, are based on biological reactions using biological components such as nucleic acid hybridization, antibody reactions, and enzymatic reactions. Biomolecules are also used for bioelectronic applications in a microchip format. Biochips could be designed to detect biological molecules (DNA, RNA, proteins, biotoxins), or non-biological chemicals.⁷⁸ It’s important to note that the term “biochip” refers to the biological basis of the chip and does not limit the class of targets to those that are biological. Because enzymes,

DNA, and antibodies all work in aqueous environments, microfluidics is an essential part of biochip technology.

There are many kinds of prototype microchips demonstrating proof of concept that have not been commercialized. Commercialized microchips are common in research and diagnostic laboratories, however the support equipment to use the microchips, such as microfluidics stations and chip readers, requires a laboratory setting, including trained personnel. Although microchips are a highly developed technology for genomics, they are an emerging technology for other applications, such as medical devices and environmental sensing.

Because of programs like the National Nanotechnology Initiative⁷⁹ (NNI, a federal R&D program established to coordinate multiagency efforts in nanoscale science, engineering, and technology) and the intense interest and promise in the field in general, it is likely that micro- and nano-based technologies will significantly contribute to product development and commercialization in the near future.

6.3.7 Microchip Surface Acoustic Wave (SAW) Technology

SAW technology has been used for decades in transceiver technology and cell phone technology. For chemical detection, SAW sensors can be configured in a microarray, with each element uniquely coated. Mass changes in a subset of elements due to interaction with a particular volatile chemical causes surface acoustic waves ($\sim 10 \text{ \AA}$ in amplitude, 1 to 100 micrometers in wavelength) which are detected by piezoelectric materials. The subset of elements that respond to a specific VOC can be recognized by software included in the sensor, allowing for a diverse list of detectable analytes.⁸⁰

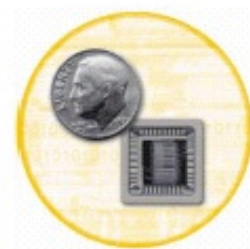
HAZMATCAD™, from Microsensor Systems, Inc. (Bowling Green, KY), features three 250 MHz SAW sensors in a hand-held portable Chemical Agent Detector instrument. Each sensor is coated with different polymers that provide a multi-pattern sensor response (fingerprint) to indicate the presence of contaminants in vapor samples.⁸¹ HAZMATCAD™ detects and identifies trace amounts of chemical warfare agents, including nerve and blister agents, and can be configured to detect phosgene and/or hydrogen cyanide. HAZMATCAD™ Plus supplements the SAW technology with electrochemical sensors for additional detection of up to four classes of toxic industrial chemicals, specifically hydride, halogen, choke, and blood agent vapors. The system operates on 20 to 120 second analysis cycle, depending on the mode selected, and the typical time to alarm is less than 60 seconds in “Fast Mode.” This device has price range of \$4,850 to \$7,950 and has been evaluated by the Army.⁸² (Image reproduced with permission from Microsensor Systems Inc.)



HAZMATCAD™
(Microsensor Systems, Inc.)

6.3.8 Microchip Chemiresistors

Cyrano™ Sciences, now a part of Smiths Detection (Edgewood, MD),⁸³ has developed miniature “electronic nose” sensors using conductive polymer films deposited in an array on a ceramic substrate. Each individual detector of the sensor array is a composite material consisting of conductive carbon black homogeneously blended throughout a non-conducting polymer. The detector materials are deposited as thin films on an alumina substrate that lie across two electrical leads, which create conducting chemiresistors. The output from the device is an array of resistance values as measured



Cyrano™ 320 and NoseChip™
(Smiths Detection)

between each of the two electrical leads for each of the detectors in the array. The polymer composite chemiresistors, are designed to absorb a diversity of analytes. The manufacturers claim that the polymer composite sensors respond to a wide range of organic compounds, bacteria, and natural products in a vapor form. The signature of 100 different analytes can be stored in the memory of the Cyrano® 320 hand-held device, which is commercially available. A penny sized version called the NoseChip™ is being used to develop future products called ChemAlert™ and ChemBioAlert™, which will be integrated into online sensor networks. Although these “electronic noses” are not able to directly measure water samples, if used with vaporizing technology, they could be adapted for water sampling (Rachel Kohn, Smiths Detection, personal communication). (Images reproduced with permission from Smiths Detection.)

6.4 Emerging Technology

Although the biosensor, IMS, and SAW technologies discussed above (Section 6.3) have commercially available products on the market for surface water or vapor media, these technologies are also being used to develop the next generation of sensors so they can also be considered an emerging technology. In addition, fiber optic cables, which are being designed to serve as continuous sensors, are discussed below. These emerging technologies are being developed by companies, national labs, and other research institutes.

6.4.1 Organism-Based Biosensors

- **Clam Biomonitor**

Similar to MosselMonitor®, discussed previously, other groups are investigating using clam responses to detect water quality issues that affect clam behavior. However, these approaches have been limited to source water monitoring. The University of North Texas, Little Miami, Inc. (Milford, OH), and EPA have a joint project to develop a Clam Biomonitoring System. The gape of 15 clams is measured at one-minute intervals and is plotted along with temperature, pH, conductivity, and dissolved oxygen. A cellular modum is used to connect to the Internet for data relay. The system is installed on the Little Miami River in Miamiville, OH.⁸⁴ This system has not been tested in chlorinated drinking water.

- **Fish Biomonitoring**

The Great Lakes Water Institute, a University of Wisconsin research group, is developing a biosensor system using transgenic zebrafish to monitor water distribution systems. The embryos of zebrafish are injected with pollution responsive reporter genes shortly after fertilization. The transgenic fish are designed to detect 18 chemical contaminants, including the biological warfare agents paraoxon and parathion, which are relatives of sarin. The contaminants trigger the pollution response elements, which then activate the production of luciferase in the fish. The enzyme causes the fish to emit light, thereby signaling the presence of a toxin in the water. The fish can be used to repeatedly analyze the same site as the monitoring process does not kill the fish.⁸⁵

The U.S. Army Center for Environmental Health Research (USACEHR) has developed an automated biomonitor-based on bluegill (*Lepomis macrochirus*) ventilatory and body movement patterns.⁸⁶ It was developed to monitor toxins in treated wastewater but has not been adapted for chlorinated drinking water.

6.4.2 Eukaryotic Cell-Based Biosensors

There are emerging technologies that incorporate eukaryotic cells or tissues in assays on microchip platforms for biosensors. The B-cell, cardiac-cell, and fish-cell systems described in this section have not yet been commercialized and are not being developed specifically for drinking water. These emerging technologies could be utilized for drinking water monitoring provided that sample volume concentration and disinfectant residual issues are addressed.

Fish cells could be used to detect toxins through changes in color and movement of chromatophores (primary cells). The cells are stored in disposable cartridges which can be monitored by a video camera through a microscope. The data would be analyzed by a computer for the changes described above. Such a system could show changes within 1 to 100 minutes and could be used in continuous or grab sample mode (Grayman et al., 2003). A prototype system, SOS Cytosensor system, is being developed by Adlyfe, Inc. (Rockville, MD).⁸⁷

A biosensor-based on mammalian cells (cardiac cells) is being developed by Dr. Gregory Kovacs at Stanford University. The cells are cultured on disposable microelectrode arrays. The toxins are detected by changes in electrical discharge, beat rate, and signal propagation velocity. The system is being designed for grab sample analyses using portable hand-held equipment. The Portable Cell-Based Biosensor is in the prototype stage. Mammalian neuronal cells have also been explored as a biosensor by the U.S. Naval Research Laboratory. The neuronal cells are carried in a transportable cell cartridge which is placed in a monitoring device for continuous monitoring for up to two days. A computer program evaluates changes in electrical patterns such as mean spike rates. The system called Portable Neuronal Microelectrode Array is commercially available (Shaffer et al., 2003).⁸⁸

6.4.3 Fiber Optic Cable-Based Sensors

The Great Lakes Water Institute, a University of Wisconsin research group, is developing a real-time water distribution system monitor utilizing fiber optic cables. The Water Security Division of the Great Lakes Water Institute is supported in part by the Water Harvesting and Water Purification Program at DARPA. The monitor consists of a fiber optic cable run through the water conduit, and

various chemical receptors and a fluorescent group are attached to a gel coating the cable. When a toxin binds to a receptor, the characteristics of the fluorescent group, or fluorophore, are altered. Laser pulses passing through the cable detect the change in the fluorophore, providing for detection from a central monitoring station. Spatial maps are generated, based on the data from the laser pulses. The Institute is developing technology to add both biological and chemical receptors to the cable in order to provide a more complete monitoring system, since the only toxins that are detected are the specific ones that the system is designed to detect.⁸⁹

Intelligent Optical Systems, Inc.'s (Torrence, CA) DICAST® technology is composed of fiber optic cables that have a glass core coated with a permeable indicator-doped cladding to achieve chemical sensitivity over their entire length.⁹⁰ Instead of having several sensors at various locations along its length, the entire length of the fiber is a sensor. Thus, it has more sensing area and less probability of missing a target molecule. Although DICAST® has been developed for sensing in air, it could be modified to work in water. The applications of this and other fiber optic sensors include monitoring water for dissolved gases, pH, bio-content, and toxic chemicals and their byproducts such as cyanide (Steven Cordero, Intelligent Optical Systems, Inc., personal communication).

6.4.4 Ion Mobility Spectroscopy (IMS)

Sionex Corporation's (Waltham, MA), MicroDMx™, technology is based on IMS in a MEMS format, but is referred to as differential mobility spectroscopy because a varying radio frequency field pulls the ions in a zigzag pattern increasing the distance they travel thereby increasing their separation.⁹¹ The company has prototype hand-held and online products in development for detection of VOCs in air. The company also has research projects ongoing for adapting the prototypes for water matrices (Joe Santos, Sionex, personal communication). (Image reproduced with permission from Sionex Corporation.)



microDMx™ Chip
(Sionex)

6.4.5 Surface Acoustic Wave (SAW) Technology

S-CAD, developed by Science Applications International Corporation (SAIC; San Diego, CA), is a portable, hand-held chemical agent detection system for air. This product features the dual detection power of an IMS cell and a SAW sensor, combined with a data fusion algorithm to reduce false alarms without affecting detection performance. The system can both identify and specify the concentration of different chemical agents, including nerve, blister, and blood agents. S-CAD has the capability to gather and store data for future analysis, and its modular design allows easy integration with nuclear and biological agent detectors and/or other application specific sensors.⁹² The company is currently examining issues regarding adaptation for water sampling (Steven Haupt, SAIC, personal communication).

Sandia National Laboratories (SNL) has developed the Micromachined Acoustic Chemical Sensor to detect VOCs, explosives, illicit drugs, and chemical warfare agents.⁹³ These miniature sensors (as small as 0.5 mm) incorporate a micromachined flexural plate wave (FPW) device as a general purpose chemical sensing platform.⁹⁴ FPW technology uses polymer films to selectively absorb the analyte of interest and is compatible with both gases and liquids. These devices are analogous to the SAW sensor, which is an extremely sensitive gravimetric detector that can be coated with a film

to collect chemical species of interest down to ppm and ppb levels of airborne contaminants.⁹⁵ The Micromachined Acoustic Chemical Sensor can be fabricated on silicon with integrated microelectronics to complete the sensor capability. Although none of these technologies has been integrated into a commercially available product nor has been designed for use in water distribution systems, SNL believes the technology has high potential for *in situ* chemical detection applications.

SNL has also developed two field prototypes for portable chemical analysis systems, called μ ChemLab, which researchers hope to combine into one complete system by 2008 (μ ChemLab/CB^{TM96}). The Gas-Phase μ ChemLab uses a combination of GC channels coupled with an array of SAW sensors to monitor volatile and semi-volatile organic species in air. This product can detect chemicals at levels as low as 10 to 100 ppb and analysis takes just seconds-to-minutes. The Liquid-Phase μ ChemLab hand-held analyzer utilizes various chip-based technological innovations such as microfluidics, capillary gel, and zone electrophoresis columns that are combined with small laser-induced fluorescence detectors. The detectors can



**μ ChemLab™ Liquid Phase
(Sandia National Lab)**

analyze biotoxins and other inorganic and high MW chemical contaminants. SNL scientists plan to further develop the system so it can detect viruses and bacteria. Nanodetex⁹⁷ (formerly MCL Technologies, Albuquerque, NM) is an SNL spin-off company licenced to develop μ ChemLab for chemical warfare agents, drug detection, and health monitoring. There is also ongoing research to adapt the Gas-Phase μ ChemLab to water applications, including automated onsite measurement of trihalomethanes, petroleum hydrocarbon contaminants, and chemical warfare agents and their hydrolysis products. The ultimate goal is to develop a low-cost, quickly deployable, and real-time discriminatory sensor for water quality determination as well as online versions of the equipment. This technology is funded under the DOE's Chemical and Biological Non-Proliferation program and is also a candidate system for the DOD's Joint Chemical Biological Agent Water Monitor project (Wayne Einfeld, SNL, personal communication). SNL, CH2M Hill (Colorado), and Tenix Investments (Australia) have signed an agreement that calls for an online water monitoring prototype, based on μ ChemLab, to be developed and begin testing by June 2005.⁹⁸ The first phase of testing will focus on detecting ricin and botulinum toxin. The development team eventually also hopes to address viruses, bacteria, and parasites. (See Appendix B for summaries of SNL research projects related to detection technologies; photo from SNL website.)

Pacific Northwest National Laboratories (PNNL; Richland, WA) has designed a SAW-based sensor system to detect chemical warfare agents in the field. The SAW sensors have chemically selective polymer coatings to provide rapid, reversible analysis of multi-component chemical vapors. Chemometric analysis is used to distinguish between multiple vapor signals, which is the application of mathematical, statistical, graphical, or symbolic methods to maximize chemical information which can subsequently be extracted from data. The system is integrated with computer control and data acquisition and has been deployed and demonstrated in the field. PNNL researchers have also improved the sensitivity of traditional SAW sensors by coating them with synthesized novel hydrogen bonding organic/inorganic copolymers. The sensors reach 90 percent of full response within six seconds of the first indication of response when exposed to nerve agent simulants and organic solvents. In tests using actual nerve agents, response sensitivity was increased at least four times over traditional sensing polymers. PNNL's new copolymers are currently being used in

commercially available chemical sensors for the detection of nerve agents. Copolymer technology is available for licensing.⁹⁹

6.4.6 Raman Spectroscopy

Real-Time Analyzers, Inc. (East Hartford, CT)¹⁰⁰ has recently been received an EPA Small Business Innovative Research (SBIR) Program Phase I award for the period of March 1, 2005, to August 31, 2005, to provide the Agency with a chemical sensor that can be multiplexed into water distribution systems to provide an EWS capability. Surface-enhanced Raman scattering (SERS) sensors will be coupled to a central Raman analyzer via fiber optics. The objective of the project is to develop sensors that will selectively detect several chemical agent hydrolysis products, toxic industrial chemicals, and pesticides at concentrations below 1 mg/L in flowing streams in 10 minutes or less.

7. Technologies that Detect Microbial Contaminants for Early Warning Systems

7.1 General Introduction to Assays and Sensors

Currently, microbial culture methods are relatively slow, requiring at least 24 to 48 hours before results are available. With traditional techniques, growth of the target organisms in culture is required for identification. Ideally, microbial monitoring methods should be rapid, providing results in two hours or less. The methods presented in this chapter begin to meet these criteria. Sensors for living organisms can target detection of genetic material (nucleic acids), proteins, or other components or activities of living cells such as adenosine triphosphate (ATP). Most sensors for detecting microbes are based on biological interactions, so they have biological components incorporated into the sensor technology. The sensor components that interact directly with sample components are called capture or recognition components. Capture molecules can be DNA, antibodies, or other molecules that bind or react with sample components. The sample component that will be detected is called the target. Generally, target refers to the actual molecule that interacts with the capture molecule, but in some cases it is used to refer to the whole organism that is indicated by the presence of the target molecule. Examples of target molecules are specific DNA sequences and antigens. Target molecules can also be chemicals. There are some sensors presented in this chapter that can detect both pathogens and chemicals, but detection of chemicals is not the primary application of the technology.

The specificity of a sensor is determined by how reliably and firmly capture molecules bind or interact with the specified target. The capture molecule-target molecule interaction is detected through various mechanisms such as light production or mass change. The sensitivity of a sensor is based both on how well the capture molecule and target interact and on how many molecules need to interact before the reaction can be detected. The reaction kinetics (binding and release of target molecules) requires that targets be relatively concentrated, so methods for concentrating microbes from larger volumes of drinking water are needed. In the case of intentional contamination, a sample concentration step may not be needed. The above discussion applies to multiple sensor platforms, such as immunoassay strips, microchips, and solution phase systems.

EPA does not endorse or recommend any of the following technologies. The summary information below was obtained from company websites, promotional literature, and personal communication with company representatives.

7.2 Available Technologies

7.2.1 Immunoassays

The principle behind rapid immunoassay technologies is to detect the antigen-antibody reaction. Specific antigens in the water are bound to corresponding antibodies through targeting of specific proteins. The presence of a microbial contaminant is “seen” when specific antigen proteins in the sample bind with the corresponding antibodies. Immunoassays have been used since the early 1980s for many research, clinical, and safety/quality control applications. A familiar example of a strip type immunoassay is a home pregnancy test.¹⁰¹ Classic examples of immunoassays are the enzyme-linked immunosorbent assay (ELISA) and the enzyme-linked fluorescent immunoassays (ELFA). Immunosorbent refers to the immobilization of the capture molecules on a surface, such as a

membrane (Alberts, 1994). The capture molecules can be either antigens or antibodies. The target molecules in the sample are antibodies if antigens are immobilized and antigens if antibodies are immobilized. Another antibody that recognizes either the sample antigens or sample antibodies, called the secondary antibody, is added. The secondary antibody is conjugated (linked) to an enzyme that forms a colored precipitate (for ELISA) or gives off light (for ELFA) in the presence of substrate. Each enzyme molecule acts catalytically, thereby amplifying the signal of a successful binding interaction. When the assay consists of capture antibodies recognizing antigens, which are in turn recognized by secondary antibodies, it is called an antibody sandwich assay. ELISAs for quantitative assays are commonly done in microtiter plates in laboratory settings and may require time consuming pipetting. However, the technology has been advanced for strip assays for onsite uses. One of the issues for many immunoassays is cross reactivity with other microbes which leads to high false-positives rates. This can be addressed with the use of specific epitope targeted monoclonals that have been verified for low cross-reactivity with other potential sample components. Immunoassay methods have primarily been developed for grab samples, but have not been applied for online water distribution monitoring systems. Variations on the basic ELISA and ELFA concepts have also been incorporated into microchip designs.

Immunoassays designed for onsite grab sample screening for intentional chemical or microbial contamination of air, food, and water are desirable because the method can determine the presence of a specified microbial contaminant or contaminants and can be completed in less than 15 minutes. Test strips are generally not quantitative, so the results usually need to be confirmed by other methods.

- **Strip Tests - Lateral Flow Assay**

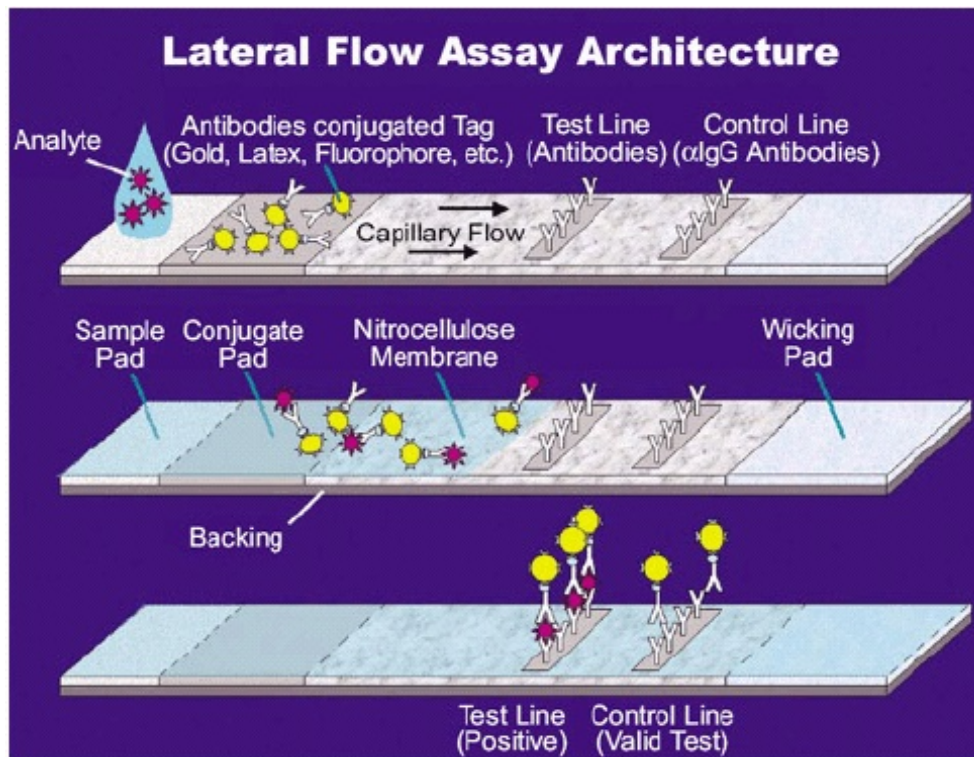
The lateral flow assay is a general technique for detecting antigens.¹⁰² It is a simplified version of ELISA. The test strip is an absorbent membrane mounted on a stiff (plastic) backing, often contained in a plastic cassette. A liquid sample is applied to one end of the strip, the sample diffuses along the length of the strip, passing several stripes (narrow regions) impregnated with high concentrations of specific antibodies, which are labeled with colored dyes or fluorescent agents. When the antigen-labeled antibody complex migrates to the test stripes, a color change or fluorescent signal indicates the presence of the target antigen. A control stripe beyond the test stripe serves as a positive control, indicating proper diffusion and appropriate functioning of strip reagents (Exhibit 7-1). Home pregnancy tests are lateral flow assays.¹⁰³ Traditional lateral flow assays produce color changes that can be detected with the naked eye. Newer fluorescent and phosphorescent reporters require excitation light and/or light detection devices.

A commercially available lateral flow assay test strip is Bio Threat Alert® (BTA) made by Tetracore (Gaithersburg, MD¹⁰⁴). Samples are put on the test strip and move along the strip membrane. A reddish band that can be seen with the naked eye on the positive line indicates the presence of specific contaminants. The following are the currently available tests and detection limits, expressed as colony forming units per milliliter (cfu/ml) (images reproduced with permission from Tetracore):

- *Bacillus anthracis* (1×10^5 cfu/mL)
- *Yersinia pestis* (2×10^5 cfu/mL)
- *Francisella tularensis* (1.4×10^5 cfu/mL)

Exhibit 7-1. Lateral Flow Assay

(image from: http://spaceresearch.nasa.gov/general_info/homeplanet.html)



- *Botulinum* toxin (10 ppb)
- *Staphylococcal* enterotoxin B (2.5 ppb)
- Ricin (50 ppm)

New Horizons Diagnostics' (Columbia, MD) SMART™ (Sensitive Membrane Antigen Rapid Test) Tickets use a similar method. The detection is provided by immunofocusing of colloidal gold-labeled antibodies and their corresponding target antigens onto small membranes. Two red lines on the strip indicate positive control and positive sample and the test is complete in 15 minutes. SMART™ tests currently available are the same as BTA with the inclusion of *Vibrio cholerae* O1. The detection limits of bacteria are 10^5 cfu/mL and for biotoxin is 50 ppb.¹⁰⁵



BioThreat Alert® (Tetracore)

SMART™ Tickets have been incorporated into Bio-HAZ™ (EAI Corporation, Abingdon, MD), a portable field kit for sample collection and analysis to detect the presence of biological contaminants (ECBC, 2002). Designed primarily for use by emergency response and forensics evidence personnel, the kit contains materials needed for liquid, solid, and air sampling and onsite biological screening. Fluorometry, luminescence, colorimetry, and sample-specific analyses, performed with hand-held equipment, identify the presence of biological contaminants



Bio-HAZ™ (EAI Corporation)

in the field. Ruggedized for field use, the kit also includes instructions to assure evidentiary integrity.¹⁰⁶ (Image reproduced with permission from EAI Corporation.)

ADVNT (Phoenix, AZ),¹⁰⁷ immunoassay detection strips called BioWarfare Agent Detection Devices (BADD), have been used by U.N. weapons inspectors in Iraq.¹⁰⁸ BADD strips are self-contained, qualitative assays for screening environmental samples for the presence of anthrax, botulinum toxin, and ricin. After a sample is transferred to the BADD test strip, dye-labeled antibodies detect trace amount of the contaminant and show its presence with two bands. After 15 minutes, the results are read visually.

RAMP Anthrax Assay by Response Biomedical Corporation (Vancouver, Canada) is a rapid immunochromatographic system. The system has a portable fluorescence reader and test cartridges for detecting anthrax, botulinum toxin, ricin, and smallpox. The cartridge is a lateral flow immunoassay device with a test and control line. The detector is an antigen-specific antibody attached to a fluorescent bead. The RAMP instrument detects the presence of fluorescent beads that attach to the capture assay line.¹⁰⁹ The RAMP Anthrax Assay has not been tested for use in drinking water systems.

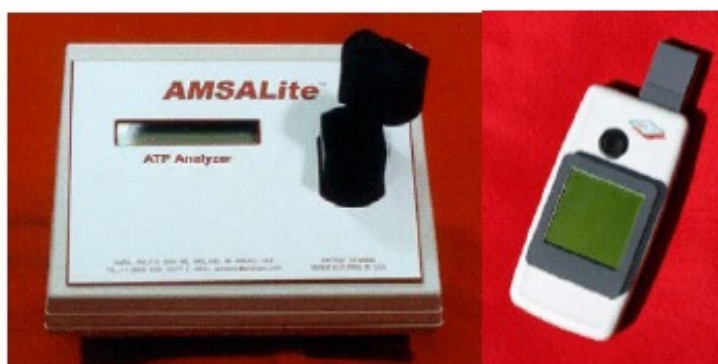
7.2.2 Detection of Bacterial - ATP

A common indicator for microbial presence used in the food and beverage industry is ATP. Tests for ATP are now being used for rapid detection of microbes in water, such as cooling towers. A small volume of water (typically < 20 milliliters) is required and the test takes between 30 seconds and a few minutes depending on the kit. Either free ATP or microbial ATP can be measured. To measure microbial ATP, cells in the water sample are lysed to release ATP into the solution. To detect only ATP contained within living bacterial cells, the water sample must first be filtered to collect the cells and rinse away non-bacterial ATP, then the cells are lysed to release ATP.

An enzyme, luciferase, and a substrate, luciferin, are present in the reaction solution. The reaction catalyzed by luciferase, that breaks down ATP and releases a photon of light from luciferin. A small hand-held/portable luminometer reads the quantity of light emitted from the reaction. The light intensity is directly related to the concentration of ATP in the sample, which is in turn an approximate indicator of biomass in the sample.¹¹⁰ The ATP test requires users to purchase a luminometer and consumable supplies (enzyme, substrate, and sample container). The ATP reaction can be amplified with adenylate kinase (AK) to measure very low numbers of cells.¹¹¹

The concentration of ATP in microbes depends on species, strain, environmental, and metabolic factors. Therefore, ATP is only an approximate indicator of biomass. Using bacteria-spiked water samples, the kits available have lower detection limits, around 1,000 cfu/mL. Since all living cells have ATP, microbial ATP needs to be separated from non-microbial ATP. However it cannot differentiate between bacterial species. In general, a single relative light unit (RLU) reading is not adequate for assessing the degree of microbial presence in a sample. It is important that routine testing establish a baseline trend for ATP results, then subsequent fluctuations in ATP can indicate a change in microbial status for the system. ATP from the human user can also be a source of false-positive readings. Numerous companies have products on the market, a few that design products for water are presented below. No third party verification was indicated for any of the products.

A few products that can detect total ATP are included because they may be useful for monitoring highly pure water samples that do not have background sources of ATP. AMSALite™ (Antimicrobial Specialists and Associates, Inc., Midland, MI)¹¹² sells an ATP detection kit that is specifically for industries using high purity water, such as printing.¹¹³ The luminometer costs about \$2,000 and several versions of the kit available. The WaterGiene™ (Charm Sciences, Inc., Lawrence, MA)¹¹⁴ test swab has a chamber with a cell lysing agent to expose cellular ATP, but it does not first rinse extracellular ATP away. (Images reproduced with permission from AMSA Inc.)



AMSALite™ **AMSALiteIII**
(Antimicrobial Specialists and Associates Inc.)

Bio Trace International (Bridgend, UK) sells an online Continuous Flow ATP Detector¹¹⁵ that can be used to discriminate between background ATP and bacterial ATP. The company claims “near real-time” results and a testing capacity that provides readings every second.

New Horizons Diagnostic Corporation’s (Columbia, MD) Profile®-1 uses its Filtravette™ disposable cartridge system to remove non-bacterial ATP arising from somatic cells (other sources of non-bacterial ATP) and other interfering compounds.¹¹⁶ This system has been demonstrated to be useful for measuring only bacterial ATP in distribution system water by Deininger and Lee (2001). The Filtravette™ allows for the free ATP to be rinsed away before the bacterial ATP is released into the assay solution. (Image reproduced with permission from New Horizons Diagnostics Inc.)



Profile®-1
(New Horizons Diagnostics Inc.)

7.2.3 Flow Cytometry- and Micro-Flow-Based Technology

Flow Cytometry is a general technique that has been used in laboratories since the 1960s for analysis of cells. More recently, flow cytometry has been used in medical applications and analysis of environmental microbial populations. A monodisperse suspension of cells flows past a laser beam (or in some more complicated instruments, multiple laser beams) and the device measures properties of each cell, such as size, granularity, green fluorescence, red fluorescence, and far red fluorescence intensities.¹¹⁷ Fluorescent tags can be used for a variety of general or specific cell components, such as DNA, RNA, proteins (antigens), or other target molecules. Some microorganisms can be distinguished on the basis of differential light scatter properties with the addition of fluorescent tags. Dyes that stain only live cells can be added to samples so that the flow cytometer can quantify the level of live versus dead cells. Nucleic acid intercalating dyes can be used to determine DNA/RNA ratios and adenine-thymine/cytosine-guanine content which helps further characterize the cells in a sample and could be used to identify microorganisms in some cases. Fluorescently labeled antibodies can be used to identify specific organisms in aerosols, water, soil, and food.

Alternatively, attachment of specific antibody to fluorescent microspheres can detect both toxins and viruses in multicolor assays. The same technology that can “see” and sort individual cells can also be used to analyze micro particles.

Microcyte Aqua® and Microcyte Field® by BioDetect (Houston, TX)¹¹⁸ are suitcase sized flow cytometers that can be used in the field to characterize particles and identify microbes if used in conjunction with fluorescent tags. Microcyte Aqua® is targeted at routine analysis of algae and other microorganisms in water. BioDetect claims that the minimal sample preparation makes the system suited for integration into an online, continuous water surveillance system. The instrument can differentiate between biological and non-biological particles, which is important for applications where correlation between the total number of particles and microorganisms does not always exist. (Image used with permission from BioDetect.)



**Microcyte Aqua®
(BioDetect)**

Brightwell Technologies (Ottawa, Canada)¹¹⁹ produces an automated Micro-Flow Imaging instrument that acts as a particle counter but actually captures digital images of the particles in the water sample. The sample is drawn through a micro-fluidic flow cell. One digital image per second is taken of the sample and images are stored that meet user-defined parameters. It takes about 5 minutes to analyze 1 mL of sample. Particles as small as 1 µm can be seen by the camera, which has a 0.2 µm resolution. Particle sizes and concentrations are analyzed and the data are presented graphically. The system requires no sample preparation and can be run continuously or intermittently for hours. The company has tested the system in drinking water and wastewater treatment applications. (Image reproduced with permission from Brightwell Technologies.)



Micro-Flow Imaging (Brightwell Technologies)

The system requires no sample preparation and can be run continuously or intermittently for hours. The company has tested the system in drinking water and wastewater treatment applications. (Image reproduced with permission from Brightwell Technologies.)

7.2.4 Bioparticulate Monitors - Light Scattering Technology

Light scattering technology is a simple scanning procedure that provides information about the presence of particles of a certain size. When a laser beam is sent through flowing water, the laser light is scattered at right angles by the presence of particles in the water. Optical devices such as photodiodes collect the scattered light, which can be analyzed to determine the size and number of particles present in the water sample.

An alert to the presence of particles in the water is useful because it can quickly alert water operators of a possible contaminant. However, the technology does not allow for the determination of specific information about the identity of the particle; furthermore, it can only detect particles within a certain size range. It often cannot differentiate between a grain of sand and a harmful microorganism. As a result, there can be a high false-positive rate associated with the technology.¹²⁰

Online turbidimeters, which measure the cloudiness of water using continuous light scattering technology, are well known and used within the water utility industry. Turbidimeters use heated tungsten filaments, light-emitting diodes, or lasers. Turbidity monitoring is required on any water produced for public consumption, and tests alert water operators that filters are failing or that the water is more conducive to bacterial growth.¹²¹ The same technology that supports turbidimeter technology can also be applied to continuous online monitoring of drinking water distribution systems to screen for the intentional introduction of pathogens. Optical techniques can overcome many of the shortfalls of traditional detection methods, which are slow, labor-intensive, and can have high variability and low recoveries.

An AwwaRF research project determined that Multi-Angle Light Scattering (MALS) can distinguish between *Cryptosporidium* and finished water matrix particles at a level great enough to serve as an early warning tool for water systems. The identification rate of *Cryptosporidium parvum* oocysts varied from 11 percent to 45 percent, and false-positive rates varied from 0.3 percent to 3 percent. The MALS system may be tuned by the user, who must understand that a higher identification rate will be accompanied by a higher false-positive rate. MALS was also able to differentiate between different physical states of *Cryptosporidium* oocysts, including oocysts treated with ozone, heat treated, or excysted from live untreated oocysts. The technology uses optical fingerprints in order to identify the different types of oocysts. This finding is important to water system operators because it allows users to determine if the potential harm from *Cryptosporidium* oocysts has been reduced by mitigation actions. The limit of detection was such that MALS could be used as an early warning tool for water contamination outbreaks. For purified water, the estimated limit of detection (ELOD) was found to be 7, 0.7, and 0.1 oocysts/mL in 1, 10, and 60 minutes, respectively. For finished drinking water samples, the ELOD was 75, 7.5, and 1 oocysts/mL in 1, 10, and 60 minutes, respectively. The researchers concluded that MALS technology has suitable applications to water distribution system monitoring (Quist et al., 2004¹²²). It was tested at the San Diego State University “Shadow Bowl,” which was organized to test new rapid-response measures to deal with a potential national security emergency during the 2003 Super Bowl.¹²³

The AwwaRF research project on MALS was developed into a commercial product called BioSentry™, by JMAR Technologies, Inc. (Carlsbad, CA; formed from LXT Group and PointSource Technologies). BioSentry™ beta units have been field tested and the product is scheduled for commercial production in late 2005. The system is composed of multiple, laser-illuminated sensor units that are networked together to provide continuous, real-time monitoring of water distribution systems. It uses 660 nm wavelength laser light and a charge-coupled device (CCD) detector to collect the scattered light. The technology uses Mie scattering, which is measured from the direction of the incoming light and is not dependent on the specific wavelength of the light. Although mie scattering has been used in other particle counting technology, this is the first application to water monitoring. The light is then collected from multiple angles, allowing for the compilation of more information about the particles than is possible with a single collection point. Desktop computers at a central location utilize LXT’s proprietary algorithms to analyze the shape, size, index of refraction, and internal structure of particles in order to identify the contaminant. The analysis of all of the factors helps reduce false-positives generated by systems that



BioSentry (JMAR)

examine particle size alone. BioSentry™ also has the ability to alert system operators to the presence of unknown or unrecognized contaminants. (Image reproduced with permission from JMAR.)

The two main challenges facing this technology are false-positives and the level of sensitivity. The application of light scattering technology using multiple collection angles and complex algorithms will yield a lower false-positive rate than its predecessor technology that simply counts particles of a certain size. However, in order for the system to be effective in protecting humans from contaminated water, the technology must be sensitive enough to detect microorganisms well below dangerous levels, perhaps one spore in 100 liters. JMAR hopes to be able to more accurately assess the effectiveness of BioSentry™ upon completion of field tests at water utilities in 2005.¹²⁴

Rustek, Ltd. (UK) has developed a Multi-Angle Laser Light Scattering (MALLS) technology that combined with pattern recognition techniques increases the technology's ability to monitor for microbial contaminants.¹²⁵ The Computing Research Centre at Sheffield Hallam University, (Sheffield, UK), is using the MALLS device patented by Rustek, Ltd. The technology is currently being used to detect bacteria in different elements of the water industry, including water companies, the bottled water industry, and breweries; in addition, the technology has applications in the medical field. The device analyzes how light is scattered in order to determine the particle content in the water sample. When a laser beam is projected through a sample, it is disrupted by particles. The resulting light picture, or how the laser beam appears after it is disrupted by particles, will vary in both the direction and speed of the light beams. Thus, the fluctuation in amplitude and frequency of intensity are measured to determine the amount of microbes present in the sample.¹²⁶

7.3 Potentially Adaptable Technology

The technologies presented in this section are potentially adaptable for finished water and distribution systems, but have not reached the fully commercial stage or undergone third party verification. The technologies either have been developed originally for source water or for non-water media (e.g., air).

7.3.1 Fiber Optic-Based Biosensor

RAPTOR™, developed by the U.S. Naval Research Laboratory and Research International (London, UK), is a portable, rapid, automatic fluorometric assay system for monitoring biological contaminants, toxins, explosives, and chemical contaminants.¹²⁷ The self-contained instrument integrates optics, fluidics, electronics, and software and is suitable for laboratory and field assays. It performs user-defined, multi-step assay protocols for monitoring fluorescently labeled chemical reactions occurring on the surface of each of the system's four disposable optical waveguide sensors. Research International's biosensor systems are based on monolayer receptor-ligand reactions taking place on the surface of injection molded polystyrene waveguides. The baseline protocol used to identify specific pathogens is called the "sandwich format" fluoroimmunoassay. Toxins and bacteria such as ricin and *B. anthracis* have been detected at levels below <1.0 ng/mL and 100 cfu/mL, respectively. According to Research International,



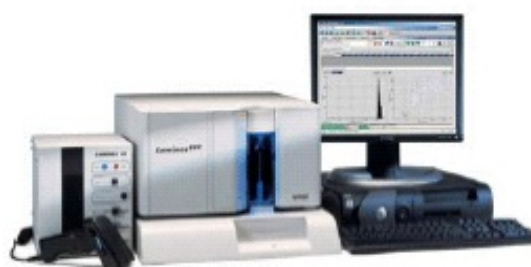
RAPTOR™
(Research International)

RAPTOR™ is capable of real-time detection of microbial pathogens with or without conventional culture. The portable unit can simultaneously process four analytes in 7 to 12 minutes. The hand-held model in development will be capable of 12 to 16 simultaneous assays (Bunk, 2002). (Image reproduced with permission from Research International.)

Daniel Lim's laboratory (University of South Florida) was involved in the development of RAPTOR™ and is currently in the process of placing a prototype array biosensor linked to a filtration/concentration system for automated, continuous online monitoring of potable water at a local water utility. The filtration/concentration system uses a hollow fiber filter that concentrates microorganisms from large volumes of water. The system will be back flushed and the back flush will be sent directly to the biosensor. It is anticipated that the biosensor will be able to identify specific microorganisms in the distribution system, including biothreat agents, should they occur (Daniel Lim, University of South Florida, personal communication).

7.3.2 Dye-Loaded Microspheres

The Luminex® Corporation's (Riverside, CA) xMAP® system consists of 5.6 micrometer polystyrene microsphere particles that are loaded with red and infrared fluorophores in ratios that allow for 100 distinct color-codes. Each microsphere can be coated with a separate capture molecule which can be involved in either nucleic acid hybridization, antibody recognition, a receptor-ligand reaction, or an enzymatic reaction. The reaction times are about three times faster than standard microarrays because the microspheres are in solution have 3-D exposure allowing for nearly solution-phase kinetics, whereas flat microarrays are limited by solid-phase kinetics. The microspheres pass through the detection chamber single file and are optically measured.¹²⁸ Luminex® markets bench top readers for genomics and proteomics applications. Researchers from Lawrence Livermore National Laboratory (LLNL) utilized Luminex® technology to develop an Autonomous Pathogen Detection System (APDS). The system has an automated sample preparation module, based on sequential injection analysis (SIA). The APDS interfaces aerosol sampling with multiplexed microsphere immunoassay-flow cytometric detection. The system performed well over five days of unattended continuous operation (Hindson et al., 2004).¹²⁹ (Image reproduced with permission from Luminex Corp.)



Luminex® xMAP® (Luminex Corp.)

7.3.3 Detection of ATP

Several ATP detection systems are available for use with water samples. Another commercially available system deserves note because it has a long-standing history of use in the food and beverage industry and may be applicable for finished drinking water. Celsis-Lumac (Landgraaf, The Netherlands) sells a cellular ATP detection system, RapiScreen™, that can be used to measure bacteria on the surfaces of meat products and in beverages.¹³⁰ Hygiena (Camarillo, CA), which also markets some of the Celsis-Lumac technology, has developed liquid stable reagents and freeze-dried reagents for ATP bioluminescence applications.¹³¹

7.3.4 Cell-Based Biosensor

The Massachusetts Institute of Technology (MIT) developed Cellular Analysis and Notification of Antigen Risk and Yields (CANARY™), which was licensed to Innovative Biosensors, Inc. (College Park, MD), and is now marketed as the BioFlash™ System. With this system, transgenic B-cells express antibodies against target antigens. When the target antigen is present in the test sample, the B-cells emit light (via green fluorescent protein), which is detected by a portable luminometer. Either liquid or solid samples can be tested. The assay protocol for liquid samples has five steps, which collectively take about 5 minutes to complete, including reading time. The sample preparation removes inhibitors such as chlorine (Hollie Kephart, Innovative Biosensors, Inc., personal communication). The original development paper cites the sensitivity as 200 cfu for *Y. pestis* (in 20 µL reaction volume), 1,000 cfu *B. anthracis* (from a swab rinsed in 1 mL of extraction buffer), and 500 pfu vaccinia virus (in 20 µL reaction volume) (Rider et al., 2003). A separate cell line must be developed for each target antigen. This system has not been verified by a third party. The company markets CANARY™ as having broad applications in food testing, animal health, biodefense, and human health care, including drug discovery and development, and disease diagnosis.¹³² (Image reproduced with permission from Innovative Biosensors, Inc.)



BioFlash™ (Innovative Biosensors Inc.)

7.3.5 Polymerase Chain Reaction

Polymerase chain reaction (PCR) is an analytical technique that detects/identifies organisms by targeting their nucleic acids (DNA/RNA). PCR is a highly developed technology for molecular biology applications. It has broad applicability for almost any situation where DNA needs to be detected and identified.

Nucleic acids are synthesized in great numbers and subsequently identified by various techniques. In terms of security applications, it can be used to detect and identify biological contaminants. The following illustrates the PCR process:

- Microbial cells are disrupted to expose the DNA/RNA. Disruptive techniques include use of lytic enzymes, freeze-thaw cycles, or bead-beating.
- DNA/RNA is extracted and purified to remove interferences such as folic acids.
- Various reagents are added (e.g., DNA primers, excess nucleotide bases, and enzymes to produce DNA).
- DNA is synthesized in great numbers via thermal cycling. The amplification of DNA occurs through a series of 30 to 45 temperature cycles producing billions of copies.
- The amplified target DNA is detected using various methods including electrophoresis, fluorescent gene probes, and fluorescence melting curves.

PCR is a sensitive and potentially rapid detection method. It can detect any organism that contains nucleic acids, including viruses, bacteria, and protozoa. The assay is selective, can be used to screen

for selected contaminants, and is getting easier to conduct using prepackaged reagents. However, the method cannot distinguish between live and dead microorganisms and can be negatively affected by natural interferences such as soil-derived humic and fulvic acids. Because PCR reactions are also carried out in small volumes, samples need to be reduced to microliter volumes. Several portable PCR-based identification devices are available.

The Ruggedized Advanced Pathogen Identification Device (RAPID), developed by Idaho Technologies (Salt Lake City, UT), has been used extensively by the military.¹³³ It can screen up to eight contaminants simultaneously, uses a closed system to reduce contamination, and all reagents are freeze-dried for convenience. It is an automated system which includes cell disruption and DNA extraction-purification necessary for PCR. Reaction volume is 10 to 20 μ L. The thermal cycler has preprogrammed tests and automatic data interpretation. It is field deployable weighing 35 pounds and can analyze samples in 30 minutes. The microbes that can be detected by the RAPID System are listed below. The nucleic acid limit of detection (NALOD) is indicated where available in parenthesis (units are genomic equivalent [GE] or plaque forming unit equivalents [pfu-e]; Tuck et al., 2005):

- *Bacillus anthracis* (5 GE)
- *Brucella* spp. (10 to 20 GE)
- *Salmonella* spp.
- *Yersinia pestis* (5 to 40 GE)
- *Francisella tularensis* (2.3 to 7 GE)
- *E. coli* O157:H7
- *Listeria monocytogenes*
- *Campylobacter*
- *Clostridium botulinum*
- Orthopox (200 to 350 GE)
- Smallpox (40 to 125 GE)
- Q fever (5 to 31 GE)
- Typhus (10 GE)
- Glanders (5 GE)
- Ebola virus (260 to 706 pfu-e)
- Marburg virus (1.9 to 4 pfu-e)
- Easter Equine Encephalitis virus (20 to 5,000 pfu-e)



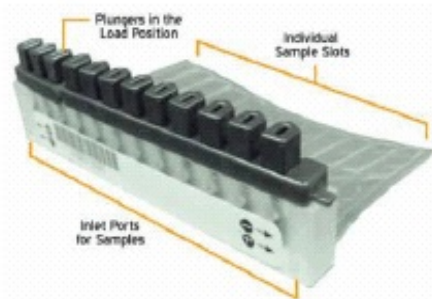
RAPID (JBAIDS)
(Idaho Technologies)

RAPID can be used to detect pathogens in water samples. The unit costs around \$55,000 with each test costing \$50. EPA and the Army are developing a prototype for water. Currently, EPA's ETV program is investigating the sensitivity, interferences, and cross-reactivity of the unit.¹³⁴ In September 2003, Idaho Technology was awarded the Joint Biological Agent Identification and Diagnostic System (JBAIDS) contract.¹³⁵ In March of 2005, RAPID underwent a two-week operational test at Brooks City-Base, TX. The Air Force Operational Test and Evaluation Center, based at Kirtland Air Force Base, NM, took the lead on the exercise, while the Army Medical Department provided training and technical assistance. After validation by a joint-service Data Authentication Group, the operational test results will be forwarded to the Joint Program Executive Office for Chemical and Biological Defense for final approval. If approved, JBAIDS will enter full-rate production in September 2005 and the DOD will distribute 450 systems throughout the services over the next three years.¹³⁶ (Image reproduced with permission from Idaho Technologies.)

Idaho Technology's latest portable PCR device, called RAZOR, comes with prepackaged freeze-dried reagents for 12 different targets already loaded into the clear flexible plastic PathFinder™ reaction pouches. Reagent grade water is required but the sample ports attached to the reaction pouches are designed



RAZOR
(Idaho Technologies)



PathFinder™ Pouches

so that volume measuring is not required. The reaction pouches are loaded into the cycling device and results are obtained after about 30 minutes. The device weighs nine pounds, including battery.¹³⁷ (Images reproduced with permission from Idaho Technologies.)

Bio-Seeq™, developed and commercially available through Smiths Detection (Edgewood, MD), is a hand-held PCR-based biological detector. A sample preparation cartridge allows samples to be taken in the field and tests run on the spot. All the necessary reagents, filters, and mixing chemicals required to process a biological or viral sample are included in the sample prep cartridge, eliminating the need for pipettors, tips, and sample vials. The unit has six detection modules (thermocycler/optics modules) that perform the thermal cycling, optical reading, and alarm detection for each test. Each module has two independent optical channels that can be used during a single test. With suitable reagents, these channels can allow the user to run a target sample with a positive control in the same tube, eliminating the need to prepare a separate positive control. The device is capable of detecting 1 cfu (in ~28 μL sample volume) in 30 minutes and costs \$25,000.¹³⁸ (Image reproduced with permission from Smiths Detection.)



Bio-Seeq™ (Smiths Detection)

LLNL has developed a “hand-held nucleic acid analyzer” (HANAA) based on real-time PCR (TaqMan). This specific technology has been licensed to Cepheid, a Sunnyvale, CA-based company that is developing biosensors for the U.S. Postal Service. HANAA can identify an organism in less than 10 minutes (Perkel, 2003).¹³⁹ It requires the operator to prepare the sample by adding reagents to a reaction tube and selecting which pathogen will be targeted. Water Environment Research Foundation (WERF) has tested HANAA with the waterborne pathogens, *Cryptosporidium parvum* and *E. coli* O157:H7 (photo from LLNL website).



HANAA (Lawrence Livermore National Lab)

Cepheid, Inc. (Sunnyvale, VA) Smart Cycler® XC is a portable PCR machine that uses the company's patented I-CORE (integrated cooling/heating optics reaction) modules to amplify up to four targets simultaneously from one sample. The amplification is monitored in real-time and can be completed in as little as 30 minutes. The company's newer GeneXpert System includes a cartridge-based sample preparation system that takes about five minutes to prepare.¹⁴⁰ In 2001, the U.S. Centers for Disease Control and Prevention (CDC)

developed and validated test kits for several bio-threat agents optimized for use with the Smart Cycler®. The Laboratory Response Network (LRN), uses the CDC validated kits and Smart Cycler® to provide nationwide screening and reference testing to respond to a bioterrorism event. In 2002, Cepheid, Inc., delivered to the U.S. Army



Smart Cycler®

(Cepheid Inc.)

GeneXpert®

Medical Research Institute of Infectious Diseases (USAMRIID) field-ready DNA test kits for rapid detection of four bio-threat agents, *Bacillus anthracis* (anthrax), *Yersinia pestis* (plague), *Francisella tularensis* (tularemia), and *Clostridium botulinum* (botulism). Developed in collaboration with USAMRIID under a DOD contract, the tests combine DNA sequences identified and validated by USAMRIID for bio-threat agent detection with Cepheid's proprietary reagent formulations and "freeze-dry" processing for prolonged stability and ease-of-use.¹⁴¹ This technology is being used in many post office sorting facilities throughout the United States. The system has a sensitivity of < 30 spores/reaction in water or buffer, a false-positive rate target of < 1:500,000 samples (99.9998 percent), no cross-reactivity with nearest neighbor organisms, and a non-determinate rate of < 1 percent. The anthrax assay has been validated by third party government agency evaluations. In 2005, the company expects to introduce a triplex cartridge for anthrax, tularemia, and plague, and a separate Orthopox cartridge (Jaymee Rosenberger, Cepheid, personal communication). For use with drinking water samples, concentration techniques would be needed to reduce large sample volumes to appropriately smaller volumes. (Images reproduced with permission from Cepheid, Inc.)

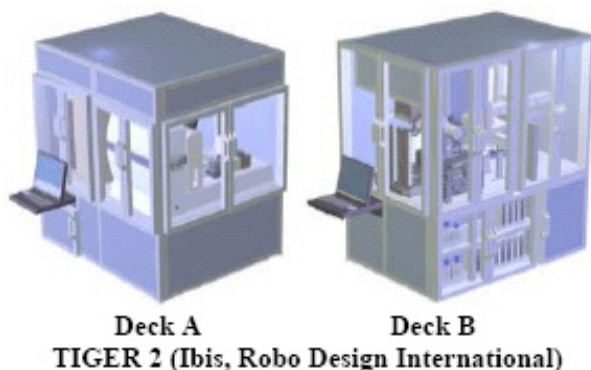
The PathAlert™ Detection System from Invitrogen Federal Systems (Frederick, MD), in conjunction with the 2100 Bioanalyzer micro-fluidics based electrophoresis system from Agilent Technologies (Palo Alto, CA),¹⁴² is a PCR based system that is able to detect biothreat agents in a single agent assay or multi-agent assay formats. Existing products include single agent assays for *B. anthracis*, *Y. pestis*, vaccinia, and *F. tularensis* with multiple target loci for each reaction. In addition, a multi-agent single reaction assay is available for the detection of these four agents. Under development are assays for additional water borne pathogens such as *E. coli* O157:H7, *Cryptosporidium parvum*, *Giardia lamblia*, *Salmonella* species, *Shigella* sp., and others.

PathAlert™
(Invitrogen Federal Systems)

The product is available in prepackaged or custom formats, where the user is able to pick four to six targets of choice for inclusion in a single multi-agent assay. PathAlert™ was tested in June 2004 as part of EPA's ETV program. During this testing, the system was able to overcome environmental inhibition from fulvic and humic acids. The system is able to operate in a standard stationary or mobile laboratory environment (Willem Folkerts, Invitrogen Federal Systems, personal communication). Although PathAlert™ is not marketed as portable, it is included in this report because the developers have specifically addressed biothreat agents and the technology has been tested in EPA's ETV program,

as well as in a technology readiness assessment (TRA) conducted at the U.S. Army's Dugway Proving Ground. (Image reproduced with permission from Invitrogen.)

One method developed around DNA base composition and PCR, that has successfully demonstrated proof-of-principle, is called Triangulation Identification Genetic Evaluation of Risks (TIGER). TIGER has been developed by Isis Pharmaceuticals, Inc. (within their Ibis Therapeutics program, Carlsbad, CA), in collaboration with SAIC, and funded by DARPA.¹⁴³ The TIGER biosensor system can identify a broad range of infectious organisms, including known, unknown, non-culturable, or bioengineered elements, within a few hours. PCR primers are designed to place unknown organisms with their related neighbors, and multiple primer pairs target multiple locations within pathogen genomes. Mass spectrometry is used to obtain mass signature data. RoboDesign International, Inc. (Carlsbad, CA) is developing TIGER 2.0, which will be an automated system and will require minimal intervention from a technician (Bunk, 2002). The footprint will be ~ 8 x 8 feet and is being transitioned to USAMRIID and CDC. The culture-independent methodology allows for flexibility with respect to the types of starting sample that can be used (e.g., blood, urine, soil, other environmental samples) (Kumar Hari, Ibis Therapeutics, personal communication). Although this technology is not field portable or online, it presents an advancement beyond standard PCR approaches where primers are designed for detecting only one known pathogen at a time. (Image reproduced with permission from Ibis Therapeutics.)



Deck A
Deck B
TIGER 2 (Ibis, Robo Design International)

7.3.6 Bio-Optoelectronic Sensor Systems (BOSS)

DARPA funds the bio-optoelectronic sensor systems (BOSS) center, which includes team members from the University of California at Berkeley, Colorado State University, Columbia University, Georgia Institute of Technology (Georgia Tech), the University of Illinois at Urbana-Champaign, the University of Michigan at Ann-Arbor, and the University of Texas at Austin, who collaborate to develop technologies to detect chemical and biological warfare threats.¹⁴⁴ Georgia Tech's, Applied Sensors Laboratory is using fiberoptic evanescent wave spectroscopy in the mid-infrared region to sense capture-target molecule interactions. The sensing area is coated with a thin polymer layer (can be a molecularly imprinted polymer; see Section 7.4.13) that forms a hydrophobic membrane, serving both as an extractor phase to enrich hydrophobic analytes in close vicinity of the sensor surface and as a suppressor of matrix interference by water absorptions.¹⁴⁵ Georgia Tech has developed sensors for marine and groundwater applications (EPA, 2003). The developers claim that "the sensor is fast, highly sensitive, and provides real-time direct measurement with no additional steps or consumable reagents...[and is] capable of detecting a wide variety of chemical and biological species in air, water, and biological samples" (Bodurow, 2005).

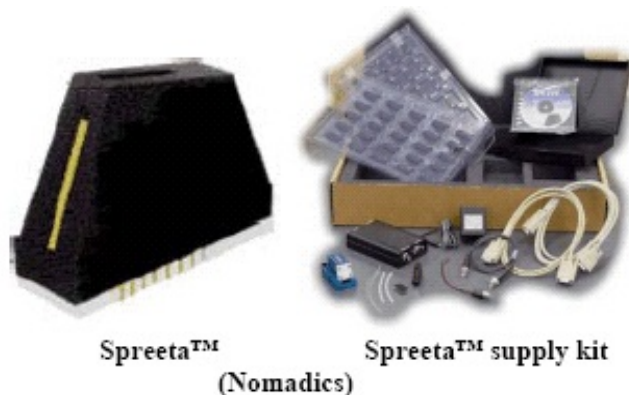
7.3.7 Surface Plasmon Resonance (SPR)

Surface plasmon resonance (SPR), detects changes in mass by measuring changes in refractive index.¹⁴⁶ The sensor chip consists of a glass support surface coated with a thin layer of gold. The

gold surface can be modified in a variety of ways to immobilize different compounds. For example, if the gold surface is modified with a carboxymethylated dextran layer, various biomolecules can be attached to this hydrophilic layer without causing denaturation. When a sample is passed over the chip surface (via microfluidics), molecules that bind/interact with the immobilized target are captured. Interactions between proteins, nucleic acids, lipids, carbohydrates, and even whole cells can then be studied. When binding occurs, the mass increases, and when disassociation occurs, the mass decreases. These changes in mass can be detected as they occur and yield quantitative information such as kinetics, affinity, and concentration of the molecule in the sample. Binding of molecules as small as 100 Daltons can be detected. Portable instruments are being developed (Karl Booksh, DMS Lab, University of Washington¹⁴⁷). A related technique, called surface plasmon-coupled emission (SPCE), is being developed at the University of Maryland, and has the potential to improve sensitivity 1000-fold over other fluorescence technologies.¹⁴⁸

Nomadics® Advanced Instrumentation Group (Stillwater, OK) offers a Surface Plasmon Resonance (SPR) Evaluation Module for researchers interested in studying specific chemical and biological contaminants on a portable SPR platform.¹⁴⁹ The Nomadics Evaluation Module is based on Texas Instruments' (Dallas, Texas) Spreeta™ biosensor that enables real-time quantitative measurement of bio-molecular interactions.

The Module contains 50 sensors (chips), a flow cell with an electronic PC interface control, and a Windows based operating system. Spreeta's design encapsulates the entire SPR optical system making the device compact and able to be integrated into various instrument designs. The sensor can be used to detect and quantify the presence of specific contaminants for applications such as agriculture, water quality, medical, and food safety applications.¹⁵⁰ Researchers at Stanford University tested Spreeta and conclude that the sensor "shows promise as an inexpensive, portable, and accurate tool for bio-analytical applications in laboratory and clinical settings" (Whelan et al., 2002).¹⁵¹ The same research team reported that the analyte concentration in their test method corresponds to the detection of 90 fmol IgG (Whelan and Zare, 2003). In 2006, Nomadics anticipates launching a Spreeta-based Life Science platform. (Images reproduced with permission from Nomadics.)



7.3.8 Electrochemiluminescence (ECL)

ECL is a detection technology that utilizes light generated by the oxidation and reduction of a ruthenium metal ion as a labeling system. Capture molecules (e.g., antibodies) are absorbed onto a support surface, such as magnetic beads or a microarray plate. The addition of target molecules from the sample and ruthenylated antibodies creates an antibody sandwich which is detected when the ruthenylated antibodies are stimulated to glow with an electrode. Background signal is limited because the electrodes only stimulate nearby ruthenium, quenching is not a problem with the 620 nm emitted light.¹⁵² As with other antibody-based technologies, volume reduction would most likely be required for ECL technologies to be adapted for distribution systems.

ECL was developed by BioVeris (formerly IGEN; Gaithersburg, MD). BioVeris' BioVerify Tests utilize two antibodies which recognize the pathogen or toxin, one immobilized on paramagnetic microparticles and the other labeled with BioVeris' BV-TAG™ label. The sample mixed with the antibody reagents is loaded into the flow based M1M Analyzer, which transports this assay mixture into a measurement cell and collects the microparticles on an electrode. The electrode stimulates the BV-TAG™ labels bound (via the antibodies and the spore) to the microparticles and the emitted light is measured. Assays that are available for M1M include *Botulinum* neurotoxins (A, B, E, F), anthrax, ricin, Staphylococcal enterotoxins A and B, *E. coli* O157:H7, *Salmonella*, *Listeria*, and *Campylobacter*. The M1M comes packed in a transportable suitcase with a separate reagent suitcase.¹⁵³ The company markets the system for biodefense applications and claims it can be used for research and environmental samples.



**M1M Analyzer
(BioVeris)**

Meso Scale Defense¹⁵⁴ (Gaithersburg, MD), a division of Meso Scale Discovery, also sells systems utilizing ECL technology. The company's MULTI-ARRAY™ and MULTI-SPOT™ microplates have electrodes integrated into the bottom of the plate. Capture molecules are immobilized onto the plates, then sample and MSD-TAG™ are washed over the array. Antibody sandwiches, which are formed when target molecules are present, are detected by a reader. Meso Scale Defense has benchtop readers on the market and is designing a portable cartridge reader for first responders.¹⁵⁵

7.4 Emerging Technology

The emerging technologies are prototype field or laboratory devices as well as technological advancements that could be integrated into a system. Systems discussed include advancements in immunoassays, proof-of-concept and prototype microchip technologies, micro beads, and light scattering technology. Immunoassay technology in general is described in Section 7.2. Some of the microchip technologies presented are used in commercial products for other applications such as genomics research or clinical analysis. The potential range of applications of these technologies for other uses is diverse and includes sensors for drinking water monitoring. Whether or not any of these technologies are ever used to develop products specifically for use with drinking water depends mostly on cost. Because it is beyond the scope of this document to analyze economic factors, technologies that could be developed into products for use in drinking water distribution systems will be presented regardless of whether costs might eventually prevent their development for water application. In addition, it is difficult to determine what the potential detection limits could be for these technologies because detection limits are based on specific contaminants in a specified matrix and these technologies have not been adapted for distribution system water or the range of threat agents that are of concern.

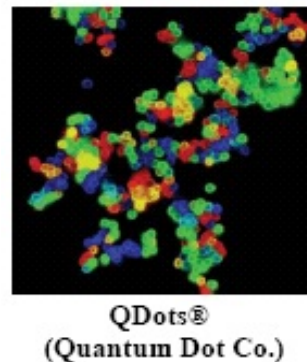
7.4.1 Lateral Flow Assay

NASA's Jet Propulsion Laboratory has developed a quantitative lateral flow assay (QLFA) for testing drinking water samples in space.¹⁵⁶ Depending on the design and the specific antibodies used, the test strip yields a rough count of the total cfus in the water sample, and a preliminary classification as to the types of organisms present—for example, viruses versus different major

classes of bacteria. The test takes only minutes to conduct and does not require growth of bacteria. Relatively low levels of antigens can be detected using newer fluorescent dyes, such as Qdots®, which are much brighter than traditional fluorescent labels (see more below¹⁵⁷).

7.4.2 Labels

Quantum Dot Company's (Hayward, CA) Qdots® are nanocrystal spheres that fluoresce at a variety of different wavelengths. The exterior surface can be coated with biological molecules such as DNA, antibodies, or receptors. Although colloiddally dispersed pigments occur naturally and have been used in paints for centuries, the breakthrough has been creating fluorescent versions that are water soluble and non-toxic to cells.¹⁵⁸ Qdots® are currently being marketed for labeling subcellular components of living cells for imaging applications.¹⁵⁹ Other researchers are also developing quantum dot technologies (Gorman, 2003).¹⁶⁰ Quantum dots have the ability to quantitatively detect biological molecules in samples. The EPA Office of Ground Water and Drinking Water (OGWDW) Technical Support Center located in Cincinnati, OH, is using quantum dots to as part of a sensor technology for determining the occurrence and prevalence of cyanobacteria and their toxins in surface and finished water (Gerald Stelma, EPA, personal communication). The biosensor EPA is developing will be portable for use in the field and eventually adapted for continuous monitoring. The goal of EPA's research is to develop molecular methods to detect cyanobacteria and to simultaneously extract and detect cyanotoxins of interest to the Agency.¹⁶¹ (Image reproduced with permission from Quantum Dot Co.)



Another newer labeling technology is Upconverting Phosphor Technology™ (UPT). SRI International (Menlo Park, CA), in collaboration with OraSure Technologies (Bethlehem, PA) and under DARPA support, has developed a lightweight, battery operated, hand-held sensor to detect multiple pathogens (bacteria, viruses) and their toxins simultaneously.¹⁶² The system uses UPT™ to color-code multiple pathogens simultaneously in a lateral flow immunoassay test strip.¹⁶³ The upconverting phosphor reporters emit visible light upon excitation by near infrared light and have the advantages of (1) single particle detection sensitivity, (2) multiplexing, (3) no autofluorescence, and (4) no photobleaching. SRI has thus far developed ten UPT™ phosphors, each producing a different color, which allows for the simultaneous detection of several contaminants in the same sample.¹⁶⁴ The sensor can detect 10 to 1,000 picograms (pg)/mL of small (e.g., virus, toxin) target antigen in < 15 min with a sample volume of less than 300 µL. For spores and bacteria, the sensitivity is as low as 1000 cfu/mL. So far, this technology has been developed for sampling of biological fluids (oral fluids, blood, etc.) but future research aims to apply UPT™ to environmental testing, including drinking water.¹⁶⁵ OraSure Technologies owns commercial rights and may develop the technology for other emerging applications, such as biological warfare defense, combinatorial chemistry, biomolecular screening, medical diagnostics, and drug testing.

7.4.3 Magnetic Beads

Dynabeads®, developed by Dynal Biotech LLC (Oslo, Norway), is a product used for rapid separation and detection of microbes, nucleic acids, proteins, and other biomolecules in liquid or viscous samples. Dynabeads® technology is based on immunomagnetic separation. The polymer

shells of these microscopic (1 to 4.5 μm) beads can be coated with a variety of ligands (antibodies, oligos, proteins, DNA/RNA probes, etc.) that will bind to specific targets. The resulting target-bead complexes are then isolated using magnetic attraction and detected using an ultraviolet laser system.¹⁶⁶ The variable combinations of bead-size and ligand type facilitate detection and identification of a wide variety of targets. This method has successfully detected *E. coli* in water samples in less than five hours (Pyle et al., 1999). Although Dynabeads® are not being marketed by Dynal as tools for CBW detection, they could be used in flow cytometry devices and other technology that can detect small labeled particles.

7.4.4 Flow-Through Columns

The Biodetection Enabling Analyte Delivery System (BEADS), developed by the PNNL (Richland, WA), is a portable, automated front-end sample preparation device for pathogen detection. The system features micro-sized glass, polymer, or magnetic beads coated with antibodies specific to a chemical or biological species of interest. The beads are color-coded to differentiate their specific chemistries for extracting and detecting multiple pathogen signatures. Liquid samples flow over renewable bead-based immunoassay columns, which serve to isolate and concentrate whole cells, proteins, nucleic acids, and/or chemicals as they bind with the beads. In addition to sample purification and concentration, BEADS has its own PCR detector, or can be linked to other detector technologies. No human interaction with the system is required for sample preparation or analysis, and field test results can be sent electronically to a remote location. The BEADS system has successfully detected trinitrotoluene (TNT), pesticide/herbicide, botulinum toxin, *E. coli*, and anthrax in a process that takes about four hours to complete (ACS, 2002).¹⁶⁷ This technology has not been third party verified.

7.4.5 Raman Spectroscopy

Biopraxis (San Diego, CA) is developing a reagentless, portable, biosensor, whose first version is known as “Doodlebug.” The biochip has biomolecules immobilized on a surface-enhanced Raman¹⁶⁸ scattering (SERS)-active metal surface. When a sample is added to the surface of the chip, the immobilized capture biomolecules selectively bind their ligands. The chip reader, a Raman microscope, illuminates the surface of the chip with a laser and the scattered light is collected. The wavelengths and intensities of the scattered light are used to analyze the unique molecular structure of the cross-reactions. The technology can detect chemicals (including explosives) and biologicals. Biopraxis is developing a biochip to detect 8 to 10 different targets at the same time (Bunk, 2002). A WERF study showed that Doodlebug could distinguish between six *Legionella* species, recently passaged (fresh) oocysts from six *C. parvum* Genotype 2 strains, three Genotype 1 strains, a *C. meleagridis* strain, and a *Giardia* sample. Results take about 60 seconds to obtain. Experiments involving the impact of environmental and water treatment conditions suggested that this technology will be able to differentiate between viable and nonviable, and possibly injured, organisms. The SERS fingerprint may even be useful in determining the “age” of an oocyst (e.g., whether it is too old to be infectious). The sensitivity of the technique eliminates the need for amplification techniques, such as PCR, fluorescent labels, and enzymatic reactions, thereby greatly reducing the potential for false responses from sample constituents that either mimic or inhibit the signals from labels or interfere with enzymatic reactions (Grow et al., 2003).¹⁶⁹ Several other companies have portable Raman spectroscopy-based instruments.¹⁷⁰

7.4.6 Microelectrode Arrays

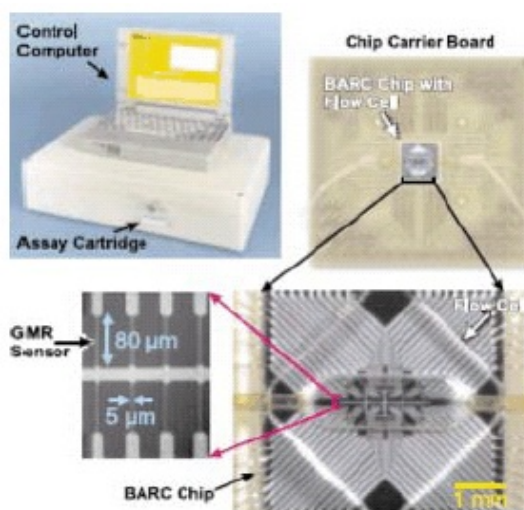
The CombiMatrix Corporation (Mukilteo, WA) is in the process of testing its biothreat detection system, Sen-Z™,¹⁷¹ a hand-held, portable, self-contained unit that captures and electronically detects a range of threat agents (e.g., anthrax spores, smallpox virus particles, ricin, and saxitoxin). CombiMatrix's core technology consists of microarrays of 1,000 to 12,000 microelectrodes in one cm². Overlaying each microelectrode is a porous reaction layer which serves as a reaction "flask." The microelectrode creates a local change in pH, which dictates where on the microarray capture molecules are synthesized or deposited. CombiMatrix microarrays have been made to detect DNA hybridization and antigen-antibody reactions. Some of the key features of the Sen-Z™ are multiplex immunochemical assays; a platform that can be quickly configured to detect a broad range of threat agents; real-time fluorescent-free electronic detection of signals by electrochemical methods; automated hands-free sample collection, preparation, detection, and analysis; and high sensitivity (ricin at 60 pg/mL). At the present time, this technology focuses on air sampling, but the company believes that the integration of agent isolation and processing technology could adapt this product for a water monitoring system (David Danley, CombiMatrix, personal communication). (Image reproduced with permission from CombiMatrix.)



Sen-Z™ (CombiMatrix Corp.)

7.4.7 Microarray of Gel-Immobilized Compounds

The Biochip Technology Center at Argonne National Laboratory developed a reusable "Micro Array of Gel-Immobilized Compounds" (MAGIChip™) that can perform thousands of biological reactions in a few seconds. MAGIChip™ is a small glass slide with up to 10,000 3-D gel pads that serve as micro-test tubes. Robots load the pads with DNA or protein fragments from bacteria, viruses, or chemicals. Bench top equipment is required to analyze the chips. Researchers at Argonne's Biochip Technology Center are developing new applications for the biochip, writing faster sample analysis programs, and working to shrink portable biochip readers. This technology has been used for gene expression, diagnosis and monitoring of genetic diseases, microbial analysis in environmental cleanups and agriculture, routine protein analysis of blood and urine, exploration for life in outer space, and forensic DNA testing.¹⁷² Although they have the potential for detecting biological contaminants in an EWS context, they have not yet been adapted for this use. In addition, volume reduction would most likely be required for this technology to be adapted for distribution systems.



BARC Chip (Naval Research Lab)

7.4.8 Magnetic Microbeads

The Bead ARray Counter (BARC) chip, developed at the Naval Research Laboratory, consists of an array of

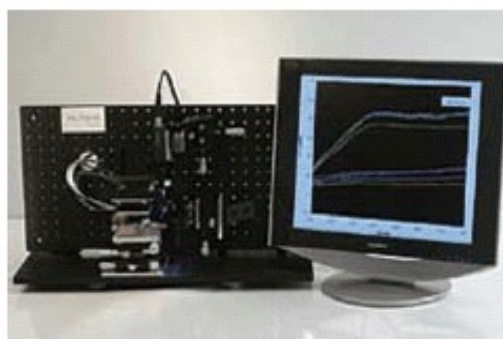
DNA spots immobilized on a surface.¹⁷³ Hybridization of sample DNA with chip immobilized DNA is detected by magnetic beads 1 to 3 μm in diameter. The chip's magnetic field microsensors are μm -scale, wire-like structures made with giant magnetoresistive (GMR) material, which can detect individual magnetic beads and is more sensitive and more compact than the optical detectors required for fluorescence-based techniques (Whitman et al., 2001; Tamanaha et al., 2002; Rife et al., 2003¹⁷⁴). The developers envision that millions of sub-micrometer GMR elements enabling simultaneous detection of thousands of DNA sequences with high sensitivity and dynamic range will be possible as the technology advances.¹⁷⁵ This technology is not yet field ready. (Photo from NRL website.)

7.4.9 DNA Microarrays

DNA microarrays (DNA chips) can contain 100,000 different spots of DNA printed on a glass microscope slide (Fitzgerald, 2002). Alternatively, photolithography and solid-phase chemistry can be used to produce microarrays containing 500,000 oligonucleotide (single stranded DNA) probes within 1.28 cm^2 (Affymetrix Genechip®).¹⁷⁶ When a sample with unknown DNA is exposed to the spots, it will hybridize (match-up) with the spots of DNA that are complementary. The sample DNA is labeled (through a PCR reaction) so a chip reader device is able to detect where on the microarray hybridization occurs. The microarrays could be designed to detect a multitude of sequences that would be unique to specific pathogens of concern.¹⁷⁷ There are several companies producing and custom designing microarrays. Microarrays are widely used for genomics research,¹⁷⁸ but face sample volume reduction problems for use with environmental samples and drinking water.

7.4.10 Micro-Cantilever System

The VeriScan™ 3000 System, produced by Protiveris (Rockville, MD),¹⁷⁹ utilizes technology licensed from Oak Ridge National Laboratory.¹⁸⁰ The bench-top system can conduct 64 simultaneous assays using a proprietary Micro-Electro-Mechanical System¹⁸¹ (MEMS)-based biochip, a patented laser reader technology, microfluidics, and advanced custom analysis software. The biochip has an array of microcantilevers that can detect interactions between proteins, antibodies, antigens, or DNA. The system, which does not require labels or amplification, delivers data in real-time as the binding interactions take place. The lower limit of detection is 0.2 ng/mL , making it competitive with the more traditional ELISA assay (Daviss, 2004). As with other technologies for detecting microbes on microchip platforms, sample volume reduction for the concentration of cells would be necessary before the technology is viable for drinking water. (Images reproduced with permission from Protiveris.)



VeriScan™ 3000 System (Protiveris)

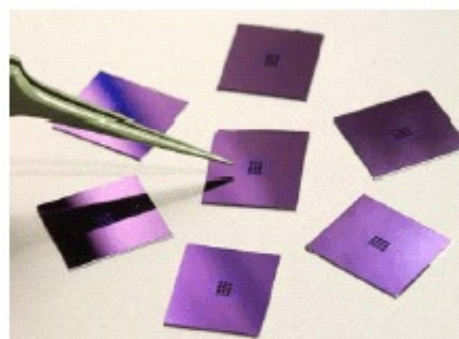
7.4.11 Photoluminescent Biochips

IatroQuest's (Verdun, Canada) Bio-Alloy™ biochips are made of silicon-based semiconductor materials that are nanostructured and chemically modified to bind to a variety of molecules, including antibodies, enzymes, nucleotides, and chemicals as recognition elements. The underlying

detection principle, based on a photoluminescence response, relies on quantum confinement and changes in the surface energy state when the material is excited with low-power blue LED light. Upon affinity binding of target contaminants to the recognition elements linked to the surface, surface energy perturbations result in an immediate change in the photoluminescence response, which is detected as an increase in green light intensity. Different formats of the material can be produced, including chips, particles, or microspheres for more end-product versatility. IatroQuest has a portable demonstration system, but no products are yet developed.¹⁸² The company has been awarded a \$3 million (Canadian dollars) development contract from the CRTI Counter-Terrorism Initiative.

7.4.12 Polymer Microbeads - Taste Chip

Scientists at the University of Texas at Austin have developed the “electronic taste chip,” based on a system of polymer microbeads that mimic human taste buds.¹⁸³ The system has been licensed to LabNow, Inc., for commercial product development. This multi-sensor array technology can generate digital fingerprints of complex fluids in near-real-time. The device functions by using a combination of micromachining, nano-chemistry sensing schemes, molecular engineering of receptor sites, and pattern recognition protocols to detect a variety of biological and chemical contaminants (e.g., electrolytes, toxins, drugs, metabolites, bacteria, blood products). Taste chips can be adapted within months to respond to new analytes, which provide for customized applications such as drinking water analysis. Their analytical characteristics (sensitivity, selectivity, detection thresholds, assay variance) have been shown to be comparable to or better than many well-established macroscopic analytical methods (Goodey and McDevitt, 2003; McCleskey et al., 2003; Kirby et al., 2004). Fully developed prototype instruments and customized microchip sets have been designed, constructed, and tested in numerous application areas including homeland defense, where hand-held units have been sent to the Defense Threat Reduction Agency for further testing (John T. McDevitt, U. Texas, personal communication; image reproduced with permission).



Taste Chip (University of Texas)

7.4.13 Molecularly Imprinted Polymers

Molecularly imprinted polymers (MIP) are synthetic receptors which can be designed for a range of toxins and some microorganisms.¹⁸⁴ MIPs have greater stability, being able to withstand climate extremes and larger sensitivity ranges, than antibodies (Haupt, 2002).¹⁸⁵ The technology is being incorporated into the UK Ministry of Defense’s development of an integrated biological detection system for battlefield use against biowarfare agents (Bunk, 2002). Some analytes for which MIPs have been developed include the algal toxins, domoic acid, and microcystin, and the fungal toxins, aflatoxin B1, and ochatoxin A.¹⁸⁶ MIPs are used very successfully in “at home” glucose detection devices for diabetics. Further refinement of MIPs for CBW detection is being pursued by multiple laboratories (Mays, 2004; Pesavento et al., 2004).

7.4.14 Magnetoelastic Sensors

Mass-sensitive magnetoelastic sensors can be used to detect antibody-antigen interactions. However the mass change must be amplified by biocatalytic precipitation. The sensor platform has immobilized capture antibodies, which recognize target antigens, then alkaline phosphatase-labeled antibodies are added to form an antigen-antibody sandwich complex. The mass of the sandwich complex is amplified by the precipitation of 5-bromo-4-chloro-3-indolyl phosphate disodium salt hydrate (BCIP). In response to an externally applied time-varying magnetic field, steady-state or pulse, the ribbonlike magnetoelastic sensors mechanically vibrate at a characteristic resonance frequency.



**Ten Sensor Array
magnetoelastic sensor
(Craig Grimes, PennState)**

These mechanical vibrations can be detected in several ways: optically from the amplitude modulation of a reflected laser beam, acoustically using a microphone or hydrophone, and by using a pickup coil to detect the magnetic flux emitted from the sensor.¹⁸⁷ *E. coli*, enterotoxin, and ricin have been detected with laboratory prototypes (Ruan et al., 2003, 2004a, 2004b). Although, this laboratory prototype sensor will not likely be adapted for water in the near future, its very low cost makes it an attractive technology. (Image reproduced with permission from Craig Grimes.)

7.5 Concentration Methods

Two AwwaRF research papers scheduled for publication in 2005 (Extraction Methods for Early/Real-Time Warning Systems for Biological Agents - Project A and B; see Appendix D) address methods for extracting biological contaminants from large sample volumes.

AwwaRF Project #2985 seeks to develop a large-volume extraction method for biological contaminants that takes less than three hours and has at least a 60 percent to 70 percent recovery efficiency. CDC is a project partner. The project builds on research being done by the DOD on the Joint Service Agent Water Monitor, which serves all of the DOD services (e.g., Army, Navy, Air Force, Marines). The objective of the program is to develop a water monitor that is portable, preferably hand-held, near real-time, and capable of detecting all agents harmful to service members in the field, while providing no false-positives. Because intentional contamination of water has historically been a concern for the military, DOD has the most focused and developed information concerning purposeful contamination of drinking water.

AwwaRF Project #2908 (see Appendix D) seeks to screen three to five different water extraction methods for biological contaminant surrogates. DOD is a research partner. AwwaRF indicates that release of the final report may involve a special protocol that requires signing a non-disclosure agreement.

7.5.1 Hollow Fiber Ultrafiltration

A persistent challenge for many detection methods is the need to concentrate the contaminants before identification and quantification. Hollow fiber ultrafiltration is a technology to simultaneously concentrate viruses, bacteria, and protozoa from large volumes of water. The ultrafiltration method can concentrate 100 liters of drinking water into 250 mL within 1 to 2 hours. The water is circulated through a filter system to catch certain molecule sizes. The retentate can be

further subdivided to permit detection of various microorganisms. This method may still have to remove concentrated inhibitors that can interfere with certain assay tests like PCR. The method is currently being developed by EPA, CDC, Army, and the Metropolitan Water District of Southern California. A study of the hollow fiber techniques on source water from four water districts showed a mean recovery of approximately 48 percent of *Cryptosporidium* oocysts. The results were comparable to the Envirochek filter. The conclusion was that hollow-fiber ultrafiltration can efficiently recover oocysts from a variety of surface waters (Kuhn and Oshima, 2002).

EPA-NHSRC and the Idaho National Laboratory (INL) have an interagency agreement to develop and produce a next generation prototype of the Ultrafiltration Concentration (UC) device previously developed by NHSRC and other stakeholders. The UC benchtop device concentrates microbial pathogens within a 100 L municipal drinking water sample into a 250 mL volume in approximately a 2-hour time frame (400-fold concentration). INL hopes to use the benchtop UC system that has been tested at the NHSRC in Cincinnati, OH, to redesign/repackage and automate the components such that the new device can be operated in the field as a near-commercial, or field prototype system (Vincente Gallardo, EPA, personal communication).

7.5.2 Hydroxyapatite Whole Cell Capture

Hydroxyapatite (HA) whole cell capture is a technology that could be applied to concentrate microbiological contaminants in water supplies in order to detect them. For both pathogenic and non-pathogenic organisms, the presence of anionic polymers on cell surfaces can be used to capture both Gram-positive and Gram-negative eubacteria. Hydroxyapatite is a form of calcium phosphate that can bind to bacterial cells with high affinity. It has been demonstrated by Berry and Siragusa (1999) that positively charged HA particles can concentrate and purify bacteria from complex matrices such as suspensions of ground beef and bovine feces. The bacteria would then be ready for identification by PCR analysis. Because the cell capture is based on van der Waals and electrostatic interactions between the bacteria cells and the HA particles, the affinity to the HA particles depends on the specific cell type. When tested, the efficiency of capture varied from 46 percent for *E. coli* to 99 percent for *Yersinia enterocolitica* (Mays, 2004).

7.5.3 Lectin and Carbohydrate Affinity

Another approach that could be used to capture microbial cells is to use lectins that target the carbohydrate rich cell envelope polymers of microbes. The carbohydrate pieces are usually fundamental structural elements of cell walls or proteins so are less likely to vary than protein sequences that can mutate or are dependent on environmental conditions. Therefore, the use of lectins is an attractive candidate for concentration methods. Lectin-based capture of several eubacteria including *E. coli* and *Salmonella* spp. has been demonstrated. A microbial capture approach analogous to using lectin affinity is to use the carbohydrate binding properties of the microorganisms themselves. It is normally critical for pathogenic bacteria to adhere to the lining of the gut in order to colonize. Well studied examples of carbohydrate binding in bacteria are adhesions used by *E. coli* and *S. flexneri*. Also, necessary host cell recognition through carbohydrates has been studied for certain viruses, such as rotavirus. It can be speculated that a collection of lectins and/or carbohydrates could be chosen to bind organisms in a semiselective manner to concentrate and purify them for detection.

Anticipated challenges to the use of hydroxyapatite and lectin/carbohydrate affinity include the difficulty of immobilization of HA and lectins onto magnetic or polystyrene beads. Also, tests would need to be performed to determine capture efficiency of the microbial contaminants of interest, and tests would be needed to determine if these methods would co-concentrate inhibitors, causing them to be of little use for detection (Mays, 2004).

8. Technologies that Detect Radiological Contaminants for Early Warning Systems

Radiation is a possible contaminant in water and is associated with carcinogenic and non-carcinogenic adverse health effects. The Federal Water Pollution Control Act (Clean Water Act), the Safe Drinking Water Act (SDWA), and the Maximum Contaminant Levels (MCLs) address protection of water systems from radiation and other contaminants. Radiation MCLs are measured at entry points, do not require routine monitoring, and currently exist for beta/photon emitters (includes gamma radiation), alpha particles, combined radium 226/228, and uranium. These regulations had been thought to be adequate in ensuring a long-term distribution of clean and safe water. However, now that terrorism is a major security concern in the U.S., the importance of the water sector's preparedness for potential attacks and accidents has become increasingly important. The Homeland Security Presidential Directives (HSPDs) and the Public Health Security and Bioterrorism Preparedness and Response Act of 2002 (Bioterrorism Act) have obligated EPA to focus on the water sectors' strategies for emergency prevention and response.

In the case of intentional contamination, realtime monitoring of radiation is important for immediate detection and response. Currently there is radiation measurement equipment that detects the total amount of radiation, as well as equipment that detects specific types of radiation by the energy levels emitted from a given source. SSS-33-5FT Drinking Water Rad-safety Monitor by Technical Associates and 3710 RLS Sampler by Teledyne Isco, Inc. (Los Angeles, CA)¹⁸⁸ (both mentioned below) are examples of devices that analyze the aggregate radiation of alpha, beta, and gamma rays. These instruments alert operators when the water has been radiated, but do not identify the specific contaminant. Other instruments identify alpha, beta, and gamma radiations separately, and will be discussed further in this section. The general information as well as many of the technology costs presented in this section are available on EPA's website,¹⁸⁹ Water and Wastewater Security Product Guide, which addresses radiation detection equipment for monitoring water assets. This website is based on information culled from the *Multi Agency Radiation Survey and Site Investigation Manual* (EPA, 2000), developed by EPA, DOE, DOD, and the U.S. Nuclear Regulatory Commission.

EPA does not endorse or recommend any of the following technologies. The summary information below was obtained from company websites and promotional literature.

8.1 General Introduction to Methods of Detection

Gamma radiation emissions are long-range electromagnetic waves that penetrate many objects and can be measured in the field with a sodium iodide (NaI) scintillation survey meter. On the other hand, it is difficult to have in-field rapid detection technology for alpha and beta radiation in water due to their physical properties. Alpha radiation emissions are positively charged particles that cannot penetrate through objects while beta radiation emission are negatively charged particles that have a moderate capacity to penetrate objects. Difficulties arise in measuring alpha and beta emissions in water because these short range types of radiation are easily blocked (attenuated) by water before they reach the detector.

Therefore, the instruments need to be placed close to the source without blocking the path of the radiation to the detector. Furthermore, gas-flow proportional counters typically evaluate alpha and beta radiation from smooth, solid surfaces. However, since water surfaces are not smooth, a large,

sensitive liquid scintillation counter in a laboratory is frequently required; thus, in-field quantification of alpha and beta radiation in water is a rare practice. This chapter, however, introduces certain devices that can detect and quantify radiation onsite.

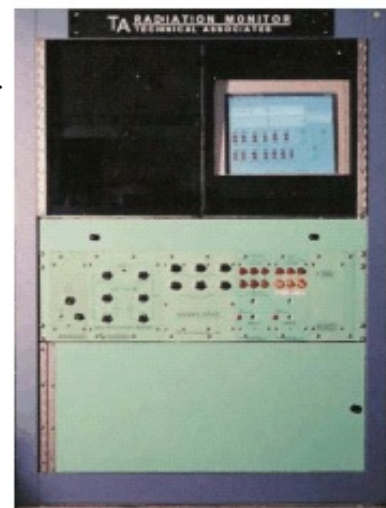
The instruments and methods can be evaluated in terms of specificity and sensitivity. EPA defines specificity as the ability of an instrument to quantify or evaluate the specific type of radiation or radionuclide for which it is designed without false-positives, (e.g., without interference from other radiation or radionuclides). Sensitivity is defined as the radiation level or quantity of radioactive material that can be measured or detected with some estimated level of confidence, and is a function of the instrumentation and the technique used. With regard to the specificity in measuring alpha and beta radiations, liquid scintillation counters are generally extremely flexible and accurate when properly calibrated and quenching effects are compensated (the full energy pulse may not reach the photo-multiplier detector). The complex multi-energy spectra of beta radiation can be quantified because its energy spectra are 10 to 100 times broader than the gamma spectra. With regard to sensitivity, this scintillation survey meter is ideal for moderate to high energy beta and alpha emitters because different radiation types can be easily distinguished by their pulse shape.

With regard to the specificity in measuring gamma radiation, some of these scintillation survey meters make the preliminary identification of specific isotopes possible with their ability to analyze selected ranges of gamma energies. The minimum sensitivity of these scintillation meters is 200 to 1000 counts per minute (cpm), and can be lower when switched to digital integrate mode. The cost of the sodium iodide scintillation survey meter is approximately \$2,000. Typically these in-line gamma radiation detectors are used only at special facilities that handle radioactive materials.

Continuous online monitoring systems can monitor the water in real-time however, there are few such units commercially available. These systems can be installed along with an alarm system that would alert operators of unusual radiation measurements. There are units for measuring radiation in wastewater but these would have to be adapted for drinking water. Grab sample units for drinking water are much more common. Very few water districts have real-time radiation monitors in place to protect water and the public.

8.2 Available Technology

The SSS-33-5FT¹⁹⁰ by Technical Associates (Los Angeles, CA) is a real-time, in-line, continuous flow-through scintillation detector of alpha, beta, and gamma radiation in ground, surface, or waste water. The detector can be applied to measure one type of radiation or all radiations combined. This easily calibrated apparatus uses ion exchange resin beads and charcoal filters, and does not require liquid scintillant. The ion exchange resin collects ions from dissolved metals, which are then measured for activity by gamma spectrum detectors. The charcoal filter collects non-ionized stray radioactives. Crushed anthracene scintillation crystals are the final detector of the radiation. The instrument measures tritium up to 100 picoCurie/mL and is equipped with a system that sends an alert if unusual readings are made. All the data can be retrieved in a spreadsheet format.



SSS-33-5FT
(Technical Associates)

This instrument is on the market for approximately \$58,000. (Image reproduced with permission from Technical Associates.)



MEDA-5T
(Technical Associates)

MEDA-5T¹⁹¹ by Technical Associates is a continuous monitor of intentional contamination or accidental spills of gamma radiation into the water source. The instrument is equipped with pumps and a scintillation detector. An automatic quick alarm will sound in the event of a radioactive water contamination. The monitor is available for approximately \$25,000. (Image reproduced with permission from Technical Associates.)

The 3710 RLS Sampler¹⁹² by Teledyne Isco, Inc. (Los Angeles, CA), detects radionuclides using 3M Empore™ Rad Disks and a known amount of flow-through. The sampler continuously monitors in water for all types of radiation. (Image reproduced with permission from Teledyne Isco Inc.)



3710 RLS Sampler
(Teledyne, Isco, Inc.)

The down-hole tritium in water detectors, SSS-33DHC and SSS-33DHC-4¹⁹³ by Technical Associates, are used to continuously monitor and detect underground plume or tritium leakage. These detectors fit in bore holes, are not influenced by other nuclides, and require no liquid scintillant. The monitors are sensitive below EPA clean drinking water levels, have a sensitivity of 1 nanoCurie/ml in 100 seconds, and their lower limit of detection is better than the FDA drinking water standard of 20,000 pCi/L average over 24 hours. These monitors cost \$72,000.

The SSS-33M8 monitor¹⁹⁴ by Technical Associates is a real-time continuous monitor for tritium in water. No liquid scintillant is required and it is sensitive to 0.1 nanoCurie/mL without being influenced by other nuclides. It is useful in monitoring leaks in type reactors, tritium in groundwater, and laboratory or plant liquid waste streams. This monitor costs \$16,500.

8.3 Potentially Adaptable Technology

Canberra (Meriden, CT) has developed several devices that detect radiation in liquid pipes such as those carrying waste streams, but these monitors are not intended for drinking water distribution systems. All of Canberra's devices can monitor liquid streams in realtime using the Radiological Assessment Display and Control Software (RADACS), which allows online access to the monitors from remote locations.

The LEMS600 Series Liquid Effluent Monitoring System (LEMS)¹⁹⁵ by Canberra has the capacity to continuously evaluate the gross gamma/beta radiation. The series consists of LEMS614, LEMS615, and LEMS616. The detectors are equipped with alarms in case of high radiation or failure conditions. The LEMS614 detects the combination of beta and gamma radiation, while LEMS615 detects gamma radiation in liquid samples between 0 to 50° C. A similar gamma

detector, LEMS616, incorporates a cooling system for liquids with higher temperatures. The cost of LEMS technologies is between \$100,000 and \$150,000.

The OLM100 Online Liquid Monitoring System¹⁹⁶ by Canberra continuously monitors liquid and gas gamma radioactivity in liquid and gaseous streams. It is available both as a clamp on model as well as a clam shell model so as to fit various pipe sizes. The device uses a gain-stabilized scintillation detector and has earned Class 1E Safety Qualifications. The instrument is an online monitor that is attached to the exterior of pipes so as to not disrupt the flow rate within. Its sensitivity/detection limit depends on a preprogrammed lower limit of detection and the normal background. The cost of OLM-100 is between \$35,000 and \$70,000.

The ILM-100¹⁹⁷ by Canberra is similar to the OLM-100 but is installed within the pipe system. The ILM-100 and OLM-100 cost between \$35,000 and \$70,000. The OLM system is typically cheaper than the ILM system because it can be clamped onto an existing pipe, whereas the ILM system must be fitted into the pipe. Both systems can be fitted into pipes of ½ inch to 16 inches, but the cost increases with the pipe size because of the additional expense of ensuring that the detector is properly installed in the pipes.

8.4 Emerging Technology

Clarion Sensing Systems, Inc. (Indianapolis, IN)¹⁹⁸ has developed an in-pipe radiation detector that the company plans to launch on the market in late 2005 (Martin Harmless, Clarion, personal communication). The Gamma Shark™ sensor detects gamma radiation in water above background levels. The device is able to expose more surface area for the radiation to contact by inserting the scintillator tube in the water stream. The monitor logs fissions detected and converts the counts per minute to normal units. The Gamma Shark™ compares the radiation levels in the water to background and detects increases in radiation in the water. The company is in the process of third party verification and the instruments are expected to be cost-effective compared to currently available technology. Clarion's radiation detectors will stand alone or interface with the company's Sentinal™ unit (see Chapter 4) to provide website display results as they are obtained.

According to a DOE publication in 2000,¹⁹⁹ Thermo Power Corporation (Waltham, MA) is developing the Thermo Alpha Monitor (TAM)²⁰⁰ under the sponsorship of DOE. This instrument is a near real-time monitor of alpha radiation, which was estimated to have a cycle time of approximately 30 minutes for 1 ppb Uranium, and approximately 5 minutes for 10 ppm Uranium. The concept was developed around the simultaneous *in situ* collection and quantification of radioisotopes on a silicon detector using a solid-state semiconductor counter. The detector is similar to those that use ionization chambers, but measures the lost energy caused by ionized radiation as an electrical current.

The PNNL (Richland, WA) is in the process of developing a in-field radionuclide sensor to detect technitium-99 (Tc-99) in groundwater.²⁰¹ The technology will incorporate the use of chemically selective beads to preconcentrate Tc-99 in the sensor in order to increase the sensitivity and selectivity of the direct measurements. The laboratory strives to create a device that can demonstrate reversible operation and the required sensitivity as well as the capability to operate the embedded controls from remote locations.

In addition, an online real-time radiation detection instrument will be available for alpha radiation in the near future. DOE tested this prototype, and further technological development has been conducted under the Los Alamos National Laboratory since 2001.²⁰² The detector is expected to be used in monitoring radioactive liquid waste and groundwater using Long Range Alpha Detection (LRAD) technology. The monitor is in real-time and is non-intrusive.²⁰³

[this page intentionally left blank]

9. Technical Evaluation of Early Warning Systems

This chapter provides a technical evaluation of the various components of an Early Warning System (EWS) for drinking water, as characterized in Chapters 3 and 4. Such an evaluation is important to allow utilities and drinking water quality officials to identify technologies appropriate to particular situations and systems. Researchers and utilities need a better sense of what systems are becoming fully developed and where there are research gaps. False-positives and false-negatives have occurred with various devices and have caused great concern among first responders, emergency agencies, and health and law enforcement officials. There are claims of performance that would benefit from additional testing and evaluation. In addition, technology is rapidly evolving and at various stages of development to detect chemical and biological contaminants. This report is divided by the level of development of early warning. The level of development is set by three categories, (1) available, (2) potentially adaptable, and (3) emerging. In Chapter 3, the desired characteristics of an EWS (e.g., detects range of contaminants, sensitive) were presented. In this chapter, an analysis is conducted on how close the existing EWS technologies meet these desired characteristics.

9.1 Approach for Technical Evaluation

A scientific and technical evaluation of EWS technologies is based on expert review of qualitative, semi-qualitative, and quantitative information sources as described below. It is important to note that the evaluation did not involve actually testing equipment or assays. The information sources include the following:

- verification studies
- degree of government involvement, support, and development for technology
- field experience and case studies
- other studies
- expert opinions

The sources are described in detail below.

9.1.1 Verification Studies

During the anthrax attacks of 2001, when hand-held assays proved unreliable, it became particularly clear that the government has a responsibility for validating the performance of CBR detection equipment (Emanuel et al., 2003). Verification, feasibility, and proof-of-concept studies of CBR detectors, with a special focus for use in water, are underway at several government and private facilities. Examples include the U.S. Army Edgewood Chemical Biological Center facility, the DOD Chemical and Biological Defense Program Test and Evaluation Executive Agent Facility for Water Monitor Test Methodology and Instrumentation Development, the EPA WATERS Facility, and various contractor facilities. Specific efforts at evaluation include the following:

- EPA's Environmental Technology Verification (ETV) program evaluates various technologies, including sensors for chemical, microbial, and radiological contaminants.
- EPA's Technology Testing and Evaluation Program (TTEP) tests the performance of technologies related to homeland security applications.

- The National Technology Alliance, through the Chemical, Biological, and Radiological Technology Alliance, examined and reported on state-of-the-art and emerging technologies in water monitoring (Black & Veatch, 2004).
- Some local water utilities, including the Pittsburgh Water and Sewer Authority, have conducted verification tests (States, 2004).
- AwwaRF has an extensive number of evaluation projects that deal with EWSs (see Appendix D). However, most are on going, and were not available for this evaluation.

The challenge remains that only a limited number of facilities can test this equipment with real chemical or biological agents.

9.1.2 Degree of Government Involvement, Support, and Development for Technology

Government and industry have sponsored research into the development of various water monitoring technologies, as well as the verification of their performance. Such research could be an indication of the potential development of the technologies. Sponsoring agencies include DHS, EPA, U.S. Army (ECBC), FDA, and CDC. For example, ECBC has an active program, including projects such as “Development of Novel DNA Probes for Emerging BW Agents,” “PCR Assay Optimization for BW Detection,” “Validation of BW Detectors,” and “Development of Enzyme-based CW Sensors.” FDA is investigating several technologies for identification of microbial contaminants, most of which are food-related, but some have applicability to the water sector. For example, in September 2003, FDA awarded five research grants on;²⁰⁴ (1) development of the Waveguide Immunoassay for *Yersinia pestis*; (2) a rapid immunoassay silver amplification test system; (3) uses of a novel, compact microchip sensing system for rapid food screening; (4) development of PCR-based assays on a microchip, and (5) use of thin layer chromatography and bioluminescence.

9.1.3 Field Experience and Case Studies

Some of the technologies have been widely used in source water or in the food industry that may enable the technology to be applicable to finished drinking water. Some utilities are using these technologies for grab samples from treated water, and a few utilities have online systems. The limited field experiences and case studies that were examined during the development of this report helped to provide insight into the technologies’ current uses. It is likely that further examination of more detailed (and confidential) case studies would yield a wealth of valuable information for the advancement of the EWS field.

9.1.4 Other Studies

There are several studies that provide evaluation information. These include the ASCE White Papers and *Interim Guidelines for Designing Online Contaminant Monitoring System* (ASCE, 2004), the CBRTA report *Water Monitoring Equipment for Toxic Contaminants Technology Assessment* (Black and Veatch, 2004) and various AwwaRF research studies (see Appendix D; Roberson and Morley, 2005).

9.1.5 Expert Opinions

Experts were contacted in various agencies and organizations, including DHS, USGS, EPA, DOD, various national labs, water associations, utilities, and consultants contracted for this project.

Using the above sources, a technical evaluation was conducted on various operational features of an EWS (e.g., data management, acquisition, security), on multi-parameter water quality monitors, on chemical sensors, on microbial sensors, and on radiological sensors.

9.2 Evaluation of Various Operational Features of EWS

This section addresses the features of the EWS that are *not* related to sensors. These EWS features include real-time data acquisition and analysis, contaminant flow predictive systems, sensor placement, alert management, security enforcement, and communications, response, and decision making.

9.2.1 Issues and Gaps

- **Real-time Data Acquisition and Analysis**

The SCADA interface is key to managing the data and identifying a contamination event. Most utilities are familiar with SCADA systems. Remote data acquisition systems are commercially available and used in many utilities for basic water quality control and monitoring. Adapting the SCADA to track sensor data is not a large challenge. However, challenges include the ability to handle the data load as well as to interpret the data that are collected. Analyzing large streams of data requires special training. Various software exists, but many algorithms for data analysis are not verified or demonstrated. Standardized methods for data analysis do not exist and may need to be developed for such EWSs. Documentation of case studies could also further guide the proper use of such data analysis techniques.

- **Contaminant Flow Predictive Modeling Systems**

There are some basic contaminant flow predictive systems, but their use by utilities for the purpose of modeling the movement of contaminants is not widespread. Many utilities do use models for tracking chlorine residuals and disinfection byproducts. However, as models undergo further development by researchers, it is necessary to calibrate and verify the models and make the models useful tools for sensor placement, for real-time contaminant flow prediction, and for identifying the location of the contaminant source. Utilities would need to expand their current use of models to include modeling for intentional contamination events. Also, utilities would either need to train personnel to operate the expanded models, or hire contractors to run the predictive flow models.

- **Sensor Placement**

Sensor placement has implications for cost. Placement is often determined by logistic factors such as location security and convenience, and access to a power source or data transmission rather than risk minimization. Although current research on combining flow models and sensor technology is a move in the right direction, such models must be verified before difficult and costly decisions are

made by the utilities. Simple guidance is needed for situations where the number of sensors is limited.

- **Alert Management**

Managing the alert process will help determine when certain proper response actions are needed. Proper alert levels will also minimize false-positives/false-negatives. It is not possible to eliminate all false-positives and false-negatives at the same time. Therefore, it is preferable to optimize the system to eliminate false-negatives and manage the inevitable false-positives in a way that minimizes undesirable impacts on the utility and community. Currently, only some utilities have experience with this as a part of their normal operations. The use of water quality parameters as a first stage alert is a particular challenge for EWSs for terrorist attacks. Detailed baseline water quality data are needed to set alerts with reasonable confidence that they do not result in too many false-positives or false-negatives. More demonstration projects are needed to assure the reasonability of certain approaches to alert management and further guide utilities to the proper use of such alert management.

- **Data Security**

Current remote monitoring products are beginning to incorporate security precautions, including encryption. However, demonstration projects are not frequent. Standardization from other data security efforts could be applied to the water sector. Programs should be developed to link utility security efforts surrounding SCADA generally with data security geared to EWSs.

- **Communications, Response, and Decision Making**

The process linking the analysis of contamination data with the decision making and response is outlined in EPA's Response Protocol Toolbox. While this guidance provides a process, the notification and communication equipment to effectively implement the process has not been extensively developed for water utilities. Tools (e.g., Water Contaminant Information Tool) to assist decision making and response are being developed.

9.2.2 Conclusions and Recommendations

Much of the data acquisition software and hardware already exist. The data acquisition systems do not represent a major issue given currently recommended sampling times by EPA. Security of SCADA systems for EWSs is a challenge but can probably be handled as the general security of SCADA systems is addressed by utilities. Recommendations on the topics in the section include the following:

- Standardized methods and guidance for data analysis and interpretation are needed. Some of the efforts by ASCE will help to guide utilities in the use of such systems.
- Projects are needed to verify contaminant flow models and then adapt the models relatively easily for use by various sized utilities.
- Simple guidance is needed, such as what to do if only a small number of sensors are available.

- A demonstration project is needed to assure the reasonableness of certain approaches to alert management. The USGS project is an example where multi-parameters sensors for water quality are being used in conjunction with alert management. Additional projects should examine alerts for other promising sensors such as mussel or bacteria monitors.
- Effective technologies should be developed to facilitate the rapid and efficient alert of decision makers and response personnel with response information.

9.3 Evaluation of Multi-Parameter Water Quality Monitors

Traditional drinking water quality monitors have been bundled together and sold commercially. They can now be monitored remotely, continuously, and in real-time. Several vendors have modular systems, so that utility companies can choose which parameters they want to measure. These multi-parameter monitors have proven valuable for maintaining daily water quality, and more recently have been evaluated as a first-tier warning of the presence of an intentional contaminant. However, combining monitors and sensors from different manufacturers is still problematic because these are limited uniformity and interchangeability in hardware, signal generation and processing, and connectivity. Several cities have used multi-parameter probes in their distribution systems both for ensuring general water quality and for water security. Usually the probes were placed at convenient sites with ready access.

An important part of developing a first stage EWS is to evaluate whether the normal operation of water distribution systems can be documented in terms of sensor responses. One purpose of the test at the WATERS Center was to determine if sensors can identify a baseline water quality or if sensor drifting takes place. Thus, the basic performance characteristics of individual commercially available sensors (in terms of use for early warning in water) were evaluated. The parameters measured include pH, DO, turbidity, free chlorine, conductivity, ORP, TOC, and ion-selective electrodes (Cl^- , NO_3^- , and NH_4^+). A basic conclusion was that specific-conductance, TOC, and free chlorine monitors drift very little when properly calibrated and serviced; therefore, these sensors are ideal for characterizing normal or safe conditions. However, it was also found that free chlorine interferes with some of the above water parameters. Additionally, the test examined if the sensors can qualitatively detect the contaminants. The contaminants injected into the system included wastewater, potassium ferricyanide, malathion, and glyphosate. The test concluded that the sensors can only provide a general indication of the contaminant class such as inorganic, organic, or a reactive species producing chlorine demand (EPA, 2004).

The USGS and EPA have an Interagency study to implement and test an EWS at actual field sites. The investigation team, composed of scientists and researchers from EPA, the USGS New Jersey District, and a water utility are involved in the project whose purpose is to identify potential EWS field sites, select sensors based on the previous EPA and USGS efforts, evaluate the distribution system hydraulics and water quality, determine sensor locations, and collect sensor data. However, no contaminants will be injected into the distribution system. The data will help determine how well the sensors work, optimize the sensor location, and develop a baseline water quality profile of the distribution system.

Another study from EPA's WATERS test facility investigated the response of a combination of off-the-shelf sensors to detect changes caused by the injection of wastewater, groundwater, a chemical cocktail, and individual chemicals, such as potassium ferricyanide, malathion, and glyphosate. The

feasibility of using the sensor information as an early warning of an attack was investigated. Initial results show that water quality sensors responded to the injection of test materials. The parameters monitored by the sensors include chloride, free chlorine, ORP, specific conductance, TOC, and turbidity. These parameters exhibited a unique and consistent pattern of signal changes upon injection of wastewater, potassium ferricyanide, malathion, glyphosate, and groundwater into a drinking water distribution system simulator. The sensor system showed promise for providing quick detection of water quality changes due to introduction of these test materials in the pipe loops. Because of the unique physicochemical properties of these test materials, a specific sensor response pattern was observed for each substance. This suggests that the sensor system may provide information on the characteristics of unknown contaminants and facilitate the subsequent identification with more sophisticated instruments. With further optimization, a system of sensors may be used as an EWS (EPA, 2004). However, because the range of test materials was narrow, additional types of contamination and scenarios should be examined to test this conclusion further.

Currently, EPA has several planned efforts to examine the use, development, and testing of multi-parameter probes. EPA has an interagency agreement with the USGS and initiated CRADAs with Hach Company, PureSense Environmental, Inc., and YSI, Inc. The goal of the partnerships is to develop technologies for both detection devices (e.g., multi-parameter probes) and data analysis software to facilitate the installation of early warning systems in the distribution networks of local water utilities. The types of multi-parameter probes include pH, ORP, specific conductance, residual chlorine, and temperature.

Another series of tests currently being conducted at the EPA WATERS facility is verifying the capability of multi-parameter water monitors for distribution systems. The testing is being performed under the auspices of the EPA-ETV Program. The multi-parameter monitors for distribution systems being used during these verification tests consist of instrument packages that can be connected to or inserted into distribution system pipes for continuous monitoring. Also included in this category are technologies that can be programmed to automatically sample and analyze distribution system water at regular intervals, as well as hand-held technologies requiring technicians to manually collect samples and perform the analysis. The monitors must be able to measure free chlorine as well as at least one other water quality parameter (e.g., alkalinity, pH, DO, ORP, temperature, turbidity, conductivity, ammonia, calcium, total carbon, chloramines).

The multi-parameter water monitors are being evaluated for the following parameters:

- *Accuracy*: Comparison to results from standard laboratory reference analyses.
- *Response to individually injected contaminants*: detection of changes in pipe loop water chemistry. (Contaminants tested will include aldicarb, arsenic trioxide, and either *E. coli* bacteria or nicotine.)
- *Inter-unit reproducibility*: comparison of results from two simultaneously operating monitors.
- *Ease of use*: general operation, data acquisition, set up, demobilization, required maintenance.
- *Presence and identification of injected contaminants (if applicable)*: A total of 17 different contaminants will be tested for identification by the appropriate monitoring system.

The monitors being verified during this series of tests include the following:

- Clarion Systems Sentinal™
- Emerson Model 1055 Solu Comp II Analyzer
- Man-Tech TitraSip SA (multi-parameter but not online)²⁰⁵
- Hach Event Monitor²⁰⁶
- Analytical Technology, Inc., Series C15 Water Quality Monitoring Module

Several manufacturers are exploring the signature monitoring approach. Using data from multi-parameter continuous monitoring devices, one company tested a number of potential water contaminants in an effort to establish signatures that could provide detection and a tentative identification. A list of 60 contaminants (chemicals, toxins, biologicals) were analyzed for possible detection. The sensors included pH, chlorine, conductivity, turbidity, and TOC. The sensors showed response to the various contaminants, however, a few contaminants did not trigger a sensor response at concentrations that are considered harmful. The manufacturer has developed a trigger algorithm to set off an alarm when conditions in water depart from expected baseline parameter values. Because utilities regularly experience changes in water quality, there are always concerns in this type of system for false-positives (King, 2004).

It was announced in October 2004 that the Army and Hach Company have signed a CRADA to complete testing of the Army's new real-time water security detection and response technology by the end of 2004. Under the agreement, ECBC, the Army Corps of Engineers, and Hach will conduct live-agent testing using Hach monitoring equipment (GLI International panel, CI-17, turbidimeter, pH, and specific conductance, as well as Hach's TOC monitor) to detect terrorist attacks on drinking water distribution systems. The ECBC is one of the few sites in the U.S. where testing on actual chemical and biological contaminants can take place. Pending verification tests, the technology is scheduled for commercial production in 2005.

Exhibit 9-1 provides an evaluation of specific water quality parameter probes in the distribution system. Exhibit 9-2 summarizes how the probes (both currently available or potentially adaptable) compare with the desired characteristics of EWSs (as described in Chapter 3).

9.3.1 Issue and Gaps

The following discussion highlights various issues and gaps in using multi-parameter water quality monitors in an EWS.

- **Baseline Data are Needed**

Although research has demonstrated proof of concept for using water quality parameter fluctuations as a signal that a contamination event has taken place, baseline data to calibrate the alarm triggers may need to be gathered over months or years for each independent system. This will likely prove to be sufficiently expensive that budgetary impacts would need to be addressed. Daily, seasonal, and event- (i.e., storm-) related fluctuations will need to be identified and characterized, so they are not confused with contamination events. Thus, systems with highly fluctuating source waters may have considerable noise in the baseline.

Exhibit 9-1. Evaluation of Water Quality Parameter Monitors

Technology	Manufacturer	Evaluation
Single Parameter Sensors		
Model A 15/B-2-1 – Free Chlorine	Analytical Technology, Inc.	This is an online sensor that uses a polarographic method to monitor free chlorine. It showed less baseline stability and sensitivity than Hach's AquaTrend Panel, which also monitors chlorine.
Hach TOC process analyzer	Hach	This is an online sensor that uses UV persulfate oxidation to monitor total organic carbon. A good baseline and high sensitivity was maintained when tested with all contaminants. Cost is \$30,000, higher than most of the other devices tested in the study.
International Model 5500 Dissolved Oxygen	GLI	This is an online sensor that uses a membrane electrode to monitor dissolved oxygen concentration.
Ion Selective Electrodes	Various vendors	No difference in chloride, nitrate, and ammonium analyzers. Nitrate electrode not properly calibrated after exposure to Cl. Chloride and ammonium sensor fail at a rate of 3-6 months. Recommend using 3 point calibration.
Specific- Conductance	Various vendors	No difference with vendors. Easy calibration, sensors last years, care during cleaning of annular-ring carbon electrodes
Dissolved Oxygen	Various vendors	Low flow technology no advantage over larger cell. DO sensor based on plan sensor technology gave positive deviation with sudden changes in Cl. Had failure rates for chip higher than manufacturer anticipated.
Oxidation- Reduction	Various vendors	Similar performance of vendors, ORP robust, other sensors (pH/electrodes) combined with ORP will fail before ORP
pH	Various vendors	Failure rates of 6 months in chlorinated water (planar sensor failed at 1-2 months, and required at least weekly calibration).
Temperature sensor	Various vendors	Rarely fail.
Turbidity Monitors	Various vendors	Very stable when properly cleaned (cleaning procedure is more difficult but only required quarterly. Calibration requires practices. Some false-positive readings when vibrated or change pressure.
Free Chlorine	Various vendors	Colorimetric reliable when serviced properly. However, sampling interval is 3 minutes. Polarographic technique very reliable but must change membranes every 2 months and need rigorous cleaning. Planar measurement failed most frequently.
Total Organic Carbon	One vendor	Very stable but need experience to operate.

**Exhibit 9-1. Evaluation of Water Quality Parameter Monitors
(continued)**

Technology	Manufacturer	Evaluation
Multi-Parameter Sensors		
Six-Cense™ continuous monitor	Dascore	This online sensor monitors dissolved oxygen, free chlorine, ORP, pH, specific conductance, and temperature. It showed an unstable baseline when monitoring ORP, specific conductance, and free chlorine.
AquaTrend panel	Hach	This online sensor monitors free chlorine, pH, specific conductance, temperature, and turbidity. For free chlorine detection, it showed the highest sensitivity and most stable baseline compared to ATI's and Dascore's free chlorine sensors. It also had the most stable baseline for turbidity monitoring. Overall, the AquaTrend showed consistent responses, stable baselines, and high sensitivity in almost all parameters measured in the study.
DataSonde 4a	Hydrolab	This online sensor monitors ammonia nitrogen, chloride, dissolved oxygen, nitrate nitrogen, ORP, pH, specific conductance, temperature, and turbidity. It performed well compared to other sensors in measuring ORP.
In-Situ Model Troll 9000	In-Situ	This online sensor monitors dissolved oxygen, ORP, pH, specific conductance, temperature, and turbidity. In measuring ORP, it was noted that the In-Situ model had a higher rate of failure than other sensors.
Signet Model 8710	Signet	This online sensor monitors ORP and pH.
YSI Model 6000 continuous monitor	YSI	This online sensor monitors ammonia nitrogen, chloride, dissolved oxygen, nitrate nitrogen, ORP, pH, specific conductance, temperature, and turbidity. The YSI model showed a more stable baseline for ammonia nitrogen and nitrate nitrogen monitoring and a higher sensitivity for chloride monitoring. Overall, the YSI model showed consistent responses, stable baselines, and high sensitivity in almost all parameters measured in the study.
Zero Angle Photon Spectrometer MP-1	Oregon State University	This online sensor uses optical measurement to monitor bacterial fluorescence, humic fluorescence, nitrate nitrogen, total fluorescence, transmission, and 245 nm UV absorbance.
STIP-scan	STIP Isco GmbH (Germany)	UV/V is a spectroscopic sensor that is capable of simultaneous measurement of nitrate, COD, TOC, spectral absorption coefficient (SAC254), total solids, sludge volume, sludge volume index, and turbidity

Sources: EPA, 2004a, 2004b.

Exhibit 9-2. Water Quality Monitors Comparison with Desired EWS Characteristics

Product	Description	Range of Contaminants	Online/Portable?	Cost	Operator Skill	Analysis Time	Currently available?	Evaluation
Various Specific Conductance probes	single-parameter water quality monitoring	conductance	online	\$1,200	low	< 5 min	available	EPA WATERS
Various Dissolved Oxygen probes	single-parameter water quality monitoring	DO	online	\$1,600	low	< 5 min	available	EPA WATERS
Various Oxidation-reduction probes	single-parameter water quality monitoring	ORP	online	\$1,450	low	< 5 min	available	EPA WATERS
Various pH probes	single-parameter water quality monitoring	pH	online	\$1,400	low	< 5 min	available	EPA WATERS
Various Temperature sensors	single-parameter water quality monitoring	temp	online	\$1,100	low	< 5 min	available	EPA WATERS
Various Turbidity monitors	single-parameter water quality monitoring	turbidity	online	\$1,100	medium	< 5 min	available	EPA WATERS
Various Free Chlorine monitors	single-parameter water quality monitoring	chlorine	online	\$3,000	low	< 5 min	available	EPA WATERS
Various Total Organic Carbon monitors	single-parameter water quality monitoring	TOC	online	\$25,000	medium	3-15 min	available	EPA WATERS
Hach TOC Process Analyzer	single-parameter water quality monitoring (total oxygen concentration)	general toxic chemicals	online	\$30,000	low, automated	3-15 min	available	EPA WATERS
Hach Water Distribution Monitoring Panel	multi-parameter water quality monitoring	general toxic chemicals	online	\$13,500	low, automated	< 5 min	available	EPA WATERS
Diascore, Inc., Six-Cense™ continuous monitor	multi-parameter water quality monitoring	general toxic chemicals	online	\$9,700	low, automated	< 5 min	available	EPA WATERS
Emerson Model 1055 Solu Comp II Analyzer	multi-parameter water quality monitoring	general toxic chemicals	online	not available from website	low, automated	< 5 min	available	none

**Exhibit 9-2. Water Quality Monitors Comparison with Desired EWS Characteristics
(continued)**

Product	Description	Range of Contaminants	Online/Portable?	Cost	Operator Skill	Analysis Time	Currently available?	Evaluation
Analytical Technology, Inc., Series C15 Water Quality Monitoring	multi-parameter water quality monitoring	general toxic chemicals	online	not available from website	low, automated	< 5 min	available	none
Analytical Technology Inc Model A 15/B-2-1	single-parameter water quality monitoring (free chlorine)	general toxic chemicals	online	\$3,700	low, automated	< 5 min	available	EPA WATERS
Clarion Systems' Sentinel	multi-parameter water quality monitoring	general toxic chemicals	online	not available from website	low, automated	< 5 min	available	none
GLI International Model 5500	single-parameter water quality monitoring (dissolved oxygen)	general toxic chemicals	online	\$3,700	low, automated	< 5 min	available	EPA WATERS
Hydrolab DataSonde 4a	multi-parameter water quality monitoring	general toxic chemicals	online	\$15,000	low, automated	< 5 min	available	EPA WATERS
Hach AquaTrend panel	multi-parameter water quality monitoring	general toxic chemicals	online	\$12,800	low, automated	< 5 min	available	EPA WATERS
In-Situ Model Troll 9000	multi-parameter water quality monitoring	general toxic chemicals	online	\$11,200	low, automated	< 5 min	available	EPA WATERS
Signet Model 8710	multi-parameter water quality monitoring	general toxic chemicals	online	\$830	low, automated	< 5 min	available	EPA WATERS
YSI Model 6000 continuous monitor	multi-parameter water quality monitoring	general toxic chemicals	online	\$15,000	low, automated	< 5 min	available	EPA WATERS
STIP-scan	multi-parameter water quality monitoring	general toxic chemicals	online	not available from website	low, automated	< 5 min	potentially adaptable	none
Clarion Systems' Sentinel	multi-parameter water quality monitoring	general toxic chemicals	online	not available from website	low, automated	< 5 min	available	none

- **Contaminant Specific Signatures are Needed**

Research has begun to develop contaminant specific signatures; however, the limited number of contaminants examined lowers the confidence of the claim that the signature really is unique. Classes of contaminants may be identifiable, but whether a wide range of specific contaminants can be identified has not yet been determined. Regular changes in water quality can be a source of false alarms (i.e., false-positives). Additionally, it is not known yet whether there are specific signatures for biological contaminants.

- **Data Storage and Manipulation are Needed**

For continuous real-time monitors, raw data can be generated on a scale that may be too large for manual manipulation in a spreadsheet. Monitors that gather this volume of data would require customized software (which vendors would usually supply) for data analysis. Utilities may choose to archive summary data in a compressed form, to meet possible later needs. For many of the techniques and devices reviewed in this report (see Chapters 5 to 8) the quantity of data generated will not present a challenge. However, utilities should be mindful of what they may want their system to handle if upgrades are planned. Approaches for storing and analyzing data are presented in Chapter 4.

- **System Can be Expensive**

Not all vulnerable utility companies are able to afford the monitoring systems currently being evaluated as EWSs. Reductions in price due to competition and technological advancements may remedy this situation in the future, but in the interim, utilities with limited financial resources will face a challenge in implementing online water quality monitoring.

- **Cost Decisions**

Current multi-parameter units cost approximately \$10,000 without TOC. Although TOC appears to be a valuable parameter to measure, it adds \$18,000 to 29,000 per unit. Research needs to determine the cost/benefit relationship of including this technology in an EWS. A basic system with 10 microprobe monitors (without TOC) linked to an existing SCADA system is estimated to cost approximately \$150,000, plus \$60,000 per year in operational costs (DSRC Meeting, 2004).

Exhibit 9-3 provides a snapshot of capabilities, issues, and gaps for multi-parameter water quality monitors.

9.3.2 Conclusion and Recommendations

Given the current developmental stage of multi-parameter technologies and based on preliminary EPA tests, parameters that appear stable in monitoring a distribution system include chloride (ISE), specific conductance (electrode), turbidity (nephelometric), free chlorine, and ORP. TOC also appears to be extremely helpful, but it is expensive to monitor. Sensor probes and monitoring systems are being developed by manufacturers. Such probes include free and total chlorine, pH, temperature, specific conductance, chloride, nitrates, turbidity, and ORP. The cost per probe ranges from a few hundred to several thousand dollars.

Exhibit 9-3. Water Quality Monitors as EWS

Capabilities	Issues and Gaps
<ul style="list-style-type: none"> • Generally reliable and accurate for WQ parameters • Training and maintenance needs considered reasonable by water utilities • Have demonstrated the ability to identify some chemical contaminants • Wealth of multi-parameter monitors available from a variety of companies • A few utilities have experience in using in distribution systems • Significant testing of systems is ongoing and will further evaluate use as an EWS component • Generally not prohibitively expensive • Selection of parameters will determine effectiveness • Free chlorine sensor had the best response for contaminants tested at EPA WATERS laboratory 	<ul style="list-style-type: none"> • Baseline data needed on regular water quality fluctuations • Contaminant specific signatures needed • Large scale data storage and manipulation needed • Systems can be expensive to install and operate depending on the parameters chosen • System not yet demonstrated for chemical warfare agents, but future efforts planned • Easy to place, but may present challenges for placement based on risk evaluation (space constraints, protection of the equipment). Also, location may be influenced by interferants created by water source mixing and routine/unexpected water quality fluctuations.

Using the multi-parameter techniques, there is some preliminary evidence to suggest that such a system appears to be able to detect an anomaly in the system. However, it is also reasonable to be concerned about false-positives and whether the system can provide definitive indications of contamination by a terrorist. Just gathering the baseline data may be prohibitively expensive. Currently, these technologies need to demonstrate the ability to detect biological contaminants or dangerous chemicals or develop a track record of field performance (e.g., how will it behave with biofilms). Additional testing is needed, most likely in the field, before widespread use could be recommended. For example, no tests have been performed on chloraminated systems. Full-scale testing by the USGS New Jersey District, EPA, and a water utility during 2006 and 2007 may help shed light on concern over false-positives and whether a system can function within the fluctuations of normal water quality.

The signatures being developed by Hach and others to identify contaminants or classes are difficult to evaluate independently or validate because their methods and algorithms are considered proprietary and therefore are not available to the research community. As additional testing is conducted using these methods and their performance is confirmed, there is less of a reason to be cautious in proposing the use of these signature methods. Also, the examination of water quality parameters for use in detecting and identifying contaminants is still being evaluated by EPA, USGS, Army, and other organizations. Yet, no field scale tests of a full EWS with these multi-parameter components have been implemented to date. This adds to the caution in currently recommending use of these water quality parameter-based EWSs.

9.4 Evaluation of Chemical Sensors

Online continuous sensors and hand-held sensors for the detection of chemical/toxins in vapors or air have been on the market and in use since before 9/11. The number of potential users of CBW sensors greatly expanded after vulnerabilities to terrorist attacks were recognized. Researchers and companies are rapidly developing technologies and products that will meet the needs of this increased pool of end users.

- Microchip and microfluidics technology is advancing the sensor field by enabling miniaturization of traditional methods (e.g., GC), as well as design of new methods.
- Portable and online gas chromatographs are available and in use by first responders. GC can reliably identify a wide range of VOCs. Several portable GCs have been tested under EPA's ETV program. In one case, an online GC has been used in water distribution systems.
- Kits that utilize bacteria to detect toxins have been developed for use with drinking water. Several kits have been verified under the ETV program.
- Daphnia, mussels, algae, and fish have been incorporated into sensors for toxins in treated waste effluent and source waters. However, only a mussel-based and a fish-based system have been used to date with chlorinated drinking water.
- Portable infrared spectroscopy, ion mobility spectroscopy, surface acoustic waves, and polymer composite chemoresistors technologies have been incorporated into portable devices that can be used by first responders for the identification of numerous toxic chemicals.
- Fiber optic cables are being coated with sensor materials to engineer continuous flexible sensors for use in water and in air.

EPA's ETV Program has investigated a number of the sensors that are sensitive to chemical contaminants. A few utilities have experience using the biosensors for grab samples in distribution systems. Another utility has experience using portable GC in the distribution system.

The following are evaluations of specific chemical detection devices starting with arsenic and cyanide and then continuing with other specific detector systems. Exhibit 9-4 summarizes how the chemical detectors (only those available now or potentially adaptable) compare favorably against the desired characteristics of an EWS (as described in Chapter 3).

- **Arsenic Sensor**

There are two basic types of technologies that are used in commercially available tests, both of which have been third party verified by EPA's ETV Program. The first type involves a color reaction kit (three manufactures evaluated) and the second employs anodic stripping voltammetry (ASV; two manufacturers evaluated). The arsenic monitor manufactured by Industrial Test Systems, Inc. (Rock Hill, SC) showed that low and high levels of interferences did not appear to affect the detection of arsenic. A very low rate of false-positives was reported, but a variable rate of false-negatives was reported. One source of error that ETV testers noted was that when samples contain concentrations exceeding optimal detection, range accuracy and precision of the associated results were reduced because of the difficulty in performing accurate dilutions in a field setting. The AS

Exhibit 9-4. Chemical Sensors Comparison with Desired EWS Characteristics

Product	Description	Range of Contaminants	Online/Portable?	Cost	Operator Skill	Analysis Time	Sensitivity	Currently available?	Verification
Arsenic detection devices	color reaction or anodic stripping voltammetry (ASV)	arsenic	portable	\$100-\$350 (color reaction); \$8,000 (ASV)	low (color reaction); high (ASV)	15 min-1 hr	< 10 ppb	available	EPA-ETV
Cyanide detection devices	colorimeter or ion selective electrodes	free cyanide	portable	\$500- \$1,500	low (colorimeter); medium (ISE)	15-30 min	< 0.1 mg/L	available	EPA-ETV
INFICON Scentograph CMS500	automated gas chromatograph	volatile organic compounds	online	not available from website	low	30-60 min	ppb	available	none
INFICON Scentograph CMS200	gas chromatograph	volatile organic compounds	portable	not available from website	high	30-60 min	ppb	available	none
INFICON HAPSITE®	gas chromatograph-mass spectrometer	volatile organic compounds	portable	\$75-\$5,000	high	30-60 min	ppb	available	EPA-ETV, AwwaRF
Constellation Technology Corp CT-1128	gas chromatograph-mass spectrometer	volatile organic compounds	portable	not available from website	high	not available from website	ppb	available	none
Severn Trent Field Enzyme Test	rapid enzyme inhibition	insecticides, nerve agents	portable	not available from website	low	5 min	ppb	available	AwwaRF
Severn Trent Eclox™	enzyme inhibition	chemicals and biotoxins	portable	\$7,900	low	5 min	detects ug/L to mg/L of contaminant	available	EPA-ETV, AwwaRF
Randox Laboratories Aquanox™	enzyme inhibition	chemicals and biotoxins	portable	not available from website	low	not available from website	not available from website	available	none

**Exhibit 9-4. Chemical Sensors Comparison with Desired EWS Characteristics
(continued)**

Product	Description	Range of Contaminants	Online/Portable?	Cost	Operator Skill	Analysis Time	Sensitivity	Currently available?	Verification
Lab_Bell inc. LuminoTox	Photosynthetic enzyme complex inhibition	chemicals and biotoxins	portable	not available from website	medium	< 15 min	ppb	available	none
Harvard BioScience, Inc. MitoScan	submicrochondrial particles inhibition	chemicals and biotoxins	portable	not available from website	medium	30 min	not available from website	available	none
Check Light LTD ToxScreen-II Rapid Toxicity Test	biomonitor (bacteria)	toxins - Aldicarb, Colchicine, Cyanide, Dicrotophos, Thallium sulfate, Botulinum, Ricin, Soman, VX	portable	reagent kit - \$300; system - \$2,895	low	30 min	< ppm	available	EPA-ETV
Hidex Oy BioTox Flash™	biomonitor (bacteria)	toxic substances	portable	reagent kit - \$128; system - \$8,900	high	5-30 min	not available from website	available	EPA-ETV
Strategic Diagnostics Inc DeltaTox®	biomonitor (bacteria)	toxic substances	portable	reagent kit - \$370; system - \$5,900	low	5-15 min	100 cfu/mL	available	EPA-ETV
Strategic Diagnostics Inc MicroTox®	biomonitor (bacteria)	toxic substances	not portable	reagent kit - \$360; system - \$17,895	low	15 min	not available from website	available	EPA-ETV none
Hach ToxTrak™ Rapid Toxicity Testing System	biomonitor (bacteria)	toxic substances	portable	reagent kit - \$380; system - \$3,950	low	45 min	not available from website	available	EPA-ETV
InterLab Supply POLYTOX™	biomonitor (bacteria)	toxic substances	portable	reagent kit - \$147; system - \$1,600	low	20 min	not available from website	available	EPA-ETV

**Exhibit 9-4. Chemical Sensors Comparison with Desired EWS Characteristics
(continued)**

Product	Description	Range of Contaminants	Online/Portable?	Cost	Operator Skill	Analysis Time	Sensitivity	Currently available?	Verification
SYSTEM Srl. microMAX-TOX	biomonitor (bacteria)	toxic substances	online	information not available	information not available	information not available	information not available	available (expected 2005)	none
Delta Consult MusselMonitor®	biomonitor (mussels)	toxic substances	online	\$2,300	low	20 min	see website for 26 contaminants	available	none
Biological Monitoring Inc. Bio-Sensor®	biomonitor (fish)	toxic substances	online	not available from website	low	< 1hr	not available from website	available	none
Aqua Survey IQ Toxicity Test™	biomonitor (daphnia)	toxic substances	portable	\$2,400 (starter kit) \$400 (maintenance kit)	medium	75 min	not available from website	potentially adaptable	EPA-ETV
bbe moldaenke Daphnia Toximeter	biomonitor (daphnia)	toxic substances	online	not available from website	low	< 30 min	not available from website	potentially adaptable	none
bbe moldaenke Algae Toximeter	biomonitor (algae)	toxic substances	online	not available from website	low		not available from website	potentially adaptable	none
bbe moldaenke Fish Toximeter	biomonitor (zebrafish)	toxic substances	online	not available from website	low	< 30 min	not available from website	potentially adaptable	none
US Army Center for Environmental Health Research	biomonitor (bluegill)	toxic substances	online	not available from website	information not available	1 hr	not available from website	potentially adaptable	none
Lumintox Gulf L.C. Lumintox	biomonitor (dinoflagellates)	toxic substances	portable	not available from website	low	2-4 hrs	not available from website	potentially adaptable	none

**Exhibit 9-4. Chemical Sensors Comparison with Desired EWS Characteristics
(continued)**

Product	Description	Range of Contaminants	Online/Portable?	Cost	Operator Skill	Analysis Time	Sensitivity	Currently available?	Verification
SensIR Technologies HazMatID™	Fourier transform infrared attenuated total reflection spectroscopy	organic chemicals, biological contaminants	portable	not available from website	low	10 min	chemicals at 100 ppm	potentially adaptable	none
ITN X-Ray fluorescence		metals	online	not available from website	information not available	not available from website	not available from website	potentially adaptable	none
Smiths Detection SABRE 4000	ion mobility spectroscopy (IMS)	explosives, chemicals warfare agents, toxic chemicals	portable	not available from website	low	< 1 min	> 5-10 ppb	potentially adaptable	none
Cyranose® 320	polymer composite chemiresistor	toxic chemicals in vapor form	portable	not available from website	not available from website	not available from website	not available from website	potentially adaptable	none
Cyranose Sciences Nosechip™	polymer composite chemiresistor	toxic chemicals in vapor form	online	not available from website	not available from website	not available from website	not available from website	potentially adaptable	none

75 arsenic test kit manufactured by Peters Engineering (Austria) showed that low and high levels of interferences did not appear to affect the detection of arsenic. A very low rate of false-positives and negatives was reported. One problem ETV testers noted was that the reagent tablet took up to 1.5 hours to dissolve.

The As-Top Water test kit offered by Envitop, Ltd. (Oulu, Finland) indicated the presence of interferences did not affect the arsenic test. The effect of operator skill level appears to be a significant factor with the As-Top Water test kit. The non-technical operator rarely detected arsenic in any samples, even those containing arsenic at over 90 ppb. The technical operator detected arsenic more frequently, though rarely at the same concentration determined by the reference method. One problem ETV testers noted was the color on the indicator did not correspond exactly to colors on the comparison card.

Monitoring Technologies International Pty., Ltd. (Perth, Australia) offers the PDV 6000 portable analyzer, which measures arsenic in water using anodic stripping voltammetry (ASV). ETV testers noted that instructions in the operation manual for water analysis were difficult to follow, indicating that the level of experience in the operation of the PDV 6000 analyzer and associated software is likely to influence the reliability of results. Low and high levels of interferences (iron and/or sulfide) adversely affected the detection of arsenic.

Another device that employs ASV technology is the Nano-Band™ Explorer made by TraceDetect (Seattle, Washington). ETV testers noted the Nano-Band™ Explorer did not appear to be affected by matrix interferences added to the samples. However, the data from the two operators were quite different, with the non-technical operator reporting no detectable arsenic in any of the 16 samples.

Cyanide Sensor

There are two basic types of technologies (colorimetric and solid sensing element) that are used in commercially available tests, both of which have been third party verified by EPA's ETV Program. Both types of technologies are used in portable devices designed for onsite rapid analysis of cyanide in water. One problem common to all four portable colorimeters tested by the ETV was that performing analyses under extremely cold conditions (sample water 4 to 6° C) negatively affected the performance of the reagents. Also, for all four colorimeters, when a lethal amount of cyanide was present, a drastic, rapid change in color was visible and no reading by the colorimeter was necessary, making lethal amounts of cyanide in water quickly detectable. Using the VVR V-1000 multi-analyte photometer, there was a slight bias for a technical operator compared to a non-technical operator. It takes approximately 17 minutes to obtain and analyze one sample. Using the 1919 SMART 2 Colorimeter, technical versus non-technical operator did not impact results. For the Mini-Analyst Model 942-032 by Orbeco-Hellige (Farmingdale, NY), the manufacturer recommends adjusting the pH of water samples to between 6.0 and 7.0. Since gaseous hydrogen cyanide can be released at a pH less than 9.0, this adjustment is not desirable from a safety standpoint, especially if lethal/near-lethal concentrations of cyanide are present. Although the model was easily transported to the field and the sample preparation instructions were clear, the liquid pyridine reagent had an offensive odor, and the granular reagent tablets were difficult to open. Also, the operators stated that it was inconvenient to keep track of the mixing and waiting times during the analysis. There was a slight bias for a technical operator. Using the AQUAfast® IV AQ4000

colorimeter by Thermo Orion (Beverly, MA), there was very little difference in results generated by the non-technical operator compared with those of the technical operator.

Using the solid sensing element, the Thermo Orion Model 9606 Cyanide Electrode required calibration and electrode polishing before every sample set. Operator bias was not tested. Also, using the solid sensing element, the Cyanide Electrode CN 501 with the Reference Electrode R503D and Ion Pocket Meter 340i (WTW ISE) by WTW Measurement Systems (Ft. Myers, FL) had a difficult to understand instruction manual. A one-hour telephone consultation with WTW was required before the WTW ISE was easy to operate. Operator bias was not evaluated.

MosselMonitor® by Delta Consult

MosselMonitor® detects toxins. One of the major problems for using the MosselMonitor® was the low food content of the water to be monitored (fast running surface waters, groundwater). An “Automated Food Device” (AFD) was developed to automatically and continuously feed algae to the mussels using a flow-through system. Mussels are very sensitive to chlorine, and addition of thiosulphate to the water minimizes the effects of free chlorine (Jan de Maat, Delta Consult, personal communication). As a result of the adaptations, the Budapest Waterworks have now successfully applied the MosselMonitor® in monitoring of chlorinated drinking water for 10 months.

Eclox™ by Severn Trent Services

Eclox™ detects chemicals and biotoxins. Sample analysis is simple and takes only five minutes. Contaminant concentrations could be detected to a limit of µg/L to mg/L, but results were not consistently reproducible. When compared to the similar detection device Microtox®, the actual contaminant values generated by these devices may vary in different types of water, especially in distilled water. It is necessary to establish site-specific baseline values (States, 2004). In another study, clean chlorinated and chloraminated water samples produced very low inhibition of light, indicating that the disinfection byproducts that may be present in drinking water do not interfere with Eclox™ results. However, false-negative results were produced by lethal doses of soman and *Botulinum* toxin. Eclox™ is easily transported and operated in the field, where similar results were produced as in the lab (EPA-ETV, 2004).

MicroTox® and DeltaTox® by Strategic Diagnostics, Inc.

MicroTox® and DeltaTox® detect chemicals and biotoxins. Sample analysis is moderately difficult and takes 45 minutes. Copper was shown to be a potential interferent. Contaminant concentrations could be detected to a limit of µg/L to mg/L, but results were not consistently reproducible. When compared to the similar detection device Eclox™, the actual contaminant values generated by these devices may vary in different types of water, especially in distilled water. It is necessary to establish baseline values for each site (States, 2004). In another study, MicroTox® had false-positive results when testing clean chloraminated water, but not when testing clean chlorinated water. Half the contaminants tested produced false-negatives when lethal doses were present. The operation of MicroTox® was easy to understand for in-lab operation. This product is not field portable. For DeltaTox®, false-positive results were produced when testing clean chloraminated water, but not when testing clean chlorinated water. Over half the contaminants tested produced false-negatives

when lethal doses were present. DeltaTox® is straightforward to operate and easily transported to the field (EPA-ETV, 2004).

Tox Screen II by Checklight, Ltd.

When using the pro-organic buffer, the low level of light production in water disinfected by chlorination or chloramination may interfere with the ToxScreen II results, resulting in false-positives. However, residual sodium thiosulfate from dechlorination may have caused these results. When using the pro-metal buffer, as long as a similar reference sample is used, water disinfected using either process is not likely to interfere with the ToxScreen II results. Operation of the ToxScreen II was relatively straight forward and the instrument was easily transported to the field when similar results as in the lab were produced (EPA-ETV, 2004).

ToxTrak™ by Hach Company

Half of the samples from a water system using chlorination were analyzed in July and the other half in September. In July, a significant amount of inhibition was noted, while in September, the same sample was largely non-inhibitory. There seems to be a risk for false-positive results due to interference of previously chlorinated water, though the reason for the difference in these results is not clear. False-positives were also experienced due to iron in the water samples. False-negative results were experienced when samples with lethal doses of contaminants were tested. The ToxTrak™ was easy for testers to operate and is field portable, but the ToxTrak™ reagent must be incubated over night at 35°C, which could be problematic for field deployment (EPA-ETV, 2004).

IQ Toxicity Test™ by Aqua Survey

Aluminum, copper, and iron are potential interferents because they adversely affected 90 percent to 100 percent of the *Daphnia* organisms. In addition, all *Daphnia* organisms exposed to drinking water from a system disinfected by chloramination were adversely affected, and therefore produced false-positives. However, the water sample from a drinking water system that uses chlorination did not adversely affect the daphnia. There were no false-negative results produced when using this test. The IQ Toxicity test™ instruction manual is easy to understand and the test is field portable, though a stock of *Daphnia* must be maintained to facilitate short-notice field testing (EPA-ETV, 2004).

BioTox Flash™ by Hidex Oy

Bacterial metabolic inhibition caused by copper and zinc may result in interference with BioTox™ results. Slightly exaggerated inhibition may result when using chloraminated water, resulting in a possible false-positive, while there is a risk for false-negatives when using chlorinated water samples. The BioTox™ is field portable, but a flat, steady surface is needed to operate the BioTox™. ETV testers found it difficult to operate the BioTox™ without an instruction manual, but once the correct procedure was determined, operation was easy (EPA-ETV, 2004).

POLYTOX™ by Interlab Supply, Ltd.

Without a baseline water sample of a matrix similar to the test water sample, there is a considerable risk that an analysis of POLYTOX™ in clean chloraminated water would produce organism

respiratory inhibition great enough to yield a false-positive result. In clean chlorinated water inhibition was low enough that false-positives were not produced. Over half of the contaminants tested produced a false-negative when present at lethal doses. The POLYTOX™ is field portable and ETV testers had no difficulty operating it (EPA-ETV, 2004).

Pesticide/Nerve Agent by Severn Trent Services

Pesticide/Nerve Agent is a rapid enzyme test that detects pesticides and nerve agents. Sample analysis is performed in five minutes and is generally simple. This test is easily conducted using concentrated or non-concentrated sample water (States, 2004).

HAPSITE® by INFICON Inc.

HAPSITE® is a field deployable gas chromatograph-mass spectrometer (GC-MS) that detects VOCs found in toxic substances and chemical warfare agents. The recent addition of a “Situ Probe” purge-and-trap sampling device enables water samples to be analyzed. The GC portion of the device detects volatile substances with a molecular weight between 45 and 300, and the MS portion of the device identifies the compound from a library of 170,000 organic compounds (States, 2004). Sample analysis takes 60 minutes but is very difficult to perform. This system has been deployed in a distribution system and could serve as a case study.

9.4.1 Issues and Gaps

This section highlights various issues and gaps in using chemical detectors for early warning for finished drinking water.

- **Cost for Some Available Technology is High**

Online and portable devices such as GC-MS are expensive, ranging from \$75,000 to \$95,000.

- **Field Kits are Not Optimal**

The bacterial monitoring kits tested by EPA’s ETV have high false-positive and false-negative rates. A common drawback for kits is the stability of reagents. Often reagents require reconstitution (if they are lyophilized) or careful measurement of reaction components to constitute a fresh reaction mixture. Kits can be subject to variability due to different users because it is difficult for users to mix and pipette in a consistent manner. They require trained personnel and have set up requirements, such as culturing log phase growth bacteria. The results do not provide specific identification of a toxin. Although these kits may be suitable for confirming the presence of a toxin, further methods would need to be utilized for specific identification.

- **Some Detection Methods Face Challenges from the Chlorine Residual**

Organism-based biomonitors are sensitive to the chlorine residuals in drinking water. Although the fish-based Bio-Sensor® and MosselMonitor® remove chlorine, broadly applicable methods for chlorine removal have not yet been developed. Although one company, Checklight, is developing

a system for removal of chlorine, the effect of chlorine removal on other biosensors has not been demonstrated.

- **Many Technologies Have Not Been Adapted for Water**

Portable infrared spectroscopy, ion mobility spectroscopy, surface acoustic waves, and polymer composite chemoresistors technologies are being aggressively pursued for air and vapor applications, but have not been developed specifically for drinking water monitoring. These techniques could be adapted for water if companies' market research indicates there is a potential market.

Exhibit 9-5 provides a snapshot of capabilities, issues, and gaps for chemical sensor technologies and techniques.

9.4.2 Conclusion and Recommendations

Portable technology (e.g., GC) is available for conducting analysis of many possible chemical contaminants. This area will continue to improve as high technology equipment is based on microchip technology (e.g., nose chip). Certain biomonitors are portable and can be used for site assessments. Chlorine would have to be removed for such analyses. The technology that is readily available and reliable are specific probes like arsenic and cyanide probes that could be effective against a narrow selection of contaminants. Online technologies are not cost effective and are not reasonably available. GC and ion mobility have cost and technical challenges. The current experience of using high-tech GC in a utility's distribution system has not been determined to be cost-effective to cover the distribution system.

Certain biomonitors may be promising if the issue of chlorine and chloramine residual interference can be resolved. For example, the mussel monitor has been recently demonstrated in finished water in Europe and there are various efforts to make other monitors (MicroTox® and ToxScreen) adaptable to finished water. The mussel monitor could be a good candidate for an EPA-ETV Program verification and perhaps used for a laboratory and/or field study on finished water or with CBR surrogates or agents. In the next three years, the field should show further development in terms of cost effective and reliable devices. A few new technologies (such as microchips) could revolutionize the chemical detection field for drinking water.

Exhibit 9-5. Chemical Sensor Technologies and Techniques

Method	Capabilities	Issues and Gaps
Arsenic and cyanide probes	<ul style="list-style-type: none"> established monitors for arsenic/cyanide reliable ETV reports available 	<ul style="list-style-type: none"> limited to one parameter identified at a time various issues (reliability) with certain methods
GC	<ul style="list-style-type: none"> range of VOCs detected online for drinking water 	<ul style="list-style-type: none"> expensive not widely used for drinking water
Enzyme Inhibition	<ul style="list-style-type: none"> detects chemicals (phenols, amines, heavy metals) detects substances toxic to cholinesterase (nerve agents and pesticides) portable (kit) 	<ul style="list-style-type: none"> requires mixing and pipetting chlorine residual interferes (false-positive source)
Bacterial biomonitors	<ul style="list-style-type: none"> detects substances toxic to bacteria portable (kit) ETV reports available online for surface water 	<ul style="list-style-type: none"> requires mixing and pipetting false-positive/false-negative rate high (ETV reports) chlorine residual interferes
Daphnia, fish, algae biomonitors	<ul style="list-style-type: none"> detects substances toxic to daphnia, fish or algae online for source and treated waste water monitoring 	<ul style="list-style-type: none"> chlorine residual adversely affects the living organisms
Mussel and fish biomonitors	<ul style="list-style-type: none"> detects substances toxic to mussels or fish online systems exist in use in a few distribution systems 	<ul style="list-style-type: none"> not proven for drinking water no third party verification
Eukaryotic cell and tissue biomonitors	<ul style="list-style-type: none"> can potentially detect substances toxic to human cells 	<ul style="list-style-type: none"> emerging technology, commercial products not available
Fiber optic cable-based sensors	<ul style="list-style-type: none"> detects toxic chemicals being designed to be on line for water distribution systems can cover long continuous areas 	<ul style="list-style-type: none"> emerging technology most advanced products are for air
Infrared	<ul style="list-style-type: none"> identifies wide range of substances portable (suitcase) 	<ul style="list-style-type: none"> water matrix interference requires use of extraction method unidentified substance must be concentrated
Ion mobility	<ul style="list-style-type: none"> detects wide range of compounds (explosives, chemical warfare agents, toxic industrial chemicals or narcotic substances) portable (hand-held) 	<ul style="list-style-type: none"> expensive developed for vapor sensing, would require accessory equipment for water
SAW-based sensors	<ul style="list-style-type: none"> detects VOCs, explosives, illicit drugs, and chemical warfare agents online for groundwater monitoring 	<ul style="list-style-type: none"> MEMS-SAW is emerging technology water applications will lag behind air applications
Microchip chemoresistors	<ul style="list-style-type: none"> detects wide range of volatile compounds portable (hand-held) 	<ul style="list-style-type: none"> developed for vapor sensing, would require accessory equipment for water

9.5 Evaluation of Microbial Sensors

Rapid microbial detection technologies are not as advanced as chemical detection technologies. However, advances in the last few decades in molecular biology, genomics, and microfluidics, have stimulated the imagination of researchers and resulted in the appearance of the first generation of detection devices for microbes. There are many technological approaches with laboratory prototypes and the beginning of commercial product development.

- Immunoassays are available in several formats including: test strips, columns, linked to fiber optics, attached to microspheres and quantum dots, and incorporated into a wide array of microchip technologies. Specific contaminants can be identified with antibody-based technologies.
- ATP is a general indicator for the presence of live cells. There are numerous small portable kits for detecting ATP that are used in the food industry. There are also portable kits for testing grab samples in water.
- Portable and rapid (30 minutes or less) PCR is a reality, with four systems currently on the market.
- Light scattering technologies have a long history of use for measuring turbidity and are now being adapted for detecting microbial cells in drinking water.
- Technologies that utilize microchips/microarrays are being aggressively pursued. The proliferation of approaches should yield some viable options for drinking water applications in the long-term.

ECBC conducts research applicable to biological and chemical defense sensors and integrated detection systems. It has conducted many studies, including some that can detect contaminants in water. In March 2002, ECBC issued the *Bio-Detector Assessment* (ECBC, 2002). The report evaluated several biological detection devices including immunoassay-based or nucleic acid-based technologies. The devices include Bio-HAZ™, FACSCount, Luminex 100, ANALYTE 2000, BioDetector, Hand-Held Assays, ORIGEN Analyzer, Tetracore Tickets, Cepheid Smart Cycler®, and Rapid System. The ANALYTE 2000 technology has been replaced by the company's newer technology, RAPTOR™. ORIGEN Analyzer technology is now being further developed by BioVeris. The evaluation used criteria including portability, reliability, time to analyze, classes detected, viability, sensitivity to bacteria, toxins, viruses, ease of use, rate of processing samples, portability, and price for consumables. The methods were evaluated using a quantitative scale and input from experts. Hand-Held Assays, Tetracore, and New Horizon (referred to as Smart™ Tickets elsewhere in this report) received the highest score of all immunoassay-based devices. PCR was credited with being specific and sensitive and not prone to false-positives. Specifically, RAPID from Idaho Technologies received high scores. Freeze-dried PCR assays are already available, and the system can be operated from a battery and connected via Internet to transmit data to remote sites to assist in response. ECBC also has a program (Early Sentinal Biomonitoring System Program) to screen and examine, and verify the performance of up to 28 technologies for rapid detection for drinking water (Stanley States, Pittsburgh Water and Sewer Authority, personal communication).

Evaluations of specific microbial detection devices are provided below. Exhibit 9-6 summarizes how the microbial detectors (those available now or potentially adaptable) compare with the desired characteristics of an EWS (as described in Chapter 3).

Exhibit 9-6. Microbial Sensors Comparison with Desired EWS Characteristics

Product	Description	Range of Contaminants	Online/Portable?	Cost	Operator Skill	Analysis Time	Sensitivity	Currently Available?	Verification
Tetracore Bio Threat Alert (BTA)	antibody lateral flow assay	biological agents including anthrax, botulinum toxin, ricin	portable	\$625 (25 strip kit) \$4,000 (strip reader)	low	15 min	anthrax - 10 ⁶ spores/mL; bot. - .02 mg/L; ricin - .0075 mg/L low	available	AwwaRF, ETV, ECBC
New Horizons Diagnostics SMART™ Tickets	antibody lateral flow assay	biological agents including anthrax, botulinum toxin, ricin	portable	\$15-20 per strip	low	15 min	bacteria 10 ⁵ cfu/mL; biotoxin 50 ppb	available	AwwaRF
EAI Corporation Bio-HAZ™ (with SMART™ tickets)	antibody lateral flow assay	biological agents including anthrax, botulinum toxin, ricin	portable	\$20,000	low	< 30 min	see above	available	ECBC
Research International RAPTOR™	antibody fluorometric assay	biological agents, toxins, chem contaminants	portable	\$50,000	medium	7-12 min	anthrax detected at < 1.0 ng/mL	potentially adaptable	none
Response Biomedical Corp Test Cartridges	antibody lateral flow assay	biological agents (anthrax, botulinum toxin, ricin)	portable	\$10,000 (25 cartridges & reader)	low	15 min	anthrax - 10 ⁷ spores/mL, bot. - 2 mg/L; ricin - 1 mg/L	available	EPA-ETV
ADVNT BADD Test Strips	antibody lateral flow assay	biological agents (anthrax, botulinum toxin, ricin)	portable	\$250 (10 strips)	low	15 min	anthrax - 10 ⁷ spores/mL; bot. > 5 mg/L; ricin - 20 mg/L	available	EPA-ETV
LLNL Autonomous Pathogen Detection System using Luminex Corporation's xMAP®	microspheres with biological capture molecule	biological contaminants	in lab; online	information not available	high	information not available	information not available	potentially adaptable	none

**Exhibit 9-6. Microbial Sensors Comparison with Desired EWS Characteristics
(continued)**

Product	Description	Range of Contaminants	Online/Portable?	Cost	Operator Skill	Analysis Time	Sensitivity	Currently Available?	Verification
BioDetect Microcyte Aqua®	flow cytometer	cells	portable	not available on website	information not available	not available on website	not available on website	available	none
Brightwell Technologies Micro-Flow Imaging	digital imaging particle counter	particles and cells	online	not available on website	information not available	1 min	particles > 2 µm in size	available	none
AMSA Lite™ Antimicrobial Specialists and Associates	luminescence	ATP	portable	\$2,000	low	< 10 min	not available on website	available	none
WaterGiene™ Charm Sciences, Inc	luminescence	ATP	portable	not available on website	low	< 10 min	100 cfu/mL	available	none
Continuous Flow ATP Detector BioTrace International	luminescence	ATP	online	\$50,000	not available on website	1 min	not available on website	available	none
Celisis-Lumac Landgraaf, the Netherlands	luminescence	ATP	portable	not available on website	not available on website	< 10 min	not available on website	potentially adaptable	none
Profile™ - I (using Filtravette™) New Horizons Diagnostic Corp	luminescence	ATP	portable	not available on website	not available on website	< 5 min	not available on website	available	none
LXT/JMAR BioSentry	light scattering	biological contaminants	online	not available on website	low	1 min	low	available 2005	none
Rustek Ltd	light scattering - MALS	biological contaminants	online	not available on website	not available on website	not available on website	not available on website	potentially adaptable	none

**Exhibit 9-6. Microbial Sensors Comparison with Desired EWS Characteristics
(continued)**

Product	Description	Range of Contaminants	Online/Portable?	Cost	Operator Skill	Analysis Time	Sensitivity	Currently Available?	Verification
Idaho Technology RAPID	PCR	biological contaminants	portable	\$55,000	medium	30 min-3 hrs	1,000 cfu/mL	potentially adaptable	AwwaRF, ECBC
Smiths Detection Bio-Seeq™	PCR	biological contaminants	portable	\$25,000	medium	30 min	1 cfu/sample volume (28 µL)	potentially adaptable	none
Invitrogen PathAlert™	PCR	biological contaminants	mobile lab	not available on website	high	30 min	10 ⁴ cfu/mL	potentially adaptable	ETV DoD
Cepheid Hand-Held Nucleic Acid Analyzer (HANAA)	PCR	biological contaminants	portable	not available on website	information not available	< 10 min	information not available	potentially adaptable	none
Cepheid Smart Cycler® XC	PCR	biological contaminants	portable	\$46,000	medium	30 min-3 hrs	< 30 anthrax spores	potentially adaptable	ECBC
Ibis Pharmaceuticals and SAIC T.I.G.E.R.	PCR	biological contaminants	portable	not available on website	not available on website	few hrs	not available on website	potentially adaptable	none
Nomadics® Spreeta™ Evaluation Module	surface plasmon resonance (SPR)	biological and chemical	portable	\$695-\$9,995	not available on website	not available on website	not available on website	potentially adaptable	none
Georgia Tech BOSS	fiber optic evanescent wave spectroscopy	biological and chemical	portable, online	information not available	information not available	minutes	information not available	potentially adaptable	none
Innovative BioSensors Inc. BioFlash™	cell-based biosensor	biological contaminants	portable	not available on website	medium	5 min	not available on website	potentially adaptable	none
BioVeris M1M	ECL	biological	mobile lab	not available on website	high	1 min	not available on website	potentially adaptable	none

BTA Test Strips by Tetracore (Gaithersburg, MD)

BTA Strips detect pathogens by rapid immunoassay. In one evaluation study, the detection limit was found to be 10^5 cfu/mL for pathogenic bacteria. They are useful for screening acute hazards, but poor sensitivity limits their usefulness in detecting low levels of contaminants in water. Analysis is simple and takes 15 minutes (States, 2004). EPA conducted a second evaluation test for anthrax, botulinum, and ricin. The anthrax test strips generated one false-positive when testing each Florida and New York drinking water sample. False-negatives were generated in water due to Ca and Mg ion presence, and in concentrated drinking water from California and New York. The strips were not able to detect spores at the vendor indicated concentration limit of 10^5 , only at levels 100 to 1,000 times greater. For *Botulinum* toxin test strips, false-positives resulted due to the presence of humic acid, fulvic acid, and lipopolysaccharides in water. There were no false-negatives. Both toxin types were detected near the vendor-indicated limit of 0.1 mg/L. For ricin, false-positives occurred in Florida drinking water while false-negatives occurred in New York drinking water. Test strips can detect to concentrations of 0.035 mg/L, as stated by vendor. All types of BTA test strips had consistency near 100 percent. A 25 test strip kit costs \$625 and the Alexeter strip reader costs \$4,000 (EPA-ETV, 2004).

In a third evaluation study, BTA Tetracore Tickets identified four of eight contaminants. Many BTA reagents are available commercially or through the government and are not likely to produce false-positives or negatives. Furthermore, there was low opportunity for error due to ease of use and it takes less than 30 minutes to set up the device and analyze one sample. It is a hand-held device and costs \$4,500. Tetracore scored one of the highest of all immunoassay-based devices in this evaluation (ECBC, 2002).

SMART™ Tickets by New Horizons Diagnostics (Columbia, MD)

SMART™ Tickets detect biotoxins by rapid immunoassay with a detection limit of 2 to 50 ug/L. Analysis is simple and takes 15 minutes; however, poor sensitivity limits their usefulness in detecting low levels of contaminants in water (States, 2004). SMART™ Tickets have been incorporated into Bio-HAZ™. In a study of Bio-HAZ™ with New Horizon SMART™ Tickets, it was able to identify all four of the bioagent classes (sporulated bacteria, vegetative bacteria, toxins, and viruses), and identified four of eight traditional bioagents identified by DOD. Some SMART™ Tickets reagents are available commercially or through the government and the method is not likely to produce false-positives or negatives. There is also low opportunity for error due to ease of use and it takes less than 30 minutes to set up and analyze one sample. It is field portable and costs \$20,000. Bio-HAZ™ scored one of the highest of all immunoassay-based devices (ECBC, 2002).

R.A.P.I.D. (Ruggedized Advanced Pathogen Identification Device) by Idaho Technology

R.A.P.I.D. uses PCR to detect pathogens and biotoxins to a limit of 10^3 cfu/mL. This device is used extensively by the military, but the detection capabilities suggest potential application for water utility personnel or contaminated drinking water investigators. The sample preparation is standardized, the kit includes positive and negative DNA controls, and initial data interpretation is automated. The effectiveness of this test is limited by its sensitivity. Analysis is moderately difficult and takes 90 minutes (States, 2004). In another evaluation study, the Rapid System identified four of eight contaminants with half of reagents being available commercially or through

the government. It was not likely to produce false-positives or negatives, but had a high opportunity for error due to difficulty of use. The Rapid System takes approximately three hours to set up the device and analyze one sample. It is field portable and costs \$55,000 (ECBC, 2002).

Eclox™ by Severn Trent Services

Eclox™ detects chemicals and biotoxins. Sample analysis is simple and takes only five minutes. Contaminant concentrations could be detected to a limit of $\mu\text{g/L}$ to mg/L , but results were not consistently reproducible. When compared to the similar detection device MicroTox®, the actual contaminant values generated by these devices may vary in different types of water, especially in distilled water. It is necessary to establish baseline values for each site (States, 2004). In another study, clean, chlorinated, and chloraminated water samples produced very low inhibition of light, indicating that byproducts of either disinfection process that may be present in drinking water do not interfere with Eclox™ results. However, false-negative results were produced by lethal doses of soman and botulinum toxin. Eclox™ is easily transported and operated in the field, where similar results were produced as in the lab (EPA-ETV, 2004).

HandHeld Assays from the Department of Defense

HandHeld Assays can identify seven of the eight traditional bioagents identified by DOD. Reagents are mostly available commercially or through the government with the assays being found to be less unlikely to produce false-positives or negatives. They have a low opportunity for error due to ease of use and take less than 30 minutes to set up and analyze one sample. HandHeld Assays scored high in the ECBC study (ECBC, 2002). In another study, HandHeld Assays were determined to have limits of detection that are many times the infectious dose. There can be false-positives because of environmental contamination and they are sometimes not used properly. The DOD determined that the HandHeld Assays are effective if used in concert with other confirmatory detectors (Emanuel et al., 2003). In another report generated by scientific experts from 14 federal agencies,²⁰⁷ HandHeld Assays had either high false-positive rates (ranging from 3 percent to 83 percent) or sensitivity problems. Thus, none of the assays could be considered reliable for field detection.

Smart Cycler® from Cepheid

Smart Cycler® identified four of eight traditional bio agents identified by DOD, but the reagents are not currently available commercially or through the government. It is less likely to produce false-positives or negatives, has high opportunity for error due to difficulty of use, and takes approximately three hours to set up the device and analyze one sample. It is field portable and costs \$35,000 (ECBC, 2002).

Light-Scatter

The identification rate of *Cryptosporidium parvum* oocysts varied from 11 percent to 45 percent, and false-positive rates varied from 0.3 percent to 3 percent. The MALS system may be tuned by the user, who must understand that a higher identification rate will be accompanied by a higher false-positive rate. MALS was also able to differentiate between different physical states of *Cryptosporidium* oocysts, including oocysts treated with ozone, heat treated, or excysted from live

untreated oocysts. The limit of detection was such that MALS could be used as an early warning tool for water contamination outbreaks. For purified water, the estimated limit of detection (ELOD) was found to be 7, 0.7, and 0.1 oocysts/mL in 1, 10, and 60 minutes respectively. For finished drinking water samples, the ELOD was 75, 7.5, and 1 oocysts/mL in 1, 10, and 60 minutes respectively. The researchers concluded that MALS technology has suitable applications to water distribution system monitoring (Quist et al., 2004, AwwaRF Project #2720, see Appendix D).

RAMP Anthrax Assay by Response Biomedical Corporation (Vancouver, Canada)

RAMP uses a cartridge that is a lateral flow immunoassay device with a test and control line. The detector is an antigen-specific antibody attached to a fluorescent bead. The RAMP instrument detects the presence of fluorescent beads that attach to the capture assay line. In the test study, three non-pathogenic strains of *Bacillus anthracis* and three non-anthraxis *Bacillus* strains were tested. The detection limit of the three *Bacillus anthracis* strains ranged from 1,000 to 2,000 spores. The non-anthraxis *Bacilli* did not cross-react and no false-positives were produced in the presence of interferents. The RAMP Anthrax Assay has not been tested for use in water systems (Heroux and Anderson). In another verification test conducted by EPA, three types of test cartridges were available for anthrax, botulinum toxin, and ricin. The anthrax cartridges produced no false-positives or negatives due to interferents, though were not able to detect anthrax spores at the vendor indicated concentration of 4×10^5 spores/mL (only at levels 100 to 1,000 times greater). The botulinum toxin cartridges had no false-positives, but were not able to detect Type B. They detected Type A to a concentration of 2 mg/L, though the vendor indicated detection limit was 0.5 mg/L. No false-positives or negatives resulted when testing the ricin cartridges, which could detect to a concentration of 5 mg/L, though the vendor indicated limit was 1 mg/L. Results from all types of cartridges were very consistent. Sample throughput was four samples per hour. The cartridges were portable and easy to use with minor direction from a trained operator. Cost is \$10,000 for 25 cartridges, a reader, carrier, and printer (EPA-ETV, 2004).

BADD Test Strips by ADVNT

Three types of test strips are available that detect either anthrax, botulinum toxin, or ricin. The anthrax strip had no false-positives, but there was one false-negative in concentrated New York drinking water. Consistency was 90 percent. Sensitivity was 4×10^7 to 8×10^7 spores/mL. The botulinum toxin strips had no false-positives or negatives due to interferents. However, the strips were not able to reproducibly detect Type B toxin, and only detected Type A at a concentration of 5 mg/L. However, the vendor stated that the limit was 0.4 mg/L for either type. Consistency was 84 percent. The ricin strips produced no false-positives, but produced false-negatives due to interferents in drinking water. Consistency was 100 percent. Sensitivity was 20 mg/L, higher than the 0.4 mg/L detection level indicated by the vendor. Cost is \$250 for a box of 10 strips. Strips are portable and easy to use; although the indicator line color was very faint sometimes, increasing the risk for false-negatives. It takes 15 minutes for an indicator line to appear. Sample throughput was 20 to 30 samples per hour (EPA-ETV, 2004).

ELISA by Tetracore

Anthrax ELISA produced false-positives due to water with humic and fulvic acid in it and no false-negatives were produced. However, the ELISA was not able to detect anthrax at the vendor-

indicated level of 2×10^4 , only at concentrations 100 times greater. Botulinum toxin ELISA had no false-positives, but false-negatives were produced when humic and fulvic acid were present in the water sample. The lowest detectable concentration for Type A was 0.02 mg/L, but it was not clear for Type B. The ricin ELISA showed no false-positives or negatives and could detect ricin to a concentration of 0.0075 mg/L, slightly higher than vendor indicated level. ELISA was easily portable, but not easily operated by an untrained user. The cost for one Tetracore ELISA (96 well plate) is \$400 (EPA-ETV, 2004).

9.5.1 Issues and Gaps

The following section highlights various issues and gaps in using microbial detectors for early warning for finished drinking water.

- **Contaminants Need to be Concentrated to be Detected**

Many microbial pathogens are a risk to human health at low concentrations. Detecting low concentrations is difficult for the binding assays that most capture-target technologies utilize. Thus, it may be necessary to concentrate large volumes of water samples to gather enough contaminant to detect. Two AwwaRF research papers expected in 2005 (Extraction Methods for Early/Real-Time Warning Systems for Biological Agents - Project A and B) may help with this issue (see Appendix D).

- **Concentration Techniques can also Concentrate Interference Compounds**

Techniques that concentrate the target contaminant will very often also concentrate other non-target contaminants and interferants that will interfere with the biosensor assay. For example, to successfully perform PCR analysis of environmental waters, it is necessary to remove analytical interferences such as humic and fulvic acids.

- **Antibodies Cross-React and are Subject to Binding Kinetics**

Antibodies may bind with known or unknown affinity to non-target antigens. The sensitivity of antibodies needs to be calibrated for each batch, even for monoclonals. Cross-reactivity is a problem if different target molecules have overlapping epitopes. Antibodies designed against specific unique epitopes would have less cross reactivity. Even the best antibody will only have detectable binding if the target antigen is sufficiently concentrated; therefore, it is necessary to concentrate drinking water samples before testing.

- **Emerging and Bioengineered Microbes Could Escape Detection**

Even with a broad selection of capture molecules, microbes will evolve such that they may lose target epitopes or DNA, and therefore escape detection. Bioengineered pathogens could be designed to evade detectors, if detailed information on capture molecules was obtained. The only technology that minimizes this problem is Triangulation Identification Genetic Evaluation of Risks (TIGER), developed by Isis Pharmaceuticals, Inc., because it integrates a variety of approaches (DNA base composition and PCR) into one analysis.

- **Reagents May Not be Stable in Field Environmental Conditions**

Reagents containing biological molecules usually degrade or become inactive within hours of being subjected to room temperature conditions. Even if partial activity is maintained, quality control is jeopardized. This problem can partially be addressed with freeze-dried reagents, but reagent-grade water at the field site is required to reconstitute the reaction solutions. Molecular stability of biomolecules on biochips is even more difficult.

- **Most Microbial Detector Technologies are for Grab Samples, Not Online**

With the exception of Micro-Flow Imaging, there are no commercial online technologies for detecting microbes. Two light scattering technologies (BioSentry and MALLS) are online and are undergoing beta testing, but are not yet on the market.

Exhibit 9-7 provides a snapshot of capabilities, issues, and gaps for microbial sensor technologies and techniques.

9.5.2 Conclusion and Recommendations

Development of an online microbial technique appears years away. Light scattering methods show some promise, but most methods are not suited for continuous online monitoring or differentiating among microbes. However, there are several potentially adaptable methods, including immunoassay, PCR, and ATP, that could be used for confirmation testing of grab samples. For drinking water, the challenge that remains with most methods is the issue of concentrating the sample. A few methods of concentration show promise including the hollow fiber, the micropump, and the PNNL BEADS technology. Generally, this does not seem like an insurmountable obstacle for some methods. However, for PCR, current technology and concentration methods still do not have the adequate level of detection. Overall, none of the methods met all requirements for rapid detection technology. Therefore, the recommended approach was to screen a sample with a generic detector (e.g., multi-parameter probe or perhaps light scatter), then use an immunoassay device in tandem with another method for identification. Detectors based on ATP are promising, but have not been verified for water (one is online for water). An ETV Program testing ATP products is recommended. In the future, microchips have great potential in online measurement, but presently the field is not sufficiently mature.

Exhibit 9-7. Microbial Sensor Technologies and Techniques

Method	Capabilities	Issues and Gaps
Strip tests (immunoassay)	<ul style="list-style-type: none"> • detects 1-4 antigens in one test • portable • seconds to complete test • EPA conducting research on use for finished water 	<ul style="list-style-type: none"> • sample concentration needed • lack of necessary sensitivity
Fiber optic-based biosensor	<ul style="list-style-type: none"> • can detect specific antigens • portable • high potential to be online 	<ul style="list-style-type: none"> • emerging for water
Microspheres	<ul style="list-style-type: none"> • can detect specific antigens 	<ul style="list-style-type: none"> • emerging for water • not in portable format
Flow cytometry and micro-flow imaging	<ul style="list-style-type: none"> • potentially identify specific microbes • can quantify • portable 	<ul style="list-style-type: none"> • sample concentration may be needed
ATP	<ul style="list-style-type: none"> • detects cellular components • portable (kits) • chlorine residual is not an issue 	<ul style="list-style-type: none"> • not independently validated for water • cannot provide microbe specific information
PCR	<ul style="list-style-type: none"> • detects specific DNA sequences • portable (suitcase and hand-held) 	<ul style="list-style-type: none"> • not designed for water • sample concentration required • current level of technology has limits of detection that are still not adequate
Light scattering	<ul style="list-style-type: none"> • detects cells, oocysts, spores, possibly species specific • potential for online • does not require concentration techniques 	<ul style="list-style-type: none"> • not widely used for pathogen detection • not independently validated for water • may be prone to false-positives • cannot detect viruses
Microchips and microarrays	<ul style="list-style-type: none"> • potential to identify many specific pathogens • small size is good for minaturized devices 	<ul style="list-style-type: none"> • portable versions are emerging technology • sample concentration probably required

9.6 Evaluation of Radiological Sensors

With the possibility of accidental radioactive spills and emerging terrorist threats, it is important that water systems have the capability to detect a surge in radioactivity as soon as it occurs. Furthermore, identifying the type of radiation and its source will greatly contribute to a rapid response and recovery effort. Continuous, online monitoring in real-time will allow for rapid detection of intentional or accidental contamination of the water system. The use of an alarm system will help alert the appropriate operators. For intentional contamination of distribution systems, radionuclides that have a high specific activity (Curies/gram), deliver a relatively high gamma and

maybe alpha/beta dose, and can be obtained and solubilized in high concentrations are the most likely contaminants of concern.

The devices described below are the instruments used for measuring alpha, beta, and gamma radiation in liquid or water. New technology that allows detection of radiation at lower levels has been emerging. In-field, gamma radiation detectors are more common than detectors for alpha and beta radiation, which have properties that make them difficult to detect. There were very few verification studies of radiation detectors for use in drinking water. They are provided below. Exhibit 9-8 summarizes how the radiological detectors (those available now or potentially adaptable) match up against the desired characteristics of radiation sensors for use in an EWS.

Isco 3710 RLS Samplers

A study by Westinghouse Savannah River Company, using Isco 3710 RLS samplers, showed that “Data collected over a four-month field test period compares very favorably with concurrent laboratory-based analyses and historical data, at a reduction in cost and significant time savings.”²⁰⁸

Thermo Alpha Monitor

Oak Ridge National Laboratory has tested this instrument and demonstrated its capabilities on water under 1 picocurie/L, and has analyzed isotopic U levels of 10 ppt natural U (15 femtocuries/L), as well as 20 ppb natural U (30 pCi/L) in under 30 minutes. This detector is still under development and requires further testing of durability and accuracy as well as peer reviews and EPA approval.

9.6.1 Issues and Gaps

The following section highlights various issues and gaps in using radiation detectors for early warning for finished drinking water.

- **Devices and Results Show Variability**

The appropriate devices and methods will vary according to local conditions such as temperature and humidity, or the properties of the radionuclide at the source of the radiation.

- **Require Special Expertise**

All of the devices mentioned in this chapter usually require specialized expertise for installation, setup, and routine calibration, even if they are labeled maintenance-free.

- **Costly for Online Monitoring**

Although online analyzers are efficient in monitoring water quality, they are expensive and limited in number. Many facilities may find grab samplers to be more appropriate. Manufacturers are in the process of developing and refining other applications of small-scale flow-through scintillation technology. Utilities will need to collaborate with manufacturers to customize the monitors for small-scale needs.

Exhibit 9-8. Radiological Sensors Comparison with Desired EWS Characteristics

Product	Description	Range of Contaminants	Online/ Portable?	Cost	Operator Skill	Analysis Time	Sensitivity	Currently Available?	Verification
Technical Associates SSS-33-5FT	continuous flow through scintillation detector	alpha, beta, gamma rays	online	\$58,000	medium to high	< 5 min	detects tritium up to 100 pCurie/mL	available	none
Technical Associates MEDA 5T	scintillation detector	gamma	online	\$25,000	medium to high	< 5 min	not available on website	available	none
Technical Associates SSS-33DHC and SSS-33DHC -4	no scintillation detector	monitors tritium and plume	online	\$72,000	medium to high	< 5min	1 nano Curie/mL	available	none
Technical Associates SSS-33M8	no scintillation detector	monitors tritium	online	\$16,500	medium to high	< 5 min	0.1 nano Curie/mL	available	none
Teledyne Isco, Inc 3710 RLS Sampler	filter	all	online	\$35,000- \$75,000	medium to high	< 5min	not available on website	available	none
GammaShark™	details not yet available	gamma	online	not yet available	information not available	< 5 min	not available on website	available 2005	planned
Canberra LEMS600 Series Liquid Effluent Monitoring	monitors radiation in liquid from outside of pipe	beta and gamma rays	online	\$100,000- \$150,000	medium to high	< 5 min	not available on website	potentially adaptable	none
Canberra OLM100 Online Liquid Monitoring	monitors radiation in liquid from outside of pipe	gamma rays	online	\$35,000- \$75,000	medium to high	< 5 min	not available on website	potentially adaptable	none
Canberra ILM 100	monitors radiation in liquid from within pipe	gamma rays	online	\$35,000- \$75,000	medium to high	< 5min	not available on website	potentially adaptable	none

- **Few Detectors are Available or Verified**

There are only a few detectors that are designed to monitor for alpha and beta radioactivity. There are also only a few detectors that are designed for online monitoring of gamma radioactivity. Verification studies have not been extensively performed on radiological detectors for finished drinking water.

- **Not Geared to Distribution Systems**

Some of these monitors are intended for waste streams rather than distribution systems due to the more stringent requirements for drinking water monitors. Waste stream monitors would be geared more towards the detection of accidental spills rather than intentional contamination.

Exhibit 9-9 provides a snapshot of capabilities, issues, and gaps for radiation sensor technologies.

Exhibit 9-9. Radiation Sensor Technologies

Radiation Detected	Capabilities	Issues and Gaps
Alpha	<ul style="list-style-type: none"> • none 	<ul style="list-style-type: none"> • difficult to detect in water
Beta	<ul style="list-style-type: none"> • continuous and real-time measurements 	<ul style="list-style-type: none"> • difficult to detect in water • typically designed for wastewater and groundwater • not verified for drinking water
Gamma (liquid scintillation)	<ul style="list-style-type: none"> • continuous and real-time measurements • has required sensitivity in water 	<ul style="list-style-type: none"> • typically developed for wastewater, not drinking water • not verified for drinking water • requires special expertise for setup, operation and maintenance • costly for online monitoring

9.6.2 Conclusions and Recommendations

There are demonstrated technologies for examining radiation in wastewater, but the transfer or adaptation to drinking water has not taken place. Only a few products claim applicability to water, some on a grab-sample basis. More products are being developed by a few vendors, but it is still unclear whether the threat merits use of these expensive products on a real-time basis. The few items that are commercially available should be verified either by EPA or by a national laboratory that specializes in radiation. Grab sampling can be performed by a number of products, but it is unclear if there is any generic monitor that can trigger this more detailed analysis. Thus, early warning for radiation detection is not currently available, and the market forces for such development may not be strong.

[this page intentionally left blank]

10. Conclusions and Recommendations

The following are conclusions and recommendations from this state-of-the-art review of technologies and techniques for EWSs. General conclusions and recommendations are provided first. These are followed by specific conclusions and recommendations organized by features of the EWS: data acquisition and analysis; flow modeling; sensor placement; alarm management; decision making and response; multi-parameter water quality technologies; and detection of chemical, microbial, and radiological contaminants. The recommendations include a list of near- and long-term knowledge and research gaps.

10.1 General Conclusions and Recommendations

Viable integrated EWSs that meet the desired characteristics and can be routinely used are several years away. Some individual components are available currently, however, others need further development. Designs of EWSs for water distribution systems are largely theoretical or in preliminary stages. Much of the required data acquisition software and hardware already exists, but software for security of EWS SCADA systems is still under development and needs verification. Distribution system modeling in general, and contaminant flow predictive systems in particular, are developing rapidly with the incorporation of graphic software; however, most utilities have not implemented software for modeling intentional contamination events. Most sensor and EWS components have not been tested or verified, and the types of contaminants and levels of exposure have not been well defined to support selection of sensor technologies. Several companies are working on alert management methods but are in preliminary stages of research, with often proprietary trigger algorithms. Linking contamination data analysis with decision making and alert response has been outlined; however, the equipment to effectively implement the process has not been extensively developed for water utilities. Research on approaches and technologies to detect engineered microbes is needed. Also, all of these technologies should be verified and affordable, and should operate consistently in the field.

Short-Term Research Needs

- *An in-depth review of EWS architecture and implementation should be conducted.*
Because a detailed examination of the basic design and features of an EWS architecture is beyond the scope of this study, follow-up studies to prioritize certain features and provide comprehensive guidance to implement the selection, linking, and testing of various EWS components are recommended. Any guidance on design should include considerations for small and large systems, public health surveillance, and consumer complaint monitoring. Also, the research should provide guidance on EWS performance, alarm, and response criteria.
- *Methods for vulnerability assessments should be adapted to focus on contamination scenarios.*
There are various vulnerability assessment methods that utilities have used. To develop an EWS, vulnerability to contamination has to be examined. It is unclear whether utilities have specifically examined their vulnerabilities for contamination or whether the existing methodologies can adequately assess contamination vulnerabilities. This is an area of further research to see how adequately utilities have examined contamination vulnerability and how such information can be incorporated into EWS architecture.

- *Research on international efforts on EWS is needed.*
EPA may find it useful to continue to engage the international research and development community to gain access to innovations and advancements being made in other countries.
- *Grab-sampling protocols and analysis technologies should be developed quickly.*
Online detectors, as part of an integrated EWS, may be years away. However, near real-time monitoring can be approached by establishing periodic grab samples that can be analyzed as appropriate by field or laboratory instruments.

Long-Term Research Needs

- *Survey case study and analysis should be performed on monitors/sensors/detectors used by utilities.*
Some water utilities have installed or tested EWS component technology, such as monitors, sensors, or detectors, in the field but the experiences are not extensive or shared. Experience gained from using these technologies in a distribution system, even if they are not part of a fully integrated EWS, as defined by this report, should be captured. A survey of such case studies can provide great insights into the validated use and capabilities/disadvantages of certain technologies. Further research efforts should be undertaken to more fully document and evaluate the case study experience of utilities using EWS components in the field.
- *EWS technologies and techniques need to undergo verification testing.*
The ETV or TTEP program should test various sensor technologies, including for example, ATP products, mussel biotectors, and radiological online detectors.
- *Potential contaminants list should be reviewed on an ongoing basis.*
The types of contaminants of concern for public health are important to evaluating EWS adequacy. Determining the specific contaminants is an area of ongoing work that is not publicly available and is generally under classified review. There will be further such classified efforts. There is a research need to continue to determine the types of contaminants that are harmful and that need to be detected by EWSs.
- *Concentrations that must be detected by a sensor should be reviewed on an ongoing basis.*
Another recognized area of research is to determine the concentration of contaminants that need to be detected by EWSs. The concentration depends on the properties of the contaminant, the routes and magnitude of exposure, and the susceptibility of the exposed population to particular contaminants. Without a determination of these concentrations, the adequacy of any specific instrument or set of instruments in reducing public health risk is difficult to determine. Continued research is recommended to fully determine concentrations that must be detected. Related to concentrations, research should also be conducted to determine the anticipated exposures and doses based on specific concentrations that impact human health, as well as to determine if decontamination efforts were sufficient to protect human health.
- *The fate and transport (including exposure levels, doses, and detectible concentrations) of contaminants, especially toxic byproducts, should be examined.*
As research occurs on the contaminants of concern, additional research should be conducted to determine the toxic byproducts of certain contaminants and to model the fate and transport of these contaminants in real world water distribution systems. The persistence, stability,

resistance to chlorine, and ease of dispersion of a contaminant in an aqueous environment are important fate and transport factors. This research area will assist with the evaluation and selection of EWS technologies.

- *Results from laboratory research by various agencies on EWSs should be replicated and the conclusions of EWS studies should be shared among government agencies and water utility stakeholders.*

There are various laboratory research efforts on EWSs in distribution systems that are sponsored or conducted by the EPA WATERS Center, U.S. Army ECBC facility, USGS facilities, and specific utilities. These efforts should be replicated when possible to verify results. The information from these efforts and other EWS studies should be shared among government agencies and water utility stakeholders.

10.2 Specific Conclusions and Recommendations

10.2.1 Data Acquisition and Analysis

Data collection by Supervisory Control and Data Acquisition (SCADA) or other automated systems is essential to handle the large volume of data from online sensors in an EWS. Existing data acquisition systems do not present a major issue given currently recommended sampling times by EPA (between 2 and 10 minutes, depending on the SCADA system setup and bandwidth, the sensor location, and the water flow rate). Because of the large amount of data generated, automated data validation processes are indispensable to ensure accurate results from data analysis. Data transmission to a central database, through hardwired or wireless systems, requires a simple yet effective protocol to ensure accuracy and completeness, and can be done by comparing data received from monitoring sites with data stored at the sensor locations. Much of the data acquisition software and hardware already exists. Software for security of SCADA systems for EWSs is still under development and needs verification, but can probably be addressed by utilities simultaneously with general security issues (e.g., encryption).

Short-Term Research Need

- *Standardized methods and guidance for data analysis and interpretation are needed.*
Specifically, further research and development in mining software to identify outlier detection is needed. Verification programs are needed to substantiate the data analysis algorithms. Some of the efforts by ASCE will help to guide utilities in the use of such systems (ASCE, 2004).

Long-Term Research Needs

- *Large-scale data storage and manipulation techniques and technologies are needed.*
For continuous real-time monitors, data are generated on a large scale. SCADA is the likely vehicle to collect the data. New ways of storing and manipulating the information for immediate and long-term uses are needed.
- *SCADA data security programs should be developed to link existing utility efforts with security characteristics inherent in EWS.*
Current remote monitoring products are beginning to incorporate security precautions including encryption. However, demonstration projects are not frequently undertaken. Standardization

from other data security efforts could be applied to the water sector. Programs should be developed to link utility security efforts surrounding SCADA with data security geared to EWSs.

10.2.2 Flow Modeling

Predicting the movement and flow of contaminants in a water distribution system EWS is important not only to prepare for a potential contamination event, but also to improve the effectiveness of the monitoring system. Distribution system modeling in general, and contaminant flow predictive systems in particular, are developing rapidly. Current contaminant flow models can also integrate data from geographic information systems and display results using computer-aided drafting (CAD) software. PipelineNet, an integration of EPANET and ArcView GIS, and commercial integration packages such as WaterGEMS and InfoWater provide direct capabilities to assess impacts of contamination events. Calibration using optimization methods or tracer studies has been increasingly used in distribution systems. Utilities are not generally using models specifically for the purpose of modeling intentional contamination events. Consumption-of-water models are also being occasionally incorporated. Utility efforts to validate and develop predictive flow models would meet the dual purposes of general planning (expansion, upgrades, repairs, maintenance) and testing intentional contamination scenarios. There are currently few established calibration criteria in the U.S., although a committee of the AWWA did propose a set of possible calibration guidelines in 1999 and the EPA is preparing a distribution system handbook which will include a section on hydraulic model calibration and validation. These possible calibration guidelines should serve as a catalyst or starting point to move forward on developing accepted calibration guidelines or standards. Incident Commanders Water Modeling Tool (ICWater) extends the capability of a previously developed RiverSpill modeling tool to allow an incident commander to analyze and react quickly to chemical and/or biological contaminants introduced into surface water sources. EPA's TEVA program incorporates a probabilistic framework for a large range of contamination attacks in assessing vulnerabilities and estimating the most appropriate sensor placements.

Short-Term Research Need

- *Improved contaminant flow models are needed.*

Research is recommended to develop improved models and methods for validating the models in specific applications. The models should be improved to better include the effect of chemical fate and byproducts.

Long-Term Research Need

- *Flow models need to be verified and then used to improve EWS design.*

Projects are needed to verify contaminant flow models and to make the tools useful for sensor placement, real-time contaminant flow prediction, and identifying the likely location of the contaminant source. These models need adaptation for ease of use by various sized utilities. There are no established calibration criteria for contaminant flow models in the U.S., although a committee of the AWWA did propose a set of possible calibration guidelines (ECAC, 1999). However these guidelines have not been officially accepted and there is no active process underway to adopt them. Using these possible calibration guidelines as a catalyst or starting point, it would be recommended to move forward on developing accepted calibration guidelines or standards.

10.2.3 Sensor Placement

Because of both budgetary and technical constraints, utilities can make only a modest initial investment in sensors within their distribution system, and therefore the utilities want to determine the most appropriate locations. Without resorting to the sophisticated experimental optimization techniques, a two-stage procedure is typically followed. In the first stage, likely sites for sensors are determined based on technological (e.g., available power source, access to communications) and physical (e.g., access) constraints. In the second stage, sensors are placed throughout the system on larger pipes that serve the most customers. Current research combining flow models and sensor technology is beginning to be developed, but such models must be verified before difficult and costly decisions are made by the utilities.

Short-Term Research Need

- *Hardware and materials to protect remote sensors are needed.*
Online sensors are typically installed using special sample taps that require interruption of water flow through pipes. New installation techniques are being developed to enable installation without interrupting the water flow or major excavation. Sensors also need to be able to withstand the harsh environment of different locations. New development in construction of materials and protective hardware is necessary to enable sensor systems to be installed in areas open to the environment (AwwaRF, 2002).

Long-Term Research Need

- *Research into sensor placement parameters is recommended.*
Simple guidance, such as what to do with a limited number of specific sensors, is needed. Also, validation of sensor placement strategies should be investigated by perhaps comparing results of several models that determine sensor placement and optimization.

10.2.4 Alert Management

Alert management systems typically consist of two general areas: (1) establishing parameters for alert triggers and (2) reducing false alarms. Any anomalies in the comparison of sensor data to the baseline trigger alerts to the operator. Establishing reliable baseline data is key, especially when water quality fluctuates. Alert management systems usually rely on strict data validation protocols or specialized software to reduce false alarms. Several companies are working on alert management, but are in preliminary stages of research, with often proprietary trigger algorithms.

Long-Term Research Need

- *Alert management approaches/technologies should be examined and sensitivity to false-positives and false-negatives should be quantified.*
A demonstration project is needed to ensure the reasonableness of certain approaches to alert management. The relationship between alert sensitivity and the potential for adverse consequences (false-positives and false-negatives) should be quantified. Additional projects should examine alerts for other promising sensors such as mussel or bacteria monitors.

10.2.5 Decision Making and Response

The process linking the analysis of contamination data with the decision making and response is outlined in EPA's Response Protocol Toolbox; however, additional tools to effectively implement the process are needed for water utilities.

Long-Term Research Need

- *Technology to support and implement decision making and response are needed.*
Tools to assist decision making and response, such as the Water Contaminant Information Tool, are being developed and will help fill a current void.

10.2.6 Multi-Parameter Water Quality Technologies

There is an active research program in the use of the multi-parameter water quality monitors as part of an EWS for distribution systems. Preliminary evidence suggests that such monitors can detect an anomaly in the distribution system and provide an initial red flag warning. However, it is also reasonable to be concerned about false-positives and whether the system can provide definitive indications of intentional contamination. Gathering baseline data may also be prohibitively expensive. Currently, these technologies need to be demonstrated to detect biological contaminants or dangerous chemicals or develop a track record of field performance. The technology has not been sufficiently evaluated to recommend widespread use; for example, no tests have been performed on chloraminated systems. However, full-scale testing by USGS, EPA, and a water utility during 2006 and 2007 may help shed light on concern over false-positives and whether a system can work with the fluctuations of normal water quality.

Given the current developmental stage of multi-parameter technologies, parameters that appear from EPA's preliminary tests to be useful to monitor in distribution systems include chloride (ISE), specific conductance (electrode), turbidity (nephelometric), free chlorine, and ORP. TOC is extremely helpful, but may be too expensive to be widely used. Probes are being developed by manufacturers to include free and total chlorine, pH, temperature, specific conductance, chloride, nitrates, turbidity, and ORP. Not all utility companies are able to afford the monitoring systems currently being evaluated as EWSs. Reductions in price due to competition and technological advancements may remedy this situation in the future, but in the interim, utilities with limited financial resources will face a challenge in implementing online (e.g., continuous) water quality monitoring.

The signatures being developed by Hach Company and others to identify contaminants or classes are difficult to independently validate or be understood because their methods and algorithms have not been made public. Also, the examination of water quality parameters in detecting and identifying contaminants is still being evaluated by EPA, USGS, the Army, and other organizations. There has yet to be a field-scale test of an EWS with these water quality parameter components. These are reasons for caution in recommending the use of water quality parameter-based EWSs.

Short-Term Research Needs

- *Verified baseline data to calibrate EWS alarm triggers are needed.*
Although research has demonstrated proof-of-concept for using water quality parameter fluctuations as a signal that a contamination event has taken place, baseline data to calibrate the

alarm triggers may need to be gathered over months or years for each distribution system. Because this is very expensive, research demonstration projects such as the USGS project are needed to advance the understanding of how baseline water quality data might influence the performance of EWSs in the field.

- *Contaminant specific signatures are needed.*
Research has begun to develop contaminant specific signatures; however, the limited number of contaminants examined to date lowers the confidence of the claim that the signature really is unique. Classes of contaminants may be identifiable, but whether a comfortable range of specific contaminants can be identified has not yet been determined. Additionally, it is not known yet whether monitors can detect biological contaminants and dangerous chemicals. Further research is needed to develop specific signatures for a wider range of contaminants and concentrations, including actual agents.
- *Validation of event detection algorithms is needed.*
It is important that the algorithms used to determine when alarm conditions are encountered are validated for a variety of real world operational conditions.

Long-Term Research Need

- *Costs and benefits (e.g., ability to detect contaminants with multi-parameter water quality monitors) of using TOC sensors should be determined and more affordable and reliable TOC sensors should be developed.*

Current multi-parameter units cost approximately \$10,000 without TOC. Although TOC appears to be a valuable parameter to measure, it adds \$18,000 to 29,000 per unit. Research needs to determine the cost/benefit relationship of including this technology in an EWS. A basic system with 10 microprobe monitors (without TOC) linked to an existing SCADA system is estimated to cost approximately \$150,000, plus \$60,000 per year in operational costs. Also, a research/development need is to have cheaper and reliable online TOC monitors. A TOC monitor for an EWS would not need to be capable of compliance monitoring but would only need to detect gross changes in TOC levels that warrant further investigation.

10.2.7 Detection of Chemical Contaminants

Portable field technology is available for conducting analyses of grab samples on site for many possible chemical contaminants. This area will continue to improve as high technology equipment evolves based on microchip technology (e.g., taste-chip). The technology that is readily available and reliable uses specific probes, such as arsenic and cyanide, that could be effective against a narrow selection of contaminants. Certain biomonitors are portable and can be used for site assessments. Chlorine in the water would have to be removed for many such analyses. In contrast to portable field technology, online chemical detection technologies are not reasonably available or are not cost-effective. GC and ion mobility have cost and technical challenges. Certain biomonitors may be promising, if the interference issue of chlorine and chloramine residual can be resolved. In one case, the mussel monitor has been recently demonstrated in finished water in Europe. There are various efforts in the U.S. to make other monitors (MicroTox® and ToxScreen) adaptable to finished water. The MosselMonitor® or Bio-Sensor® could be a good candidates for an EPA-ETV Program study and perhaps used for a laboratory and/or field study on finished water or with CBR surrogates or contaminants. In the next three years, the field should show further development in terms of cost-

effective and reliable devices. A few new technologies (such as microchips) could revolutionize the chemical detection field for drinking water.

Short-Term Research Need

- *The impact and removal of chlorine and other residues on accuracy of detection should be examined.*

Organism-based biomonitors are sensitive to the chlorine residuals in drinking water. Although the fish-based Bio-Sensor® and MosselMonitor® remove chlorine, broadly applicable methods for chlorine removal have not yet been developed. Although one company, Checklight, is developing a system for removal of chlorine, the effect of chlorine removal on other biosensors has not been demonstrated.

Long-Term Research Needs

- *Reliable field kits should be developed.*

The bacterial monitoring kits tested by EPA's ETV Program have high false-positive and false-negative rates. A common drawback for such kits is the stability of reagents. Often reagents require reconstitution (if they are lyophilized) or careful measurement of reaction components to constitute a fresh reaction mixture. Kits can be subject to variability due to different users because it is difficult for users to mix and pipette in a consistent manner. They require trained personnel and have set-up requirements, such as culturing log phase growth bacteria. The results do not provide specific identification of a toxin. Although these kits may be suitable for confirming the presence of a toxin, further methods would need to be utilized for specific identification.

- *Existing state-of-the-art detection technologies should be adapted for use in EWSs.*

Portable infrared spectroscopy, ion mobility spectroscopy, surface acoustic waves, and polymer composite chemoresistors technologies are being aggressively pursued for air and vapor applications, but have not been developed specifically for drinking water monitoring. Research could examine whether these techniques could be adapted for water with further research if there is a potential market.

10.2.8 Detection of Microbial Contaminants

Development of an online microbial technology appears years away. An exception to this may be the light-scattering methodology, which shows some promise. Most methods are not suited for continuous online monitoring or for differentiating among microbes. However, to confirm a contaminant using a portable field unit with grab samples, there are several potentially adaptable methods from which to choose, including immunoassay, PCR, and ATP. These methods have not yet been exploited to their full potential, so will likely continue to be incorporated into new monitoring devices and systems. Grab sampling could include sampling at scheduled intervals or taking composite samples (e.g., collecting small volumes of sample continuously over time). In any sampling, the microbial integrity must be ensured. For drinking water, the challenge for most methods is the need to concentrate the sample. A few methods of concentration show promise including the hollow fiber, the micropump, and related efforts by Pacific Northwest National Laboratory. Generally, this does not seem like an insurmountable obstacle for some methods. However, for PCR, current online technologies and concentration methods are not sufficiently advanced to detect microbes at levels that threaten public health. Overall, none of the methods by

themselves provide sufficiently rapid detection. Therefore, one recommended approach is to screen a sample with a generic detector (e.g., multi-parameter probe or perhaps light scatter), then use an immunoassay device in tandem with another method for identification. Detectors based on ATP are promising, but have not been verified for water (one is online for water). ATP detection products should be third party evaluated for EWS application. In the future, microchips have great potential in online measurement, but presently the field is not sufficiently mature.

Short-Term Research Needs

- *Extraction and concentration technologies need improvement.*
Many microbial pathogens are a risk to human health at low concentrations. The concentration of pathogens that needs to be detected to adequately protect public health is a policy issue. However, it is widely acknowledged that current detection methods for online or near continuous use are not sensitive enough to detect the lowest microbial concentrations that may be a concern for human health. Therefore, microbial contaminants need to be sufficiently concentrated to be detected. Detecting low concentrations is difficult for the binding assays that most capture-target technologies utilize. Thus, it may be necessary to concentrate large volumes of water samples to gather enough contaminant to detect. Two AwwaRF research papers expected in 2005 (Extraction Methods for Early/Real-Time Warning Systems for Biological Agents - Project A and B) and research at Idaho National Laboratory in Idaho Falls, ID may help with this issue.
- *Methods to distinguish concentrated interferants from target compounds are needed.*
Concentration techniques could also concentrate interference compounds. Techniques that concentrate the target contaminant will very often also concentrate other non-target contaminants that will interfere with the biosensor assay. For example, to successfully perform PCR analysis of environmental waters it is necessary to remove analytical interferences such as humic and fulvic acids.
- *The development of field-stable reagents is needed.*
Reagents may not be stable in field environmental conditions. Reagents containing biological molecules usually degrade or become inactive within hours of being subjected to room temperature conditions. Even if partial activity is maintained, quality control is jeopardized. This problem can be partially addressed with freeze-dried reagents, but reagent-grade water at the field site is required to reconstitute the reaction solutions. Molecular stability of biomolecules on biochips is even more difficult.

Long-Term Research Needs

- *Antibodies for unique epitopes that would show less cross-reactivity should be developed.*
Antibodies cross-react and are subject to binding kinetics. Antibodies may bind with known or unknown affinity to non-target antigens. The sensitivity of antibodies needs to be calibrated for each batch, even for monoclonals. Cross-reactivity is a problem if different target molecules have overlapping epitopes. Antibodies designed against specific unique epitopes would have less cross-reactivity.
- *Research on additional approaches and technologies that can detect emerging, evolving, and engineered microbes is needed.*

Emerging and bioengineered microbes could escape detection. Even with a broad selection of capture molecules, microbes will evolve such that they may lose target epitopes or DNA, and therefore escape detection. Bioengineered pathogens could be designed to evade detectors, if detailed information on capture molecules was obtained. The only existing technology that minimizes this problem is Triangulation Identification Genetic Evaluation of Risks (TIGER), developed by Isis Pharmaceuticals, Inc., because it integrates a variety of approaches (DNA base composition and PCR) into one analysis.

10.2.9 Detection of Radiological Contaminants

There are demonstrated technologies for examining radiation in wastewater, but the transfer or adaptation to drinking water has not yet taken place. Only a few products claim applicability to water, some on a grab-sample basis. Also, the appropriate devices and methods will vary according to local conditions, such as temperature and humidity, or the properties of the radionuclide at the source of the radiation. More products are being developed by a few vendors, but it is still unclear whether the threat merits use of these expensive products on a real-time basis. The few items that are commercially available should be verified either by EPA or by a national laboratory that specializes in radiation. Grab sampling can be performed by a number of products, but it is unclear if there is any generic monitor that can trigger this more detailed analysis. In addition, all of the radiological monitoring devices mentioned in this study usually require specialized expertise for installation, set-up, and routine calibration, even if they are labeled maintenance-free. Thus, early warning for radiation detection is not currently available, and the market forces for such development may not be strong.

Short-Term Research Need

- *Beta and gamma radioactivity detectors should be developed and verified for drinking water monitoring applications.*

There are only a few detectors that are designed to monitor for alpha and beta radioactivity. There are also only a few detectors that are designed for online monitoring of gamma. Verification studies do not seem to have been performed on detectors that are geared to radiation terrorist attacks on drinking water.

Long-Term Research Needs

- *Low-cost, online, radioactivity monitors are needed.*

Although online analyzers are efficient in monitoring the water quality, they are expensive and limited in number. Many facilities may therefore find grab samplers to be more appropriate. Manufacturers are in the process of developing and refining other applications of small scale flow-through scintillation technology. Utilities will need to collaborate with these manufacturers to research and customize the monitors for small scale needs.

- *Monitors should be developed that are specifically intended for water distribution systems.* Some of these monitors are intended for waste streams rather than distribution systems due to the more stringent requirements for drinking water monitors. Waste stream monitors would be geared more towards the detection of accidental spills rather than intentional contamination.

REFERENCES

- ACS (2002) American Chemical Society. "PNNL Research: Biodetection Enabling Analyte Delivery System." *Chemical and Engineering News*. 80(20):32-36.
- ASCE (2004) Interim Guidelines for Designing an Online Contamination Monitoring System, American Society of Civil Engineers.
- Alberts, B; Bray, D; Lewis, J; Raff, M; Roberts, K; Watson, JD. (1994) *Molecular Biology of the Cell*. Third Edition Garland Publishing Inc. New York.
- AWWA Workshop (2004) Contamination Monitoring Technologies sponsored by the American Water Works Association, Richmond, VA; May 2004.
- AwwaRF (2002) Online Monitoring for Drinking Water Utilities (Project #2545) Order number 90829. Report prepared by: E. Hargesheimer, O. Conio, and J. Popovicova.
- Bahadur, R; Samuels, W; Pickus, J. (2003a) Case Study for a Distribution System Emergency Response Tool. AwwaRF, Denver, CO.
- Bahadur, R; Samuels, W; Grayman, W; Amstutz, D; Pickus, J. (2003b) PipelineNet: A Model for Monitoring Introduced Contaminants in a Distribution System. World Water & Environmental Resources Congress, Environmental & Water Resources Institute - ASCE.
- Baxter, CW; Lence, BJ. (2003) A Framework for Risk Analysis in Potable Water Supply. World Water & Environmental Resources Congress, Environmental & Water Resources Institute - ASCE.
- Berry, ED; Siragusa, GR. (1999) Integration of hydroxyapatite concentration of bacteria and semi-nested PCR to enhance detection of *Salmonella typhimurium* from ground beef and bovine carcass sponge samples. *J. Rapid Methods Automation Microbiol.* 7:7-23.
- Berry, J; Hart, W; Phillips, C; Uber, J. (2004) A General Integer-Programming-Based Framework for Sensor Placement in Municipal Water Networks. World Water & Environmental Resources Congress, Environmental & Water Resources Institute - ASCE.
- Black & Veatch (2004) "Water Monitoring Equipment for Toxic Contaminants Technology Assessment" General Dynamics, and Calspan/University of Buffalo Research Center, October 2004.
- Bodurow, CC; Campbell, DP; Gottfried, DS; Xu, J; Cobb-Sullivan, JM; Caravati, KC. (2005) A low-cost, real-time optical sensor for environmental monitoring and homeland security. EPA Science Forum 2005. http://www.epa.gov/sciforum/2005/pdfs/oeiposter/bodurow_catherine.pdf
- Bravata, DM; Sundaram, V; McDonald, KM; Smith, WM; Szeto, H; Schleinitz, MD; Owens, DK. (2004) Evaluating detection and diagnostic decision support systems for bioterrorism response. *Emerging Infectious Diseases*. 10(1):100-108.
- Bunk, S. (2002) Sensing Evil. *The Scientist*. 16(15):13.

Carlson, K; Byer, D; Frazey, J. (2004): Section 5.2 - Candidate Instruments and Observables. Section 5.3. - Models. May, 2004 Draft of Methodology and Characteristics of Water System Infrastructure Security.

Cross, H. (1936) Analysis of Flow in Networks of Conduits or Conductors. Univ. of Illinois Eng. Experiment Station Bulletin. Page 286.

DARPA (2004) Chemical and Biological Sensor Standards Study. LTC John Carrano, Study Chair.

Daviss, B. (2004) A Springboard to Easier Bioassays. *The Scientist*. 18(4):40. March 1, 2004.

Deininger, R; Lee, JY. (2001) Rapid determination of bacteria in drinking water using an ATP assay. *Analytical Chemistry and Technology*. 5(4):185-189.

DSRC Meeting (2004) Distribution System Research Consortium Draft Summary Report. Distribution System Research Consortium Meeting, presentations by Vowinkle, Uber, and McKenna: August 25-26, 2004, Cincinnati, Ohio USEPA.

ECBC (2002) *Bio-detector Assessment*. ECBC-TR-171, March 2002, Walther, Emanuel and Goode. Edgewood Chemical Biological Center.

Emanuel, P; Chue, C; Kerr, L; Cullin, D. (2003) Validating the Performance of Biological Detection Equipment: the Role of the Federal Government, BioSecurity and Bioterrorism: Biodefense Strategy, Practice and Science.

ECAC (1999) Engineering Computer Applications Committee Calibration Guidelines for Water Distribution System Modeling. Proc. AWWA ImTech Conference, 1999.

EPA (2000) Multi Agency Radiation Survey and Site Investigation Manual. (EPA 402-R-97-016), August, 2000.

EPA (2003) A Review of Emerging Sensor Technologies for Facilitating Long-Term Ground Water Monitoring of Volatile Organic Compounds. (EPA 542-R-03-007.)
<http://www.epa.gov/tio/download/char/542r03007.pdf>

EPA-ETV (2004) U.S. Environmental Protection Agency, Environmental Verification Program
<http://www.epa.gov/etv/>

EPA (2003/2004) Response Protocol Toolbox: Planning for and Responding to Drinking Water Contamination Threats and Incidents. Modules 1-6. 2003/2004.

EPA (2004) Office of Research and Development, Shaw Environmental, Draft Report Evaluation of Water Quality Sensors in Distribution Systems; May 2004 and EPA, Office of Research and Development, Shaw Environmental, Draft Report: Water Quality Sensor Responses to Chemical and Biological Warfare Agent Simulants in Water Distribution Systems July 2004.

EPA (2005) Distribution System Water Quality Report: A Guide to the Assessment and

Management of Drinking Water Quality in Distribution Systems. ORD NRMRL Water Supply and Water Resources Division. June 2005 Draft.

Fitzgerald, DA. (2002) Microarrays on the spot. *The Scientist*. 16(4):42.

Fontenot, E; Ingeduld, P; Wood, D. (2003) Real-time Analysis of Water Supply and Water Distribution Systems, World Water & Environmental Resources Congress, Environmental & Water Resources Institute - ASCE.

Goodey, AP; McDevitt, JT. (2003) Multishell Microspheres with Integrated Chromatographic and Detection Layers for Use in Array Sensors. *J. Am. Chem. Soc.* 125(10):2870-2871.

Gorman, J. (2003) NanoLights! Camera! Action! Tiny semiconductor crystals reveal cellular activity like never before. *Science News*. 163(7):107.

Grayman, W; Roberson, A; States, S. (2003) AWWA Contamination Monitoring Technologies Seminar; Richmond, VA. May 2003.

Grayman, W; Deininger, R; Males; Gullick, R. (2004a) Source water early warning systems. Chapter in *Water Supply Systems Security*. Edited by Larry Mays, McGraw-Hill and Companies, New York, NY.

Grayman, WM; Clark, RM; Harding, BL; Maslia, M; Aramini, J. (2004b) Reconstructing Historical Contamination Events. Chapter in *Water Supply Systems Security*. Edited by Larry Mays, McGraw-Hill and Companies, New York, NY.

Grayman, W; Rossman, L; Deininger, R; Smith, AC; Smith, J. (2004c) Mixing and aging of water in distribution system storage facilities. *J. AWWA*. 96(9).

Grow, AE; Deal, MS; Thompson, PA; Wood, LL. (2003) Evaluation of the Doodlebug: a biochip for detecting waterborne pathogens. Water Intelligence Online IWA (WERF).

Hasan, J; States, S; Deininger, R. (2004) Safeguarding the security of public water supplies using early warning systems: A Brief Review. *J. of Contemporary Water Research and Education*. 129:27-33.

Haupt, K. (2002) Creating a good impression. *Nature Biotechnology*. 20:884-885.

Heroux, K. and Anderson, P. (No date) "Evaluation of a Rapid Immunoassay System for the Detection of *Bacillus anthracis* Spores." U.S. Army Edgewood Chemical Biological Center, Aberdeen Proving Ground, MD. <http://www.responsebio.com/pdf/EdgewoodEvaluation.pdf>

Hindson, BJ; Brown, SB; Marshall GD; McBride, MT; Makarewicz, AJ; Gutierrez DM; Wolcott DK; Metz, TR; Madabhushi, RS; Dzenitis, JM; Colston, BW Jr. (2004) Development of an automated sample preparation module for environmental monitoring of biowarfare agents. *Analytical Chemistry*. 76(13):3492-3497.

Hrudey, SE; Rizak, S. (2004) Discussion of rapid analytical techniques for drinking water security investigations. *J. AWWA*. 96(9):110-113.

Kessler, A; Ostfeld A; Sinai, G. (1998) Detecting accidental contaminations in municipal water networks. *J. of Water Resources Planning and Management*. 124(4):192-198.

King, KL. (2004) Presentation by K.L. King, Event Monitor for Water Plant or Distribution System Monitoring; Hach Homeland Security Technologies; AWWA Water Security Congress; April 25-27, 2004.

ILSI (1999) Early Warning Monitoring to Detect Hazardous Events in Water Supplies. International Life Sciences Institute-Risk Science Institute. <http://rsi.ilsio.org/file/EWM.pdf>

Jentgen, L; Conrad, S; Riddle, R; Von Sacken, EW; Stone, K; Grayman, WM; Ranade, S. (2003) Implementing a Prototype Energy and Water Quality Management System. AwwaRF/AWWA.

Kirby, R; Cho, EJ; Gehrke, B; Bayer, T; Park, YS; Neikirk, DP; McDevitt, JT; Ellington, AD. (2004) Aptamer-based sensor arrays for the detection and quantitation of proteins. *Analytical Chemistry*. 76(14):4066-4075.

Koblizek, M; Maly', J; Masoji' dek, J; Komenda, J; Kucera, T; Giardi, MT; Mattoo, AK; Pilloton, R. (2002) A biosensor for the detection of triazine and phenylurea herbicides designed using photosystem ii coupled to a screen-printed electrode. *Biotechnology and Bioengineering*. 78(1):110-116.

Kretzmann, H; Van Zyl, J. (2004) Stochastic Analysis Of Water Distribution Systems. World Water & Environmental Resources Congress, Environmental & Water Resources Institute - ASCE.

Kuhn, R; Oshima, K. (2002) Hollow-fiber Ultrafiltration of *Cryptosporidium parvum* oocysts from a wide variety of 10-L surface water samples. *Canadian J. of Microbiology*, 48(6):542-549.

Lee, B; Deininger, R; Clark, R. (1991) Locating monitoring stations in water distribution systems. *J. AWWA*. 83(7):60-66.

Li, Z; Buchberger, S; Tzatchkov. (2005) Importance of Dispersion in Network Water Quality Modeling. Proc. World Water & Environmental Resources Congress, Environmental & Water Resources Institute - ASCE. 2005.

Li, Z; Buchberger, S. (2004) Effect of Time Scale on PRP Random Flows in Pipe Network. World Water & Environmental Resources Congress, Environmental & Water Resources Institute - ASCE.

Mays, LW. (2004) *Water Supply Systems Security*. New York: McGraw-Hill.

McCleskey, SC; Griffin, MJ; Schneider, SE; McDevitt, JT, Anslyn, EV. (2003) Differential receptors create patterns diagnostic for ATP and GTP. *J. Am. Chem. Soc.* 125(5):1114-1115.

Murray, R; Janke, R; Uber, J. (2004) The Threat Ensemble Vulnerability Assessment Program for Drinking Water Distribution System Security, Proceedings of the World Water and Environmental Resources Congress, Salt Lake City, June 2004.

Ostfeld, A. (2004) Optimal Monitoring Stations Allocations for Water Distribution System Security. Chapter in *Water Supply Systems Security*. Edited by L. Mays, McGraw-Hill.

Ostfeld, A; Salomons, E. (2004) Optimal layout of early warning detection stations for water distribution systems security. *J.WRPM, ASCE*. 130(5):377-385.

Perkel, JM. (2003) Microbiology vigil: probing what's out there. *The Scientist*. 17(9):40.

Pesavento, M; D'Agostino, G; Alberti, G. (2004) Molecular Imprinted Polymers as Sensing Membrane for Direct Electrochemical Detection of Pollutants, IAEAC: The 6th Workshop on Biosensors and BioAnalytical μ -Techniques in Environmental and Clinical Analysis ENEA - University of Rome "La Sapienza": October 8-12, 2004 - Rome, Italy.

Powell, J; Clement, J; Brandt, M; Casey, R; Holt, D; Grayman, W; LeChevallier, M. (2004) Predictive Models for Water Quality in Distribution Systems. AwwaRF-AWWA, Denver, CO.

Pyle, BH; Broadway, SC; McFeters, G. (1999) Sensitive detection of *Escherichia coli* O157:H7 in food and water by immunomagnetic separation and solid-phase laser cytometry. *Applied and Environmental Microbiology*. 65:1966-1972.

Quist, GM; DeLeon, R; Felkner, IC. (2004) Evaluation of a Real-time Online Continuous Monitoring Method for *Cryptosporidium*. AwwaRF Project #2720.

Rider, TH; Petrovick, MS; Nargi, FE; Harper, JD; Schwoebel, ED; Mathews, RH; Blanchard, DJ; Bortolin, LT; Young, AM; Chen, J; Hollis, MA. (2003) A B cell-based sensor for rapid identification of pathogens. *Science*. 301:213-215.

Rife, JC; Miller, MM; Sheehan, PE, Tamanaha, CR; Tondra, M; Whitman, LJ. (2003) Design and performance of GMR sensors for the detection of magnetic microbeads in biosensors. *Sensors and Actuators A*. 107:209-218.

Roberson, JA; Morley KM. (2005) Contamination Warning Systems for Water: An Approach for Providing Actionable Information to Decision-makers. American Water Works Association. <http://www.awwa.org/Advocacy/pressroom/pr/index.cfm?ArticleID=424>

Rosen, JS; Miller, DM; Stevens, KB; Ergul, A; Sobrinho, JAH; Frey, MM; Pinkstaff, L. (2003) Application of Knowledge Management to Utilities. AWWA Research Foundation. ISBN 1-P-4.5C-90895-2/03-CM.

Rossman, L. (2000) EPANET Version 2 User's Manual. USEPA.

Ruan, C.; Zeng, K; Varghese, OK; Grimes, CA. (2004a) A staphylococcal enterotoxin B magnetoelastic immunosensor. *Biosensors and Bioelectronics*. 20:585-591.

Ruan, C; Varghese, OK; Grimes, CA; Zeng, K; Yang, X; Mukherjee, N; Ong, KG. (2004b) A magnetoelastic ricin immunosensor. *Sensor Letters*. 2:1-7.

Ruan, C; Zeng, K; Varghese, OK; Grimes, CA. (2003) Magnetoelastic immunosensors: amplified mass immunosorbent assay for the detection of *Escherichia coli* O157:H7. *Analytical Chemistry*. 75:6494-6498.

Shaffer, KM; Gray, SA; Fertig, SJ; Selinger, JV. (2003) Neuronal Network Biosensor for Environmental Threat Detection. Internet abstract found at: <http://www.nrl.navy.mil/content.php?P=04REVIEW118>.

States, S. (2004) Rapid Screening, How Good Is it for Security Investigations? AWWA Jan 2004.

Tamanaha, CR; Whitman, LJ; Colton, RJ. (2002) Hybrid macro-micro fluidics system for a chip-based sensor. *J. of Micromechanics and Microengineering*. 12:N7-N17.

Tuck, K; Powers, M.; Millward, H; Chen, Y; Zharkikh, L; Wall, M; Li, W; Gundry, C; Pavlov, I; Ditty, S; Hadfield, T; Karaszkiwicz, J; Nielsen, D; Teng, DH-F. (2005) Joint Biological Agent Identification and Diagnostic System (JBAIDS): Stability and Sensitivity of Freeze-Dried Real-Time PCR Assays. American Society of Microbiology 2005. Abstract 089/Y-018.

Uber, J; Janke, R; Murray, R; Meyer, P. (2004a) Greedy Heuristic Methods for Locating Water Quality Sensors in Distribution Systems. Proc. World Water & Environmental Resources Congress, Environmental & Water Resources Institute - ASCE, 2004.

Uber, J; Shang, F; Rossman, L. (2004b) Extensions to EPANET for Fate and Transport of Multiple Interacting Chemical or Biological Components. World Water & Environmental Resources Congress, Environmental & Water Resources Institute - ASCE.

van Bloemen Waanders, BG; Bartlett, R; Biegler, L; Laird, C (2003) Nonlinear Programming Strategies for Source Detection of Municipal Water Networks. World Water & Environmental Resources Congress, Environmental & Water Resources Institute - ASCE.

Walski, TM; Chase, DV; Savic, DA; Grayman, W; Beckwith, W; Koelle, E. (2003) Advanced Water Distribution Modeling and Management, Haestad Methods. Waterbury CT: Haestad Press.

Watson, J; Greenberg, HJ; Hart, WE. (2004) A Multiple-Objective Analysis of Sensor Placement Optimization in Water Networks. World Water & Environmental Resources Congress, Environmental & Water Resources Institute - ASCE.

Whelan, RJ; Wohland, T; Neumann, L; Huang, B; Kobilka, BK; Zare, RN. (2002) Analysis of biomolecular interactions using a miniaturized surface plasmon resonance sensor. *Analytical Chemistry*. 74:4570-4576.

Whelan, RJ; Zare R.N. (2003) Surface plasmon resonance detection for capillary electrophoresis separations. *Analytical Chemistry*. 75:1542-1547.

Whitman, LJ; Sheehan, PE; Colton, RJ; Miller, RL; Edelstein, RL; Tamanaha, CR. (2001) Naval Research Laboratory Review/Chemical/Biochemical Research.

WHO (2004) Public Health Response to Biological and Chemical Weapons: World Health Organization Guidance. <http://www.who.int/csr/deliberpidemics/biochemguide/en/index.html>

[this page intentionally left blank]

APPENDIX A

WaterSentinel Overview

Promoting the security of the nation's water infrastructure is one of the most significant undertakings and responsibilities of the U.S. Environmental Protection Agency (EPA) in a post-September 11 world. An attack, or even a credible threat of an attack, on water infrastructure could seriously jeopardize the public health, infrastructure, and economic vitality of a community. Although historical evidence suggests that the probability of intentional contamination of the drinking water supply is relatively low, experts agree that it is possible to contaminate a portion of a drinking water system, resulting in adverse public health consequences. Furthermore, the probability of a contamination threat (the mere indication that contamination of the drinking water supply may have occurred) is relatively high. Given that it is possible to contaminate drinking water at levels of public health concern, and the probable occurrence of contamination threats in the water sector, there is a need to evaluate the credibility of any contamination threat and identify appropriate response actions in a very short period of time.

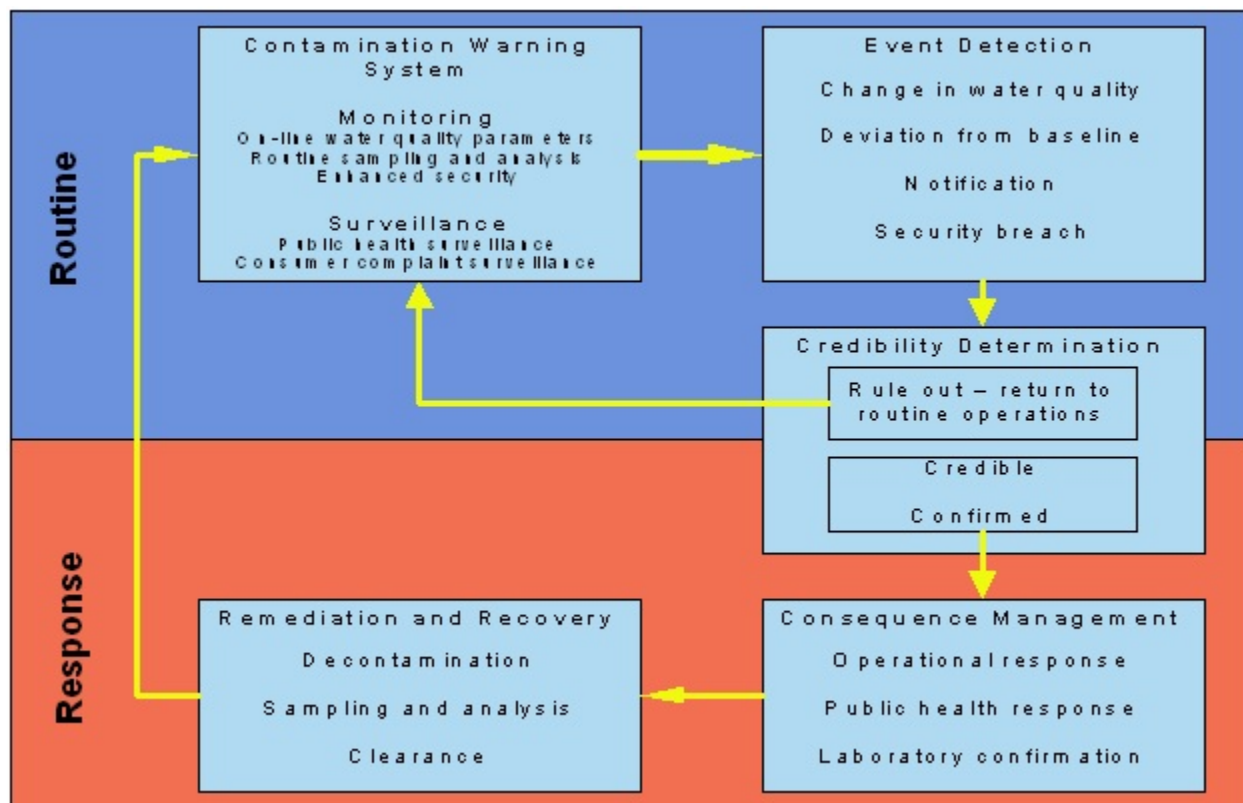
In recognition of this threat and in response to Homeland Security Presidential Directive 9, EPA developed the proposed WaterSentinel initiative. HSPD-9 directs EPA to:

- “develop robust, comprehensive, and fully coordinated surveillance and monitoring systems . . . for . . . water quality that provide early detection and awareness of disease, pest, or poisonous agents”; and
- “develop nationwide laboratory networks for . . . water quality that integrate existing Federal and State laboratory resources, are interconnected, and utilize standardized diagnostic protocols and procedures.”

The proposed WaterSentinel initiative will build on existing EPA efforts to design and deploy a contamination warning system (CWS). A CWS is an evolution of the “early warning system” concept and involves the active deployment and use of monitoring technologies/strategies and enhanced surveillance activities to collect, integrate, analyze, and communicate information to provide a timely warning of potential water contamination incidents and initiate response actions to minimize public health and economic impacts.

The key to an effective and timely response to a water contamination threat is to minimize the time between indication of a contamination incident or change in water quality and implementation of effective response measures through early detection of threat warnings of potential contamination. Identification of a contamination threat leads to response actions designed to determine whether or not a threat is credible and to protect public health in the case of a credible threat. Early detection can be achieved through the implementation of a CWS. A CWS is not merely a collection of monitors and equipment placed throughout a water system to alert of intrusion. Fundamentally, it is an exercise in information management. Different information streams must be managed, analyzed, and interpreted in a timely manner to recognize potential contamination incidents in time to respond effectively.

Figure 1 presents an overview of the components of the proposed concept of operations for the WaterSentinel contamination warning system (WS-CWS). Although an effective CWS should be designed to maximize the detection of contamination incidents, accidental or intentional, it is

Figure 1 Overview of the WS-CWS Concept of Operations

important to demonstrate the effectiveness of the design and integration of CWS components through a systematic process that can be expanded and adapted over time to ensure sustainability.

In the design of the WS-CWS, EPA will partner with drinking water utilities, key water sector stakeholders, technical experts, representatives from public health, law enforcement, and other federal agencies to focus on first-generation CWS components that initially address a representative subset of priority contaminants to improve a utility's ability to respond to any contamination threat or incident. In addition, the WS-CWS will yield operational benefits for non-security related water quality issues and enhance collaboration/integration of water utilities and local health departments. Through working with these partners, EPA will use the results of the WaterSentinel initiative demonstration project to develop a sustainable model for a CWS that can be implemented by utilities throughout the nation.

Major Components of the WS Initiative

The major components of the WS initiative include the following:

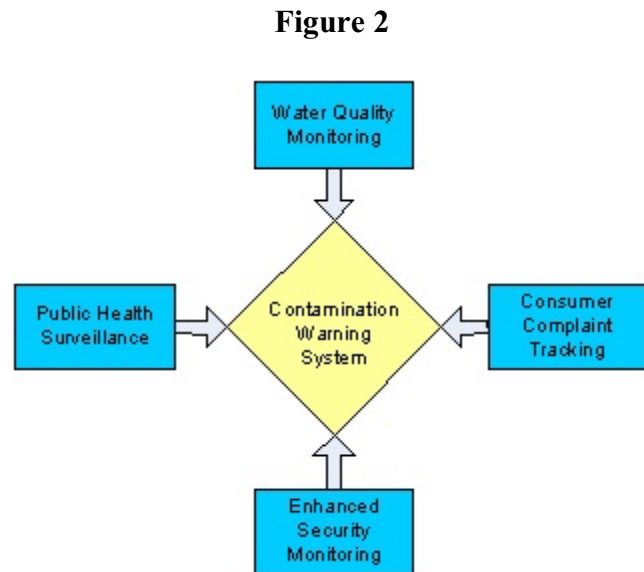
- System architecture and program design
- Selection of baseline contaminants
- Laboratory support and the Water Laboratory Alliance
- Event detection and credibility determination

- Consequence management
- Data management

System Architecture and Program Design

The WS system architecture will define the conceptual approach for the WS-CWS and document the most effective combination of CWS components to yield a sustainable program that can be adopted and implemented by drinking water utilities. The key components of a CWS are shown in Figure 2 and are described as follows:

- **Water quality monitoring.** Multiple approaches are available for monitoring water quality as part of a CWS. The WS-CWS will focus primarily on two options as described below.



- **Online monitoring for changes in water quality parameters.** Online monitors for water quality parameters, such as chlorine residual, pH, conductivity, turbidity, etc., can potentially detect an identifiable change from an established water quality baseline and serve as an indicator of potential contamination in the WS-CWS.
- **Routine sampling for select contaminants.** Water samples can be collected at a predetermined frequency or in response to a trigger and analyzed for specific, targeted contaminants. It may also be possible to detect some non-target analytes if the analytical techniques used in the routine monitoring program are sufficiently robust and if the analysts are trained and encouraged to investigate tentatively identified contaminants.
- **Consumer complaint surveillance.** Consumer complaints regarding unusual taste, odor, or appearance of the water are often reported to and recorded by water utilities, which conventionally use them to identify and address water quality problems. Using an appropriate methodology, WS could track and analyze these complaints to look for unusual trends that may be indicative of a contamination incident.
- **Public health surveillance.** Syndromic surveillance by the public health sector as well as reports from 911 call centers and poison control hotlines might serve as a warning of a potential drinking water contamination incident if there is a reliable link between the public health and drinking water utilities.
- **Enhanced security monitoring.** Security breaches, witness accounts, and notifications by the perpetrator, news media, or law enforcement can be monitored through enhanced security practices.

Factors for consideration in the development of the WS system architecture for a given utility include the following:

- *Sustainability and dual use:* The ability of utilities to operate and maintain the WS-CWS to benefit water security as well as routine operations and water quality concerns.
- *Cost-benefit of implementation:* The ability to demonstrate that the cost of implementing, operating and maintaining the WS-CWS is justified by the benefits. This factor is directly related to the previous consideration of sustainability and dual use.
- *Universal application:* The ability to adapt and implement the WS-CWS design, in some manner, at any drinking water utility regardless of size, treatment type, location, or complexity.

Under the proposed initiative, EPA would work with utilities to determine sensor placement and sampling locations, develop and enhance communication and coordination between the utility and public health community, identify approaches for enhancement and integration of consumer complaint and public health surveillance, and define dual use benefits of implementation of the WS-CWS.

Selection of Baseline Contaminants

Many potential monitoring and surveillance components that could be integrated into a CWS, and evaluated during WS demonstration project, have not been thoroughly demonstrated in a CWS application. Thus, it is critical that the WS demonstration project be limited to contaminants for which technologies/strategies are well understood or characterized through other water monitoring application. For example, there is substantial experience with technologies used to monitor basic water quality parameters, such as chlorine residual, pH, and conductivity. Use of such established technologies during the WS demonstration project will allow for the focus on the performance of the contamination warning system, without introducing additional uncertainty associated with research techniques. Once the concept of a CWS has been demonstrated, novel detection technologies could be evaluated in the context of this proven system.

The WS initiative is intended to increase protection against those contaminants that could cause serious harm to public health or economic well-being if introduced into a drinking water system. Thus, selection of candidate contaminants for the WS initiative should consider the threat posed by potential contaminants. Therefore, the first step in the development of the WS initiative is to identify those baseline contaminants that will be included in the demonstration project.

The objectives of the WS contaminant selection process are to:

- Select a reasonable number of baseline contaminants that provide coverage for all categories of priority contaminants using a combination of different monitoring and surveillance technologies/strategies.
- Identify research priorities related to sampling and analysis methods that can be initiated in the near term for evaluation in the WS demonstration project.
- Identify long-term research priorities related to sampling and analysis to ensure future coverage of all priority contaminants.

Laboratory Support and the Water Laboratory Alliance

To provide necessary analytical support for both routine monitoring and response actions, the Water Laboratory Alliance (WLA) is intended to establish capability and capacity at drinking water utility laboratories for routine monitoring of baseline contaminants. The WLA is a network of laboratories with extensive capability for the analysis of water samples for a wide range of potential contaminants. It is proposed that the WLA integrate existing water quality labs with the existing Laboratory Response Network (LRN), established by the U.S. Center for Disease Control and Prevention (CDC) to support analysis of potential biothreat agents.

Required confirmatory and response analysis capabilities and capacities should be established to support the WS initiative. Since many CWS components may provide non-specific indicators of potential contamination, laboratories that are part of the WLA should be proficient in the screening and analysis of unknown samples for chemicals, pathogens, and radionuclides. In addition to the development of laboratory capabilities to support the WS-CWS, the development of standardized analytical methods that can be utilized for screening, presumptive, and confirmatory analysis will be a key focus of research activities.

Event Detection and Credibility Determination

While the WS initiative is designed to gather and integrate information from a number of sources that might be indicative of a contamination threat, the information is only useful in the context of a CWS if it can be quickly and effectively used to make appropriate response decisions. Thus, there is a need for decision support tools.

In the WS-CWS model, event detection is defined as a signal from the CWS that is indicative of a possible contamination incident. This signal could be a pattern of unusual water quality, a cluster of unusual consumer complaints, or unusual symptoms picked up by a public health surveillance program. Although public health surveillance systems have their own event detection algorithms, these do not exist, or are not widely deployed, for water quality and consumer complaints. Thus, there is a need to develop event detection software (EDS). The most important function of the EDS is to filter out the anomalies that normally occur, or which have known causes, and signal only those events that are likely to be possible contamination incidents. In short, the purpose of the EDS is to reduce the false-positive rate without missing potential events.

Although the EDS can indicate a possible contamination threat, it cannot indicate a credible threat that requires response actions to protect public health. Furthermore, the human element cannot be removed from the credibility determination step. However, it is possible to develop a tool to support officials in decision making by guiding them through the evaluation process and aiding in the synthesis of information necessary to make timely and appropriate response decisions. Ultimately, the decision will always rely on human judgment and evaluation of incomplete information. However, this decision tool can be a great aid in the process, and might substantially reduce the time to make critical response decisions.

Consequence Management

Early detection of a contamination incident is only beneficial in minimizing public health or economic impacts if effective response decisions also can be made in a timely manner. A consequence management protocol will provide a decisionmaking framework that governs when, how, what, and who will be involved in making decisions in response to contamination threat warnings to minimize the response timeline and implement operational or public health response actions appropriately. Availability of a robust and tested consequence management protocol will be a key factor in initiation of monitoring and surveillance activities.

The systematic approach for assessing credibility in response to contamination threat warnings ensures that all available information is analyzed in a timely and efficient manner to minimize both false alarms and over-response to a trigger that has not been determined to be credible. While the system architecture will identify an integrated set of contamination threat warnings that provide input for consequence management decisions, the consequence management protocol will be independent and able to inform response decisions and containment strategies for existing triggers and contamination threat warnings in the absence of a formal CWS.

Data Management

A CWS is not merely a collection of monitors and equipment placed throughout a water system to alert of intrusion. Fundamentally, it is an exercise in information management. Different information streams must be managed, analyzed, and interpreted in a timely manner to recognize potential contamination incidents in time to respond effectively.

The elements of the WS-CWS present a rich topography of information needs to be collected, integrated, and analyzed to make response decisions. For each CWS component, EPA and partners in the WS initiative would identify the requirements of the technology employed to analyze data and distinguish a potential incident from the established baseline.

Based on CWS components identified through WS system architecture and program design, data may need to be extracted from a combination of SCADA systems, laboratory information management systems (LIMS), consumer complaint surveillance systems, security monitoring systems, and public health surveillance systems in a manner that allows for timely decision making and response.

Next Steps

WaterSentinel has been proposed as a demonstration project to commence in Fiscal Year 2006. EPA will launch this project by building on existing efforts. Throughout Fiscal Year 2005, EPA will continue to work with the water sector on activities that could lay the groundwork for WaterSentinel. Such activities could include the design of a model contamination warning system, analysis of contaminants that could be effectively monitored for a timely response, the development of consequence management protocols for response to a potential incident, and research into technologies that could be candidates for deployment.

APPENDIX B

Agencies Involved in Early Warning Systems

The following are brief descriptions of agencies involved in research, evaluation, or development of early warning systems.

Federal Agencies (Research and Programs)

The U.S. Environmental Protection Agency

EPA plays a lead role in protecting the water sector. In National Strategy for Homeland Security (July 2002), EPA is designated as responsible for protecting our national water supply. Also, under the Homeland Security Presidential Directive-9 (January 2004), EPA is one of the Federal Agencies responsible for agriculture, food, and water security to “develop robust, comprehensive, and fully coordinated surveillance and monitoring systems, ... that provide early detection and awareness of disease, pest, or poisonous agents.”

To spearhead the research efforts on water security, EPA formed the National Homeland Security Research Center (NHSRC) in the Office of Research and Development (ORD). EPA has initiated many efforts related to early warning systems, including the following:

- Drafting the Water Security Research and Technical Support Action Plan (Action Plan), which provides the basis for this project.
- Initiation of an NHSRC’s Water Awareness Technology Evaluation Research Security (WATERS) Center to conduct research projects including an evaluation of various sensor technologies and data acquisition systems.
- Use of EPA’s Environmental Technology Verification (ETV) Program to provide credible performance data for commercial-ready environmental technologies including homeland security technologies (e.g., early warning systems).
- Sponsoring efforts by the American Society of Civil Engineers to develop Guidance for Designing Online Contamination Monitoring System.
- Forming the Distribution System Research Consortium (DSRC) in June 2003 to provide a forum for information exchange on a diverse water distribution system security topics including early warning systems research (e.g., sensor, field studies, sensor placement).
- Forming the Threat Ensemble Vulnerability Assessment (TEVA) Research Program for Drinking Water Distribution System Security. One of the products is the help in designing early warning systems and for evaluating strategies for locating sensors in the distribution system.
- Developing various guidance on emergencies and early warning systems.

Department of Homeland Security

The Department of Homeland Security was established in 2002 in order to protect the nation from terrorist attacks.²⁰⁹ As part of this mission, DHS has the responsibility to protect the nation’s drinking water. DHS has established the Ready Campaign for the purpose of educating the public on a continuous basis so that communities will be ready in case of an emergency scenario.²¹⁰ The 2004 Homeland Security Presidential Directive/HSPD-9 also requires DHS to protect the agriculture and food systems from attacks, disasters, and other emergencies.²¹¹ Part of this directive’s

Awareness and Warning section is to enhance intelligence operations in securing water assets, such as implementing effective monitoring and detecting capabilities. The directive also orders further research and development of detection, prevention, characterization, response, and recovery countermeasures. Furthermore, DHS, in conjunction with EPA and other agencies, is involved reviewing the available information on technology performance.²¹² DHS has also provided grants to projects involved with the research and development of technologies that could be used for early warning systems in water, such as the SCADA systems.²¹³

Department of Defense

The danger of nuclear, biological, and chemical arms has been a concern of the Department of Defense (DOD) even before the 9-11 terrorist attacks. Programs such as the Joint Service Agent Water Monitor Program and other detector and sensor programs were formed since the late 1990s.²¹⁴ Now, under E2.1.20. Food and Water Security of the Antiterrorism Program from Directive number 2000.12 of 2003, the Department of Defense is obligated to protect food and water sources from disruption and contamination or other terrorist attacks. DOD must fulfill this requirement by taking action to detect, prevent, and mitigate the effects from intentional contaminations of food and water sources.²¹⁵ DOD is thus continuously supportive of the research and development of more advanced water contamination detective devices such as detectors that are faster, lighter, and smaller and can be used in-field.²¹⁶ DOD strives to achieve this by funding organizations, such as SNL, that are developing EWS technology. Finally, DOD contributes to the development of EWS through its research and development programs, such as the Defense Advanced Research Projects Agency (DARPA), further described below. A list of other DOD-funded R&D organizations is available at <http://www.dtic.mil/ird/websites/orgsites.html>.

Defense Advanced Research Projects Agency

DARPA is the main research and development organization under DOD and strives for superior military technology.²¹⁷ For water security measures, DAPRA is looking for fast, highly sensitive, and highly specific biosensor systems.²¹⁸ The four thrust areas of the Biosensors Technologies Program are, (1) Mass-Based Identification Technologies, (2) Surface-Based Identification Technologies, (3) Nucleic Acid-Based Identification Technologies, and (4) Breath Analysis-Based Identification Technologies.²¹⁹ The Biosensors Technologies Program is conducted in collaboration with 20 universities and laboratories. As mentioned in this report, the DARPA Chemical and Biological Sensors Standards Study presents methods for evaluating sensors by capturing the performance trade-offs between sensitivity, probability of correct detection, false-positive rate, and response time.

Naval Research Laboratory

The Naval Research Laboratory (NRL) is the corporate research laboratory for the Navy and Marine Corps. The focus of this laboratory encompasses scientific and technology research and development particularly for maritime applications as well as atmospheric and space sciences and technologies.²²⁰ NRL has been researching and developing methods to detect contaminants in the environment. In collaboration with GeoCenters, Inc., these efforts have resulted in the development of a method to detect radioactive material such as uranium on a microchip.²²¹ Under the sponsorship of the Office of Naval Research, NRL also developed a field test method in potable water for

cyanide that did not require laboratory testing.²²² NRL also developed a microchip for detecting cyanide in vapor and drinking water,²²³ in a collaborative effort with GeoCenters, Inc., the New Mexico State University, and the University of California. NRL is currently developing a high-sensitivity biosensor for monitoring airborne and water-borne contaminants in the environment. The force amplified biological sensor can detect the force between DNA and antigen molecules.²²⁴ Other advancements include the development of RAPTOR™ and the Bead ARray Counter (BARC) chip, as discussed in this report. RAPTOR™ is a portable, rapid, automatic fluorometric assay system for monitoring biological agents, toxins, explosives, and chemical contaminants. The BARC chip consists of an array of DNA spots immobilized on a surface,²²⁵ detecting hybridized sample DNA using magnetic beads.²²⁶ The development of BARC was sponsored by DARPA and ONR.²²⁷

Edgewood Army Proving Grounds

Although Edgewood Army Proving Grounds was originally founded as a chemical weapons research, development, and testing facility, Edgewood now focuses on chemical weapon defensive measures, and responds to the Army Chemical and Biological Defense Command, which oversees the Army's nonmedical chemical and biological defense activities.²²⁸ Army Edgewood Joint Service Agent Water Monitor Program is actively looking at sensors for distribution using the following proven classes of detection technologies: conventional, optical techniques, polymers/materials, assays, and sentinel species. Additionally, it is examining new areas of MEMS (Micro-Electro-Mechanical Systems) and MOEMS (Micro Optical Electro Mechanical Systems), which rely on a concept proven in one of the other classes. Edgewood is collaborating with EPA in order to heighten homeland security efforts.²²⁹

U.S. Geological Survey

Water quality has been a large focus for the U.S. Geological Survey. USGS has evaluated many different real-time continuous water quality monitoring stations.²³⁰ In addition, USGS was part of workshops such as the ILSI monitored *Early Warning Monitoring to Detect Hazardous Events in Water Supplied* in 1999,²³¹ as well as the 2004 National Monitoring Conference, "Building and Sustaining Successful Monitoring Programs" by the National Water Quality Monitoring Council.²³² USGS has also supported EWS projects such as the development of the Efficient Hydrologic Tracer-test Design Program, which provides scenario simulations of a release event so that water systems can test their preparedness.²³³

National Laboratories

Sandia National Laboratories

Since well before 2001, Sandia National Laboratories' (SNL) Chem/Bio Program has been involved in the development of advanced sensor technologies for rapid detection of chemical and biological warfare agents.²³⁴ Most of these technologies are pre-commercial and in various stages of prototyping, including the μ ChemLab and Micromachined Acoustic Chemical Sensor. However, SNL believes that once mature, its technologies should offer cost-effective monitoring alternatives. SNL's specific water sensor development activities include (Wayne Einfield, SNL, personal communication) the following:

- 1) *Adaptation of gas-phase μ ChemLab for detection of trihalomethanes and hydrolysis products of chemical agents in water.* Researchers are building a “front-end” for an existing chip-based gas chromatograph. The system is initially being developed for analysis of trihalomethanes in water as well as hydrolysis products of chemical agents. They anticipate the completion of a field-ready prototype in 2005.
- 2) *Use of liquid-phase μ ChemLab for the continuous online detection of biotoxins in water.* This is probably the most mature of the SNL portfolio of technologies. A proteomics-based analysis scheme utilizes microfluidics-based capillary-zone and capillary-gel analyses for biotoxin separation coupled with laser induced fluorescence detection, all in a hand-held, field portable package. SNL is in final discussions with two major cooperative research and development agreement (CRADA) partners and a successful agreement will launch an aggressive project to optimize and test this system for use as a real-time device for water distribution system monitoring.
- 3) *Preconcentration of bacterial species in water using insulative dielectrophoresis and microfabricated fixtures.* This project is aimed at the development of a preconcentrator for biological species in water that offers promise to separate various types of bacteria based on their mobility in an electric field. Researchers have demonstrated the ability to differentiate between live and dead *E. coli* cells as well as the ability to differentiate between bacteria and inert particles in the water matrix.
- 4) *Microfabricated electroanalysis system for the detection of inorganics in water.* This project is aimed at the detection of various electroactive species in water (e.g., lead, cadmium, arsenic) and utilizes a microfabricated multi-electrode array to measure various species by anodic stripping voltametry. SNL researchers have a table-top prototype that is being optimized for lead analysis, however, they anticipate that the functionality of this instrument could be expanded as one of a suite of early warning sensors.
- 5) SNL, CH2M Hill (Colorado), and Tenix Investments (Australia) have signed an agreement that calls for an online water monitoring prototype, based on μ ChemLab, to be developed and testing to begin by June 2005.²³⁵ The first phase of testing will focus on detecting ricin and botulinum toxin. The development team eventually also hopes to address viruses, bacteria, and parasites.

Lawrence Livermore National Laboratory

Lawrence Livermore National Laboratory (LLNL) is a national laboratory operated by the University of California for U.S. Department of Energy. Although LLNL was founded as a nuclear weapons design laboratory, it has broadened its field of work to include energy, biomedicine, and the environment.²³⁶ LLNL has been developing a wide range of technologies for sensors.²³⁷ As discussed in this report, LLNL utilized Luminex® technology to develop an Autonomous Pathogen Detection System (APDS). The system has an automated sample preparation module based on sequential injection analysis (SIA). Also discussed in this report is the “hand-held nucleic acid analyzer”(HANAA) based on real-time PCR (TaqMan) developed by LLNL.

Oak Ridge National Laboratory

The Oak Ridge National Laboratory (ORNL) is a multiprogram science and technology laboratory managed by UT-Battelle, LLC for the DOE.²³⁸ ORNL conducts research and development in the areas of energy, environment, and national security. In addition, the laboratory produces isotopes, manages information and technical programs, and provides research and technical assistance to other organizations.²³⁹ ORNL is one of the leading laboratories in developing biosensors and bioreporters.²⁴⁰ With regard to EWS in water, ORNL has developed the Large-Scale Water Supply Sentinel, a device that analyzes the characteristics of algae photosynthesis, in response to concerns for military and municipal water safety.²⁴¹ ORNL also licensed the VeriScan™ 3000 System, produced by Protiveris.²⁴² In addition, ORNL is associated with organizations such as the Center for Advanced Biomedical Photonics, and the Advanced Biomedical Sciences and Technology Group.²⁴³ ORNL researchers are collaborating with Gary Saylor, University of Tennessee on biosensor and nanotechnology projects (Gary Saylor, U. of Tennessee, personal communication).

Pacific Northwest National Laboratory

The Pacific Northwest National Laboratory (PNNL) is a national laboratory operated by Batelle for DOE. PNNL conducts research and development and supports education in the areas of environment, energy, health and national security, and economics.²⁴⁴ Homeland security has been a focus of PNNL even before 9/11. In the area of chemical, nuclear, and biological weapon detection, PNNL has contributed to the development of sensor and measurement technology, electronic (including controls) and system integration application requirements.²⁴⁵ The Sensors and Electronics branch of PNNL is developing its electronics and systems in the areas of biological sensors, chemical sensors, physical property sensors, nuclear radiation sensors, and macro property measurement.²⁴⁶ In order to supplement the rapid detection of biological threats, PNNL has developed the Biodetection Enabling Analyte Delivery System (BEADS). BEADS automated technology that isolates bacteria, spores, viruses, and their DNA from water, air, or dirt samples without requiring any manual preparations of samples.²⁴⁷

Idaho National Laboratory

On February 1, 2005, the Idaho National Engineering and Environmental Laboratory and Argonne National Laboratory-West became the Idaho National Laboratory (INL²⁴⁸). EPA-NHSRC and INL have an interagency agreement to develop and produce a next generation prototype of the Ultrafiltration Concentration (UC) device previously developed by NHSRC and other stakeholders. The UC bench top device concentrates microbial pathogens within a 100 L municipal drinking water sample into a 250-mL volume in approximately a 2-hour time frame (400-fold concentration). INL hopes to use the bench top UC system, which has been tested at the NHSRC in Cincinnati, to redesign/repackage and automate the components such that the new device can be operated in the field as a near-commercial, or field prototype system

Other Agencies/Organizations

Pittsburgh Water & Sewer Authority

The Pittsburgh Water & Sewer Authority is one of the organizations that the Water Environment Research Foundation and EPA are funding in order to identify, screen, and treat contaminants to ensure water security. For example, the Authority has conducted verification tests on many of the newer technologies for rapid detection in drinking water. It is also determining the risks and toxicity associated with biological, chemical, and radiological agents introduced to sewers, analyzing the fate and transport as well as treatment methods in the wastewater treatment facility, and developing emergency operating/containment procedures.²⁴⁹

National Academy of Sciences: Water Science and Technology Board

The Water Science and Technology Board (WSTB) was organized in 1982 by the National Research Council to provide a focal point for studies related to water quality and water resources.²⁵⁰ Projects administered by the WSTB related to EWS include “Public Water Supply Distribution Systems: Assessing and Reducing Risks”,²⁵¹ and the “Review of EPA Homeland Security Efforts: Panel on Water System Security Research.”²⁵²

American Water Works Association Research Foundation

The American Water Works Association Research Foundation (AwwaRF) is an international nonprofit organization that sponsors research efforts for its subscribing member organizations to provide safe and affordable drinking water.²⁵³ AwwaRF has been sponsoring many water security projects with the support of governmental agencies such as CDC and EPA, national and international research foundations, city and state water departments, and universities. These projects cover a wide range of water security topics including assessment of technologies, online monitoring and early warning systems, communication, assessing microbial contamination, and disaster response.

AwwaRF projects relevant to early warning systems for drinking water have focused on the early detection of pathogens, chemicals, radioactivity, and biotoxins so that utilities can appropriately respond in case of an intentional contamination of the water system. As terrorist concerns heighten, the ability to quickly detect and identify contaminants is vital. One of the major focuses of the AwwaRF projects is to develop a portable hand-held water monitor capable of real-time detection of all harmful agents and implement Supervisory Control and Data Acquisition (SCADA) systems to facilitate and advance monitoring and communication. Projects are developing and advancing methods to correctly identify *E. coli* and the different stages of *Cryptosporidium parvum* using technology such as the Multi-Angle Light Scattering (MALS). Other projects are focusing on strategy planning, from preventing intrusions into the drinking water systems, selecting water sampling locations and methods, and protecting utility SCADA equipment, to emergency management planning. Finally, some projects are focused beyond water treatment and distribution systems. For example, point-of-use drinking water devices may be useful as a short-term emergency response option. AwwaRF Project Summaries are presented in Appendix D.

Water Environment Research Foundation

The Water and Environment Research Foundation (WERF), created in 1989, funds wastewater and water quality research.²⁵⁴ The subscribers of the Foundation are utilities, municipalities, corporations and industrial organizations, all with a common interest in promoting research and development in water quality science and technology. The vast majority of WERF's research embraces a broad spectrum of scientific and technical disciplines (e.g., microbiology, wastewater ecology, toxicology, biological sciences, environmental engineering, and instrumentation) as well social/behavioral sciences (e.g., communications and public perception).

Prior to 9/11, WERF has undertaken studies on sensors with a view to study influent toxicity monitoring and process control. Since 9/11, WERF, under the aegis of a security grant from EPA, has been carrying out projects in the areas of (i) chemical, biological, and radioactive contamination events (accidental or purposeful), (ii) design of expert support systems for tracking anomalies in wastewater characteristics, (iii) GIS-based modeling of contaminants travel in piped conveyance systems, (iv) design of intelligent sensors for online, real-time upset early warning devices (UEWD) for tracking chemical and biological contaminants, and (iv) cyber security related to process control systems at water/wastewater utilities. WERF undertook a review of UEWDs in Yr 2000 that recommended that fundamental studies would be needed to articulate the links between how an influent event (the source) leads to an intermediate biochemical/physiochemical response (the cause) that results in an observable disruption in the treatment process (the effect). In Yr 2004, WERF sponsored sensor technology studies for water quality monitoring using fiber-optic biosensors (for rapid pathogen detection), bioluminescent biosensors (for toxicity-screening) and x-ray fluorescence spectroscopy (for waterborne metals). WERF also organized a sensor workshop (August 30-31, 2005) to prioritize research and development needs for rapid online contaminant monitoring.

American Society of Civil Engineers - Water Infrastructure Security Enhancements (WISE) - Standards Committee

EPA has contracted WISE to produce a guidance document to assist water utility companies to design and implement online contamination monitoring systems to detect intentional contamination events.

Rutgers University

With the support of EPA, Rutgers University has been involved in the research on EWSs. For example, they recently sponsored an annual Workshop on Advanced Technologies in Real-Time Monitoring and Modeling for Drinking Water Safety and Security.²⁵⁵

[this page intentionally left blank]

APPENDIX C

List and Criteria for Selecting Products and Technologies

The goal of this EWS document is to report on the state-of-the-art techniques for detecting contaminants, specifically chemical/microbial/radiological agents in drinking water distribution systems. To focus on the most promising products/technologies in this relatively new area, the following criteria were developed for including technologies/products in this document. The list of technologies is included at the end of this appendix.

The following three categories of technology development were designated:

- **Available** now (being used or could be used by water utilities)
- **Potentially adaptable** technology used (but needs additional steps to address specific challenges for use with water distribution system)
- **Emerging** technologies that may be applicable

The overriding criterion for categories is the focus on field portable (carried into field) and online technologies (not benchtop). Also, because an analysis of market viability was beyond the scope of the document, technologies/products are presented regardless of whether they would be at some point cost effective for the water utility industry. However, some costly technologies/products may not be considered because the manufacturers already determined that their products are too expensive for the water utilities market and thus have not actively developed or adapted their products for water detection.

Category 1. Available now:

Criteria:

- used/available now for water
- may be validated for water, perhaps for distribution conditions

Elaboration on Criteria:

- Portable and online products that are on the market and are specifically marketed for drinking water distribution systems. This includes basic water quality online monitors, since they may be adapted to provide early warning for CBW agents. This also includes toxicity kits that are marketed to water utilities. This will cover the online technologies listed in the ASCE Guidance and include additional portable kits and devices.

Category 2. Potentially adaptable technology used, but needs additional steps to address specific challenges for use with water distribution system:

Criteria:

- demonstrated bench top version for water with ongoing work on field portable version (carried into the field)
- portable products for water, but have some hurdles (sample concentration, chlorine removal)

- available for detecting CBW agents (in use for other media such as food or air) and can be adapted to water (accessory equipment)
- technology used in similar application (source water)

Elaboration on Criteria:

Several technologies that are in use for applications other than drinking water testing could be used for drinking water if additional sample preparation steps are taken.

- **Systems that would require removal of chlorine residuals** - Cell- and organism-based biomonitors, are presented. Their adaptation for drinking water relies on the development of methods for removing chlorine residuals. These methods are in the research stage, but are highly desired, so should be forthcoming.
- **Concentration of sample volume** - Some technologies, such as portable PCR systems, could be used with drinking water samples if used in conjunction with methods for concentrating large sample volumes into reaction-size volumes. These products are presented with the expectation that sample concentration techniques are forthcoming.
- **Vaporization/Volatilization** - Some of the portable and online vapor phase detectors that are on the market for detecting CBW agents and are used by first responders can read water samples if used with accessory equipment. There are existing methods/equipment for vaporization and volatilization. This technology would not be suggested for microbial detection. Specific vapor phase sampling products will be presented with the note that they have not been validated for use with water samples. Companies are interested in adapting existing products for use with water.

Category 3. Emerging technologies

Criteria:

- considered technologies defined as promising, given funding/grants from organization working directly on EWS technologies (AwwaRF, EPA, DHS, DOD)
- appears in literature numerous times (could be various researchers) at recognized Detection Conferences. Efforts from company, university, national laboratory, or government, and/or are now being licensed to company for development/testing of prototype or product
- proof-of-concept has been demonstrated and the technology is still being aggressively pursued
- could be utilized for drinking water sampling with further development

Elaboration on Criteria:

The following conference abstracts were examined to determine which technologies are current hot topics:

- 2004 Biodetection Technologies, Washington DC, June 2004²⁵⁶
- Detection Technologies, Arlington, VA, December 2003²⁵⁷
- Research, Technologies and Applications in Biodefense, Washington, DC, August 2003²⁵⁸
- 2003 Biodetection Technologies, Arlington, VA, June 2003²⁵⁹

- Biosensing Research and Development, World Technology Evaluation Center, Inc. National Institutes of Health, December 2002²⁶⁰
- Detection Technologies, Arlington, Va, December 2002²⁶¹
- Workshops on Advanced Technologies in Real-Time Monitoring and Modeling for Drinking Water Safety and Security, Rutgers CIMIC, Newark, NJ, June and December 2002²⁶²
- BioMEMS & Biomedical NANotech World 2002, Columbus, Ohio, September 2002²⁶³
- Biodetection Technologies, Alexandria, VA, May 2002²⁶⁴

Additionally, Army Edgewood Joint Service Agent Water Monitor Program is actively looking at sensors for distribution systems using the following proven classes of detection technologies: conventional, optical techniques, polymers/materials, assays, and sentinel species. It is also examining new areas of MEMS (Micro-Electro-Mechanical Systems) and MOEMS (Micro Optical Electro Mechanical Systems), which rely on a concept proven in one of the other classes.

What was not covered:

- Benchtop products for drinking water analysis.
- Portable products designed specifically for clinical samples.
- Sporadic research papers that have not gained wide attention.
- Technologies/products that were either only conceptual or were not currently envisioned to apply to water.

In the report, technologies are classified based on the categories above (e.g., available, potentially adaptable, emerging) and details are provided on the level of verification, proof of concept, pilot/field tested, or round robin, if the information was available. Note that for most products, except where noted, **manufacturer's claims have not been evaluated by independent sources and products mentioned are not endorsed by EPA**. The following is a list of technology products by the type of contaminant detected (e.g., chemical, microbial, or radiological), the status of the technology development (e.g., available now, potentially adaptable, or emerging), and the chapter that it appears in the document; the assay type, and the primary contaminant monitored.

The tables presented in Chapter 9 that compare detectors to desired EWS characteristics (Exhibits 9-2, 9-4, 9-6, and 9-8) are based on information obtained from references cited in the main text in Chapters 5-8 where the technologies are discussed. In some cases information is incomplete because the information was not available on the public part of the company website. In cases where there is no vendor website or the product has not yet been released, information was also not available.

List of Technologies and Techniques

Product	Company or Developer	Technology Status	Chapter
GENERAL WATER QUALITY			
Series C15 Water Quality Monitoring	Analytical Technology Inc.	Available	5 & 9
Sentinal™	Clarion Systems	Available	5 & 9
Six-Cense™	Dascore	Available	5 & 9
Model 1055 Solu Comp II Analyzer	Emerson	Available	5 & 9
AquaTrend panel	Hach	Available	5 & 9
TOC Process Analyzer	Hach	Available	9
Model A 15/B-2-1	Analytical Technology Inc	Available	9
Model 5500	GLI International	Available	9
DataSonde 4a	Hydrolab	Available	9
Model Troll 9000	In-Situ	Available	9
Signet Model 8710	Signet	Available	9
Model 6000 continuous monitor	YSI	Available	9
STIP-Scan	STIP Isco GmbH	Potentially Adaptable	5
CHEMICAL			
Quick™ tests	Industrial Test Systems, Inc	Available	6.2.1 & 9
AS 75 arsenic test kit	Peters Engineering (Austria)	Available	6.2.1 & 9
As-Top Water test kit	Envitop Ltd. (Oulu, Finland)	Available	6.2.1 & 9
PDV 6000 portable analyzer	Monitoring Technologies International Pty. Ltd. (Perth, Western Australia)	Available	6.2.1 & 9
Nano-Band™ Explorer	TraceDetect (Seattle, Washington)	Available	6.2.1 & 9
CHEMetrics VVR	CHEMetrics	Available	6.2.2 & 9
1919 SMART 2 Colorimeter	LaMotte Company (Chesterton, MD)	Available	6.2.2 & 9
Mini-Analyst Model 942-032	Orbeco-Hellige (Farmingdale, NY)	Available	6.2.2 & 9
AQUAfast® IV AQ4000	Thermo Orion (Beverly, MA)	Available	6.2.2 & 9
Thermo Orion Model 9606 Cyanide Electrode	Thermo Orion (Beverly, MA)	Available	6.2.2 & 9
Cyanide Electrode CN 501 with the Reference Electrode R503D and Ion Pocket Meter 340i	WTW Measurement Systems (Ft. Myers, FL)	Available	6.2.2 & 9
Scentograph™ CMS500	Inficon	Available	6.2.3 & 9
Scentograph™ CMS200	Inficon	Available	6.2.3 & 9

**List of Technologies and Techniques
(continued)**

Product	Company or Developer	Technology Status	Chapter
CT-1128	Constellation Technology Corporation with Agilent's (5973N MSD)	Available	6.2.3 & 9
HAPSITE®	Inficon	Available	6.2.3 & 9
Field Enzyme Test	Severn Trent		6.2.4 & 9
Aquanox™	Randox Laboratories	Available	6.2.4 & 9
Eclox™	Severn Trent	Available	6.2.4 & 9
Tox Screen	Check Light, Ltd	Available	6.2.5 & 9
Tox Screen II	Check Light, Ltd	Available	6.2.5 & 9
ToxTrak™	Hach Company	Available	6.2.5 & 9
Bio Tox™ Flash	Hidex Oy	Available	6.2.5 & 9
Polytox™	Interlab Supply, Ltd	Available	6.2.5 & 9
Microtox®	Strategic Diagnostics Inc.	Available	6.2.5 & 9
DeltaTox®	Strategic Diagnostics Inc.	Available	6.2.5 & 9
microMAX-TOX Screen	SYSTEM Srl. (Italy)	Available	6.2.5 & 9
MosselMonitor®	Delta Consult	Available	6.2.5 & 9
Bio-Sensor®	Biological Monitoring Inc.	Available	6.2.5
LuminoTox	Lab_Bell inc.	Potentially Adaptable	6.3.1
MitoScan	Harvard BioScience, Inc	Potentially Adaptable	6.3.1
IQ-Toxicity Test™	Aqua Survey	Potentially Adaptable	6.3.2 & 9
Daphnia Toximeter	bbe moldaenke, Germany	Potentially Adaptable	6.3.2 & 9
Algae Toximeter	bbe moldaenke, Germany	Potentially Adaptable	6.3.2 & 9
Fish Toximeter	bbe moldaenke, Germany	Potentially Adaptable	6.3.2 & 9
Fish and Daphnia Toximeter	bbe moldaenke, Germany	Potentially Adaptable	6.3.2 & 9
Lumitox®	Lumitox Gulf L.C.	Potentially Adaptable	6.3.2 & 9
HazMatID™	SensIR	Potentially Adaptable	6.3.3 & 9
X-ray fluorescence	ITN	Potentially Adaptable	6.3.4
SABRE 4000	Smiths Detection	Potentially Adaptable	6.3.5 & 9
HAZMATCAD™	Microsensor Systems Inc. (Bowling Green, KY)	Potentially Adaptable	6.3.7 & 9
Cyranose 320®	Cyrano™-Smiths Detection	Potentially Adaptable	6.3.8 & 9
Nosechip™	Cyrano™-Smiths Detection	Potentially Adaptable	6.3.8 & 9
Clam Biomonitoring	U. North Texas-EPA	Emerging	6.4.1
Transgenic zebrafish	Great Lakes WATER Inst.	Emerging	6.4.1
Fish Biomonitoring System	US Army Center for Environmental Health Research	Emerging	6.4.1

**List of Technologies and Techniques
(continued)**

Product	Company or Developer	Technology Status	Chapter
SOS Cytosensor	Adlyfe Inc.	Emerging	6.4.2
Portable Cell-Based Biosensor	Gregory Kovacs at Stanford University	Emerging	6.4.2
Portable Neuronal Microelectrode Array	U.S. Naval Research Laboratory	Emerging	6.4.2
Dicast®	Optical Security Sensing (Optech Ventures LLC)	Emerging	6.4.3
Fiber optic	Great Lakes WATER Inst.	Emerging	6.4.3
MicroDMx™	Sionex	Emerging	6.4.4
SAW based sensor	PNNL	Emerging	6.4.5
Micromachined Acoustic Chemical Sensor	SNL	Emerging	6.4.5
Micro-ChemLab CB™	SNL	Emerging	6.4.5
S-CAD	Science Applications International Corporation	Emerging	6.4.5
Surface enhanced raman	Real-Time Analyzers	Emerging	6.4.6
MICROBIAL			
Bio-HAZ™	EAI Corporation	Available	7.2.1 & 9
SMART™ Tickets	New Horizons Diagnostics	Available	7.2.1 & 9
Bio Threat Alert (BTA)	Tetracore	Available	7.2.1 & 9
BADD	ADVNT	Available	7.2.1 & 9
RAMP	Response Biomedical Corporation	Available	7.2.1 & 9
AMSALite™	Antimicrobial Specialists and Associates Inc.	Available	7.2.2 & 9
Continuous Flow ATP Detector	BioTrace International	Available	7.2.2 & 9
WaterGiene™	Charm Sciences Inc.	Available	7.2.2 & 9
Profile™ -1 (using Filtravette™)	New Horizons Diagnostic Corp.	Available	7.2.2 & 9
Microcyte Aqua® and Microcyte Field®	BioDetect	Available	7.2.3
Micro-Flow Imaging	Brightwell Technologies	Available	7.2.3
BioSentry	LXT/JMAR	Potentially Adaptable	7.2.4 & 9
Light scattering technology	Rustek Inc.	Potentially Adaptable	7.2.4 & 9
RAPTOR™	Research International (Naval RL)	Potentially Adaptable	7.3.1 & 9
xMAP® / Automated Pathogen Detection System (APDS)	Luminex and LLNL	Potentially Adaptable	7.3.2 & 9

**List of Technologies and Techniques
(continued)**

Product	Company or Developer	Technology Status	Chapter
RapiScreen™	Celsis-Lumac	Potentially Adaptable	7.3.3 & 9
BioFlash™	Innovative Biosensors	Potentially Adaptable	7.3.4
Smart Cycler® XC System	Cepheid	Potentially Adaptable	7.3.5 & 9
HANAA	Cepheid	Potentially Adaptable	7.3.5 & 9
TIGER	Ibis	Potentially Adaptable	7.3.5 & 9
RAZOR	Idaho Technologies	Potentially Adaptable	7.3.5 & 9
Ruggedized Advanced Pathogen Identification Device (RAPID)	Idaho Technologies	Potentially Adaptable	7.3.5 & 9
Bio-Seq™	Smiths Detection	Potentially Adaptable	7.3.5 & 9
PathAlert™	Invitrogen	Potentially Adaptable	7.3.5
BOSS	Georgia Tech	Potentially Adaptable	7.3.6
Spreeta™	Nomadics	Potentially Adaptable	7.3.7 & 9
MIM	BioVeris	Potentially Adaptable	7.3.8
Meso Scale cartridge reader	Meso Scale Defense	Emerging	7.3.8
Quantitative lateral flow assay (QLFA)	NASA	Emerging	7.4.1
Qdot™	Quantum Dot Co. /EPA research project	Emerging	7.4.2
Upconverting Phosphor Technology™	SRI International-OraSure Technologies	Emerging	7.4.2
DynaBeads®	Dynal	Emerging	7.4.3
BEADS	PNNL	Emerging	7.4.4
Doodlebug	Biopraxis	Emerging	7.4.5
Sen-Z	CombiMatrix	Emerging	7.4.6
MAGIChip	Argonne/DARPA	Emerging	7.4.7
Bead Array Counter BARC	Naval Research Lab	Emerging	7.4.8
GeneChip	Affymetrix	Emerging	7.4.9
VeriScan™ 3000	Protiveris	Emerging	7.4.10
Bio-Alloy™	IatroQuest Corporation	Emerging	7.4.11
“electronic taste chip”	University of Austin John T. McDevitt)	Emerging	7.4.12
Molecularly Imprinted Polymers		Emerging	7.4.13
Magnetoelastic Sensors	Grimes Group	Emerging	7.4.14
RADIOLOGICAL			
SSS-33-5FT	Technical Associates	Available	8.2 & 9
SSS-33DHC	Technical Associates	Available	8.2 & 9

**List of Technologies and Techniques
(continued)**

Product	Company or Developer	Technology Status	Chapter
SSS-33DHC-4	Technical Associates	Available	8.2 & 9
SSS-33M8	Technical Associates	Available	8.2 & 9
MEDA-5T	Technical Associates	Available	8.2 & 9
3710 RLS Sampler	Teldyne Isco	Available	8.2 & 9
LEMS-600	Canberra	Potentially Adaptable	8.3 & 9
OLM-100 Online Liquid Monitoring System	Canberra	Potentially Adaptable	8.3 & 9
ILM-100	Canberra	Potentially Adaptable	8.3 & 9
GammaShark™	Clarion Systems	Emerging	8.4
Online real-time alpha radiation detection instrument	DOE, now Los Alamos National Laboratory	Emerging	8.4
Groundwater radiation detector	PNNL	Emerging	8.4
Thermo Alpha Monitor	Thermo Power Corp.	Emerging	8.4

APPENDIX D
Summary of Early Warning System and Other Applicable Research Projects
Sponsored by American Water Works Association Research Foundation

Title	Project Description	Contractor and Project Manager	Investigator	Date of Completion
<p>Applications of Online Monitoring #2516</p>	<p>Will document successful online monitoring operations as well as problems encountered to identify operational, maintenance, and calibration requirements. Will focus on existing problems which includes:</p> <ul style="list-style-type: none"> • Poor design of sample-handling systems (plugging of sample lines) • Uncertainty in results and poorly implemented quality assurance • Inappropriate application of the instruments, resulting in misleading information. 	<p>McGuire Environmental Consultants, Inc. Project Manager: Ryan Ulrich</p>	<p>9 participating organizations; see website</p>	<p>8/15/2001 To be published in late 2004</p>
<p>Design of Early Warning and Predictive Source-Water Monitoring Systems #2527</p>	<p>Developed early warning and source water monitoring systems for real-time contaminant monitoring. These systems will allow operators to predict water quality events that may tax subsequent treatment processes. This study showed that an integrated approach that considers all parts of the water delivery system should be adopted in designing and operating an early warning system. A general-purpose, one-dimensional spill model for use in rivers that was developed and applied to the Ohio River could be easily adapted for use in a wide range of rivers. Additionally, a systematic method for designing and operating early warning systems that considers the highly variable, probabilistic nature of many aspects of the system was developed and demonstrated.</p>	<p>Walter Grayman Consulting Engineer and University of Michigan Project Manager: Albert Ilges</p>	<p>Partner: EPA and 5 other participating organizations; see website</p>	<p>1/1/2002 Published in 2001</p>

APPENDIX D
Summary of Early Warning System and Other Applicable Research Projects
Sponsored by American Water Works Association Research Foundation
(continued)

Title	Project Description	Contractor and Project Manager	Investigator	Date of Completion
Online Monitoring for Drinking Water Utilities #2545	AwwaRF and the Italian research organization CRS-PROAQUA recognized the drinking water industry's need for a comprehensive resource covering online monitoring technology and initiated this project to develop such a publication. Provides state-of-the-science practical, and reference information about physical, inorganic, organic, and process online instruments. Also includes information on data handling, case studies, and emerging online technologies. Many of the analytical methods upon which the identified technologies are based are included in <i>Standard Methods for the Examination of Water and Wastewater (1998)</i> .	Awwa Research Foundation and CRS PROAQUA (Italy)	Participants: Azienda Mediterranea Gas e Acqua Spa	Published in 2002
Development of Event-Based Pathogen Monitoring Strategies for Watersheds #2671	Will develop and validate a strategy for selection of sampling locations, frequencies, and methods to accurately depict pathogen occurrence and variability in relation to various sources within watersheds during and after weather, hydrologic, or land-use events.	University of Massachusetts at Amherst Project Manager: Linda Reekie	Partner: EPA and Metropolitan District Commission	38716

APPENDIX D
Summary of Early Warning System and Other Applicable Research Projects
Sponsored by American Water Works Association Research Foundation
(continued)

Title	Project Description	Contractor and Project Manager	Investigator	Date of Completion
Evaluation of Real-Time Online Monitoring Method for <i>Cryptosporidium</i> #2720	This project was looking to develop a more utility-friendly real-time continuous online monitoring method. The multi-angle light scattering (MALS) technique was found to be useful as an early warning tool for the rapid detection of large scale water contamination outbreaks since it enabled the estimation of the <i>Cryptosporidium</i> oocyst detection limit. MALS can also discriminate between different physical states of oocysts, including oocysts that were treated with ozone, heat treated, or excysted from live untreated oocysts. The technology tested in this project has the potential to provide an impact on the drinking water industry through distribution system monitoring, treatment optimization, end-user protection and monitoring, and influent monitoring and source water selection.	PointSource Technologies, Inc., And Metropolitan Water District of Southern California (LA) Project Manager: Misha Hasan	—	12/1/2004 To be published in 2004

APPENDIX D
Summary of Early Warning System and Other Applicable Research Projects
Sponsored by American Water Works Association Research Foundation
(continued)

Title	Project Description	Contractor and Project Manager	Investigator	Date of Completion
<p>Conventional and Unconventional Approaches to Water Service Provision #2761</p>	<p>While some unconventional options have been examined in connection with specific contaminants and regulations, future regulatory scenarios have not been taken into account. Unconventional approaches may turn out to be more cost effective and feasible in meeting new stringent standards. This project will compare conventional and unconventional water treatment and distribution providing quality water to customers, including POU and point-of-entry (POE) devices, small neighborhood systems, and bottled water. Will include capital costs, operational and maintenance costs, ability to meet health standards, and aesthetic quality goals. Will also consider risk associated with the options, long-term reliability of the options, and practical engineering considerations. Will assume plausible stringent future regulatory scenarios and consumer demands for high quality and aesthetically pleasing drinking water. See also Project #2924.</p>	<p>Stratus Consulting Inc. Project Manager: India Williams</p>	<p>Participants: California Urban Water Agencies</p>	<p>3/15/2004 To be published in 2005</p>

APPENDIX D
Summary of Early Warning System and Other Applicable Research Projects
Sponsored by American Water Works Association Research Foundation
(continued)

Title	Project Description	Contractor and Project Manager	Investigator	Date of Completion
Water Utility Self-Assessment for the Management of Aesthetic Issues #2777	The lack of regulation for aesthetic qualities may be the reason many utilities are not proactive in routinely analyzing the taste-and-odor (T&O) of the water. Although AwwaRF has produced numerous reports on T&O control, much of the knowledge contained in them has not yet be widely applied, nor does it provide guidance on communication during these events. Self-assessment programs already exist in AWWA's QualServ and the Partnership for Safe Water; however, these programs address only the treatment component of the utility business. These programs could serve as models for the development of a self-assessment program on aesthetic issues. Provides guidance for utility self-assessment in three areas: identification of potential and real T&O problems, management of T&O problems when they occur, and communication during T&O events within the utility and with the public.	McGuire Environmental Consultants, Inc. Project Manager: Albert Ilges	—	7/31/2003 Includes a CD-ROM. Published in 2004
Innovative Systems for Early Warning Water Monitoring #2779	Will develop and evaluate new and innovative systems to rapidly detect chemicals (individual or classes), radioactivity, pathogens, or biotoxins in water in order to help make these systems more viable for use by the drinking water community.	Kiwa N.V. Project Manager: Ryan Ulrich	Partner: Kiwa N. V.	9/1/2004 Will be published by Kiwa

APPENDIX D
Summary of Early Warning System and Other Applicable Research Projects
Sponsored by American Water Works Association Research Foundation
(continued)

Title	Project Description	Contractor and Project Manager	Investigator	Date of Completion
Rapid Detection of Bioterrorism Agents in Water Supplies #2852	Will develop and evaluate new and innovative systems to rapidly detect chemicals (individual or classes), radioactivity, pathogens, or biotoxins in water in order to help make these systems more viable for use by the drinking water community.	University of Cincinnati Project Manager: Ryan Ulrich	Partner: EPA Participants: University of Cincinnati, EPA, Cincinnati Water Works	To be completed in 2005
Application of DNA Microarray Technology to Simultaneously Detect and Genotype Isolates of Pathogens in Water #2896	Some of the difficulties in developing a universal method include the physical differences between pathogen groups, the need to concentrate large-volume water samples to detect low target concentrations of certain pathogen groups, the need to remove co-concentrated inhibitors from the sample, and the problem of standardizing a culture-independent endpoint detection method. This project will design a DNA microarray as the endpoint detector that simultaneously targets several well characterized virulence genes such as <i>E. coli</i> O157:H7 and <i>Cryptosporidium parvum</i> .	Battelle Pacific Northwest Laboratories Project Manager: Misha Hasan	—	To be completed in 2005
Molecular Methods for Microsporidia Detection (MMMD) #2901	Will assess the suitability of an automated extraction method and real-time PCR assay for the detection of Microsporidia in source water. Source water specimens will be seeded with Microsporidia spores to provide test samples with which to characterize assay performance. The assay will be optimized to provide the lowest possible detection limit, efficiency, and reproducibility.	Southern Arizona Veterans Administration Health Care and University of Arizona Project Manager: Alice Fulmer	Participants: SAVAHCS/BRFSA University of Arizona CH Diagnostics & Consulting Services Inc.	To be completed in 2005

APPENDIX D
Summary of Early Warning System and Other Applicable Research Projects
Sponsored by American Water Works Association Research Foundation
(continued)

Title	Project Description	Contractor and Project Manager	Investigator	Date of Completion
Extraction Methods for Early/Real-Time Warning Systems for Biological Agents A #2908	Will screen three to five different water extraction methods for biological agent surrogates. This project will develop a portable water monitor, preferably hand-held, that is capable of real-time detection of all harmful substances, while providing no false-positives.	New Mexico State University Project Manager: Misha Hasan	Partner: DOD Participants: U.S. Bureau of Reclamation (d45510)	To be completed in 2005
Results From the Water Utility Vulnerability Assessment Lessons Learned Study #2909	Captures lessons learned and provides a forum for information exchange on vulnerability assessment conducted by large drinking water utilities.	Sandia National Laboratories Project Manager: Frank Blaha	—	12/1/2003 Report Available
Case Study for a Distribution System Emergency Response Tool #2922	Evaluates the feasibility and applicability of the PipelineNet, a distribution system modeling tool available to water utilities free of charge through EPA, in different water utility settings for monitoring of distribution systems.	Science Applications International Corporation Project Manager: Frank Blaha	Partners: EPA	5/31/2003 Published in 2003; available only in PDF format
Security Implications of Innovative and Unconventional Water Provision Options #2924	Provide utilities with a security-oriented evaluation of water service provision options that they may be considering now or in the future. Also helps utilities evaluate and plan short-term emergency response options using bottled water, POU, and other approaches (see also Project #2761).	Stratus Consulting Inc. Project Manager: India Williams	4 Participating organizations; see website	Completed in 2003 Report available

APPENDIX D
Summary of Early Warning System and Other Applicable Research Projects
Sponsored by American Water Works Association Research Foundation
(continued)

Title	Project Description	Contractor and Project Manager	Investigator	Date of Completion
<p>Disaster Response, Recovery, and Business Continuity Planning for Water Utilities #2929</p>	<p>Emergency management planning consists of four principal functions: planning, crisis management, consequence management, and mitigation. Better preparation will minimize damage and financial losses, reduce recovery time, and improve public credibility. The ability to respond and recover is greatly enhanced if a water utility has developed in conjunction with stakeholders a disaster response, recovery, and business continuity plan and conducted routine training.</p>	<p>Stratus Consulting Inc. Project Manager: India Williams</p>	<p>Partner: EPA and 21 other participants: see website.</p>	<p>To be completed in 2006</p>
<p>Vulnerable Points in Water Distribution Systems #2931</p>	<p>Identifies the vulnerable points in a typical distribution system by determining likely points of intrusion. Also creates reasonable scenarios outlining the consequences of purposeful contamination to the drinking water system. Develops recommendations to reduce the vulnerability of critical elements and sub-elements of the distribution system.</p>	<p>Economic and Engineering Services, Inc. Project Manager: Frank Blaha</p>	<p>Partner: USEPA and 9 other participating organizations; see website.</p>	<p>Completion 2005 Report available</p>

APPENDIX D
Summary of Early Warning System and Other Applicable Research Projects
Sponsored by American Water Works Association Research Foundation
 (continued)

Title	Project Description	Contractor and Project Manager	Investigator	Date of Completion
Cyber-Security for SCADA Systems #2969	Supervisory control and data acquisition (SCADA) systems are increasingly susceptible to hacker intrusions. The Gas Technology Institute (GTI) recommended in 1999 that the gas industry adopt the Digital Encryption Standard (DES), the Rivest, Shamir, Adelman (RSA) public key algorithm, and the Diffie-Hillman number generating algorithm as a suite of algorithms. This cyber-attack protection includes preventing assailants from studying the system by listening to the communications, from altering authorized commands to lead to unauthorized operations, and to originate unauthorized commands. It is also possible to prevent a single insider from performing an unauthorized operation.	Gas Technology Institute Project Manager: Frank Blaha	Partner: Gas Technology Institute Participants: TSWG EPRI Gas Technology Institute Chicago Department of Water Management	To be completed in 2005
Extraction Methods for Early/Real-time Warning Systems for Biological Agents B#2985	Will develop a large-volume extraction method for biological agents that is rapid (< 3 hours) and efficient (60 percent to 70 percent recovery) by shortening the extraction step. This project will build upon research being done by the DOD on the Joint Service Agent Water Monitor (JSAWM).	Battelle Memorial Institute Project Manager: Misha Hasan	Partner: CDC-Division of Parasitic Diseases	To be completed in 2006

APPENDIX D
Summary of Early Warning System and Other Applicable Research Projects
Sponsored by American Water Works Association Research Foundation
 (continued)

Title	Project Description	Contractor and Project Manager	Investigator	Date of Completion
Point-of-Use Drinking Water Devices for Assessing Extent of Microbial Contamination in Distribution Systems #2986	This project will determine the feasibility of using POU drinking water devices in the event of a bioterrorism attack to help identify the contaminant, contaminant dissemination, and the public health impacts. POU devices exist that remove contaminants and have their performance certified by credible testing regimes administered by independent organizations, but have not been tested and certified for their effectiveness in reducing chemical or biological sabotage agents. Several studies have researched extraction of bacteria from granular activated carbon cores, and will constitute a starting point for this project. Some standard methods utilize fiber filters as a means to concentrate microorganisms (e.g., <i>Cryptosporidium</i>) when large water volumes have to be sampled. The intent of this study is to better understand possible patterns of delivery of the contaminant in the distribution system.	New Mexico State University Project Manager: Misha Hasan	Partner: CDC/DPD	To be completed in 2006
Assessing and Improving Water Quality Sampling Programs in Drinking Water Distribution Systems #3017	The data collected from sampling and monitoring networks in distribution systems are often of limited use for detecting and diagnosing important changes in water quality. This project will develop methods and tools to help utilities scientifically evaluate existing sampling plans and improve them. This project will also include the development of procedures and algorithms to address multiple purposes and benefits.	Malcolm Pirnie Inc. Project Manager: My-Linh Nguyen	Partner: EPA	To be completed in 2007

APPENDIX D
Summary of Early Warning System and Other Applicable Research Projects
Sponsored by American Water Works Association Research Foundation
(continued)

Title	Project Description	Contractor and Project Manager	Investigator	Date of Completion
Data Processing and Analysis for Online Distribution System Monitoring #3035	Research is needed to explore data-processing methods that can distinguish normal variability in distribution system conditions from patterns related to unacceptable water quality trends or events. This project will develop a general data processing approach to assist water quality managers and water system operators detect abnormal patterns in online monitoring data.	CSIRO (Commonwealth Scientific and Industrial Research Organisation) Project Manager: My-Linh Nguyen	—	To be completed in 2007
Model for Quality of Water in Distribution Systems #3038	Will develop a system of integrated, hierarchical models that not only describe the fundamental processes that determine water quality in pipe systems, but also simulate the temporal and spatial behavior of water quality in the complete network.	UKWIR and UK Engineering and Physical Sciences Research Council. Project Manager: Jian Zhang	—	To be completed in 2007

APPENDIX D
Summary of Early Warning System and Other Applicable Research Projects
Sponsored by American Water Works Association Research Foundation
 (continued)

Title	Project Description	Contractor and Project Manager	Investigator	Date of Completion
Security Measures for Computerized and Automated Systems at (Water) and Wastewater Facilities #3045	Will identify, organize, prioritize, and describe the most probable electronic security threats; risks associated with the various security weaknesses; the available technology that can prevent unauthorized and willful attacks; secure and stable infrastructure options for data communication; the best practices for implementing each of the available security and data communication options; and critical areas of uncertainty. Will document proven implementations of the listed technologies at water and wastewater facilities. Will also document existing implementations of data communication and security options, studies demonstrating the feasibility of options not currently in use, and the effectiveness of each solution to eliminate the security weaknesses discovered.	EMA, Inc. Project Manager: India Williams	Partner: Water Environment Research Foundation (WERF)	To be completed in 2006
Emergency Communications With Local Government and Communities #3046	Will develop and provide written and oral message statements that can be used by public agencies (water and wastewater utilities) and elected officials to communicate with the public following disasters, as well as during disaster warning alerts. Will also include an action plan for working with the public to increase public awareness of potential public health risks, and appropriate responses.	To be determined Project Manager: Frank Blaha	Partner: Water Environment Research Foundation	To be completed in 2007

APPENDIX D
Summary of Early Warning System and Other Applicable Research Projects
Sponsored by American Water Works Association Research Foundation
 (continued)

Title	Project Description	Contractor and Project Manager	Investigator	Date of Completion
Decision Support System for Water Distribution System Security #3086	Will provide a broad and substantial knowledge base for utilities about the impact of a toxicological attack on a distribution network, and cost-effective approaches for detecting and mitigating such attacks.	Charleston (S.C) Commission of Public Works Project Manager: Frank Blaha	Participants: Colorado State University Advanced Data Mining	To be completed in 2007; need special protocol for release
Integrated Program for Early-Warning-System Sensors for Safeguarding Water Supply Systems #3093	<p>Will integrate research on sensors and early warning systems to enhance benefits and cost-effectiveness of the research. Will consist initially of nine subordinate studies:</p> <ul style="list-style-type: none"> • Online Monitoring Using a UV-Probe • Organic Contaminant Detection Using an Online HPLC and GC Analysis • Combined Daphnia and Zebrafish Monitor • Detection of Cholinesterase-Inhibiting Contaminants • Feasibility Study on the Use of Chemical-Optical Sensors for the Detection of Organic Micro-Pollutants • Annual Reporting on Developments in the Fields of Sensors and Detection Techniques Data Handling for Detection Systems Containing Single or Multiple Sensors, and Procedures for Follow-up on Alarms • Strategies for Network Clean-up After Contamination • Exploring the Opportunities for Co-funding and Collaboration in Sensor Development and Implementation 	Project manager: Frank Blaha	Partner: KIWA NV - Water Research	To be determined

APPENDIX D
Summary of Early Warning System and Other Applicable Research Projects
Sponsored by American Water Works Association Research Foundation
(continued)

Title	Project Description	Contractor and Project Manager	Investigator	Date of Completion
Pilot Study on the Integration of Customer Complaint Data With Online Water Quality Data As an Early Warning System #3140	Will undertake a joint pilot-study project that will integrate customer complaint and online water quality data into an early warning system. Will include 8-10 large and medium-sized utilities, covering both geographical distribution and source water (surface water and groundwater).	Virginia Polytechnic Institute & State University Project Manger: India Williams	Partner: American Water Works Association	To be determined

ENDNOTES (including website references)

- ¹ http://cfpub.epa.gov/safewater/watersecurity/home.cfm?program_id=9
http://www.epa.gov/safewater/watersecurity/pubs/action_plan_final.pdf
- ² <http://www.whitehouse.gov/news/releases/2004/02/20040203-2.html>
- ³ <http://www.whitehouse.gov/homeland/book/>
- ⁴ <http://www.whitehouse.gov/news/releases/2004/02/20040203-2.html>
- ⁵ <http://www.epa.gov/ordnhsrc/index.htm>
- ⁶ <http://www.epa.gov/etv/>
- ⁷ <http://www.epa.gov/ordnhsrc/news/news031005.htm>
- ⁸ <http://www.ewrinstitute.org/wisesc.html>
- ⁹ <http://www.epa.gov/safewater/security/index.html>
http://cfpub.epa.gov/safewater/watersecurity/home.cfm?program_id=8#response_toolbox
- ¹⁰ http://cfpub.epa.gov/safewater/watersecurity/home.cfm?program_id=9
http://www.epa.gov/safewater/watersecurity/pubs/action_plan_final.pdf
- ¹¹ <http://www.epa.gov/ordnhsrc/pubs/fsTTEP031005.pdf>
- ¹² <http://www.awwa.org/conferences/congress/>
- ¹³ <http://www.awwa.org/education/seminars/index.cfm?SemID=47>
- ¹⁴ <http://www.ewrinstitute.org/wisesc.html>
- ¹⁵ <http://www.infocastinc.com/tech/rapid.html>
- ¹⁶ <http://www.who.int/csr/delibepidemics/en/chapter3.pdf>
<http://www.who.int/csr/delibepidemics/biochemguide/en/index.html>
- ¹⁷ <http://www.verdeit.com/VPages/SpiralDev.htm>
- ¹⁸ <http://www.aoac.org>
- ¹⁹ <http://www.stowa-nn.ihe.nl/Summary.pdf>
- ²⁰ <http://www.epa.gov/ORD/NRMRL/wswrd/distrib.htm#Table%202.0%20Proposed%20DSS>
- ²¹ <http://www.hydrarms.com/brochurepdf.pdf>
- ²² <http://www.waterindustry.org/Water-Fact/Hach-1.htm>
- ²³ http://www.tswg.gov/tswg/news/2004TSWGReviewBookHTML/ip_p18.htm

- ²⁴ <http://www.nsf.gov/eng/general/sensors/vanbrie.ppt>
- ²⁵ <http://www.epa.gov/NHSRC/pubs/fsPureSenseCrada060204.pdf>
- ²⁶ <http://www.7t.dk/company/default.asp>
- ²⁷ www.waterisac.org
- ²⁹ <http://www.hach.com>
- ³⁰ http://www.hach.com/hc/search.product.details.invoker/PackagingCode=6950000/NewLinkLabel=Hach+Event+Monitor+Trigger+System/PREVIOUS_BREADCRUMB_ID=HC_SEARCH_KEYWORD/SESSIONID|Bmd5TURZME56SW1aM1ZsYzNSUFZVOUNWREV4TVE9PUNEazVOag==
- ³¹ <http://www.instrument.org/Newsletter%20Articles/Summer%202003/Innovative%20Monitoring.pdf>
<http://www.swig.org.uk/Nick%20Sutherland.pdf>
- ³² <http://www.emersonprocess.com/raihome/liquid/articles/06-14B-2004.asp>
http://www.emersonprocess.com/raihome/documents/Liq_Brochure_91-6030_200408.pdf
http://www.emersonprocess.com/raihome/liquid/products/Model_1055.asp
- ³³ <http://www.afcintl.com/water3.htm>
- ³⁴ <http://www.clarionsensing.com/howitworks.shtml>
- ³⁵ <http://www.elscolab.be/e/Stipscan%20iem%202003%20july1.pdf>
<http://www.elscolab.be/e/stipscan.pdf>
<http://www.stateoftheheart.it/STIP-Buoy-SCAN.htm>
http://www.baumpub.com/publications/arc/cep_04may/avensys.htm
<http://www.epa.gov/watersecurity/guide/chemicalsensortotalorganiccarbonanalyzer.html>
- ³⁶ EPA Press Release May 19, 2004.
<http://yosemite.epa.gov/opa/advpress.nsf/b1ab9f485b098972852562e7004dc686/754a0739ba5bc9c985256e99005a9f60!OpenDocument>
- ³⁷ <http://www.epa.gov/ORD/NRMRL/wswrd/distrib.htm#Table%202.0%20Proposed%20DSS>
- ³⁸ Phone conversation with Dr. Ryan James, Battelle Laboratory Advance Monitoring Systems, Center Verification Test Coordinator, 19 August 2004; Interviewer - Stanley States
- ³⁹ Presentation by K.L. King, Event Monitor for Water Plant or Distribution System Monitoring; Hach Homeland Security Technologies; AWWA Water Security Congress; April 25-27, 2004
- ⁴⁰ <http://www.inficonvocmonitoring.com/downloads/pdf/haps-smart.pdf>
<http://www.inficonvocmonitoring.com/downloads/pdf/situprobe.pdf>
<http://www.inficonvocmonitoring.com/downloads/pdf/Scentograph%20CMS200%20Brochure%20-%20Screen.pdf>
- ⁴¹ http://www.contech.com/Chemical_Detection_Products.htm
- ⁴² <http://www.awwa.org/education/seminars/index.cfm?SemID=47>

- 43 http://www.epa.gov/etv/pdfs/vrvs/01_vr_eclox.pdf
<http://www.quotec.ch/services/qeclox.htm>
<http://www.wateronline.com/content/Downloads/SoftwareDesc.asp?DocID={13C2390F-C9B1-4362-A1F0-4C3BDDD04B97}>
- 44 <http://www.randox.com/products.asp>
- 45 <http://www.epa.gov/etv/verifications/vcenter1-27.html>
- 46 <http://www.checklight.co.il/pdf/manuals/ToxScreen-II%20manual.pdf>
- 47 http://www.epa.gov/etv/pdfs/vrvs/01_vr_toxscreen.pdf
- 48 <http://www.hidex.com/index.php?a=4&b=12&c=12>
- 49 http://www.epa.gov/etv/pdfs/vrvs/01_vr_biotox.pdf
- 50 <http://www.azurenv.com/dtox.htm>
- 51 http://www.epa.gov/etvprgrm/pdfs/vrvs/01_vr_deltatox.pdf
http://www.epa.gov/etv/pdfs/vrvs/01_vr_microtox.pdf
- 52 http://www.epa.gov/etv/pdfs/vrvs/01_vr_toxtrak.pdf
- 53 <http://polyseed.com/html/polytox.htm>
- 54 http://www.epa.gov/etv/pdfs/vrvs/01_vr_polytox.pdf
- 55 <http://www.mosselmonitor.nl/>
- 56 <http://www.biomon.com/biosenso.html>
- 57 <http://www.sparkdesigns.co.uk/biopapers04/papers/bs171.pdf>
<http://abstracts.co.allenpress.com/pweb/pwc2004/document/?ID=42895>
http://www.alga.cz/mk/papers/bios_02.pdf
http://www.lab-bell.com/main.jsp?c=/content/gestiondeseaux_en.html&g=left_produits_en.html&l=en
http://www.lab-bell.com/main.jsp?c=/news/new.jsp&n_id=30&l=en
- 58 http://www.alga.cz/mk/papers/bios_02.pdf
- 59 <http://www.mitoscan.com/Applications.htm>
<http://www.mitoscan.com/technol.htm>
- 60 <http://www.detect-water-terrorism.com/>
- 61 http://www.epa.gov/etv/pdfs/vrvs/01_vr_aqua_survey.pdf
- 62 <http://www.bbe-moldaenke.de/>
- 63 <http://www.bbe-moldaenke.de/>
- 64 <http://www.bbe-moldaenke.de/>

- 65 <http://www.lumitox.com/bioassay.html>
<http://www.dewailly.com/LUMITOX/lumitox.html>
<http://www.bioinfo.com/dinoflag.html>
- 66 <http://www.smithsdetection.com/PressRelease.asp?autonum=25&bhcp=1>
- 67 <http://www.sensir.com/newsensir/Brochure/ExtractIR%20Product%20Note.pdf>
- 68 <http://www.hazmatid.com/>
- 69 <http://www.itnes.com/>
- 70 http://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.abstractDetail/abstract/7477/report/0
- 71 <http://www.etgrisorse.com/pubblicazioni/contamination.PDF>
<http://pms.aesaeion.com/ionpro/Products/theory>
- 72 http://www.chemistry.org/portal/a/c/s/1/feature_ent.html?id=7635201a690a11d7f2a16ed9fe800100
- 73 http://www.emedicine.com/emerg/topic924.htm#section~ion_mobility_spectroscopy
- 74 <http://www.smithsdetection.com/prodcat.asp?prodarea=Life+sciences&bhcp=1>
- 75 <http://www.healthtech.com/2003/mfl/index.asp>
- 76 <http://www.memsnet.org/mems/what-is.html>
- 77 <http://www.memsnet.org/mems/beginner/>
- 78 <http://www.biochipnet.com/EntranceFrameset.htm>
- 79 <http://www.nano.gov/index.html>
- 80 <http://www3.sympatico.ca/colin.kydd.campbell/>
<http://www.sensorsmag.com/articles/1000/68/main.shtml>
- 81 <http://www.microsensorsystems.com/index.html>
http://www.army-technology.com/contractors/nbc/microsensor_systems/
<http://media.msnet.com/NA/USA/PortableInstruments/ToxicGasandOxygenIndicators/HazmatcadAndPlus/HazmatcadProductAnnounce.pdf>
<http://www.raeco.com/products/toxicagents/hazmatcad.pdf#search='HAZMATCAD'>
- 82 http://hld.sbcom.army.mil/downloads/reports/hazmatcad_detectors_addl_info.pdf
- 83 <http://www.smithsdetection.com/PressRelease.asp?autonum=12&bhcp=1>
- 84 http://www.ias.unt.edu/~jallen/littlemiami/Clam_Page.html
<http://www.ias.unt.edu/~jallen/clampage.html>
- 85 <http://www.uwm.edu/Dept/GLWI/cws/projects/carvan.html>
- 86 http://usacehr.detrick.army.mil/aeam/Methods/Fish_Bio/

- 87 <http://www.adlyfe.com/adlyfe/home.html>
- 88 <http://www.nrl.navy.mil/content.php?P=04REVIEW118>
- 89 <http://www.uwm.edu/Dept/GLWI/cws/>
- 90 <http://www.optech-ventures.com/products.htm>
http://www.intopsys.com/markets_brochures/Continuous-CableFOCSensor.pdf
- 91 <http://www.sionex.com/technology/index.htm>
- 92 <http://www.saic.com/products/security/pdf/S-CAD.pdf>
<http://www.saic.com/products/security/s-cad/>
- 93 <http://www.sandia.gov/media/acoustic.htm>
http://www.isa.org/Content/ContentGroups/InTech2/Features/20012/2001_October/Surface_acoustic_waves_to_the_mission_control/Dangerous_chemicals_in_acoustic_wave_sensorsandNum8217;_future.htm
- 94 <http://www.sandia.gov/mstc/technologies/microsensors/flexural.html>
- 95 <http://www.sensorsmag.com/articles/1000/68/index.htm>
- 96 <http://www.mdl.sandia.gov/mstc/documents/uchembrochure.pdf>
http://www.ca.sandia.gov/chembio/factsheets/chemlab_chemdetector.pdf
<http://www.sandia.gov/water/projects/ChemLab.htm>
http://www.sandia.gov/water/FactSheets/WIFS_SensorDevNew.pdf
http://www.ca.sandia.gov/chembio/tech_projects/detection/chemlab_gas.html
http://www.ca.sandia.gov/chembio/tech_projects/detection/chemlab_liquid.html
<http://www.mdl.sandia.gov/mstc/technologies/microsensors/chem.html>
http://www.oit.doe.gov/sens_cont/pdfs/annual_0602/robinson.pdf
http://www.ca.sandia.gov/chembio/tech_projects/detection/factsheets/chemlab-bio-detector2.pdf
<http://www.ca.sandia.gov/chembio/microfluidics/index.html>
<http://www.ca.sandia.gov/news/2003-news/031110news.html>
http://www.ca.sandia.gov/chembio/tech_projects/detection/factsheets/famebrochure.pdf
- 97 <http://www.nanodetex.com/index.html>
- 98 http://www.ca.sandia.gov/news/2004_news/120704Mercury.html
- 99 <http://www.technet.pnl.gov/sensors/chemical/projects/es4cwsen.stm>
<http://www.technet.pnl.gov/sensors/chemical/projects/es4selct.stm>
<http://www.technet.pnl.gov/sensors/chemical/projects/ES4SurfWvSnsr.stm>
<http://availabletechnologies.pnl.gov/chemmaterials/chem.stm>
- 100 http://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.abstractDetail/abstract/7487/report/0
- 101 http://www.medical-test.com/product119/product_info.html
- 102 http://www.pall.com/OEM_4154.asp

- ¹⁰³ <http://www.idmscorp.com/pregnancytest.html>
http://www.qdots.com/live/upload_documents/wQDVOct03_pg8-9.pdf
- ¹⁰⁴ <http://www.tetracore.com/products/domestic.html>
- ¹⁰⁵ <http://www.nhdiag.com/index.htm>
- ¹⁰⁶ http://www.eaicorp.com/products_sca_bh.htm
- ¹⁰⁷ <http://www.baddbox.com/>
- ¹⁰⁸ http://www.osborn-scientific.com/PDF/Positive_test_for_terror_toxins_in_Iraq.htm
- ¹⁰⁹ http://www.responsebio.com/pdf/summaryanthrax_aug02.pdf
- ¹¹⁰ <http://user.fundy.net/pjwhalen/adenosinetriphosphate.html>
Biosensors & Food Safety Diagnostics (Paul S. Satoh Neogen Corporation March 1, 2004)
- ¹¹¹ <http://www.celsis.com/products/pdfs/cels0150.pdf>
- ¹¹² <http://www.amsainc.com/atp.asp>
- ¹¹³ <http://www.amsainc.com/atp-numbers.asp>
- ¹¹⁴ http://www.charm.com/pdf/400-6505-503-300-01_WaterG.pdf
- ¹¹⁵ <http://www.biotrace.com/content.php?hID=2&nhID=16&pID=16>
- ¹¹⁶ <http://www.geneq.com/catalog/en/profile-1.htm>
- ¹¹⁷ <http://www.bio.umass.edu/micro/immunology/facs542/facsprin.htm>
- ¹¹⁸ <http://pcfcij.dbs.aber.ac.uk/aberinst/mcytmain.html>
<http://www.biodetect.biz/products/mc.shtml>
<http://www.biodetect.biz/products/MC.pdf>
<http://www.biodetect.biz/applications/app303.pdf>
- ¹¹⁹ http://www.brightwelltech.com/pdf_files/Micro-Flow_Imaging.pdf
http://www.brightwelltech.com/applications/app_notes/wtp.php
- ¹²⁰ “JMAR Technologies, Inc. Plans Launch of Laser-Based Early-Warning System to Detect Microorganisms in Water Supplies” JMAR Technologies, Inc. Press Release.
http://biz.yahoo.com/bw/040621/215346_1.html;
- ¹²¹ ETV Technology Profile: On-Line Turbidimeters http://www.epa.gov/etv/pdfs/techprofile/01_turbid.pdf
- ¹²² AwwaRF #2720: Continuous Monitoring Method for Cryptosporidium (abstract from website)
<http://www.awwarf.com/research/TopicsAndProjects/projectSnapshot.aspx?pn=2720>
- ¹²³ <http://www.connect.org/members/april.htm>
<http://www.awa.asn.au/news&info/news/26jan03.asp>

- ¹²⁴ “JMAR Technologies, Inc. Plans Launch of Laser-Based Early Warning System to Detect Microorganisms in Water Supplies” JMAR Technologies, Inc. Press Release.
- ¹²⁵ http://www.shu.ac.uk/scis/artificial_intelligence/IntelMALLS.html
- ¹²⁶ http://www.shu.ac.uk/scis/artificial_intelligence/biospeckle.html
- ¹²⁷ <http://www.nrl.navy.mil/pressRelease.php?Y=2004&R=26-04r>
http://www.resrchintl.com/pdf/spie_wqm.pdf
http://www.resrchintl.com/product_bibliography_source.htm
<http://www.resrchintl.com/raptor.html>
http://www.resrchintl.com/pdf/raptor_2%20.pdf
- ¹²⁸ http://www.luminexcorp.com/01_xMAPTechnology/08_Tutorials/How_xmap_works
http://www.luminexcorp.com/01_xMAPTechnology/02_Applications/01_index.html
- ¹²⁹ http://www.ncbi.nlm.nih.gov/entrez/query.fcgi?cmd=Retrieve&db=pubmed&dopt=Abstract&list_uids=15228315
- ¹³⁰ <http://www.celsis.com/products/pdfs/cels0158.pdf>
http://www.celsis.com/products/products_dairy.php
- ¹³¹ http://www.vectech.com/newsletters/2003/November_Newsletter.pdf
- ¹³² <http://www.innovativebiosensors.com/overview.htm>
<http://www.innovativebiosensors.com/tech.htm>
- ¹³³ <http://www.idahotech.com/rapid/index.html>
- ¹³⁴ http://www.idahotech.com/pdfs/RAPID_pdfs/ETV%20Report-RAPID-short-release.pdf
- ¹³⁵ http://www.idahotech.com/pdfs/RAPID_pdfs/SocietyScopeV6.3.pdf
- ¹³⁶ <http://www.defenseindustrydaily.com/2005/05/jbaidas-a-step-forward-for-bioweapon-detection/index.php>
- ¹³⁷ <http://www.idahotech.com/razor/index.html>
http://stm2.nrl.navy.mil/~lwhitman/pdfs/nrlrev2001_BARC.pdf
- ¹³⁸ <http://www.smithsdetection.com/product.asp?product=Bio%2DSeeq&prodgroup=Bio%2DSeeq&prodcats=Biological+Agent+Detection&prodarea=Trace+detection&division=Detection>
- ¹³⁹ http://www.the-scientist.com/asp/Registration/login.asp?redir=http://www.the-scientist.com/yr2003/may/lcprofile_030505.html
- ¹⁴⁰ <http://www.wrenwray.com/images/pdf/CEPHEIDA.PDF>
- ¹⁴¹ <http://news.moneycentral.msn.com/ticker/sigdev.asp?Symbol=CPHD&PageNum=1>
- ¹⁴² <http://www.chem.agilent.com/Scripts/PCol.asp?IPage=50>
<http://www.securitypronews.com/news/securitynews/spn-45-20050407InvitrogenandAgilentTechnologiesToCoMarketPathAlertDetectionSystem.html>

- ¹⁴³ <http://www.ibisrna.com/>
<http://www.robodesign.com/tiger2.shtml>
- ¹⁴⁴ <http://www.micro.uiuc.edu/boss/bossframes.htm>
<http://www.darpa.mil/mto/optocenters/presentations/cheng.pdf#search='Georgia%20Tech%20BOSS%20sensor%20system'>
- ¹⁴⁵ http://asl.chemistry.gatech.edu/research_ir-sensors-frame.html
<http://gtresearchnews.gatech.edu/newsrelease/ESMART.html>
http://asl.chemistry.gatech.edu/pdf-files/conference%20abstracts/Mizaikoff_SIcon_031301.pdf#search='evanescent%20field%20sensor'
- ¹⁴⁶ <http://www.cpac.washington.edu/~campbell/projects/spr.html>
<http://www.photonics.com/spectra/features/XQ/ASP/artabid.745/QX/read.htm>
- ¹⁴⁷ http://www.ee.washington.edu/research/denise/www/Lab/files/mike_spr_final.ppt
- ¹⁴⁸ <http://www.bitc.unh.edu/annual.reports/2004BITCfactsheet.pdf>
- ¹⁴⁹ http://www.aigproducts.com/surface_plasmon_resonance/spr_considering.htm
http://www.aigproducts.com/surface_plasmon_resonance/spr_evaluation_module.htm
<http://www.nomadics.com/products/spr3/>
- ¹⁵⁰ http://www.aigproducts.com/surface_plasmon_resonance/spr.htm
- ¹⁵¹ <http://www.stanford.edu/~bohuang/Research/Anal%20Chem%202002.pdf>
- ¹⁵² <http://www.bioveris.com/technology.htm>
<http://www.mesoscaledefense.com/technology/ecl/diagram.htm>
<http://www.mesoscaledefense.com/technology/ecl/walkthrough.htm>
<http://www.sbs-archi.org/02pres/Umek.pdf>
- ¹⁵³ http://www.bioveris.com/products_services/life_sciences/instrumentation/ml_analyzer.htm
- ¹⁵⁴ http://www.biospace.com/news_story.cfm?StoryID=17104620&full=1
http://us.diagnostics.roche.com/press_room/2003/072403.htm
- ¹⁵⁵ http://www.mesoscaledefense.com/coming_soon.htm
- ¹⁵⁶ http://spaceresearch.nasa.gov/general_info/homeplanet.html
- ¹⁵⁷ http://www.qdots.com/live/upload_documents/wQDVOct03_pg8-9.pdf
- ¹⁵⁸ <http://www.qdots.com/live/render/content.asp?id=47>
- ¹⁵⁹ <http://www.qdots.com/live/render/content.asp?id=87>
http://www.bio-itworld.com/archive/021804/horizons_dot.html

- ¹⁶⁰ <http://www.sciencenews.org/articles/20030215/bob10.asp>
<http://www.sciencedaily.com/releases/2002/11/021127071742.htm>
http://www.eurekalert.org/pub_releases/2004-06/uosc-qds061404.php
http://www.smalltimes.com/document_display.cfm?document_id=3811
<http://www.llnl.gov/str/Lee.html>
- ¹⁶¹ <http://www.epa.gov/OGWDW/methods/current.html>
- ¹⁶² <http://www.bravurafilms.com/projects/projectrep/phosphors.html>
<http://www.orasure.com/products/default.asp?cid=10&subx=4&sec=3>
<http://www.sri.com/news/releases/02-17-98.html>
<http://www.sri.com/rd/chembio.html>
- ¹⁶³ <http://www.orasure.com/products/prodsubarea.asp?cid=1&pid=126&sec=3&subsec=4>
- ¹⁶⁴ <http://www.sri.com/rd/chembio.html>
- ¹⁶⁵ <http://www.nanobioconvergence.org/speakers.aspx?ID=33>
<http://www.orasure.com/products/prodsubarea.asp?cid=2&pid=126&sec=3&subsec=4>
- ¹⁶⁶ <http://www.dynal.net/>
- ¹⁶⁷ <http://www.technet.pnl.gov/sensors/biological/projects/ES4BEADS-Sys.stm>
<http://www.pnl.gov/breakthroughs/win-spr02/special3.html#biothreat>
- ¹⁶⁸ <http://www.chem.vt.edu/chem-ed/spec/vib/raman.html>
http://en.wikipedia.org/wiki/Raman_spectroscopy
- ¹⁶⁹ <http://www.iwaponline.com/wio/2003/04/wio200304WF00HHE8UR.htm>
- ¹⁷⁰ <http://www.deltanu.com/companyinfo.htm>
<http://www.chemimage.com/products/>
- ¹⁷¹ http://www.combimatrix.com/news_NBCKing5Aug04.htm
http://www.combimatrix.com/products_biothreat.htm
- ¹⁷² <http://www.promega.com/geneticidproc/ussymp11proc/content/llewellyn.pdf>
<http://www.eurekalert.org/features/doe/2003-11/dnl-lft031804.php>
- ¹⁷³ <http://www.foresight.org/conferences/MNT8/Abstracts/Colton/>
http://stm2.nrl.navy.mil/~lwhitman/pdfs/nrlrev2001_BARC.pdf
- ¹⁷⁴ http://stm2.nrl.navy.mil/~lwhitman/pdfs/Rife_Sensors_Actuators_A_published.pdf
- ¹⁷⁵ <http://www.gwu.edu/~physics/colloq/miller.htm>
- ¹⁷⁶ <http://www.affymetrix.com/technology/manufacturing/index.affx>
- ¹⁷⁷ <http://www.dsls.usra.edu/meetings/bio2003/pdf/Biosensors/2149Stahl.pdf>
- ¹⁷⁸ http://www.sciencemag.org/feature/e-market/benchtop/biochips3_10_18_02.shl

- ¹⁷⁹ http://www.protiveris.com/new/products_folder/veriscansystem.html
<http://www.buscom.com/nanobio2003/session3c.html>
- ¹⁸⁰ http://pharmalicensing.com/news/headlines/1070473459_3fce20f35628c
- ¹⁸¹ <http://www.memsnet.org/mems/what-is.html>
- ¹⁸² <http://www.iatroquest.com/En.htm>
<http://www.iatroquest.net/Linked%20Docs/IatroQuest%20Corporation%20Fact%20Sheet%20040217-1334.pdf>
- ¹⁸³ http://www.cm.utexas.edu/mcdevitt/ET_Broch.pdf
<http://www.cm.utexas.edu/mcdevitt/tastechip.htm>
- ¹⁸⁴ <http://www.silsoe.cranfield.ac.uk/staff/apturner.htm>
<http://www.cranfield.ac.uk/ibst/ccst/mips/sensors.htm>
- ¹⁸⁵ <http://www.scs.uiuc.edu/suslick/pdf/pressclippings/naturebiotech.0902-884.pdf>
- ¹⁸⁶ http://www.tekes.fi/ohjelmat/diagnostiikka/diag_esitykset/turner.pdf
- ¹⁸⁷ <http://www.ee.psu.edu/grimes/sensors/>
- ¹⁸⁸ http://www.isco.com/WebProductFiles/Product_Literature/201/Specialty_Samplers?3710RLS Radionuclide_Sampler.PDF
- ¹⁸⁹ <http://www.epa.gov/watersecurity/guide/radiationdetectionequipmentformonitoringwaterassets.html>
U.S. EPA, Radiation Detection Equipment for Monitoring Water Assets, Water and Wastewater Security Product Guide
- ¹⁹⁰ <http://www.tech-associates.com/dept/sales/product-info/sss-33-5ft.html>
Drinking Water Rad-Safety Monitor Model #SSS-33-5FT. Updated 1/31/2002.
- ¹⁹¹ <http://www.tech-associates.com/dept/sales/product-info/meda-5t.html>
Updated in 2002.
- ¹⁹² http://www.isco.com/WebProductFiles/Product_Literature/201/Specialty_Samplers?3710RLS Radionuclide_Sampler.PDF
- ¹⁹³ <http://www.tech-associates.com/dept/sales/product-info/sss-33dhc.html>
- ¹⁹⁴ <http://www.tech-associates.com/dept/sales/product-info/sss-33m8.html>
- ¹⁹⁵ <http://www.canberra.com/products/802.asp>
- ¹⁹⁶ <http://www.canberra.com/products/803.asp>
- ¹⁹⁷ <http://www.canberra.com/products/801.asp>
- ¹⁹⁸ <http://www.clarionsensing.com/home.shtml>
- ¹⁹⁹ <http://apps.em.doe.gov/ost/pubs/itsrs/itsr312.pdf>

- 200 <http://www.cpeo.org/techtree/ttdescript/alpharad.htm> Last updated 10/2002.
- 201 <http://www.technet.pnl.gov/sensors/nuclear/projects/ES4Tc-99.stm>
- 202 <http://www.epa.gov/watersecurity/guide/radiationdetectionequipmentformonitoringwaterassets.html>
- 203 <http://www-emtd.lanl.gov/TD/WasteCharacterization/LiquidAlphaMonitor.html>
- 204 <http://www.cfsan.fda.gov/~dms/fssupd72.html#grants>
- 205 <http://www.johnmorris.com.au/html/Mantech/titrasip.htm>
- 206 http://www.hach.com/hc/search.product.details.invoker/PackagingCode=6950000/NewLinkLabel=Hach+Event+Monitor+Trigger+System/PREVIOUS_BREADCRUMB_ID=HC_SEARCH_KEYWORD/SESSIONID|B3hNRFkwTIRRNE56RTROekVtWjNWbGMzUk5Sdz09QWxKYVZ6RQ==
- 207 FBI/CDC June 2002 Evaluation of Hand-Held Immunoassays for Bacillus anthracis and Yersinia pestis
- 208 http://www.isco.com/WebProductFiles/Product_Literature/201/Specialty_Samplers/3710RLS_Radio_nuclide_Sampler.PDF
- 209 http://www.dhs.gov/dhspublic/theme_home1.jsp
- 210 <http://www.dhs.gov/dhspublic/display?theme=36>
- 211 <http://www.globalsecurity.org/security/library/policy/national/hspd-9.htm>
- 212 <http://www.epa.gov/etv/homeland/>
- 213 <http://www.dhs.gov/dhspublic/display?theme=38&content=4014&print=true>
<http://www.fcw.com/fcw/articles/2004/0419/web-scada-04-19-04.asp>
http://www.dhs.gov/dhspublic/interapp/editorial/editorial_0359.xml
- 214 <http://www.fas.org/man/dod-101/army/docs/astmp98/sec3k.htm>
- 215 <http://www.dtic.mil/whs/directives/corres/pdf2/d200012p.pdf>
- 216 http://www.defenselink.mil/news/Sep2004/n09032004_2004090304.html
- 217 <http://www.darpa.mil/index.html>
- 218 <http://www.darpa.mil/dso/thrust/biosci/biotech.htm>
- 219 <http://www.darpa.mil/dso/thrust/biosci/biosensor/enabtech.html>
http://www.darpa.mil/mto/People/PMs/carrano_dtec.html
<http://www.darpa.mil/dso/thrust/biosci/biotech.htm>
<http://www.darpa.mil/dso/thrust/biosci/biosensor/enabtech.html>
http://www.darpa.mil/dso/thrust/biosci/biosensor/auburn_d.html
http://www.darpa.mil/dso/thrust/biosci/biosensor/auburn_i.html
<http://www.darpa.mil/dso/thrust/biosci/biosensor/sandia.html>
http://www.darpa.mil/dso/thrust/biosci/biosensor/rush_med.html
<http://www.darpa.mil/dso/thrust/biosci/biosensor/argonne.html>

- http://www.darpa.mil/body/procurements/old_procurements/jan2000/mtojan00.html
- 220 <http://www.nrl.navy.mil/content.php?P=ABOUTNRL>
- 221 <http://pubs.rsc.org/ej/CC/2000/b003185m.pdf>
- 222 <http://www.nrl.navy.mil/content.php?P=04REVIEW115>
- 223 <http://www3.interscience.wiley.com/cgi-bin/abstract/107061018/ABSTRACT>
- 224 <http://www.nrl.navy.mil/pao/pressRelease.php?Y=1996&R=26-96r>
- 225 <http://www.foresight.org/conferences/MNT8/Abstracts/Colton/>
http://stm2.nrl.navy.mil/~lwhitman/pdfs/nrlrev2001_BARC.pdf
- 226 http://stm2.nrl.navy.mil/~lwhitman/pdfs/Rife_Sensors_Actuators_A_published.pdf
- 227 http://stm2.nrl.navy.mil/~lwhitman/pdfs/nrlrev2001_BARC.pdf
- 228 <http://www.globalsecurity.org/wmd/facility/edgewood.htm>
- 229 <http://www.epa.gov/ordnhsrc/>
- 230 http://water.usgs.gov/wicp/acwi/monitoring/conference/2004/conference_agenda_links/power_points_etc/06_ConcurrentSessionD/90_Rm15_Vowinkel.pdf
- 231 <http://www.ilsa.org/publications/publist.cfm?pubentityid=13&publicationid=268>
- 232 http://water.usgs.gov/wicp/acwi/monitoring/conference/2004/conference_web_agenda.html
- 233 http://water.usgs.gov/ogw/karst/kig2002/msf_development.html
- 234 <http://www.mdl.sandia.gov/mstc/technologies/microsensors/techinfo.html>
<http://www.sandia.gov/sensor/noframes.htm>
http://www.ca.sandia.gov/chembio/news_center/ST2002v4no3.pdf
- 235 http://www.ca.sandia.gov/news/2004_news/120704Mercury.html
- 236 <http://www.llnl.gov/llnl/001index/02about-index.html>
- 237 http://www.llnl.gov/sensor_technology/SensorTech_contents.html
- 238 <http://www.ornl.gov/ornlhome/about.shtml>
- 239 <http://www.ornl.gov/ornlhome/about.shtml>
- 240 http://www.ornl.gov/info/ornlreview/rev29_3/text/biosens.htm
- 241 http://www.ornl.gov/sci/engineering_science_technology/sms/Hardy%20Fact%20Sheets/Countermeasures.pdf
- 242 http://pharmalicensing.com/news/headlines/1070473459_3fce20f35628c

- 243 <http://www.ornl.gov/sci/biosensors/>
<http://www.ornl.gov/adm/tted/LifeSciencesTechnologies/LifeSciencesTechnologyList.htm>
- 244 <http://www.pnl.gov/main/welcome/>
- 245 <http://www.pnl.gov/main/sectors/nsd/%20homeland.pdf>
- 246 <http://www.technet.pnl.gov/sensors/>
- 247 <http://www.pnl.gov/main/sectors/nsd/%20homeland.pdf>
- 248 <http://www.inl.gov/index.shtml>
- 249 <http://www.amsa-cleanwater.org/meetings/04winter/ppt/ppt/30%20--%20FRI%20-%20Reinhardt,%20Glen/AMSA%20-%20Security%20Panel%20Discussion%20-%20GR.pps>
- 250 <http://www7.nationalacademies.org/wstb/index.html>
- 251 <http://www4.nationalacademies.org/webcr.nsf/CommitteeDisplay/WSTB-U-04-06-A?OpenDocument>
- 252 <http://www4.nas.edu/webcr.nsf/5c50571a75df494485256a95007a091e/5d3beab7fa3bb8bc85256d0b00705acf?OpenDocument>
- 253 <http://www.awwarf.org/theFoundation/>
- 254 WERF's website: www.werf.org
- 255 <http://civic.rutgers.edu/epa-workshop.html>
- 256 <http://www.knowledgepress.com/>
- 257 http://www.knowledgepress.com/events/7011409_p.pdf
- 258 <http://www.healthtech.com/2003/btr/>
- 259 http://www.knowledgepress.com/events/12111105_p.pdf
- 260 <http://www.wtec.org/biosensing/proceedings/>
- 261 http://www.knowledgepress.com/events/7191716_p.pdf
- 262 <http://civic.rutgers.edu/epa-workshop.html>
<http://civic.rutgers.edu/workshop2.html>
- 263 <http://www.healthtech.com/2002/bms/abstracts/symposium3.htm>
- 264 http://www.knowledgepress.com/events/11071420_p.pdf



PRESORTED STANDARD
POSTAGE & FEES PAID
EPA
PERMIT NO. G-35

Office of Research and Development
National Homeland Security Research Center
Cincinnati, OH 45268

Official Business
Penalty for Private Use
\$300

EPA/600/R-05/156
December 2005