Water and Sustainable Development: Opportunities for the Chemical Sciences - A Workshop Report to the Chemical Sciences Roundtable

Parry Norling, Frankie Wood-Black, and Tina M. Masciangioli, Editors, Chemical Sciences Roundtable, National Research Council

ISBN: 0-309-53173-X, 106 pages, 8 1/2 x 11, (2004)

WATER AND SUSTAINABLE DEVELOPMENT

OPPORTUNITIES FOR THE CHEMICAL SCIENCES

A WORKSHOP REPORT TO THE CHEMICAL SCIENCES ROUNDTABLE

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Chemical Sciences Roundtable

Board on Chemical Sciences and Technology

Division on Earth and Life Studies

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THE NATIONAL ACADEMIES PRESS
Washington, D.C.
www.nap.edu

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This study was supported by Research Corporation under Grant No. GG0066; the U.S. Department of Energy under Grant No. DE-FG-02-95ER14556; the National Institutes of Health under Grant No. N01-OD-2139, Task Order 25; and the National Science Foundation under Grant No. CHE-0328197. Any opinions, findings, conclusions, or recommendations expressed in this publication are those of the author(s) and do not necessarily reflect the views of the organizations or agencies that provided support for the project.

International Standard Book Number 0-309-09200-0 (Book)
International Standard Book Number 0-309-053173-X (PDF)

Additional copies of this report are available from the National Academies Press, 500 Fifth Street, N.W., Lockbox 285, Washington, DC 20055; (800) 624-6242 or (202) 334-3313 (in the Washington metropolitan area); Internet, http://www.nap.edu

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Preface

The Chemical Sciences Roundtable (CSR) was established in 1997 by the National Research Council (NRC). It provides a science-oriented, apolitical forum for leaders in the chemical sciences to discuss chemically related issues affecting government, industry, and universities. Organized by the NRC's Board on Chemical Sciences and Technology (BCST), the CSR aims to strengthen the chemical sciences by fostering communication among the people and organizations—spanning industry, government, universities, and professional associations—involved with the chemical enterprise. The CSR does this primarily by organizing workshops addressing issues in chemical science and technology that require national attention.

A workshop was organized by the Chemical Sciences Roundtable of BCST on the topic Water and Sustainable Development: Opportunities for the Chemical Sciences. The workshop brought together top experts in the area of water science and technology and leaders in chemistry and chemical engineering from government, industry, and academia. This interaction was intended to enhance the synergy between these two communities and help engage a broader cross section of the chemical sciences community in this important arena of science and technology. The workshop sessions provided technical background and explored enhanced roles that the chemical sciences R&D community might play in identifying and addressing the issues that make water a critical limiting factor in human economic development and sustainability. The goal of the workshop was to inform the Chemical Sciences Roundtable. In that process, it may also engage the broad chemical sciences community in addressing the question of how to ensure the adequate supply of water that is required for public health, sustainable agriculture and food security, energy generation, and economic growth.

This report is largely an edited transcript of speaker and discussion remarks at the workshop. The discussions were edited and organized around major themes to provide a more readable summary. In accordance with the policies of the CSR, the workshop did not attempt to establish any conclusions or recommendations about needs and future directions, focusing instead on issues identified by the speakers.

Parry Norling and Frankie Wood-Black
Workshop Organizers

Acknowledgment of Reviewers

This report has been reviewed in draft form by individuals chosen for their diverse perspectives and technical expertise, in accordance with procedures approved by the National Research Council's Report Review Committee. The purpose of this independent review is to provide candid and critical comments that will assist the institution in making its published report as sound as possible and to ensure that the report meets institutional standards for objectivity, evidence, and responsiveness to the study charge. The review comments and draft manuscript remain confidential to protect the integrity of the deliberative process. We wish to thank the following individuals for their review of this report:

Arthur Daemmrich, Chemical Heritage Foundation
Jean H. Futrell, Pacific Northwest National Laboratories
Raymond Hamelin, Université Pierre et Marie Curie (retired)
David Rea, DuPont Company (retired)
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Although the reviewers listed above have provided many constructive comments and suggestions, they were not asked to endorse the conclusions or recommendations nor did they see the final draft of the report before its release. The review of this report was overseen by **Perry L. McCarty**, Silas H. Palmer Professor Emeritus, Stanford University. Appointed by the Division on Earth and Life Studies, he was responsible for making certain that an independent examination of this report was carried out in accordance with institutional procedures and that all review comments were carefully considered. Responsibility for the final content of this report rests entirely with the authors and the institution.

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Introduction and Summary

Frankie Wood-Black
ConocoPhillips

Parry Norling
DuPont Company (retired)

At the World Summit on Sustainable Development, held in 2002 in Johannesburg, South Africa, concern for safe water supplies and adequate sanitation was noted as a key issue in the protection and management of natural resources for economic and social development. The report issued from the World Summit indicated a number of commitments that are directly related to water and sustainability—the focus and the topics of discussion at this workshop. Perhaps one of the most challenging of these commitments, outlined in Section IV of the Implementation Plan of the report),[1] is to launch a program of actions to achieve the millennium development goal (outlined in the Millennium Declaration) for safe water. The goal is, by the year 2015, to halve the proportion of people unable to reach or afford safe drinking water and the proportion of people without access to basic sanitation. Meeting this challenge will require the talents of chemists and chemical engineers, in addition to economists, city planners, and engineers in other fields. Greater understanding is needed of the fundamental causes of the problems and how to develop innovative technologies to reduce water scarcity (improved desalination, water conservation, water recycle); purify available water (analysis, treatment, pollution prevention); and manage water resources.

Many of the specific technical challenges and opportunities for the chemical sciences are well understood, but most responses have yet to be formulated and funded. Much of the public debate has focused on the problems and not the solutions, especially where the chemical sciences have answers. This workshop of the Chemical Sciences Roundtable sought to focus on solutions or paths to solutions in three sessions: Context and Overview, Water Quality and Supply, and Business Opportunities and Responsibilities. In the scope and time frame of this workshop it was impossible to cover all aspects of sustainable water supplies.

It should be noted that this meeting occurred at a fortuitous time. On June 2, 2003, the G8 leaders released a Water Action Plan that built on the principles and goals of the $1 billion Water for the Poor Initiative of the United States. That initiative was created to improve sustainable management of freshwater resources and to accelerate and expand international efforts to achieve the United Nations Millennium Declaration Goal. Initiative efforts include improving access to clean water and sanitation services, improving watershed management, and increasing the productivity of water. The G8 plan included two components from the U.S. initiative: (1) point-of-use technologies (chlorine-based solutions and filters used in the household), which are effective in combating disease and saving lives, and (2) revolving funds, which allow communities to finance capital-intensive water infrastructure projects over an affordable period of time at competitive rates.

CONTEXT AND OVERVIEW

To understand the opportunities for the chemical sciences in dealing with water-related problems, it is important to understand various aspects of the issues related to the current global agenda, impacts on water quality, water supplies (quantity and availability), and potential problems raised by water pollution. In this session, presentations were given by **Alan Hecht**, White House Council on Environmental Quality (currently at the U.S. Environmental Protection Agency); **Dennis Hjeresen**, Green Chemistry Institute; and **David Krabbenhoft**, U.S. Geologic Survey. Their talks framed the context of the issues surrounding water and provided a global perspective, appreciation of the role of green chemistry, and a specific challenge from a single contaminant—methylmercury.

[1]The Report of the World Summit on Sustainable Development Johannesburg, South Africa, August 26-September 4, 2002, can be found at *http://www.johannesburgsummit.org/*.

Here, it was pointed out that 80 percent of diseases in the developing world are water related, 4 billion to 7 billion people will face water scarcity in 2050, and water has become a priority issue for economic development throughout the world. The chemical sciences were called upon to address issues such as sanitation (the number-one means of reducing disease), water management (including use of innovative technology), and national water strategies. Other challenges mentioned include the shift of water use from agricultural to industrial applications; accessibility of water supplies; and dilemma of who pays for the treatment, transportation, and infrastructure necessary to deliver water to end users.

There was discussion about getting bright young scientists and engineers more interested in the world's water problems. It was suggested that the water issue lacks a "glamour factor" and that although the world's water concerns are great, there does not appear to be a major driver for attracting the best and brightest toward this fundamental problem that impacts every individual.

It was noted that developing countries currently have the opportunity to avoid the mistakes of the developed world. Instead of following the model of "develop first and clean up later," they might "leapfrog" with current and new technologies. A number of examples in which current technologies are far superior and can minimize the impact on water resources were provided.

Another key point raised involved the water-energy balance. It was pointed out that it takes energy to produce or transport water to the areas that are in need, and that current population densities in the arid and semiarid regions, the water-intensive nature of both agriculture and industry, and the sources and uses of water are all at the crux of this balance.

A number of places where green chemistry will eliminate the use of hazardous reactants (potential water pollutants), conserve water, and increase both the quality and the quantity of pure water were discussed. In one example, a systems approach is being used in industrial water treatment to protect infrastructure from corrosion, scaling, and bacterial growth with the use of more benign chemicals at lower levels. Another example highlighted the use of unique catalysts that are making hydrogen peroxide an economical and viable replacement for chlorine as an oxidant in a number of processes. Praise was also given to closed-loop systems that eliminate the use and contamination of water. It was noted that such systems are now in place for photographic film processing.

This session concluded with a look at mercury, the leading environmental contaminant that often results in consumption advisories for fish in the United States and around the world. Sources of mercury emissions in the environment, biological processes that transform mercury to the more biologically available methylmercury, and chemical conditions that favor such transformations were described. It was suggested that greater understanding of the true toxicological impacts of mercury is needed, and concern was raised about the way in which wetland restoration projects have been carried out. Such efforts, it was noted, can actually increase the presence of methylmercury in the environment.

WATER QUALITY AND SUPPLY: ANALYSIS AND TREATMENT

In this session, technical approaches to analysis and treatment of water problems were discussed by **Thomas E. Hinkebein,** National Desalination Roadmap Program manager and manager of the Geochemistry Department, Sandia National Laboratories; **Richard Luthy,** Silas H. Palmer Professor of Civil and Environmental Engineering Stanford University; and **Elias Greenbaum, c**orporate fellow and research group leader, Oak Ridge National Laboratory, and professor of biological physics, University of Tennessee.

The link between population growth and stresses on water supplies was emphasized. It was pointed out that significant growth is taking place in areas with limited water supply. Since 54 percent of the U.S. population lives within 60 miles of the ocean, often in a marginal environment, it was suggested that the opportunity exists for development of viable desalination water sources. However, without a clear plan for the future, it was predicted that water supply issues will limit growth, rely on case-by-case government support, and cause more conflict between states that have water and those that do not.

Challenges of desalination were discussed within the context of the jointly developed Desalination and Water Purification Technology Roadmap of the Bureau of Reclamation and Sandia National Laboratories. This roadmap serves as a strategic research pathway for desalination and water purification technologies to meet future water needs. Near-term and long-term objectives were discussed and included extending existing technologies, requiring technology breakthroughs such as reducing capital costs, increasing energy efficiency, reducing operating costs, and reducing cost of zero liquid discharge processes. It should be noted that in the time since this workshop was held, the National Research Council's Water Science and Technology Board has reviewed the roadmap (see Appendix D).

Detection of organic contaminants (especially compounds that are persistent, bioaccumulative, and toxic [PBTs], such as polychlorinated biphenyls [PCBs]) in water and in sediments was also discussed during this session. Details of work on mitigating the effects of contaminants in sediments and reducing the risk to health by decreasing the bioavailability of the chemicals were described. This work involves adding carbonaceous material to sediments to facilitate binding of contaminants. It was explained that these treatments may be superior to dredging, which is planned for PCBs in the Hudson River.

The types of analytical tools and bioavailability tests now available to address some of these questions were discussed; however, it was pointed out that no single tool or currently available test will allow these questions to be answered. It was suggested that tools must be used with prudence to avoid misapplication and care must be taken to avoid "short cuts" when dealing with living systems since impacts may not be known until years later. It was noted that partnerships between the disciplines and the regulatory agencies are essential in allowing the scientific community to address, understand, and tackle these complex problems.

The conclusion of the afternoon session centered on a device that uses the natural fluorescence associated with the photosynthesis of algae to detect the health of the drinking water supply. The basic concept behind this technology is that if a chemical agent or other contaminant entered a body of water, the algae would be affected in real time. This would impact its ability to photosynthesize and provide a useful signal for monitoring water quality.

In the evening, workshop participants heard from **Virginia Grebbien,** general manager of the Orange County Water District in California, about the status and challenges faced by the water district, which is considered one of the most innovative in the United States. She outlined some solutions that the district has implemented to address these challenges. Once again, the scientific community was called on to engage in helping to meet the future needs of this water district as well as others around the country. The importance of understanding the impacts of contaminants; how to deal with them; and how to develop fast, reliable, and inexpensive monitoring methods was highlighted.

BUSINESS OPPORTUNITIES AND RESPONSIBILITIES

The final session of the workshop focused on what industry and the scientific community can do to help meet the challenges presented in the first two sessions. This session looked at the market opportunities and responsibilities faced by the regulated industries (i.e., industrial users and suppliers), as well as the regulatory agencies. Presentations were given by **Floyd Wicks,** president and chief executive officer of American States Water Company; **Bhasker Davé,** R&D manager of advanced recycle technology and membrane separations technology at Ondeo Nalco; **Carol Jensen,** vice president of global research and development for performance chemicals, Dow Chemical Company; and **Bruce Macler,** national microbial risk assessment expert in the Water Division of the U.S. Environmental Protection Agency, Region 9.

A number of important issues facing private water supply companies were also outlined during this session. It was pointed out that about half of the 60,000 water systems in the United States are privately owned and that investor-owned water utilities serve approximately one in seven people. It was also suggested that a fundamental challenge to the industry is that there is an increased perception of risk, yet research dollars in this area are declining.

The overall process of managing the costs and risks in industrial water management as a critical component of sustainable development was highlighted. Here, sustainable development was described as development that is socially desirable, ecologically sustainable, and most importantly, economically viable. Solutions in integrated water management that follow this path were presented, such as how industries can minimize their water usage by conserving, recycling, and cascading water. It was pointed out that this involves matching the water purity to the needs of the process and stepping-down water from high-purity-requirement processes to lower-purity-requirement processes. Three areas of industrial waste management in which the chemical sciences can provide the needed innovation—green chemistry, novel equipment (e.g., membrane technology), and smart operations (e.g., use of modeling and sensors to allow automation)—were also discussed.

Another company's effort as a water user and as a supplier of clean water technology was presented. It was reported that a significant amount of fresh water is used by industry each year and that there is heavy investment in annual water acquisition, treatment, and disposal. To reduce the rising expenses, efforts are being made to integrate best practices in water, manage resources and technology, and optimize supplier relationships across the entire company. Success stories and discussion of technologies being developed helped illustrate industry's awareness and commitment to the proactive and intelligent management of water.

The formulation of regulations and current problems facing the regulatory agencies were the final topics of discussion. It was pointed out that regulations are intended to minimize the danger from contamination. They also deal with the public perception of safety and its social, political, and economic implications. In order to continue to improve the regulatory structure for water, several challenges were outlined for the research community. These included the need for robust technology to monitor environmental problems, an understanding of how to control persistent organics, knowing how to minimize disinfection by-products, and continued improvement in membrane technology. It was predicted that in the near term (within the next five years) the need to control pollutants such as arsenate and perchlorate, will continue and tools to monitor these materials will be required. However, the longer term (10 years plus) will require approaches to control a broad spectrum of persistent organics in the environment, as well as improvements in brine and sludge disposal techniques.

KEY QUESTIONS

The presentations and discussions that followed raised some important questions for further consideration:

- What constitutes safe drinking water and who decides what safe is?
- What roles should industry and government play in water management?
- Where do cost-benefit analyses come into play?
- Should all water be treated to the same standards?
- What is the future of desalination, and is it limited?
- How should water be valued more appropriately?

Context and Overview

1

Meeting the Global Water Challenge

Alan D. Hecht
White House Council on Environmental Quality[1]

DEVELOPMENT CHALLENGES

Today, 1.1 billion people worldwide live in poverty without access to safe drinking water and another 2.4 billion have no access to proper sanitation. Water-related diseases are among the most common cause of illness, affecting mainly the poor in developing countries. In 2000, the estimated mortality due to water- and hygiene-associated diarrheas and other diseases was 2.2 million, the majority of whom are children under the age of 5. For the developing world, achieving clean water and improving sanitation are crucial elements of development and poverty alleviation. It is no wonder that access to clean water and sanitation has become a priority international issue.

DEVELOPMENT GOALS FOR WATER

The United Nations Millennium Development Goals and the World Summit on Sustainable Development (WSSD) Action Plan target two key water-related issues: By 2015, halve the proportion both of people without access to safe drinking water and of people without adequate sanitation. Achieving the goal of access to safe drinking water alone requires addressing the needs of approximately 125,000 people every day until 2015.

The United States is aggressively pursuing several programs to address these basic human needs. At the WSSD in September 2003, the United States launched a nearly $1 billion Water for the Poor Initiative aimed at significantly increasing access in the developing world to clean water and sanitation. A major element of the U.S. initiative is the promotion of safe drinking water systems at the household level.

The 2002 World Health Organization (WHO) world health report attributed 2.2 million deaths annually, mainly from infectious diarrhea, to the lack of safe drinking water, sanitation, and hygiene. These constitute the third-highest risk factor for disease and disability in the developing world, after malnourishment and unsafe sexual practices. Meeting the internationally agreed water goal on sanitation requires a frontal attack on eliminating waterborne diseases.

SAFE WATER SYSTEMS

The WHO report has identified the provision of water disinfection capacity at point of use (POU) as the most cost-effective approach to reducing waterborne disease. Regardless of whether or not collected household water is initially of acceptable microbiological quality, it often becomes contaminated with pathogens of fecal origins during transport and storage. Cost-effective technologies already exist to treat water at its POU, including locally produced water disinfectant and dilute chlorine-based solution. A variety of candidate technologies for treatment of household water have been developed and employed in different parts of the world. New technologies are being field-tested. Proctor and Gamble has pioneered the development of a coagulating and water purification tablet called PUR, which has been field-tested in Nicaragua and the Philippines by the U.S. Centers for Disease Control and Prevention (CDC). The product, especially designed for the low-income market, has demonstrated significant reductions in diarrheal disease in test markets. PUR will soon be available to join other products to serve as a tool for point source purification of water.

When these technologies are coupled with education and hygiene programs, field experience shows that a 50 percent or greater reduction in water-related disease can be achieved relatively quickly. According to the WHO (2002) world health report: "There is now conclusive evidence that simple, acceptable, low-cost interventions at the household and com-

[1]Dr. Hecht is now director for sustainable development in the Office of Research and Development at the U.S. Environmental Protection Agency.

munity level are capable of dramatically improving the microbial quality of household stored water and reducing the risks of diarrhea disease and health in populations of all ages in the developed and developing world."

SOCIAL MARKETING

Once the market for these technologies has been established, it tends to grow on its own and becomes self-sustaining. Market development is advanced by *social marketing*, which involves both behavior change and product development. Social marketing combines education to motivate healthy behavior with the provision of needed health products and services to lower-income persons by marketing through the private sector. The United States has been a leader, along with the United Kingdom, in the social marketing of other health commodities (e.g., condoms, insecticide-treated nets, oral rehydration salts). Test cases show remarkably good results. In Zambia and Madagascar, $600,000 in donor funding has helped create a market for POU technologies that has now reached more than 2 million people. Collaborative efforts by WHO, UNICEF (the United Nations Children's Fund), CDC, and Population Services International (PSI) are operating in more than 20 low-income countries.

In the world today, 4 billion to 7 billion people also face possible water scarcity by 2050 (Figure 1.1). Water shortages in many parts of the world, including the U.S.-Mexico border, underscore the need for effective water management and greater water efficiencies, especially in agricultural use. Forty percent of the world's population depends on the waters of 263 river basins that are shared by two or more countries. Regional security, human resource development, poverty alleviation, and human health needs are all served by effective international cooperation on water resource management. U.S. international financial and technical assistance aims to strengthen institutions for regional water cooperation. For example, the U.S. Agency for International Development (USAID) is a partner in the West Africa Water Initiative, a new alliance of 12 organizations worldwide announced at WSSD. USAID has provided $4.4 million to this initiative, complementing more than $36 million in total resources, to invest in small-scale potable water supply and sanitation, hygiene, and water management, primarily in poor rural and urban communities.

U.S. WATER CHALLENGES

Domestic U.S. water needs are also a focus of attention. Aging infrastructures, growing U.S. population demands on water, and nonpoint sources of pollution are all stressors on U.S. water resources. Administration efforts are under way to ensure better water resource management, more efficient operation, full cost pricing, and promotion of watershed approaches.

Domestic and international good governance, innovative financing, and applications of science and technology are essential tools to address global water issues. Development

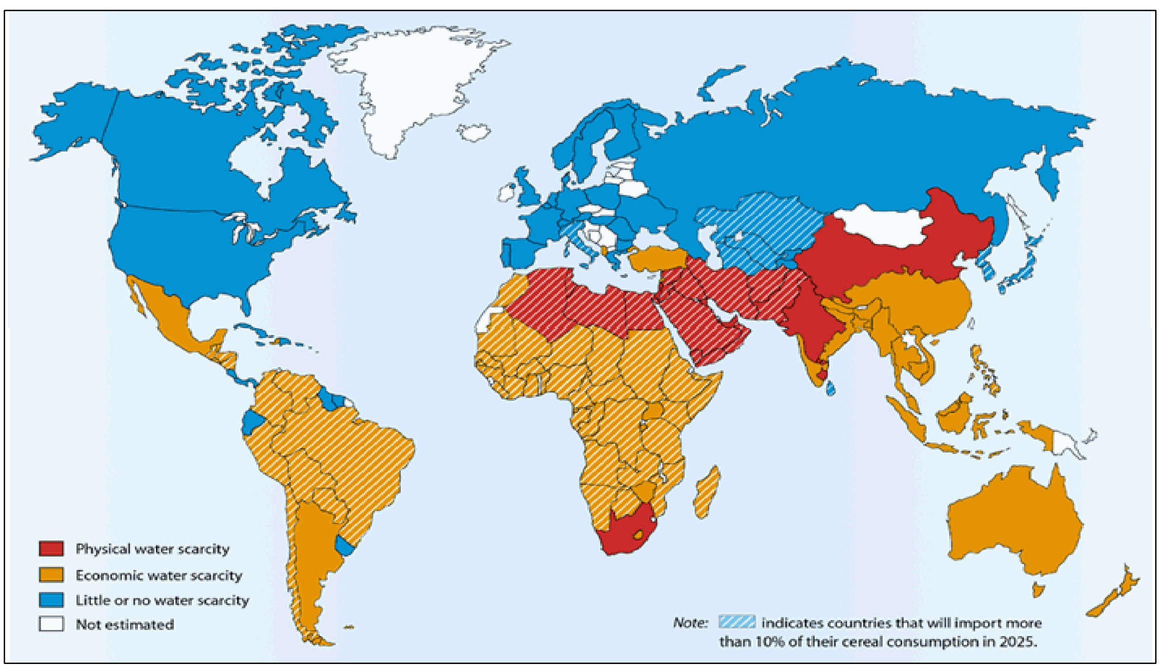

FIGURE 1.1 Water scarcity in 2050. SOURCE: UN WWAP (2003).

and application of simple technologies can go a long way in addressing some of the world's key water and health problems and reducing excessive water use. Global water challenges cross all scientific disciplines. The chemical sciences can be a key player in improving the lives of billions of people around the world.

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DISCUSSION

The World Water Forum

Jess Purl, of Chicago Chem Consultants, raised concerns about prospects for future international consensus addressing water issues. He referred back to the World Water Forum (held March 16-23, 2003, in Kyoto, Japan) mentioned earlier by Dr. Hecht and pointed out that among the very disparate groups that attended the forum in Kyoto, there was very little understanding of the basic fundamental issues of sanitation and human health. Mr. Purl was concerned that such inadequacies in the discussion decrease the likelihood for involvement of the current U.S. administration in future negotiations on water issues.

Dr. Hecht agreed that many of the groups weighing in on water issues at the forum lacked a balanced view of threat issues. For example, protests against privatization of water overwhelmed much of the discussion; and yet, he believes that ownership or management of water systems by private companies is not very prevalent throughout the world and is overall not a major issue. However, Dr. Hecht felt that the current administration is committed to water issues, and he is hopeful that it will stay engaged in any international agreements concerning water that come up in the future.

Dr. Hecht reiterated how this administration is looking at new ways to address environmental problems in general that would lead to improvements in water. Resource use and environmental health will be improved through U.S. development strategies to address fundamental infrastructure needs, political infrastructure, corruption, and overall good governance of developing countries. He was not clear on what form these efforts might take, but he believes that there would have to be increases in development aid to make this happen.

Dr. Hecht thinks that water and other resource and environmental issues must be addressed through capacity building, development of systems, and education. He spent a great deal of time at the World Water Forum in bilateral meetings explaining better ways of financing developing countries. However, Dr. Hecht believes that although the issues resonated with these countries, they will need an enormous amount of help from the United States and other development assistance efforts. He hopes that the current administration will support such efforts.

Need Versus Economic Reality

Denny Hjeresen, of the American Chemical Society, brought up a problem associated with addressing the needs of developing countries when there is no viable economic market to do so. He mentioned a meeting he attended several years ago for water ministers from across Africa at which the minister from Senegal stood up and said what they really needed was water treatment at the rate of $1 per person per year that would also be provided for free.

Dr. Hjeresen wanted to know, as the United States makes this commitment to water worldwide, how the economics of providing some of these solutions will be addressed. He talked about the very strong focus on the private sector market in the United States and said that at a dollar per person per year, there will not be many companies interested in working in this area. He pointed out that in looking at the sales growth chart Dr. Hecht presented, 22,000 units at 60 cents per unit is not much economic incentive for most businesses.

Dr. Hecht agreed that it is not likely that the private sector is going to invest heavily in this area because water is not profitable. He also pointed out that public funding is becoming less of an option as developed countries cut back on overseas development assistance. He said that France supports doubling the current $80 billion in overseas development assistance (ODA) provided by G8 countries, whereas the White House opposes any increased funding. Therefore, developing countries will have to look for other financing.

Dr. Hecht recommended that as long as the ODA exists, it should be spent on building capacity and training people to develop financing approaches. He said that there are several examples in which such efforts have been effective, such as in India and South Africa.

Water Quantity Versus Water Quality

Steve Cabaniss, of the University of New Mexico, wanted to know how much of the conflict over water between the United States and Mexico has to do with quantitative water transfer versus water quality and salination issues.

Dr. Hecht responded that both issues are important, however, the water quantity problem is more serious politically because it has its basis in treaty. Under the 1944 Boundary Water Treating Act, water is exchanged between the United States and Mexico. He said that in the last number of years, Mexico has fallen behind its transfers of water to the United States because of a long-term drought. Before the Iraq war, this issue had reached very high political levels and was discussed many times by Presidents Fox and Bush.

Dr. Hecht said that this point of contention continues to be a significant issue, given that there are farmers in Texas managing an approximate $3 billion agricultural industry that remains relatively dependent on Mexican water. Even the National Security Council became involved in U.S.-Mexico water issues and helped facilitate agreement on a transfer of Mexican water to Texas. The problem continues because Mexico still suffers from drought conditions and poor water management. Dr. Hecht said that regardless of the details, the amount of water that has been transferred between these two countries has not met the treaty obligation. This has kept water, along with immigration and other issues, festering and will potentially become a more serious problem in the future.

Water Profitability

Fareed Salem, with ConocoPhillip, said that he has been involved in the water business for a long time and has not earned much money from it. He has observed, however, that technology innovation is a key factor to water and profitability.

Mr. Salem also said that the role of government in sustainability efforts should be facilitation rather than leadership. He thought that a business approach should be taken where communities set up water sustainability business councils. He felt that sustainability efforts should be community driven because the priorities for each community are different.

Dr. Hecht responded by saying that the role of government is very important because someone has to pay for clean water. Water treatment, storage, and transfer must be fairly priced. He brought up the fact that the current pricing of clean water does not reflect these costs and addressing this is essential for solving the looming water problems. Dr. Hecht also expressed concerns that were raised at the talks in Kyoto that the poor will not be well served if governments do not play a role in providing clean water sources. Dr. Hecht agreed that the private sector should play a big role in sustainability efforts together with communities, but major hurdles exist to provide fairly priced water sources that are also profitable.

Water Trouble Spots and Global Impacts

Jan Dell, of CH2M Hill, posed questions dealing with how the effects of poor sanitation or water issues in one region can have global impacts. She wanted to know about water issues that might be analogous to those posed by the movement of air pollution from one region to another. Ms. Dell also commented on her experience working for multinationals and their water supply chains. She asked about the potential link between sanitary treatment in southern China and the outbreak of SARS (severe acute respiratory syndrome).

In response, Dr. Hecht talked about industry's role in addressing global pollution issues. He mentioned a group at the Commerce Department called the Environmental Technologies Trade Advisory Committee that is working with industries developing facilities overseas to get them to think more broadly about their capability as a service to the communities. Dr. Hecht said that great potential exists for these plants—whether they manufacture soda pop, pharmaceuticals, or computer chips—as they process water for their own needs and expand operations to provide water supplies for the local community.

On the issues of treatment, sanitation in China, and the SARS outbreak, Dr. Hecht was not aware of a link. He did highlight the CDC's efforts on international environmental health and sanitation issues and the success of the safe drinking verification programs around the world (*www.cdc.gov/safewater*). He also pointed out that, surprisingly, China was not part of the bilateral negotiations at the World Water Forum in Kyoto and that most of the focus there was on Africa and Central America.

Population and Water Supply

Don Phipps, of the Orange County Water District, felt that there are inconsistencies in discussing sustainable water supplies when the consuming organism is not a sustainable resource—that is, its population is not constant.

Mr. Phipps mentioned how for years technology has enabled water supplies to be provided in areas with growing populations, but it is becoming increasingly difficult to continue doing this. He expressed concern that if the world population does not stabilize, it will be impossible to meet water supply needs.

Dr. Hecht agreed that improved use of resources is critical. He went on to say that population impacts water supplies most significantly in areas that are urbanizing rapidly. Currently, he said, Africa is the continent that has the highest rate of urbanization and is the least equipped to deal with it. Finally, Dr. Hecht and Mr. Phipps agreed that addressing the issue of population in some form is a part of the holistic approach necessary to solve the world's water supply needs.

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Green Chemistry: The Impact on Water Quality and Supplies

Dennis J. Hjeresen
Los Alamos National Laboratory and the Green Chemistry Institute

INTRODUCTION

Most experts agree that water will be the next major environmental stress issue, rivaling and perhaps exceeding global climate change for technical and management solutions in the coming decades. The source of the water crisis is simple but exceedingly difficult to address, water resources are finite and the population that depends on those supplies is increasing inexorably. Virtually all of the global environmental impacts attributable to this population growth have ties to or severe impacts on water resources:

- Deforestation resulting from the demand for agricultural land, housing, and fuel
- Loss of biological species in forests and in waters
- Desertification, erosion, and salination of farmland from unsustainable agricultural practices
- Pollution of fresh and marine waters, further depleting food sources
- Introduction of persistent organic pollutants into the ecosystem
- Changing climate with as yet unpredictable changes in the hydrologic cycle having manifestations in flood, drought, sea-level change, and the spread of infectious diseases

Among water issues facing the world today, land-based sources of water pollution are among the most pressing. Adequate supplies of satisfactory-quality water are essential for the natural resources and ecological systems on which all life depends. An estimated 20 percent of the world's freshwater fish and 80 percent of estuarine-dependent fish species, for example, have been pushed to the brink of extinction by contaminated water and loss of or damage to their habitat.

Green chemistry, however, offers a scientifically based set of solutions for protecting water quality. This paper highlights examples of green chemistry approaches to avoiding water pollution.

GREEN CHEMISTRY

In the broadest sense, green chemistry is about preventing upstream pollution. It is the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture, and application of chemical products. It is really a very simple approach that can have profound impacts for more complicated problems. Individuals, organizations, and companies turn to green chemistry for myriad reasons including those outlined below.

Voluntary Alternative

It can be highly beneficial for an organization to do something that is in its best interest as opposed to the rulemaking strategy. Rulemaking has been somewhat effective, but has proven overall to be insufficient. The tendency of other countries such as China is to think that if they just had more regulations, they would be able to improve their water systems. However, more regulations are not always the answer. For example, the Soviet Union on paper had the toughest environmental regulations on the planet, but enforcement was sorely lacking and thus its regulations were essentially ineffective in cleaning up pollution. Green chemistry presents an alternative to the command-and-control approach to environmental protection.

Economics

What has really influenced progress on environmental issues is a closer look at economics. The American business community receives a lot of criticism for its quarterly profit mentality. Yet when companies began looking at their profit sheets, they found that there were two fundamental ways to increase profit: (1) increase your price, but this puts you at a disadvantage relative to your competition, or (2) decrease your cost. Many companies began looking for areas in which they could exercise more control over their costs and found that many of these costs lie in the environmental arena.

Life-cycle analysis (LCA), a tool of green chemistry, is a way of examining the total environmental impact of a product through every step of its life—from obtaining raw materials, through making the product in a factory, selling it in a store, using it in the home, and disposing of it. LCA reveals true waste costs. Companies have wasted a lot of money over the years on waste disposal and waste treatment, not to mention litigation. In looking at these costs, it makes sense that companies began to realize very quickly that control over process efficiency was also a control over cost. Decreasing pollution fundamentally increased profit, so movement into this area happened quickly.

This issue has also emerged internationally. Much of international competition is now based on control over costs: raw materials, labor, regulations, and environmental control. Early on there was a movement to ship a lot of U.S. manufacturing overseas because the laws were less stringent and the labor was less expensive. This is no longer the case.

Incomplete Safety Analysis

There are on the order of 75,000 chemicals manufactured, imported, or in commercial use in the United States according the U.S. Environmental Protection Agency's (EPA) Toxic Substances Control Act Chemical Substance Inventory. About 3,000 of the substances listed are released into the environment every year in quantities of 1 million pounds or more. At the same time, toxicological data on most of the chemicals on the inventory are incomplete and falling behind. The EPA uses eight tests to analyze the safety of chemical substances. About 43 percent of the 75,000 registered chemicals have gone through just one EPA test and only 7 percent have been screened through all eight. The regulatory accountability for manufacturing new and existing chemicals with such incomplete safety analysis has become increasingly problematic for businesses and for the EPA. Safety concerns can thus be addressed through the use of alternative environmentally benign chemical substances.

Limited Regulatory System

In the United States, toxic substance discharges into the environment are fairly well regulated. About 650 chemicals and compounds are registered on the EPA Toxics Release Inventory. In 1999, U.S. toxics releases from 22,639 different facilities totaled about 7.8 billion pounds (3.5 billion kilograms). Releases of toxic substances to surface and injection wells added up to about 540 million pounds in our water supply in 2000 (Table 2.1). Avoiding such discharges in the first place is thus a goal of green chemistry efforts.

TABLE 2.1 Annual U.S. Water Releases to Surface and Injection Wells

Year	Surface Releases	Injection Wells	Total Releases (lbs)
1995	180,516,139	236,194,397	416,700,536
1996	173,288,209	204,329,109	373,617,318
1997	218,371,916	219,513,898	437,885,859
1998	233,365,761	210,639,389	434,005,150
1999	253,591,816	199,547,803	453,139,619
2000	260,882,385	279,036,646	539,919,031

CHEMISTRY AND ENVIRONMENTAL ISSUES

Chemistry has often been seen as a detriment to the environment. The history of the twentieth century was that chemical substances tended to wind up in the environment, typically not intentionally. A good example is the bioaccumulation of persistent organic pollutants in the ecosystem. The original intention of these chemical applications was very good. Over time, however, dealing with the impact of a chemical once it is in the environment is extremely expensive and is less likely to be undertaken.

This legacy is a serious problem, not only for the environment, but for the field of chemistry in general. There are many potential chemistry students who feel that they want to do something important for the environment, but they do not choose chemistry as their primary discipline. The number of students going into chemistry is dropping steadily. If it were not for foreign students coming to the United States for a chemical education, many chemistry departments would be closing down.

It seems all of the bad examples would be sufficient to motivate a change in behavior in the right direction. In many cases, behaviors have changed, but overall there is a relation between chemistry and the environment that really has to be addressed at the upstream level.

ADDRESSING GLOBAL CHALLENGES

As evident from projections by the United Nations, population demands on water resources will continue to climb. For the 4 billion to 7 billion people projected, in addition to supplies of food and water, will there be adequate goods and services? Will there be plastic bags? Will there be floors and ceilings? When this equation of population growth is carried out into the products, goods and services, and rising standard of living that is being demanded, it ties back to what the chemical community has to supply.

On the one hand, this presents a growth market. On the other, by continuing down the path of "pollute first, clean up later," chemistry is really not in a position to help. Chemistry must take a role in providing some alternatives. Leapfrog technology is required because when you look at population growth, the vast majority of it is going to take place in the developing world, not the developed world.

There is an opportunity here to leapfrog technology in the same way that China, Thailand, and India have in telecommunications. Instead of investment in landline phones, it has all gone to cellular. Similar approaches are being taken in chip manufacturing and new industries. Western companies are going into these countries with the latest in environmental technology, which then sets the standards for local production. It does not always catch up right away, but it does.

GREEN CHEMISTRY EXAMPLES

The EPA, along with the National Science Foundation, the National Institute of Standards and Technology, and a number of the other stakeholders, sponsors the annual Presidential Green Chemistry Challenge Awards. Examples of some award winners are presented below and illustrate how chemistry relates to water. The examples given here focus on a holistic approach to water rather than a chemical-by-chemical approach. In general, green chemistry applies to issues far outside the traditional chemical industry.

Oxidative Technologies—Chlorine Alternatives

One of the environmental issues with which many are struggling now is endocrine disruption and the combination of chemicals in the environment in ways that they were not originally released. There are two problems, one having to do with the actual chemicals that cause endocrine disruption and the other relating to chlorine in particular. Approximately 70,000 organochlorine compounds are presently detectable in the environment. The vast majority of these were not produced directly by manufacturing processes. Rather, the majority of them result from the combination of chlorine with other molecules in the environment that has created new chemical species. These new compounds have not been tested for their safety.

The impact of these endocrine disruptors on mammalian and aquatic systems is largely unknown. This is also not something that EPA has the budget to monitor adequately. The result is that a rather large-scale ecological test is being run in real time. However, other issues of industrial waste treatment, water conservation, the marine environment, and particularly agriculture can be addressed that are important to the overall equation of sustainable development.

For example, Terry Collins at Carnegie Mellon University has taken a broad systematic approach to addressing chlorine molecules in the environment. Because chlorine is used predominantly for oxidation, he thought it might be possible to approach the problem overall by seeking out alternative oxidants. One of the great oxidants available is hydrogen peroxide. However, it is not an efficient enough oxidizer for most industrial applications. Over the last few years, Terry Collins and his group have developed the new set of tetraamino macrocyclic ligand (TAML®) catalysts to activate hydrogen peroxide and improve its efficiency.

The TAML catalysts that Collins has developed are now rapidly being commercialized for the replacement of chlorine in a number of oxidation applications, such as pulp and paper, fabric treatment, and disinfection.

This example illustrates one of the key points of green chemistry. That is, for almost any one of the major contaminants being talked about, there are a whole range of industrial applications. Thus, when taking on a problem, the solution can also be applied to a wide range of industrial applications.

By applying this technology broadly, it becomes more cost competitive. Conversely, as the technology becomes cost competitive, it can find more applications. Costs are particularly competitive when the life cycle of disposal and treatment of wastewaters is factored into the equation.

Photographic Chemicals—A Closed-Loop Approach

The ways in which water sources become contaminated are sometimes surprising. Photographic processing, for example, is one of the great "out-of-sight, out-of-mind" sources of water contamination. People across the world send their photographs out for processing each day, quite unaware of the major source of contamination that comes from photographic chemical developer simply dumped down drains. In the United States alone, the amount of photographic development waste adds up to about 1,200 million gallons of water containing 15 million gallons of developer and contaminants such as hydroquinone, ammonia, and silver.

DuPont has come up with a new photographic development system called DuCare™ that addresses this waste issue. With the DuCare system, hydroquinone developer is replaced with erythorbic acid, and 99 percent of the developer and fixer is recycled at a central facility. The chemicals are actually distributed in containers that once used are returned to DuPont for recycling. Thus, not only is the chemistry of the developer replaced, the way in which the photographic chemicals are distributed is as well. Overall, DuPont changed the nature of the business. Instead of just being a chemical supplier, it now provides a valuable service. DuPont came up with a way of delivering fixers and developers to stores that enables elimination of water use and contamination and is great for its bottom line. The only water involved now is what is originally put in the DuPont photographic processing system. Utilization of this system has the potential to the save about 395 million gallons of water per year in the United States alone. Other companies around the world are also working on incorporating this type of closed-loop approach into photographic development.

Industrial Waste Treatment

It is important to think of the scale of the economics being talked about here. The numbers are easy to come by in terms of the chemicals. The United States sells about $3.5 billion in this world market for chemical treatment, but a $5-billion-a-year market in chemicals for water treatment is actually very little. Although, it sounds like a big number, the one underlying it is substantially bigger. In terms of the industrial infrastructure, more than a trillion dollars is being protected from corrosion, from scaling, and from bacterial growth, which are huge economic problems.

When you talk about replacing these chemicals or about avoiding pollution, you have to have an idea of the scale that is being considered. Another Presidential Green Chemistry Challenge Award winner Ondeo Nalco also uses this closed-system approach.

Ondeo Nalco used to be a chemical supplier for water treatment, including chemicals for corrosion, scaling, and bacterial growth. It was quite a lucrative business too. In recent years, however, Ondeo Nalco has taken a very different approach to business. Similar to DuPont, Ondeo Nalco now provides more of a service to its customers rather than merely supplying chemicals. For its customers it provides a systematic analysis of facility use, substitute chemistry to decrease toxicity, and precise control of chemical use. Fundamentally, what has happened is that now Ondeo Nalco sells substantially fewer chemicals, which has reduced the amount of chemicals going out in water. At the same time its profit is high because it has provided an effective service for the purchaser.

Lithographic Technologies—Water Conservation

The next example involves semiconductor fabrication. Semiconductor manufacturing is somewhat deceptive because semiconductor plants do not typically have smokestacks with pollutants billowing out. Also, the industry provides high-paying jobs and other features unlike the manufacturing jobs of the past. However, semiconductor manufacturing plants are essentially chemical factories with electronic output.

The resource intensity of semiconductor manufacturing is enormous. In a recent article (Williams, E.D.; Ayres, R.U.; Heller, M. *Environ. Sci. Technol.* 2002, 36(24); 5504-5510), it was found that 1.7 kg of chemicals and fuels are used to manufacture every 2-g, 32-MB DRAM chip produced. If you just consider water, 32,000 g of water are required for every 2-g chip. However, a lot of the water is recycled in plants and a lot of it is reused, but the water is deionized, which translates into fairly high energy content. There are also 45 g of chemicals used per 2-g chip.

Water is really a huge issue here. The average semiconductor fabrication plant will go through 2 million to 3 million gallons of deionized water a day. Typically the plants are located in semiarid regions of the country (e.g., Austin, TX; Albuquerque, NM; San Jose, CA; and Irvine, CA) that already struggle with water issues. However, this water use has not been much of an issue for the industry because economically the industry could afford it. For example, at its plant in Albuquerque, New Mexico, Intel has bought water rights from farmers up and down the Rio Grande in order to have a sufficient volume of water for its processing. Because of the very high-value product being made, paying such a high price for water was justified.

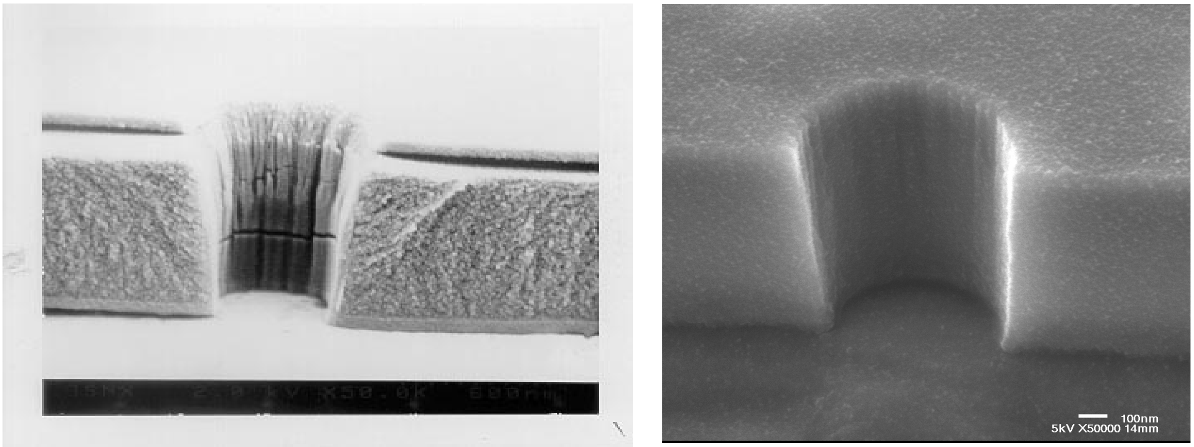
Then something occurred that changed this happy scenario. The industry hit a physics problem. The ratio of the width of features to their depth (aspect ratio) started to cause problems. Water with aqueous chemicals was used to clean the wafers as the chip features were produced. However, as the aspect ratio of the features increased, the high surface tension of the water inhibited it from being able to penetrate between the features. The industry then had to look for alternatives to water for cleaning.

A solution to this problem came out of Los Alamos National Laboratory. It was found that supercritical fluids, especially supercritical CO_2, could be used for cleaning instead of water. This is because in the supercritical state, CO_2 has no surface tension and can penetrate the small spaces with the addition of propylene carbonate, a food additive. Figure 2.1 shows the improved performance of cleaning with supercritical CO_2. This technology has been commercialized, and the supercritical fluid technology has won a Presidential Green Chemistry Challenge Award. Now six other companies are beginning the construction of new equipment for the semiconductor industry to bring this kind of technology to bear. Again, it was a rate-limiting problem, but one of the benefits is that 2 million to 3 million gallons of water a day are available for other uses. Thus, it is important to consider conservation of water resources, as well as reduction of contamination in the equation.

Marine Environment—Anitfoulants

A $4-billion-a-year problem for the shipping industry is marine fouling in coastal water regions. Every ship has this problem of buildup of marine organisms (Figure 2.2). Organisms on ships' surfaces increase drag and fuel costs, but cleaning them off is an expensive process, and takes a ship out of service. The typical approach to this problem has been the use of tributyltin in paint. Tributyltin kills marine organisms, but unfortunately, it also bioaccumulates and becomes toxic to larger organisms. In coastal regions, immune, reproductive, and mutagenic effects in marine organisms are now

A



B

FIGURE 2.1 Comparison of a semiconductor component showing sidewall polymer (A) prior to cleaning, and (B) after cleaning with supercritical CO_2.

quite high. This makes less food available in coastal regions and has led to some very long term impacts.

Rohm and Haas looked at this problem and developed the new Sea-Nine® antifoulant, 4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one (DCOI). The metabolic breakdown products of DCOI are nontoxic and do not bioaccumulate. DCOI is also cost competitive with tributyltin. It thus made sense for shipowners to switch to the less toxic alternative. Adoption of the new antifoulant was also facilitated by the number of international regulations beginning to ban the use of tributyltin. Again, regulation coupled with effective chemistry tools has helped shipowners move to use of the more environmentally friendly alternative and eliminate the use of tributyltin.

Agriculture

At the heart of sustainable development are food and water. It would not be possible to support the current population or that of the future without being able to provide food in a sustainable way. Providing enough food and water has a lot to do with the chemical industry. The chemical revolu-

FIGURE 2.2 Marine fouling a major economic and environmental issue.

tion of the 1950s and 1960s made it possible to grow enough food to sustain the planet's population. The agricultural chemicals industry is big, with $12 billion a year in pesticides alone. That is a fairly healthy dollar figure, but it is not healthy in terms of persistence and bioaccumulation. Really, the environmental movement began with Rachael Carson in the 1950s identifying the pathways of bioaccumulation of dichlorodiphenyltrichloroethane (DDT) in organisms.

Chemistry is going to have a critical role in a sustainable future, but what kind of chemistry will it be? In terms of herbicides and pesticides, they are not a problem for the most part when applied in correct doses in a scientifically responsible way. However, around the world, these chemicals are often mishandled, and proper safety procedures are not followed. Even here in the United States the typical person applying herbicides and pesticides to a lawn does not always read or follow the safety instructions provided.

The issue is how to avoid contamination of the environment in the first place. Over the last few years a number of Presidential Green Chemistry Challenge Awards have gone for agricultural applications and pesticide applications. There are even more examples such as the area of roach protection, ant protection, and other household uses. Companies are going to very different systems of alternative pesticides, including the biomimetic approach. Instead of using a broad-scale neurotoxin to go after a species, more specific targets are being sought.

For example, Dow and Rohm and Haas separately have developed biomimetic pesticides that mimic the hormonal input that causes molting. Insects do not eat when they molt. If they are forced to molt early, they starve to death. These are endocrine hormones that essentially dissipate very quickly in the environment and are also effective in small doses. Thus, instead of having to use large quantities across fields, very small quantities can be used.

Another approach that is somewhat more controversial is the use of genetic engineering. What Eden Biosciences did is essentially study the plant biology. Plants have what can be thought of as the equivalent to an immune system that, when challenged with a disease or by insect infestation, leads to a protein cascade while the plant tries to fight it off. These proteins were identified, and now Eden is engineering them. When they are applied to the plants, increased growth and increased resistance to both disease and drought are obtained.

There are two or three advantages presented by these examples from the green chemistry community. One is that smaller doses are being used, and this means increased worker safety. The UN Food and Agriculture Organization has estimated that 10,000 agricultural workers die annually from pesticide poisoning. There is thus a very good reason to put things on the market that are less harmful, not only to the environment, but to the people who are working in the field. Another great advantage of the examples presented is the decreased water use, not only decreased water contamination.

Donlar Corporation won another award for its polyaspartic acid (PAA), which it uses in disposable diapers and other applications that require absorbents. Now it has also developed an agricultural application of PAA as an absorbent around the roots of plants that creates a sink for water and chemicals. It draws water from the surrounding area into the plant, which means less water use.

SUMMARY

Addressing sustainability issues such as water and food production cannot be a choice between resources or the environment. Instead, there have to be more innovative solutions. Fundamentally, water quality is going to have to be tackled along with water quantity. Desalination can be used to deal with water quantity, but it requires a large use of energy and can lead to significant water contamination. A desalination plant also does not put clean water back into the environment. Concentrated brine is created as part of the process at least in a 2-to-1 ratio, and it takes energy to produce that. For rich countries that have energy surpluses, this is certainly an option. However, for countries with fewer resources, other options are needed.

For example, 70 percent of the water in China is contaminated and unusable for human consumption. This is typical of many developing countries. A lot of contamination is human waste. That can certainly be managed with infrastructure: collection and treatment. However, there is also a lot of industrial waste containing persistent metals and organics that must be avoided from the beginning. Water quantity will not be dramatically increased so water quality must be addressed.

Part of the answer for developing countries therefore is to be able to reuse water repeatedly. Green chemistry is really a viable approach to such global environmental problems. Solutions may come on a process-by-process basis. Each chemist uses processes and develops processes. Part of the issue for the chemical community is how to make environmental design as much a criterion at the development stage of a process or a product as any other factor. If something can be designed to be red, it can be designed to be "green" as well.

In conclusion, green chemistry is a viable approach to global environmental problems. However, success requires an effective and complex blend of technical, social, economic, and political contributions.

DISCUSSION

Adequacy of Green Chemistry Tools

Dave Layton, of Lawrence Livermore National Laboratory, began the discussion by raising concerns about the use of experimental and simulation tools to replace problem chemicals with those that are benign. He felt that it is difficult to anticipate and screen for long-term problems, and that the tools available cannot adequately mimic complex environmental situations, such as contaminants moving from one medium to another.

Dr. Hjeresen agreed that historically it was difficult to look ahead and foresee that something like chlorofluorocarbons would cause ozone depletion. However, he felt that by applying toxicology at the inception of programs rather than as an external regulatory function it may be possible to act preventively.

As an example, Dr. Hjeresen discussed ionic liquids. Early on in the development of ionic liquids, people considered them to be overall environmentally benign. Then researchers started looking at the toxicology of the compounds. Problems were found at the early stages of development, and this enabled new directions to be taken to make truly environmentally benign liquids. Dr. Hjeresen agreed that there of course would be surprises, but that this is no reason not to try the more benign path.

Adequacy of Chemical Industry Voluntary Measures

Jay Means, of Western Michigan University, expressed concern about the adequacy of the chemical industry's voluntary measures. He felt that before looking abroad to international issues it would be necessary to look at home and determine what the political, economic, and social systems would be willing to do or not do. Mr. Means was concerned that these challenges are not being met domestically.

He provided an example of how the Great Lakes have relatively enlightened neighbors in the nation of Canada; and yet decades ago, 43 or so areas of concern were identified that limit the uses of fresh water in the Great Lakes. To date, in both Republican and Democratic administrations, Mr. Means knew of no areas that had been cleaned up.

Mr. Means stated that chemistry and the chemical industry are part of both the problem and the solution and that government can neither look only to a business to regulate itself, nor look only to its own bottom line for the choices it makes to support problem solving.

Mr. Means was concerned in looking at the language put forward earlier, that there is a deep desire to help but not much commitment. He felt that having a deep desire to do something does not translate to action, and a willingness to help suggests that the solution has to come from the ground up. He continued that in many cases these societies, particularly in the international domain, do not have the capability to even begin to raise themselves up.

Further, Mr. Means remarked that given such a situation, it is no wonder that the United States is viewed as the enemy in many of these domains. Thus, bringing chemical technology to some of these countries, in light of their inability to manage even simple systems with their governments and societies, would really be the wrong approach.

Dr. Hjeresen thought that Mr. Means provided some excellent points of discussion for the meeting. He agreed that these are very difficult problems with no simple solution. For example, he said that in the United States alone there are 17 different agencies at the federal level that have something to do with water, even before you get to states, water districts, and others. He said that it is good that everyone has a stake in this, but is bad when you are trying to make a decision. When you are talking about a fixed commodity such as water, he said, a decision always implies that there is some differential parceling of that resource, there is no good political mechanism to address this.

Dr. Hjeresen thought that the world situation is quite different in that there are grades to work with. He discussed the very high level of response in the United States, Western Europe, and Japan, but stated that there is also a middle level in countries that are at a middle level of industrial development where he thinks a technological approach could have a significant impact. There are a lot of people in these countries: China, India, Pakistan, and Brazil. Dr. Hjeresen thinks that targeting the middle state of economic development has the greatest chance of success.

He agreed that poorer areas—villages of Africa or Bangladesh—are where it is necessary to provide clean water at a dollar per person per year, with someone giving them the dollar. That is partially a money issue, a commitment issue, and a human rights issue.

Dr. Hjeresen stated that the chemical community is actually much stronger in that middle range where it is possible to essentially shut off the flow of contaminants from a known factory into a known water supply in a fixed amount of time. This is where he felt that technology could play the greatest role.

He continued that the difficulty with approaches to sustainable development is that it often requires having too many people to make it happen. With the green chemistry approach, you can take a look at everything a chemist does and it becomes more manageable.

Dr. Hjeresen said that he thinks the chemical community has a lot more to add here, that even in the poorest countries there are a lot of things that chemistry can do to make a difference. He continued that it is a daunting problem that cannot be solved all at once.

Life-Cycle Approach

Don Phipps, of the Orange County Water District, suggested that what Dr. Hjeresen proposed is a paradigm shift rather than an outright solution. He agreed that such an approach makes sense because it is impossible to guarantee that anything released to the environment will always remain benign. It is possible, however, to adopt a paradigm to use the best technology available to determine the fate of compounds and track what they do. Mr. Phipps agreed that it is very important that there be a shift from simply looking at the short-term solution—you develop a product that serves a single purpose, move on, and do not worry about what happens after its use—to more of a chemical recycling paradigm.

Dr. Hjeresen agreed that just looking at the life cycle of chemical processes is a very important first step to make.

Business Drivers

Dan Askenaizer, of Montgomery Watson and Harza, was very interested in the examples presented for DuPont and Ondeo Nalco. In regard to the DuPont photographic system he wanted to know more about what influenced DuPont to move in such a direction—what were the drivers? Was it only economics? Also, he wanted to know how this service has worked out for DuPont.

In response, Dr. Hjeresen said that it is often the case that companies venture into such efforts due to being "beaten with a stick." He talked about how the Union Carbide isocyanate disaster in Bhopal, India, significantly impacted the chemical industry, especially in the United States. The event prompted the industry to take action to improve its operations and led people to start thinking more in terms of the triple bottom line of social, economic, and environmental issues.

He continued that such decisions almost always start at the bottom by people looking for a path to do the right thing, but that implementation comes from a champion for the idea at the upper levels of the organization. He said that the biggest problem in general with most organizations is middle management interfering with the flow of such ideas. Once they are implemented, he said, most companies find their efforts to be very successful.

Commenting on the success of DuPont's efforts, Dr. Hjeresen said that he thinks the technology has not penetrated to the degree it would hope for but that this is common with a lot of environmentally benign technologies. However, he gave the example of supercritical CO_2 for semiconductor applications, which has been readily accepted. Supercritical CO_2 for dry cleaning has not been accepted as readily. A number of good products have come out that can replace perchloroethylene as a dry cleaning substitute, with much less contamination of groundwater. However, the only place this has really taken over is on ships and in large cities where a dry cleaner is on the first floor of a building and perchloroethylene fumes reach the upper floors. Also, since California banned the use of perchloroethylene, more and more businesses have started noticing, and the orders for alternative machines shot up.

Dr. Hjeresen concluded that often a combination of regulatory measures and strong economic incentives is necessary to implement voluntary efforts such as those of DuPont and Ondeo Nalco.

Voluntary Versus Command and Control

Jeff Perl, of Chicago Chem, commented further on voluntary approaches versus command and control. He briefly discussed how the 1990 Pollution Prevention Act essentially involved a voluntary action and represented an effort to make that shift happen. Yet because of the legacy of command and control, the water system is used to make money from industry putting water down the drain so the incentive for reducing water use is not there. He wondered if Dr. Hjeresen had any thoughts about how to move more in the direction of a voluntary system and whether perhaps we would be better served by directing some of the metropolitan water funds into industries that reduce their water use.

Dr. Hjeresen felt that the answer is unique to each country, region, or municipality; he said the key, regardless of geographical location, is to address how to appropriately value water. He felt that the intrinsic value of water is underappreciated throughout the world.

3
Methylmercury Contamination of Aquatic Ecosystems: A Widespread Problem with Many Challenges for the Chemical Sciences

David P. Krabbenhoft
U.S. Geological Survey, Water Resources Division

INTRODUCTION

Mercury, as an issue, had a rebirth in the late 1980s, especially in Wisconsin's most precious tourist area, the northern Wisconsin Lake District. More than 50 percent of the fish in the district during that time were contaminated with levels of mercury exceeding those provided in advisories limiting the consumption of fish for certain people. With such a pristine area being contaminated, people became very concerned and wanted some explanation.

In this paper, the development and current understanding of this problem are explored. Two examples are given of current projects that are at the crossroads of politics and policy; both are directly trying to answer the question of just how responsible current emissions are in driving this problem versus historic contamination that now blankets the world's sediments and soils from a legacy of mercury releases.

Mercury Contamination

It is difficult to not currently be aware of this issue. It is on the front page of about every newspaper and magazine, and it is there for a very good reason. Methylmercury formed by bacterial action on ionic mercury (Hg(II)) is far and away the leading environmental contaminant for consumption advisories of fish in the United States, as well as globally. This is because mercury emissions are ubiquitous, and almost no other contaminant bioaccumulates to the extent of methylmercury. Typical bioconcentration factors are a million- to a hundred million-fold more than water concentrations, giving levels of toxicological concern even in the most remote sections of the planet. This makes the issue highly visible today, along with discussion of reducing mercury emissions from coal-burning facilities and compliance with the Clean Air Act and its proposed amendments with the Clear Skies Initiative.

There are direct health effects on humans and fish-eating wildlife from methylmercury contamination of fish. Last year it was found that mercury is, in fact, a major endocrine disrupter and that mercury, specifically methylmercury, is a significant inhibitor of selenium uptake by humans, wildlife, or any invertebrate system. Selenium deficiency can thus come from mercury exposure. In addition, concern has increased about sociocultural damage to people in fish-eating communities whose culture would be affected if they had to switch their food base.

Global Loading Sources

The impacts on the globe from mercury releases before and after industrialization are shown in Figure 3.1. There is three- to ten-fold more mercury now compared to pre-industrialization.

It is not clear how loadings from mining, atmospheric, and other sources compare to each other. Most of the effort for geochemists now lies in trying to understand what controls the availability of various mercury sources once they are released to the environment. It is known that mercury sources cannot be traced back to mercury releases atom for atom. However, it is not known why. That is an area in which the chemical sciences can play a very big role in helping to understand what happens to mercury, especially how it is made biologically available.

Where does mercury come from globally? About a third of the mercury currently released to the world's atmosphere comes directly from human activities. Another third comes from the oceans through photoreduction at the surface and volatilization because mercury is incredibly photosensitive. Speciation changes take place by the hour whether in a lake, a stream, or an ocean and are difficult to study because they depend on time of day and light intensity. For a geochemist this is a big challenge. The third source comes from soil emissions, again, mostly through photoreduction. The ma-

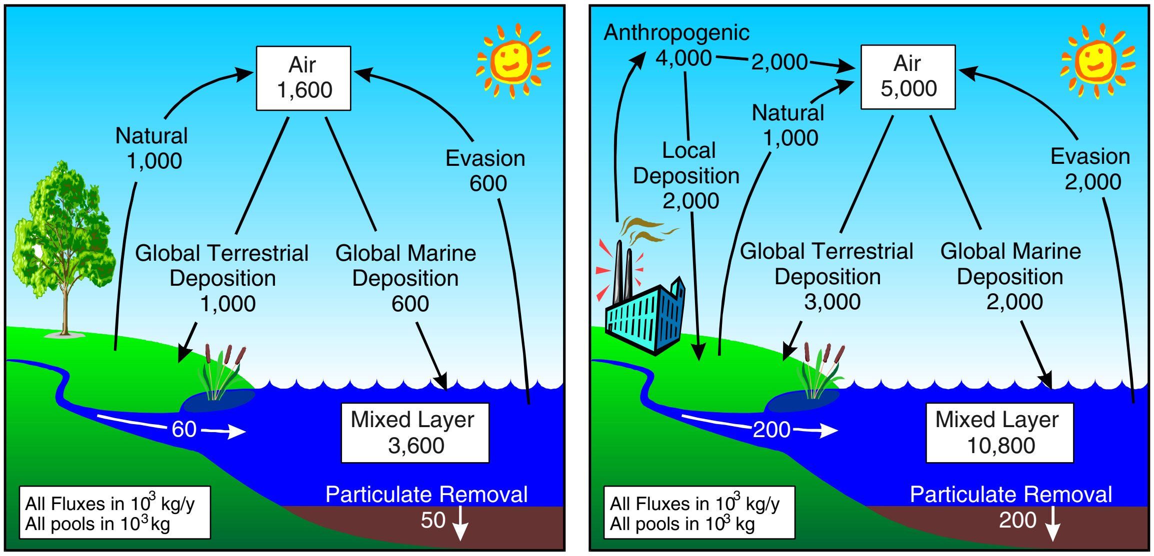


FIGURE 3.1 Pre-industrial (*left*) and current (*right*) global mercury cycle. SOURCE: Adapted from Mason, R. P.; W. F. Fitzgerald; F. M. M. Morel. 1994. The biogeochemical cycling of elemental mercury: Anthropogenic influences, *Geochimica et Cosmochimica Acta*, 58(15): 3191-3198.

jority, then, probably two-thirds of the emissions are actually reemissions of anthropogenic sources of mercury in the oceans and soils of the world. Current efforts are focused on determining how quickly these emissions can be reduced. To do this a better quantitative context is needed for establishing how quickly the world's ecosystems will respond to any proposed mercury emissions reduction strategies.

A number of developing countries, particularly China, are the biggest mercury emitters worldwide, primarily because of their use of energy generated from coal combustion. The use of coal is by far the most significant source of mercury emitted to the atmosphere and for the last decade has contributed to the emission and deposition of an immense amount of mercury into the ecosystems of China. When the third largest reservoir in the world, Three Gorges Dam, is filled, the mercury now present in those areas that are going to be flooded will be methylated at a high rate since the highest-efficiency route to methylate mercury is to flood an area. Many of the people who live on the Yangtze River are fishermen, and they will undoubtedly receive more methylmercury as a result of that dam construction, coupled with the large-scale use of coal in the last decade. Such a result has already been demonstrated in Canada where there were five- to twenty-fold increases in mercury concentrations in fish after the creation of a reservoir.

Modeling

More information is available for the United States than most other countries because a great deal of effort is put into understanding mercury emissions and deposition patterns. Data from the Toxic Release Inventory coupled with an atmospheric mercury model can be used to predict mercury deposition patterns around the United States. It turns out that mercury deposition is as much a function of rainfall patterns in the United States as it is of the actual sources of emissions.

Rainfall amount alone can completely account for the differences observed because the atmosphere is presently never depleted of mercury from rainfall. The amount that can be stripped out from a rainfall event is an infinite pool. There is heterogeneity to the earth's skies, particularly in industrialized areas such as the United States, but the stripping mechanism that brings mercury to the earth, most importantly, is rainfall.

The model suggests that mercury deposition rates differ by up to three orders of magnitude across the United States. It might be on the order of a factor of 10 or so, but the greatest deposition occurs in the eastern United States, where there are more mercury emissions due not only to more incineration and more coal combustion, but also to more rainfall.

Mercury Cycling

It is now known that mercury coming out of stacks is speciated primarily in three different forms: elemental (zerovalent Hg) as a vapor, particulate (organic Hg(II) compounds), and ionic (inorganic Hg(II) compounds, primarily mercuric chloride). Elemental mercury travels around the globe, while particulate mercury is not transported very far and ionic mercury is transported intermediate distances. The ionic form of mercury probably has a significant impact on ecosystems since it is a very soluble species and quickly becomes part of a methylation cycle.

Mercury would not be such a concern if it were not methylated. All of the mercury in consumable fish tissues and just about all vertebrate systems is methylmercury. This is the only form of mercury that bioaccumulates in humans and wildlife, the only form of mercury that crosses the blood-brain barrier where it causes most of its problems, and the only form that accumulates in human neurological tissues. Not only does methylmercury bioaccumulate more once it is in the body, but it can also access areas that elemental mercury cannot. About half of the mercury in humans probably comes from dental fillings, but that inorganic mercury does not get to the more sensitive parts of the body.

It is very important to understand the connection between where methylmercury is produced, where it is absorbed, and its behavior in the body (Figure 3.2). The path from release to the formation of ionic mercury involves photochemical processes, deposition, and then formation of methymercury at the sediment-water interface in most aquatic ecosystems. The primary methylating agents in most of these aquatic ecosystems are sulfate-reducing bacteria, which are ubiquitous in the top centimeter where most sediments transition from aerobic to anaerobic. Sulfate diffuses down from the water just above this area, and if mercury is present, the sulfur will be in the form of Hg(II) compounds such as $HgS(HS)^-$, $Hg(HS)_2$, and $Hg(S_n)HS^-$ that are then converted to methylmercury.[1]

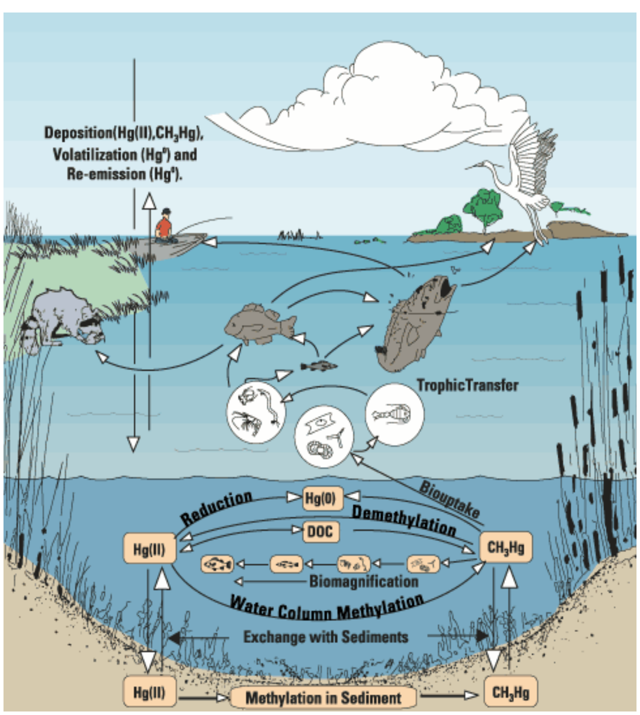


FIGURE 3.2 Aquatic cycling of mercury.

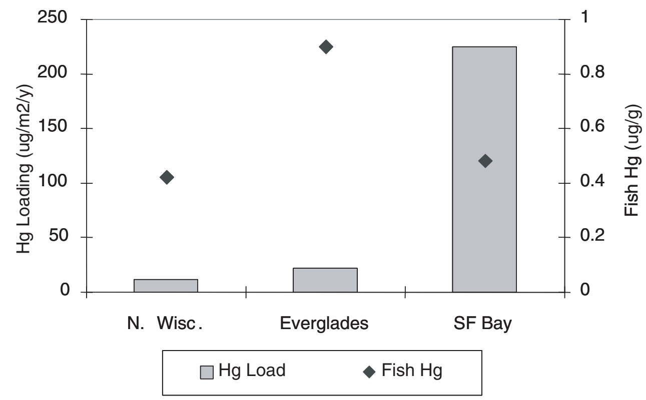


FIGURE 3.3 Relating sources and loading to bioaccumulation—bioavailability is the key.

Mercury Loading and Ecological Restoration

Until 15 years ago, mercury was not considered as much of a problem as it is today. About 27 million pounds of mercury were largely unaccounted for in the Sierra Nevadas from the 1849 Gold Rush in California. That mercury is still making its way out of the Sierra Nevadas through the central valley drainage system and into San Francisco Bay where it is now a very large issue.

Hundreds of tons of mercury currently enter the California bay delta system. At the same time, the bay is slated for a substantial effort of ecological restoration, and the number-one activity for spending money in that ecological restoration is the construction of wetlands. It is now known that the best way to make methylmercury in the environment is to put mercury into wetlands. When this was realized a few years ago, in the San Francisco area, it created a major problem for local, state, and federal agencies.

However, this is not just a case of mercury loading in the water or on land. Figure 3.3 shows estimates of the atmospheric loading rates. The value for Wisconsin is only milligrams per square meter per year anywhere in the state. The riverine load from the Sierras draining the historical contaminated areas of the Gold Rush, by comparison, dwarfs that in Wisconsin.

However, the average mercury concentration in a predator fish or sport fish represented by diamonds in Figure 3.3 is as high for the bay delta of California as it is for northern

[1]F.M.M. Morel, A.M.L. Kraepiel, and Marc Amyot. 1998. The chemical cycle and bioaccumulation of mercury. *Annual Review of Ecology and Systematics*, 29:543-566.

Wisconsin. More effective means than controlling mercury load are thus needed to address mercury toxicity in ecosystems.

EXAMPLES

Ideally, available research findings could prescribe a "safe" level of mercury exposure to ecosystems that would result in an acceptable amount of mercury in fish. However, it is presently not known if "new," recently deposited mercury is what drives mercury levels in fish or if vast pools of "old" mercury currently residing in soils and sediments from decades to centuries of deposition are the driving factor and could sustain the problem for many decades to come. To fill this information gap, researchers are currently conducting two different mercury loading studies in the United States (the Aquatic Cycling of Mercury in the Everglades [ACME] project) and Canada (the Mercury Experiment to Assess Atmospheric Loading in Canada and the United States [METAALICUS] Project), using stable isotopes of mercury that effectively distinguish between new and old mercury.[2]

Aquatic Cycling of Mercury in the Everglades (ACME) Project

The ACME project began in 1995 and has changed tremendously over the last eight years. This is a completely in-field experimental approach to understand mercury cycling processes and is ready to interface directly with the $8 billion Everglades restoration program. This is the largest restoration program ever attempted in the United States, and although it is not intended to make the mercury conditions in the Everglades worse, it may.

The large series of in-field experiments mimic what may happen as a result of restoring this ecosystem. This is being done to see what impact the current approach will have. When a wetland is drained and its soil is oxidized, the wetland cannot be recreated from that soil. Now about 50 percent remains of what was once the Florida Everglades, often described as a "river of grass."

Agricultural Impacts

There are many complicating factors in the attempt to restore this large wetland area, and many come from the Everglades agricultural area. This is a very important vegetable and sugarcane growing area for the United States and is the source of many vegetables in winter.

One of the detrimental actions in the Everglades agricultural area occurs because these former Everglades soils lack free nutrients. To grow crops, farmers must make phosphate available. Because alkaline soils bind all the nutrients, farmers add elemental sulfur by the ton to adjust the soil pH and free the nutrients. Sulfur is converted to sulfate (sulfuric acid) by bacterial action. This feeds the sulfate-reducing bacteria that make methylmercury. As it turns out, it is evident that sulfate additions in this agricultural area have more to do with the methylmercury problem in the Everglades than mercury falling from the sky. Efforts are now being made to work out what the primary controlling set of processes is and the external factors that led to this large problem of mercury contamination in the Everglades.

South Florida is an area with ecosystem-wide postings for mercury, unique to fish consumption advisories for mercury in the United States. Only in South Florida does it say that no one should eat fish. Everywhere else, advisories state that one can eat one fish per month if you are not pregnant or of childbearing age. The eating and catching of fish are curtailed as revenue of hundreds of millions of dollars is being lost because tourists no longer come to fish.

Drainage canals in the agricultural area keep fields from becoming flooded, but they also convey the sulfate put on fields to the Everglades. The result is a 100-mile-long sulfate gradient that runs from the agricultural area just south of Lake Okeechobee all the way down to Everglades National Park. Right now the only way for the national park to be affected by agricultural activities is by short-circuiting the canals, draining nutrients straight down into the park. In fact, this is the first step that was undertaken in the Everglades restoration, opening these floodgates to get water down there as quickly as possible.

Hydrologic Restoration Versus Water Quality Restoration: Sulfates

It has been difficult to express discontent with the approach being used in the hydrologic restoration of the Everglades, which ignores the quality of that water. It is understandable that Everglades National Park people want water as soon as possible; their ecosystem is greatly diminished by the lack of water. Water and appropriate breeding habitat for those fish-eating wading birds that historically were found in great numbers in South Florida are needed for the success of the ecosystem.

However, if water is shunted down there too fast, sulfur is going to be there for a very long time. It will continue to cycle and may eventually get buried, but it is going to have a very long history and cause continuing problems.

Population Impacts

An additional point is that in South Florida presently, there are plans for a very large scale aquifer storage and recovery system to support what is anticipated to be a dou-

[2]For additional details on the ACME project, see *http://sofia.usgs.gov/people/krabbenhoft.html*, and for the METAALICUS project, see *http://www.biology.ualberta.ca/old_site/metaalicus//metaalicus.htm*.

bling of the population over the next 25 years. To meet and integrate with sustainable water development needs, the waters that are being sent into the aquifer will be recovered later, not only for use as drinking water, but also to feed the ecosystem when it needs its water laden with sulfate. Efforts are being made to see just how great an impact this will have in the near future.

Flooding

Flooding previously exposed lands can have a huge impact. Flooding also occurs naturally in the Everglades. Every year, every other year, every third year, depending on whether it is a wet or a dry cycle, the Everglades naturally go through this dry-down and rewetting, moving the whole ecosystem into much, much higher levels of methylmercury, much higher than in environments that remain wet.

To most people in South Florida restoring the Everglades is equivalent to restoring the natural hydrology of the system. Water quality in the Everglades is synonymous with phosphorus abatement, but phosphate has no impact on methylmercury formation.

There are many other chemical concerns in the Everglades that have not been addressed because phosphorus gets all the attention. In South Florida, the hydrologic restoration will call for specifically more wetting and drying, higher high waters, and longer periods of dry-out and oxidation of the soils. As the soils become wet again, it is necessary to know what mercury is the source of the newly formed methylmercury.

Is it mercury already in the soil, derelict contamination, or mercury in rainfall that rewet the system? If it is mercury in rainfall that rewet the system, it is still possible to improve the situation. If it is mercury that is already in the soil, it becomes a much more difficult problem.

By the use of the stable isotopes in experiments in meter-wide tanks (mesocosms), it is possible to distinguish between mercury that has been added and mercury that is already in the ecosystem. It was found that the older mercury is less available to *Gambusia*, the little mosquito fish ubiquitous across the Everglades and a very good biomarker across the system (Figure 3.4). What was observed however is that over this range of loading in the Everglades, there was a very linear and positive relationship between the amount of mercury added and the amount of mercury in the fish. This is mercury added, not remobilized mercury from sediments.

It was very important to establish that, in fact, in contaminated ecosystems there is still a positive response between the amount of mercury that is added and the amount of mercury found in fish.

Mercury Aging

Studies were also carried out to understand the effects of the age of mercury sources on bioavailability. A comparison was made between the percentage of two sources of mercury in fish, one six weeks old (^{200}Hg) and the other six months old (^{202}Hg). The same amount of each mercury isotope was added to the same mesocosm. It was found that six-week-old mercury was three times more prevalent in fish than mercury that was four and a half months older. This is the so-called mercury aging effect. It has been found in the last few years that ecosystems do not cycle old mercury and new mercury equivalently.

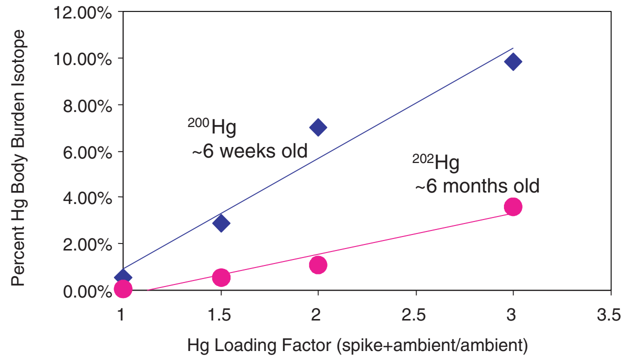


FIGURE 3.4 Bioaccumulation of new versus old mercury by *Gambusia*.

These experiments have been repeated with the same results. In these very same mesocosms—now two years old—fish were gathered again and it is no longer possible to find either one of these isotopes that are still present in sediment. They are seen in sediment, but not in fish.

Mercury accumulation in fish is being driven by new mercury coming in. Now a third isotope can be added and it ends up in fish at the same amount added, but the mercury that gets into sediments is stabilized, probably by reduced sulfur groups in the soils. It does not cycle anywhere near as actively as the new mercury.

Then a series of mixed experiments was conducted and it was found, for example, that adding dissolved organic carbon (DOC) with mercury greatly increased the amount of mercury that became methylated and bioaccumulated in fish.

Low amounts of added sulfate resulted in considerable methylmercury formation. By adding more, sometimes there would be more, but if there is a high amount of sulfate in the mesocosms, methylation is shut down because the bioavailability of the mercury decreases. What does this mean for the Everglades? A series of hypotheses are being tested presently with a model to see whether any of this can be predicted.

It is now believed that if sulfate loads are reduced coming into the ecosystem, the peak of methylmercury formation will be moved further north, but there will still be a zone in which sulfur levels are so high that there will be inhibition. There will also be an optimal zone for methylmercury formation, but the overall size of the peak will be less. Under a restorative flow condition with no attention to water quality, sulfate transport into the system will increase; instead of having just a peak of methylmercury formation in one area, there will be an entire southern Everglades system with high methylmercury levels. This is undesirable.

METAALICUS Project—Ecosystem Level Response to Changes in Mercury Loading

One of the criticisms of the work conducted in the Florida Everglades is that the experiments are run inside meter-wide-diameter cylinders giving "mesocosm effects," with results that are not representative of the surrounding environment. An approach to deal with this criticism is to dose an entire watershed in northwestern Ontario with mercury, and not only do that, but dose a whole watershed with mercury isotopes to answer two questions: (1) What is the true ecosystem-scale response to a change in mercury load, looking at the same time at new versus old mercury? (2) Which is more important at the watershed scale?

The project is known as METAALICUS. The list of participants is very long. It is a large project, and the mercury isotopes alone cost about a million dollars a year, but this is the only way to really answer these questions. The major questions to be answered deal with the ecosystem-level response to a change in mercury loading. Next, it has been stated over and over again that a hundred years of derelict contamination exists in soils and sediments across the globe. Will things improve if mercury emissions are reduced? Third, can the vast sedimentary pools of mercury sustain the problem for very long periods of time? Last, do new and old mercury behave similarly in the environment, and if not, why?

Mercury-202 is being added to the lake; mercury-199 to the wetlands, which are on the western edge of the lake; and mercury-200 to the entire forested catchment. The mercury is added to the wetland and the catchment by a very brave aviator who flies right above the treetops in driving rainstorms (Figure 3.5).

This is being done at a rate of about 20 $\mu g/m^2$ per year; similar to what is seen in the eastern United States. An area that presently gets about 5 µg of mercury is being increased to about 20 µg. It should be noted that the amount of mercury being added to the ecosystem is so small that the best mass spectrometers would not detect it. The added mercury is thus not an environmental concern.

Mercury Aging

It was found that mercury-202 added directly in the lake is methylated at a five to seven times higher rate than native mercury, providing further evidence in a completely different ecosystem (not confined by a cylinder or anything else) to show that new mercury is responsible for the formation of methylmercury. It is not old mercury that has facilitated the problem. This is not to say that old mercury has nothing to do with it, but atom for atom, the old mercury is not nearly as involved.

There continues to be a significant amount of ambient mercury moving off the uplands into the lake, at about 1,500 mg per year. However, almost none of the spike put down it has moved—only about 1 percent. Mercury, when applied to the surface of a green plot, whether it is grassland, wetland, or just a place with plants, tends not to move until it penetrates deeper into the soil, into the humus zone where the great mobilizer of mercury in the environment, dissolved organic carbon, is generated.

Deep Temperate Lake versus South Florida Wetlands

In this project a cohort of yellow perch was followed that were born in the spring of 2001 with no mercury. At the end of their first growing season, the vast majority of the mercury that they had accumulated was ambient mercury not the spike. Even though a four- to five-year pulse was added to the lake, it contributed very little of the mercury in the fish.

Now about a third of the bioaccumulated methylmercury in the second year is coming from the spike. This differs from the situation in the Everglades where both very rapid responses to additions and very quick dissipations of the effect of that new mercury are seen. Here, a deep temperate lake and arboreal ecosystem seem to have longer time lags, which can probably be expected in lake settings across the northern United States and southern Canada.

Next Steps

This project, now in its third year, is going to be a five- to ten-year effort. Thus far, it has been a mercury loading study. The debate in Washington right now centers on the effect of a reduction. The group of scientists that planned this study was thinking about that seven years ago when it was decided that a mercury reduction study cannot be done until a loaded system is available. So the idea all along with this project was to load up an ecosystem in order to be able to watch the response when reduction occurs. This was the last year of additions; next year, the reduction phase and probably the more interesting part of this study starts.

At each site, scientists have observed the same basic processes operating on the added mercury, but at different rates due to the very different environmental conditions—the warm, hot wetlands of the Everglades and the cold, boreal lake in Canada. At both study sites, however, the new mercury gets converted into methylmercury (the most toxic and bioaccumulated form of mercury) more efficiently than the old (Figure 3.5).

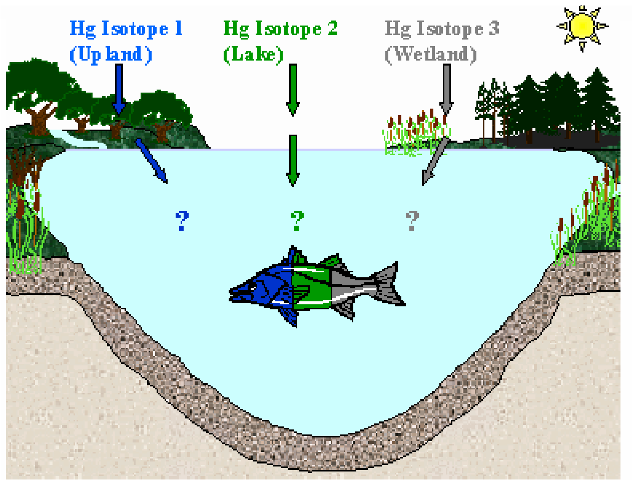


FIGURE 3.5 Movement of mercury isotopes.

DISCUSSION

Incident at Lake Apopka

Tom Dillion, of Science Applications International Corporation, noted that in late 1998 at Lake Apopka in Florida, some mud farms were flooded resulting in the worst bird kill ever. He questioned whether the incident was a result of the mercury phenomenon.

Dr. Krabbenhoft responded that the decline in wading birds got people's attention, and mercury was assumed to be the culprit. Mercury loading studies have been performed on adult birds. It was determined that adult birds have a unique way of dealing with methylmercury; they shunt all their methylmercury straight to their feathers and can withstand almost anything. However, eggs put all the methylmercury into body growth and internal organ development, resulting in a substantial decline in the survival rate of eggs upon exposure to methylmercury. He does not think the Lake Apopka response was methylmercury, although many may disagree.

Policy Implications

Debbie Elcock, of Argonne National Laboratory, requested some conclusions about the policy implications.

Dr. Krabbenhoft replied that there are three ways to deal with the mercury problem: fish consumption advisories, emissions reductions, and landscape management. Unfortunately, fish consumption advisories do not help the wildlife. Emissions reductions will decrease the new mercury available for methylation in the environment; however, old mercury still exists there. For instance, it is necessary to consider whether hydrologic restoration in South Florida needs to move forward more quickly than the water quality restoration. Florida's Governor Bush signed an amendment to the Everglades Forever Act delaying achieving the water quality criteria until 2016 instead of meeting those criteria in two more years. From Dr. Krabbenhoft's vantage point delaying achieving those water quality criteria but continuing with the hydrologic restoration could potentially be a disaster. It might be better if they did not proceed with hydrologic restoration at all until they are comfortable moving ahead with water quality restoration at the same time.

Furthermore, mercury is a concern of the current administration and many federal agencies. The proposed Clear Skies Act and the proposed Clean Air Act have specific emission reduction levels in them, and Dr. Krabbenhoft is not aware of any studies that pinpoint the appropriate level of reduction. He and his colleagues are very curious about where these reduction levels came from.

The United Nations has an environmental program that is also addressing the mercury issue. Two or three meetings have been held in the last year at which mercury was one of the topics. The United States and other U.N. nations are entertaining thoughts of global mercury reductions as a way of addressing the problem.

Alan Hecht, of the White House Council on Environmental Quality (now at the Environmental Protection Agency), commented that engineers are already starting to release water in the marshlands in Iraq to try to restore them. Releasing the water without a look at the chemistry may lead to greater problems down the road. The Everglades is an area that has to be drawn into the policy arena more quickly because actions are being taken that may have unintended consequences.

Dr. Krabbenhoft replied that Iraq has experienced that many times with mercury. About 40 or 50 years ago, the United States sent seeds to Iraq to help them grow wheat. The Iraqis thought the seed would also be a good source of wheat for flour. Unfortunately, labels on the seeds were only printed in English, so the Iraqis could not read that the seed was sterilized with phenylmercuric acetate. Use of the seed for flour resulted in the deaths of thousands of people. He gave this example to illustrate that good intentions sometimes lead to misfortune because of lack of follow-through.

Reactionary Responses

Dennis Hjeresen, of the Green Chemistry Institute, thought it seemed that attention to various chemical contaminants in the environment goes to the "current poster child." In the past, dichlorodiphenyltrichloroethane (DDT) and trichloroethylene (TCE) were focused on, while currently mercury, perchlorates, and nitrates get the attention. However, it does not seem that, within the scientific community, there is a very good way of anticipating, setting priorities, or setting up an infrastructure to study the broader issues. It would appear that many of the biological and ecosystem issues are going to be the same across contaminants, but the money seems to flow only when there is a crisis.

Dr. Krabbenhoft's big breakthrough as a researcher came when the Florida panther died of mercosis in the early 1990s. He said the response occurred because there was a crisis: something as precious and as artful as a Florida panther died of a specific contaminant. He might not have been able to study the problem if a Florida panther had not died.

However, he felt that things may be changing. Some colleagues are now doing research on emerging contaminants, hormones, and pharmaceuticals. In this way, they are working in more of an anticipatory rather than a reactionary framework. However, it is highly unlikely that a researcher will receive funding unless the research can meet a need. Generally, it is more common to react than to prevent.

Water Quality and Supply: Analysis and Treatment

4

Desalination: Limitations and Challenges

Thomas Hinkebein
Sandia National Laboratories

INTRODUCTION

In 2001, Congress directed the Bureau of Reclamation (BOR) to partner with Sandia National Laboratories (SNL) in developing a desalination technology research plan for the United States. BOR has been responsible for the development of desalination in the United States since the 1950s and has great understanding of membrane processes. SNL has expertise in program planning, including roadmapping, and in a number of technologies that are able to advance the science of desalination beyond what membrane sciences are capable of accomplishing. To implement the resulting national program, the participation by all of the national desalination organizations, including the U.S. Geological Survey (USGS), the U.S. Environmental Protection Agency (EPA), water research institutions, manufacturers, and utilities will be needed.

Why think about desalination? There are certainly three factors: drought, climate change, and population growth. The largest parts of the country have very little water: Arizona and Nevada, with their respective 40 and 60 percent growth rates per decade, and Texas, New Mexico, and California are all in dire need of water. The recent persistent drought in the Southwest has only added to the problem.

Problems

How much water is needed? The population of the United States is going to increase 30 percent in the next 20 years, but the problem is worse in certain regions where water shortages are already occurring. The amount of water that has to be added is enough to take a quarter of the outflow of all the Great Lakes: 16 trillion gallons per year (50 million acre-feet), with the amount of water available to the population remaining constant. Water supplies in some areas are also not as abundant as one might think. For example, the water level in Lake Superior, the largest freshwater body in the world, has decreased about 18 inches over the past decade. Thus, there is a great need for sustainable water supplies. One of the consequences of the current state is that water supply will limit growth.

Desalination is a possible solution, but the projected expenditure for desalination equipment and systems has been placed at $15 billion over the next five years and very little R&D is being done to improve this technology. The other problem is that most of the companies that make desalination equipment see incredibly small profit margins, single digit in most cases, with a lot of competition. Most of the big companies that used to be involved have gone out of the business; DuPont for example is no longer in the business of making reverse osmosis (RO) membranes. Other companies are struggling. Currently, desalination projects are funded on a case-by-case basis where 10-40 percent of the actual capital cost to build new desalination plants comes from some kind of government subsidy. A historical look at desalination costs for seawater RO shows that the price has come down an order of magnitude, currently in the range of $2-3 per thousand gallons. Brackish water has shown a similar decrease, down to the $1-1.50 range.

Alternative Cost Scenarios

Two alternative cost scenarios for the development of desalination technology are illustrated in Figure 4.1. The first assumes continued evolutionary improvement in treatment cost resulting from a modest government-sponsored research program centered on improving existing technologies. Concurrent with this research program, government subsidies continue in order to allow utilities to produce water to meet regional growth in demand. The current rate of spending on new desalination capacity in the United States is approximately $1 billion per year, and the current 10-25 percent federal subsidies will result in a substantial federal investment. The second scenario assumes an R&D program to create revolutionary advances to meet a treatment cost target

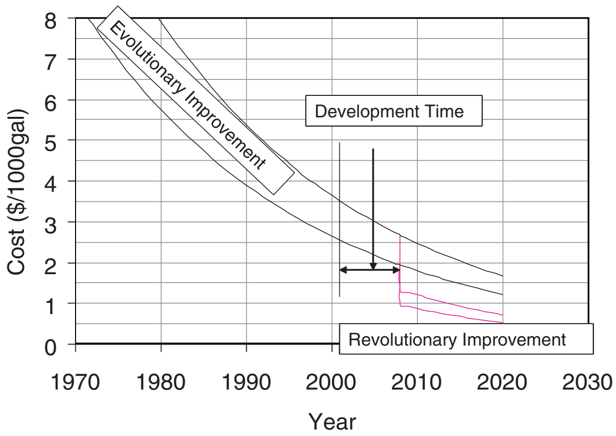


FIGURE 4.1 Projected desalination costs: brackish water, sea water, evolutionary and revolutionary development.

that is comparable to current conventional treatment costs. The cost of conventional water treatment processes declines to about $0.50 per 1,000 gallons.

If a municipality is going to meet growing water demands by using water from impaired sources, rather that nearby unimpaired sources, then the costs must be comparable to conventionally treated water cost. Also, the target price must be achievable, and in the case of desalination, it is. However, it is unlikely to be achieved by the simple extension of currently available membrane technologies. This target is a stretch goal that will require the development of revolutionary technologies. If a reasonable research program is launched, there is hope for some revolutionary kinds of improvements. This is the direction to be followed.

THE ROADMAP

The U.S. Desalination and Water Purification Roadmap is now available on the web (*http://www.sandia.gov/water/docs/RoadmapV21.pdf*) and is the first product of the Roadmap's executive committee. Several smaller meetings and one large meeting were held to arrive at this point in the Roadmap development. Future meetings will involve a more diverse involvement to complement the current work and to arrive at an integrated implementation strategy.

The Roadmap presents a summary of the water supply challenges facing the United States and suggests areas of R&D that may lead to technological solutions (as viewed by the Roadmap committee) to these challenges. This Roadmap is a living document and a process, and updates will be made on a periodic basis to ensure that it remains current and relevant. These updates will have two foci: (1) a management plan that will contain discrete research objectives and priorities and (2) an integrated implementation strategy to address broader issues extending beyond R&D on desalination processes to ensure that new developments can be implemented. The Roadmap helps identify discrete research objectives and priorities, leading to an integrated implementation strategy aimed at solving a very difficult problem—one in which people end up trying to decide what the problem really is and how to deal with it.

The process started with a vision that by 2020, desalination and water purification technologies will contribute significantly to ensuring a safe, sustainable, affordable, and adequate water supply for the Unites States. High-level needs include meeting drinking water standards, meeting agriculture and industry standards, enhancing water security, meeting today's need without compromising our future supplies, providing water in the future at a cost comparable to today's, and ensuring local and regional availability through periods of episodic shortages (droughts).

There are a number of ways to solve the problem—pricing, conservation, a part of the demand equation, and then supply (Figure 4.2). There are management approaches such as trading water from one place to another and having integrated solution approaches. Dams have a huge impact on the way the BOR ends up supplying water to the West. In fact, almost of all of Southern California is based on a water supply that comes from dams and diversions.

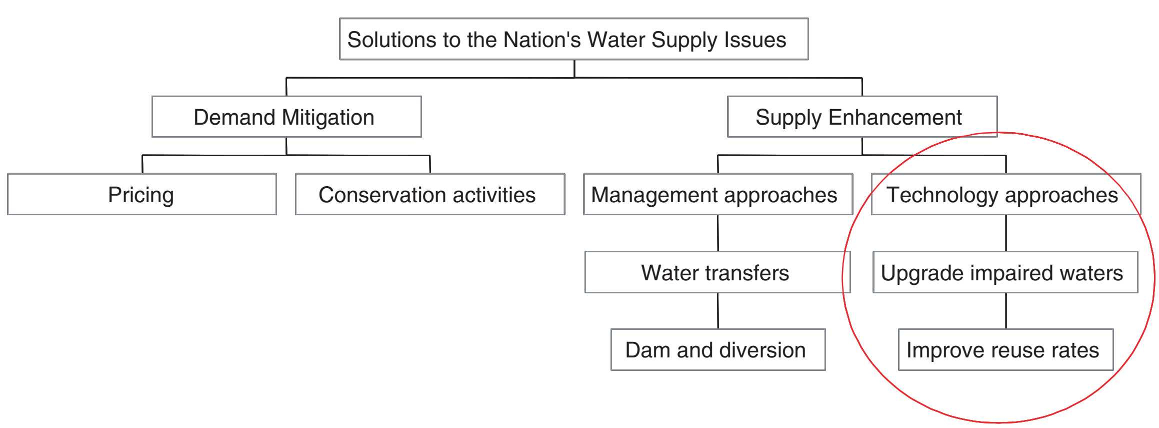


FIGURE 4.2 Hierarchy of the nation's water solution.

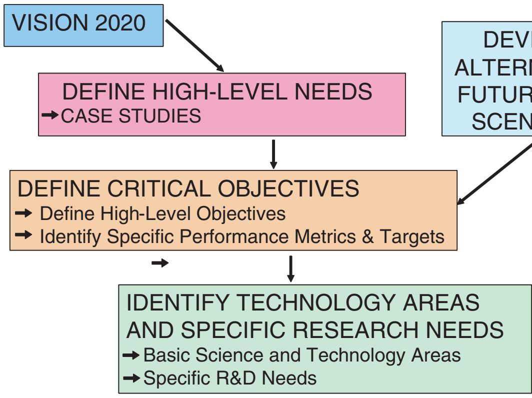


FIGURE 4.3 The architecture of the roadmap process.

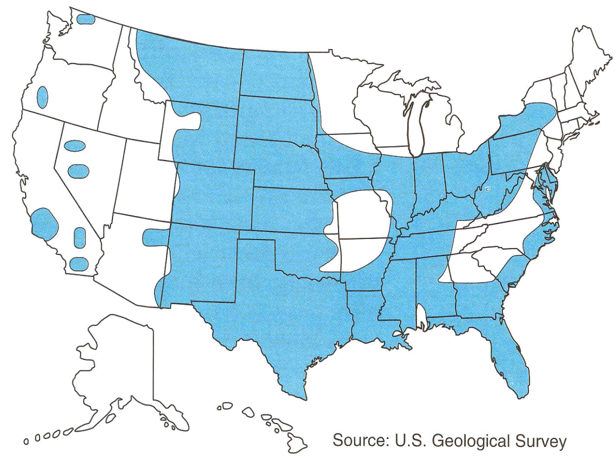


FIGURE 4.4 Potentially usable saline aquifers in inland urban and rural areas.

The focus in the Roadmap is on technology approaches to the problem—ways of upgrading impaired waters and also improving reuse. The technologies involved in both of these activities are very similar, and are captured in the Roadmap. The structure of the Roadmap is outlined in Figure 4.3. It cascades from the vision but really involves an interactive process and defines high-level critical objectives, which are the driving force for the map. The next steps involve defining the technology areas that might be used to solve the problem.

Needs

Based on the challenges outlined in the Roadmap, the desalination needs identified include reducing costs, ensuring the quality of reclaimed saline water, and enabling the disposal of concentrate. Reduction in the cost of the desalination process is especially critical for small towns. In some places, the cost of desalination processes is so high that local communities are unable to have any kind of development. Efforts must also be made to control the amount of organic or biological materials that remain in reclaimed water. Disposal of concentrate is of particular concern to inland cities. In Phoenix, for example, there is a natural inflow of 1 ton of salt per person per day into the valley, but no water that flows out. A possible solution is to develop beneficial uses for the concentrate. Figure 4.4 shows the distribution of saline aquifers in the United States, indicating the need for salt to be managed on a regional basis. Also, if drinking water is to be reclaimed from saline water, there will have to be better understanding of existing problems and better characterization of saline aquifers.

Coastal communities face different desalination challenges. A majority of the U.S. population lives within 60 miles of the coast, and this percentage is growing. Different coastal regions also have varying needs. For example, in Tampa Bay, aquifer replenishment is a major issue. There are 973 people moving to Florida each day. These are new, permanent residents, and the population is growing by almost a thousand people per day. At the same time, the area receives 55 inches of rain a year. Unfortunately, this rainfall is not able to penetrate into the groundwater system and provide an adequate supply of fresh water because of carbonate substrata underneath the ground. Only 10 percent of the water penetrates. The reality is that the Everglades and other areas in Florida are very close to a marginal water environment.

Related to desalination needs also is the need to reduce reliance on surface waters. Around 1970, the amount of groundwater withdrawals in the United States reached its peak. For the past 35 years, there have been no increases in groundwater withdrawals. All of the water added since the mid-1970s has been in surface water. Oil and gas reservoirs and coal bed methane represent huge potential new sources of water. The typical oil and gas or oil field production facility produces seven times as much water as it does oil, which means that there is available water. New Mexico is considering adding some of that water to the Pecos River as a way of meeting interstate compacts between Mexico and Texas. The main issue relative to oil and gas is developing cost-effective pretreatment to deal with small hydrocarbon residuals, again reducing the cost and ensuring water quality standards.

Objectives

Critical objectives are the highest-level milestones defining the targets that a technology must meet by a given time. They are motivated by a specific need, measured by a well-defined metric, and aimed at a specific target. In the Roadmap document, near-term objectives are for 2008, and these were set to extend current technology. Longer-term objectives were set by the Roadmap committee to meet

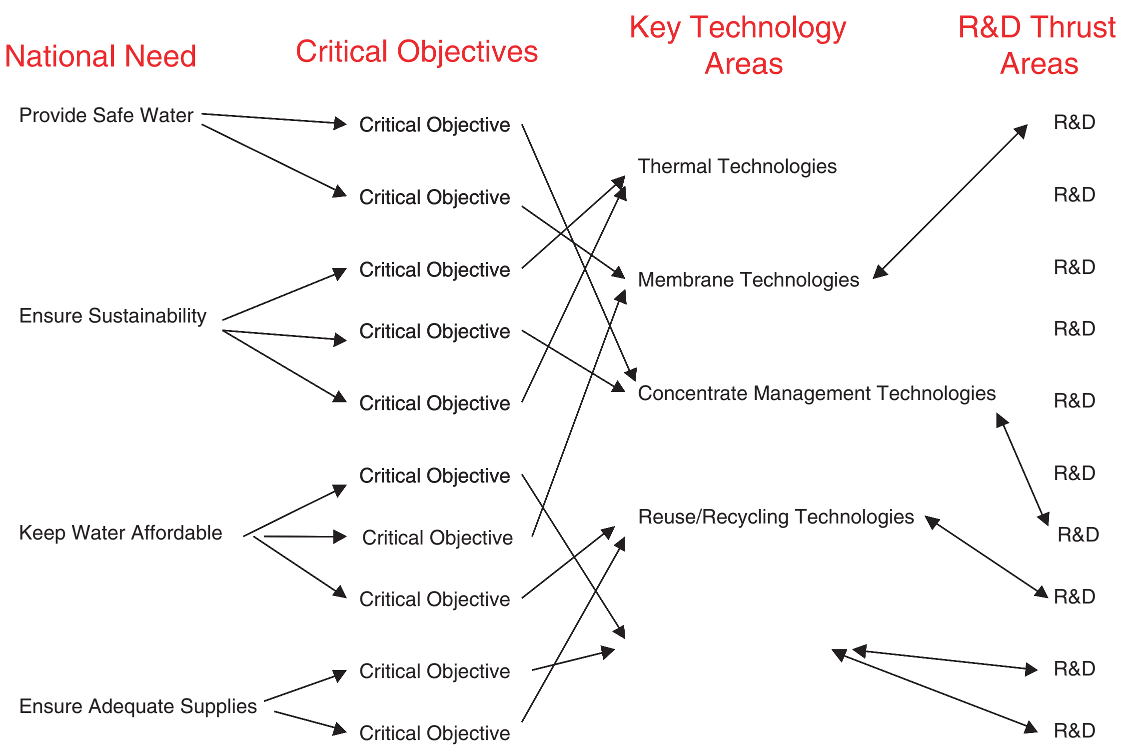


FIGURE 4.5 The Roadmap structure.

longer-term national needs and to end up with ways of meeting the full spectrum of water users.

The Roadmap structure (Figure 4.5) shows the central role that the critical objective plays in the process; critical objectives apply for all of the technologies. For example, the national need to keep water affordable is addressed by critical objectives that provide specific reduction milestones. Examples of near-term critical objectives include a 20 percent reduction in cost, a 20 percent increase in efficiency, and a 20 percent reduction in the cost of zero liquid discharge; all are deemed possible. There is no single "right" way of meeting the metrics for a critical objective—multiple technologies or combinations of technologies may provide radically different solutions that all meet a given metric. Five broad technology areas were identified that encompass the spectrum of desalination technologies and may, individually or in combination, meet a given (or several) critical objectives. Current-generation desalination technologies are drawn from these five technology areas, and it is from these areas that revolutionary, next-generation desalination technologies are expected to emerge.

Figure 4.6 gives the standard breakdown of the costs to treat water; roughly 37 percent of seawater desalination is assigned to fixed charges, and this translates into things such as flux through membranes because that defines the plant size. Electronic power is 44 percent of the cost to treat seawater—one place for a significant amount of improvement. The longer-term critical objectives are much more aggressive.

There are many diagrams in the Roadmap similar to Figure 4.7 that highlight all of the technologies and show their relation to the critical objectives.

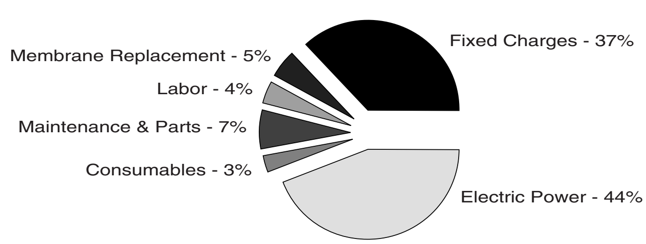


FIGURE 4.6 Standard breakdown of costs to treat water.

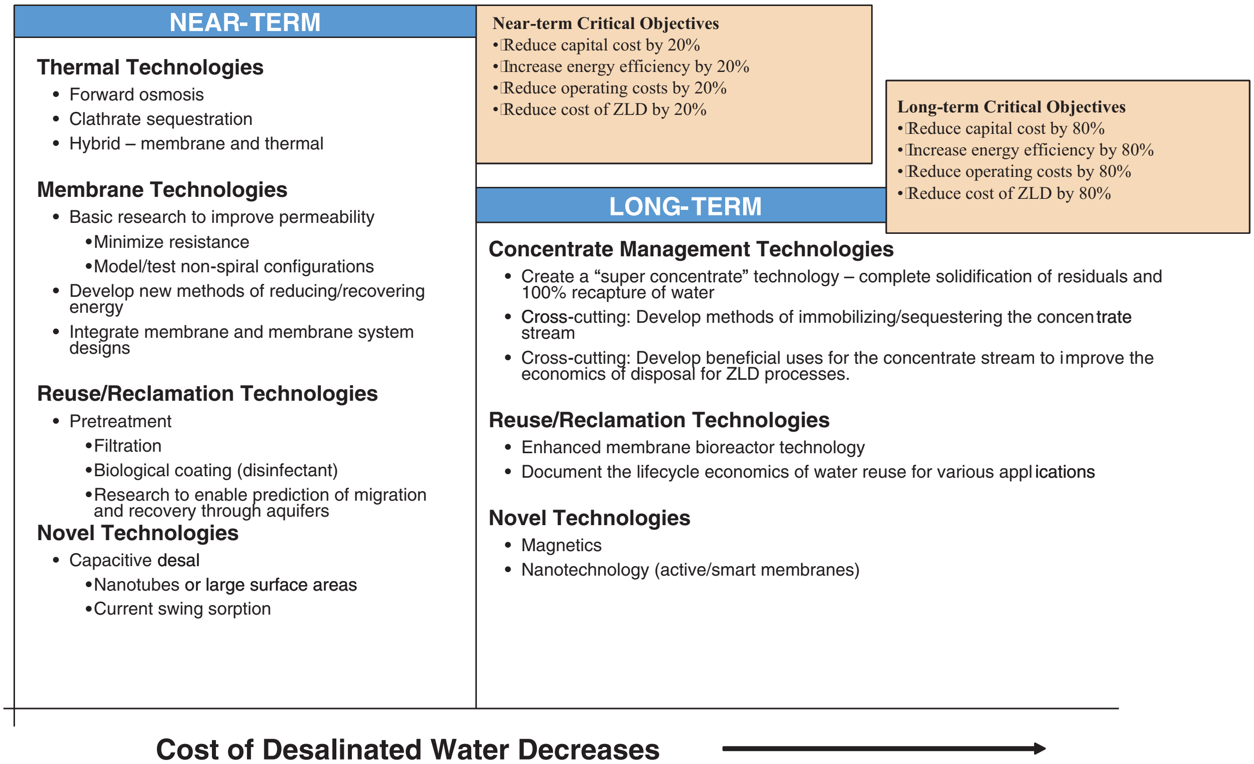


FIGURE 4.7 Technologies related to desalination objectives

Technology

Five technology groupings were identified by the Roadmap executive committee. These groupings are based on historical areas of research. Thermal technologies were invented some 2,000 years ago. Membrane technologies were invented in the 1960s. Research thrust areas for membrane technologies are shown in Box 4.1. Reuse and recycling employ many of the same concepts present in the first two technology areas; however, they are aimed at reclaiming previously used water. Concentrate management is now growing in importance as we realize that disposal of concentrate in many cases is the limiting part of desalination processes. Alternative technologies include any desalination methodology not included in the other areas.

Example Technology: VARI-RO

One solution methodology that was suggested is a variable flow, integrated pumping, and energy recovery system for supplying feedwater to RO membranes, called the VARI-RO (Figure 4.8). Normally, in an RO plant you have to pressurize water to drive it through some membrane. The VARI-RO process seeks to conserve energy by using the return pressure from the RO membrane to assist in powering this piston-driven process. For seawater RO, the input water pressure is about 1,200 psi (pounds per square inch). The discharge pressure from the membrane is 1,150 psi. All RO systems seek to use this energy. The standard method is use of the Pelton wheel. Because of fluid slip, conventional technologies are not completely efficient. The VARI-RO process has fewer losses. In normal operation three pistons operate in sequence and smooth water flow results.

In the integrated pumping and energy recovery (IPER) model, pumps are driven by electric motors and these systems may save 25 percent of the energy cost. In the direct drive engine (DDE) model, the engine is connected directly to the pump and this system is projected to conserve 70 percent of the energy used. Benefits are 25-70 percent energy savings. The IPER model of this unit has been pilot tested, and energy savings have been demonstrated. The DDE version is conceptual, and no model has yet been built.

This particular method for gathering, protecting, or saving a lot of the energy that was originally part of the VARI-RO process has not generated a lot of enthusiasm in the industry because other techniques come very close. As much as 95 percent of the energy that is part of this reject stream is

BOX 4.1
R&D Thrust Areas: Membrane Technologies

Near-Term Thrust Areas

- Mechanistic or fundamental approach to membrane design
  - CFD of feed channel
  - Conduct research to gain understanding of molecular-level effects
  - Design-in permeability
- Develop understanding of whole system (based on current knowledge)
  - Develop model of optimization
  - Research sensitivity of parameters for model
- Develop fundamental understanding of fouling mechanisms to develop indicators
  - Understand how to mitigate fouling (understand biofouling and optimize operational controls)
- Basic research to improve permeability
  - Minimize resistance
  - Model and test nonspiral configurations
- Develop new methods of reducing and recovering energy
- Integrate membrane and membrane system designs

Long-Term Thrust Areas

- Smart membranes
  - Sense contaminant differential across the membrane (in real time); automatically change performance and selectivity
- Sensor development
  - Model compounds for organics, on-line viral analyzer
  - Micro-, in situ, built-in EPS sensor to detect biofilms; particulate fouling sensor
- Membrane research
  - Operate in range of pHs (mechanical and chemical cleaning)
  - Adjust removal capability based on feed water quality and removal needs (2014—pharmaceutical removal based on molecular weight, hydrophilicity)
  - Biofilm-resistant surfaces

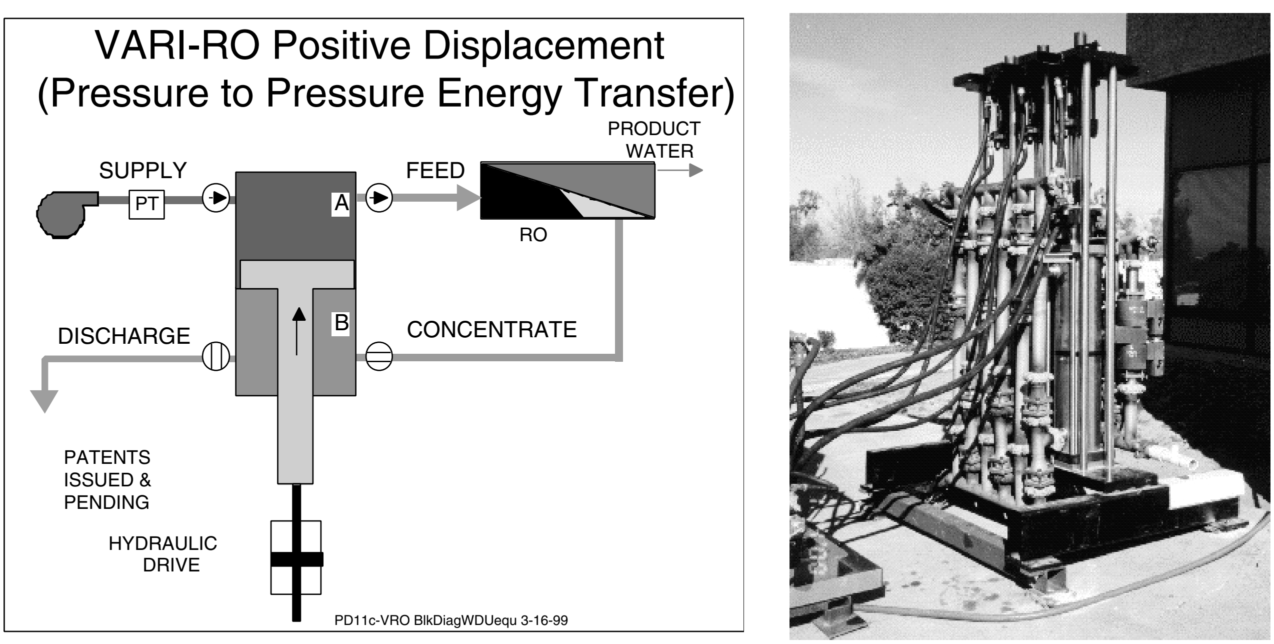


FIGURE 4.8 The VARI-RO positive displacement process and pilot plant.

already recovered. The amount of improvement by this technology is very small. However, another part of this process is interesting. Energy use was 44 percent of the cost, but a large part of that is electrical energy, which is 30 percent more efficient to generate. The idea then is to couple a Brayton cycle engine to this. Instead of an electrical power source, a primary fuel (fossil, hydro, etc.) is used. In using the primary fuel, potential savings could be half of that 44 percent of energy use.

Thermal Technologies

This approach involves a thermal distillation process to produce fresh water from seawater and represents about one-half of the world's installed desalination capacity. R&D thrust areas for thermal technologies are shown in Box 4.2.

One advantage of thermal technologies is that even though a lot of energy is put into them to deal with evaporating water, the potential exists for recovering almost all of it if the waste heat is used. For example, Jim Beckman at Arizona State developed a process in which the evaporating fluid and the condensing fluid are separated by a thin membrane, with intimate transfer of heat from one side to the other. In the chemical engineering sense, there are thousands, if not more, theoretical trays existing in this process with very efficient transfer of heat and the potential for significant energy savings. This particular process might be used for concentrate streams, trying to recover as much of the concentrate left over as possible. In seawater desalination dealing with the concentrate is not such a big issue.

BOX 4.2
R&D Thrust Areas: Thermal Technologies

Near-Term Thrust Areas

- Hybrid—Membrane and thermal to reduce waste stream
- Development of solar ponds for energy and concentrate management
- Enhanced evaporation
- Renewable energy (in small communities)—Geothermal, solar, wind, biomass
- Water harvesting from air
- Membrane distillation
- Forward osmosis

Long-Term Thrust Area

- Clathrate sequestration

Concentrate Management

In concentrate management, one idea is to develop a superconcentrate technology, complete solidification of the residuals, and 100 percent recapture of the water. R&D thrust areas for concentrate management are shown in Box 4.3. The technique that SNL is examining at present is one in which you sequester salts in a nonleachable solid. By adding sodium chloride to the nonleachable solid, a supernatant develops that is clean of salts and has some potential for being applicable in a lot of desert environments under conditions where one must worry what to do with salts.

There are many advantages to this particular process. The solids may be additives that are used as construction materials if they are truly nonleachable. Reactions do occur at ambient conditions. The real problem is one of economics. Any time you use materials for the treatment of a commodity such as water, you must worry about all of the materials that are used.

Alternative Technologies

In alternative technologies, using magnetism is an option. Most are familiar with the idea of electric field-driven transfer of ions. Electric field-driven transfer of ions is a very reasonable option because if you make a separation smaller, there is no limit to the energy requirements. R&D thrust areas for alternative technologies are listed in Box 4.4.

A group at Sciperio has been investigating this alternative approach. The proposed device concept is capable of deionizing any fluid using magnetic fields and their resultant Lorentz forces. This effort is being funded by the Defense Advanced Research Projects Agency (DARPA) and is referred to as the Lorentz Ionic Separation Apparatus (LISA). The Sciperio team estimates that LISA will be able to improve water flux, decrease energy consumption by three- to fivefold, and provide sizable improvements in the ability to process in-line ionic contaminants in the water stream.

RESEARCH PROGRAM STRUCTURE AND IMPLEMENTATION STRATEGY

The diagram in Figure 4.9 illustrates the structure of research and technology development that will be driven by the framework provided by the Roadmap. The structure of a research program that will develop novel technologies must be carefully considered. Using the technology Roadmap as a framework, the sequence of technical qualification of research, followed by laboratory-scale experimentation, then pilot-scale evaluation, and finally demonstration must be carried out for each technology thrust area.

The implementation of novel technologies in a tight financial market requires that any new technology be com-

BOX 4.3
R&D Thrust Areas: Concentrate Management Technologies

Near-Term Thrust Areas
- Develop science-related, concentrate-specific regulations for dispersion modeling of mixing zones and ion imbalance for surface water discharge R&D project
- The biology of salty water, including understanding environmental impacts, using bacteria for beneficial treatment, etc.
- Research into engineered ecology and bioengineering to discover how to engineer disposal so that at least it does not harm ecosystems and, if possible, benefits them
- Natural analogues to current treatment

Long-Term Thrust Areas
- Create a "superconcentrate" technology—complete solidification of residuals and 100 percent recapture of water
- Explore beneficial uses of concentrate including irrigation, farming, solar pond, cooling water, manufacturing, agriculture, repair of dead-end stagnant canals, energy recovery, artificial wetlands, recreations, halophilic irrigation, aquaculture
- Decentralized (point-of-use) treatment and recycling as a way of managing concentrate
- Cross-cutting: develop methods of immobilizing or sequestering the concentrate stream
- Cross-cutting: develop beneficial uses for the concentrate stream to improve the economics of disposal for zero liquid discharge (ZLD) processes

BOX 4.4
R&D Thrust Areas: Alternative Technologies

Near-Term Thrust Areas
- Capacitive desalination
- Nanotubes or large surface areas
- Current swing sorption

Long-Term Thrust Areas
- Biomimetic
- Active membranes, biological sensors/signaling capabilities
- Ion sorption
- Sodium pump, biomimetic
- Advanced membranes, separation
- Porcelain, thin-film, biologic, bioreactors
- Magnetics
- Nanotechnology (active or smart membranes)

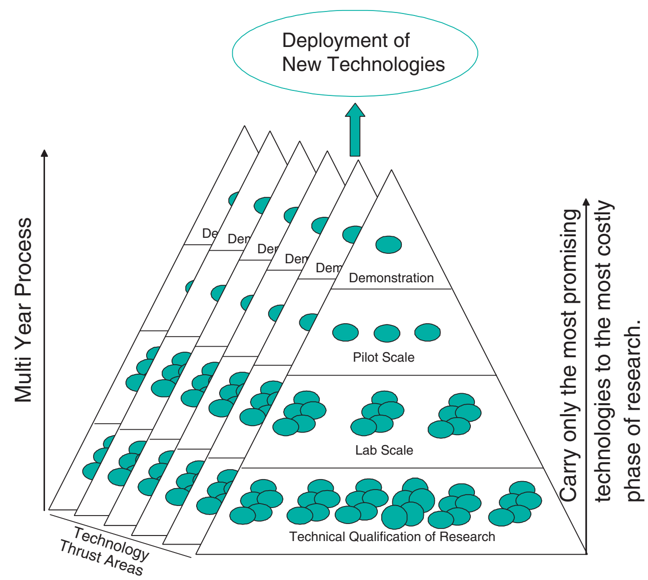


FIGURE 4.9 Structure of the research and technology development.

pletely proven in order to achieve its full deployment. Completely proving a new technology requires that this technology proceed through the demonstration stage. By carrying only the most promising research to the next and more costly levels, a cost-effective research program is constructed.

The other part of desalination that ends up being a problem is that we function in an environment where the rates of return are incredibly small. We have single-digit rates of return for most water utilities. The end result is that when you think about how it is that we are going to get new technologies deployed, you need to, as part of some kind of government program, establish some method of assisting with the deployment of new technologies.

In the low-risk, low-reward environment, there is little driving force for utilities to try field processes on their own. The end result is that the only way you get a lot of new

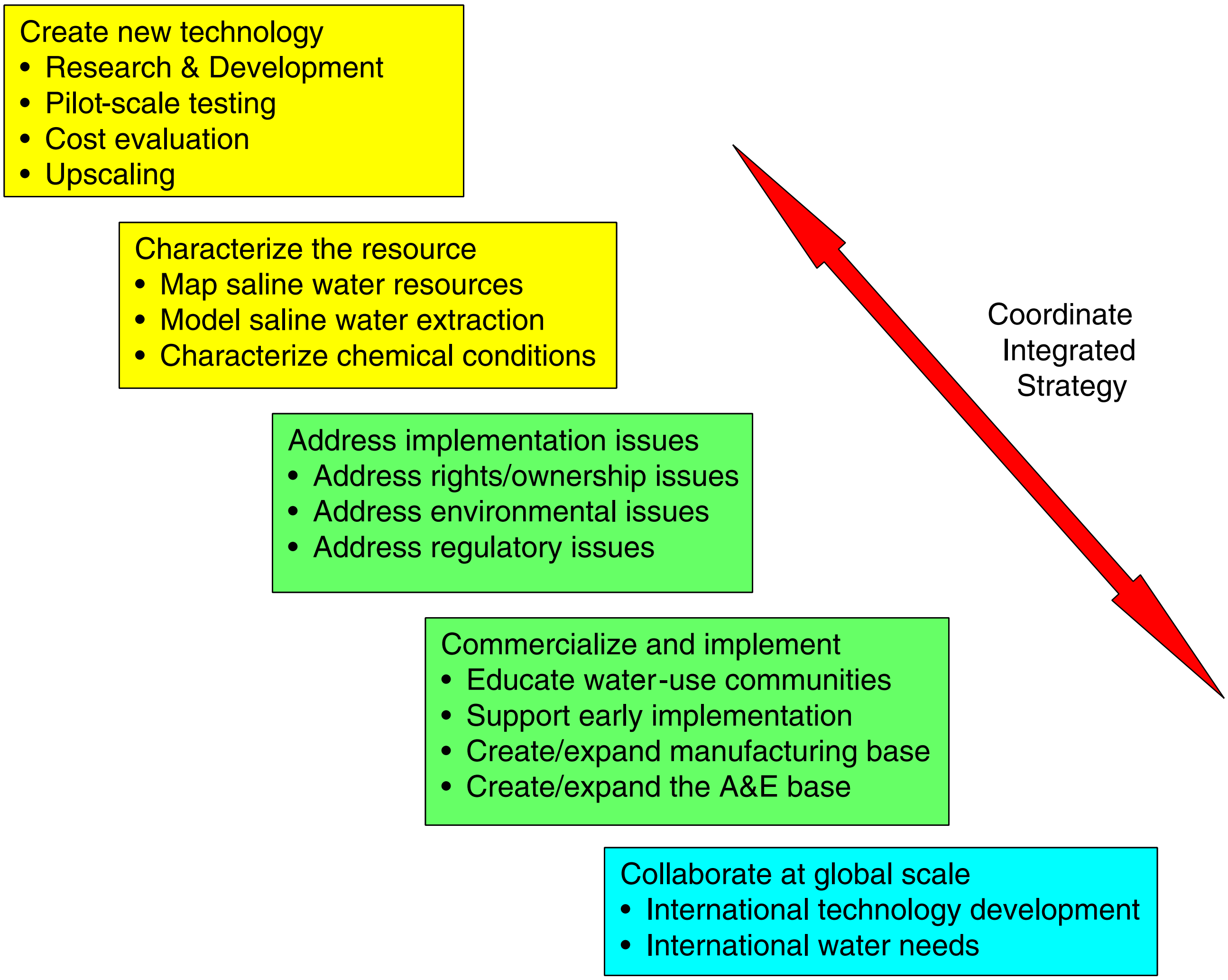


FIGURE 4.10 Integrated implementation strategy

technologies in the field is by having demonstration projects. The program that we have been trying to move forward with the government, with both congressional and administration support, is to have a demonstration facility that actually helps with this high end of moving the technologies to the field, which implies that there is a huge amount of work that goes on underneath that.

Figure 4.10 provides a view of the comprehensive implementation strategy. The Roadmap actually sits in the upper left-hand corner, where new technologies are developed. Activity is also needed that deals with characterizing the resource. Many implementation issues such as owners' rights, states' rights, and regulatory issues must be dealt with. The whole idea of commercializing a new venture requires an additional level of interaction. To deploy any of these strategies on a global scale, they will have to be advanced through the process.

DISCUSSION

Changing Technologies

Don Burland, of the National Science Foundation, remarked that the discontinuity illustrated in Figure 4.1 is caused by changing technologies. He wondered if Dr. Hinkebein knew of any technologies that can bring the trajectory down in that way.

Dr. Hinkebein said such potential future advancements will be in the area of cross-fertilization technologies currently in existence for other applications. These technologies are now being looked at for water applications. He said that broadly examining all separation technologies many lead to solutions for the future.

In particular, Hinkebein thought recent advances in understanding the nanometer scale might bring such improvements. He said that when you start to look at the energy requirements to move water through a RO membrane, there is a minimum amount of energy required. Currently this is only about three to five times the minimum energy in the typical RO membrane. Therefore, there is still room for growth, but the methods to make that growth occur will have to be evolutionary in scope, and not revolutionary.

Dr. Hinkebein also said that with nanotechnology, it becomes possible to move ionic species very small distances. This presents the potential for separating fresh water and concentrate in a different kind of environment where the minimum energy is constrained only by how small the flow field can be made.

Escalating Costs

Tom Dillion, of Science Applications International Corporation (SAIC), wanted to know how the escalating cost of energy might affect the future of this technology.

Dr. Hinkebein replied that if the cost of energy and the state of the environment stay relatively stable, RO could be made more efficient. He said that scenario was presented here. The other scenario is one in which the cost increases as you go forward in time. You try to make the same kind of improvements, recognizing that future costs are not going to look as they do on the continuation scenario.

Disposal Issues

Tom Dillion, of SAIC, was also interested in specific solutions for dealing with brine issues in Southern California.

Relative to concentrate disposal, Dr. Hinkebein said that there are a couple of issues in Southern California. For facilities that are located on the sea, where you have in essence a huge source of saline water and a huge sink of saline water, the primary issues that have to be addressed are the regulatory issues of how to meet the required concentrations and conditions when we send our rejected water back to the sea.

Dr. Hinkebein discussed brine disposal issues from when he worked on the Gulf coast. He said that the EPA required that brine be deposited about 7 miles offshore so that there would be at least 500 m of ocean or water above the point of discharge.

A similar exercise could be done on the West Coast, Dr. Hinkebein said, and it would be at a small cost—slightly higher than the cost of disposal. He said that it would be about a penny additional cost and in the global scheme of things this would be negligible.

RO Implementation

Fareed Salem, of ConocoPhillips, congratulated Dr. Hinkebein on developing the Roadmap. He felt it was greatly needed. He also pointed out that the current status of desalination is due to U.S. government-funded research that started in the 1960s. Mr. Salem said that despite the fact that a lot of RO needs are overseas, he did not feel that other governments, at least those who greatly need this technology, have invested in basic development or in putting together a Roadmap like the one presented here.

Mr. Salem also gave some words of caution about the water industry. He said that it is very conservative and whenever a new technology comes along it takes a long time before it gains acceptance. He said he hoped that equal weight would be given to the implementation of these technologies as well as to the risks associated with the acceptance of newer technologies.

Dr. Hinkebein agreed that barriers exist in implementing and accepting new desalination technologies. He gave an example of an energy recovery system that a company had difficulty placing within continental U.S. boundaries. He said that even though the company demonstrated the effectiveness of the system in field tests and a variety of other applications, no place would take the risk of putting that technology in its plant and no funding was available from the standard mechanisms in the United States. Dr. Hinkebein said the company ended up going offshore to gain the necessary operational experience to bring the technology back to the United States and sell it. He said this is a very common problem, and it is one that is recognized as a huge impediment to getting new technology in the field.

Definition of Desalination

Eli Greenbaum, of Oak Ridge National Laboratory, wanted a clarification of the definition of desalinated water, in terms of percentage salt reduced.

Dr. Hinkebein responded that there are many answers to this question. He said that in general, desalinated water is one that meets the objective or the stated need of the water. For example, if the need is to meet drinking water secondary standards, the secondary standards for sodium chloride are about 500 mg NaCl per liter.

Dr. Greenbaum further wanted to know what percentage reduction that would be from the starting amount.

Dr. Hinkebein said that it depends. If the water source is inland brackish material it would be about 25 percent of the starting point, or in starting with seawater it would be about a 95 percent reduction.

Dr. Greenbaum additionally wanted to know if the factor of three to five in energy that was mentioned early was from the minimum energy of separation (mixing).

Dr. Hinkebein responded that the reduction is from the osmotic pressure that is required to drive the water through the membrane with a certain salt concentration. He said that it depends on the molal concentration of each species in the water.

RO and Power Plants

Tom Torre, of Accumulated Technologies, commented that desalination plants being proposed in San Diego are taking an alternative approach to the disposal issue by working with power plants. He said that this is beneficial for two reasons. The hot water coming from the plant gets used, which means improved efficiency in the RO system, and the amount of concentrate going into the outflow is negligible.

Mr. Torre emphasized that the water business is very conservative. He felt that it would be difficult to get enough return on investment to get private industry to do much. He said that as someone pointed out earlier, it was the situation in Iraq that actually pushed the technology along.

Dr. Hinkebein said that he agreed and explained that this was one of the reasons SNL got involved. As a national issue, SNL recognizes that long-term water supply issues in the United States represent a destabilizing environment in which all of us are functioning now. The destabilizing environment, both inside and outside the country, is something that has to be dealt with to make the world a more stable place. He agreed that the government does not expect private industry to do a lot.

Demonstration Projects

Jeff Perl, of Chicago Chem, supported the need for demonstration projects. He said that it would be difficult to convince anyone to go forward without demonstrated effectiveness and economic viability.

Mr. Perl said that another related area includes turndown ratios using environmental "pump-and-treat" projects. He talked about Dr. Hinkebein mentioning that oil fields have a 7-to-1 turndown ratio and that with pump-and-treat the ratio is infinity to one. He said that essentially all of the water being pumped out of the ground is water with a very small level of contaminants. He said that EPA has a very nice test bed testing program with the Department of Defense (DOD), the Environmental Security Testing Program, and others. He wondered if Dr. Hinkebein had looked at teaming up with the EPA to demonstrate the improvements. He also wanted Dr. Hinkebein to comment on the pump-and-treat water generated.

Dr. Hinkebein responded that relative to teaming with the EPA, the next stage of this process is the development of a strategy that includes pairing up with a number of partners. He said that all of the work that EPA, DOD, and DARPA are doing is definitely part of the issue. The Nuclear Regulatory Commission, Army Corps of Engineers, and others will be among the future partners involved. Probably some of the biggest groups to get involved are industry research foundations such as the American Water Resources Association and National Water Research Institute.

5
Organic Contaminants in the Environment: Challenges for the Water/Environmental Engineering Community

Richard G. Luthy
Stanford University

INTRODUCTION

Hydrophobic organic compounds, such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), bind strongly to sediments. They can thus serve as a long-term source of contaminants in water bodies and biota long after the original source has been removed. Advances in analytical techniques make it possible to measure even the smallest amount of anthropogenic contaminants present in sediment. Yet the ability to relate sediment concentrations to water quality, biological availability, and toxicological effects is hindered by inadequate understanding of the binding and release of the contaminants in sediment. The inherent heterogeneity of sediment makes it difficult to describe in terms of bulk sediment physicochemical parameters such as total organic carbon content, surface area, and particle size distribution. Management of sediments and the control of sediment contaminants are among the most challenging and complex problems faced by environmental engineers and scientists and will become increasingly more so as other organic contaminants enter the environment in greater quantities.

SEDIMENT CHEMISTRY AND BIOUPTAKE

Sediments typically consist of a few weight percent of organic matter and minerals. The organic carbon environment acts as an attractor or accumulator of hydrophobic compounds, such as PCBs. Organic carbon fraction is thus taken as a measure of the sorption capacity for regulatory purposes. This enables normalization of the aqueous equilibrium relationship for sediments containing different amounts of organic carbon. However, organic carbon in sediment comes in different forms that may have very different sorption capacities for hydrophobic organic compounds. In addition to natural sources such as vegetative debris, decayed remains of plants and animals, and humic matter, sediment organic carbon is also derived from particles of coal, coke, charcoal, and soot that are known to have extremely high sorption capacities. A comparison of reported organic carbon-normalized phenanthrene partition coefficients (K_{oc}) for different sorbents is shown in Figure 5.1. These data indicate that hydrophobic organic compounds associated with soot- or coal-type carbon may be orders of magnitude less available in the aqueous phase than those associated with natural organic matter in soils and sediment.

As discussed previously (Ghosh et al., 2003), several groups have carried out work indicating the possible importance of soot carbon in sorption processes. For instance, it was shown that elevated PAH partitioning in sediment samples could be explained on the basis of the soot carbon content and known high PAH sorption capacity of soot. It was concluded that sorption of PAHs on soot-phase carbon in sediments may impact in situ bioavailability of PAHs. It is not clear though from any of the studies conducted whether natural organic matter or black carbon in sediments comprises the predominant repository of hydrophobic contaminants such as PCBs and PAHs. However, in earlier work (Ghosh et al., 2000), it was found from direct analysis of separated fractions and particle-scale microanalysis that the majority of PAHs in sediment are associated with coal-derived particles and that these PAHs are strongly bound, unavailable for biological treatment, and unavailable for uptake in earthworms.

More recently the particle-scale understanding of PCB and PAH distributions in sediments has been extended by comparing sediments from three different geographical locations and by illustrating the effect of PAH association with particle types on bioslurry treatment (Figure 5.2). When sediments were sampled from Hunters Point in San Francisco Bay, an area with high PCB concentrations, the sediment was carefully analyzed and compared with that from the other areas. Once again, coal, char, wood, charcoal, and other carbon-containing compounds were found. It was found that

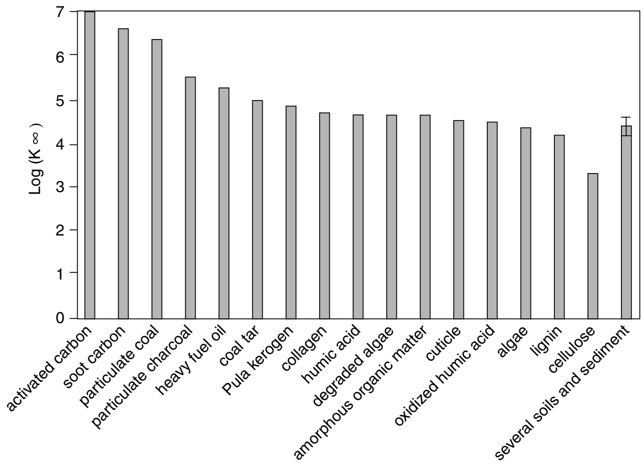


FIGURE 5.1 Organic carbon-normalized partition coefficient for phenanthrene for different types of organic carbon. SOURCE: Ghosh et al. (2003).

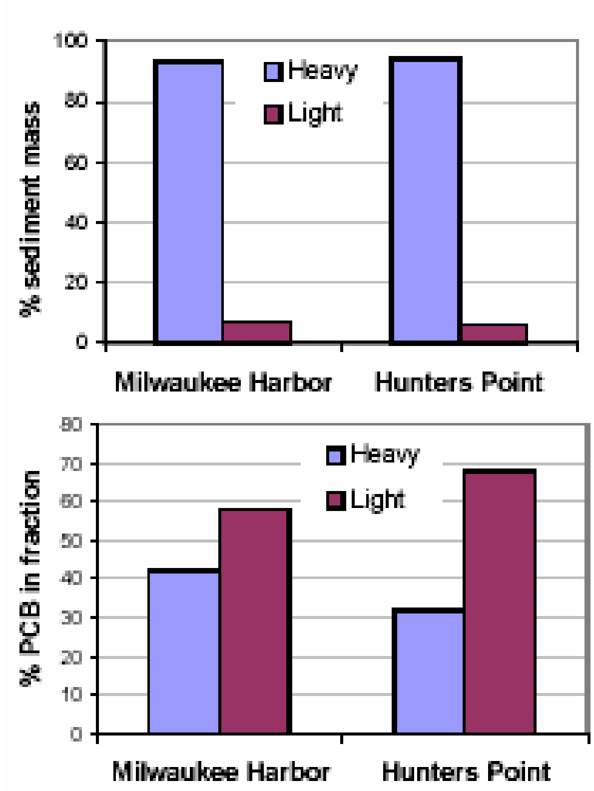


FIGURE 5.2 Distribution of PCBs in sediments.

such material in sediments from the field tended to bind or accumulate PAHs and PCBs (Ghosh et al., 2003).

It was further found that for Milwaukee Harbor and Hunters Point, the lighter-weight coal, charcoal, wood, and particulate organic carbon comprised a small percentage of the sediment; about 5-6 percent (or 7 percent by weight). It was in this small percentage of organic carbon that two-thirds of the PCBs analyzed for were found. It appears that over a period of time perhaps decades, PCBs naturally undergo a repartitioning process to the material in sediment. There is no indication that the PCBs and that material were co-disposed; rather over a long time, PCBs tend to accumulate with this material, strongly bond, and become less bioavailable.

These results suggest a new way of dealing with these contaminants and sediments, taking advantage of an ability to change the chemistry. Perhaps, the bioavailability of these hydrophobic compounds depends on the particle type to which they are bound, and the bioavailability can be changed by adding sorbent carbonaceous particles. Thus, the new strategy is to manage contaminated sediments using in situ stabilization.

ORGANIC SEQUESTRATION AND BIOAVAILABILITY CONTROL

This greater understanding of the interactions of organic contaminant with sediments may enable improved methods of sequestering and controlling the bioavailability of those contaminants. Removal of these contaminants can pose significant problems because such efforts often lead to additional release of contaminants into the aqueous environment. An excellent example of this is Lauritzen Channel, a Superfund site in Richmond Harbor, San Francisco Bay, that was contaminated with DDT (dichlorodiphenyltrichloroethane) over many years. Although the site was dredged as part of a Superfund site cleanup, postremediation monitoring found that unacceptably high levels of pesticides remain in Lauritzen Channel.

One possible approach to more effectively address the presence of organic contaminants in sediments is to change the chemistry of the sediment—not to destroy the compounds in situ, or dig them up and haul them off somewhere else—in order to change the bioavailability of the contaminants. This approach involves adding activated charcoal to sediments to prevent organic contaminants from entering the aqueous environment.

Absorption Efficiency Tests

Activated carbon is used in water treatment, but never before was it thought that adding activated carbon to sediments would achieve any benefit. The effect of activated carbon on sequestration of organic contaminants in sediments was tested here using benthic organisms indigenous to the San Francisco Bay (Figure 5.3). Clams (*Macoma*), worms (*Neanthes*), and arthropods (*Leptocheirus*) were each added to separate, activated, carbon-treated sediment samples from Hunters Point.

The results of the clam tests show that for sediment treated

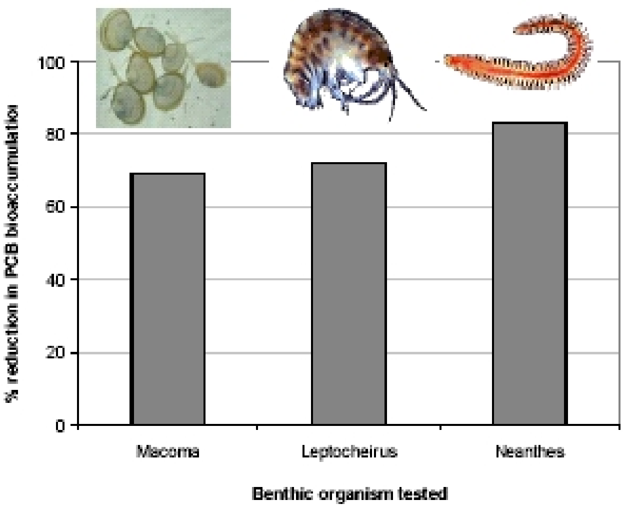


FIGURE 5.3 Species comparison of PCB bioaccumulation reduction.

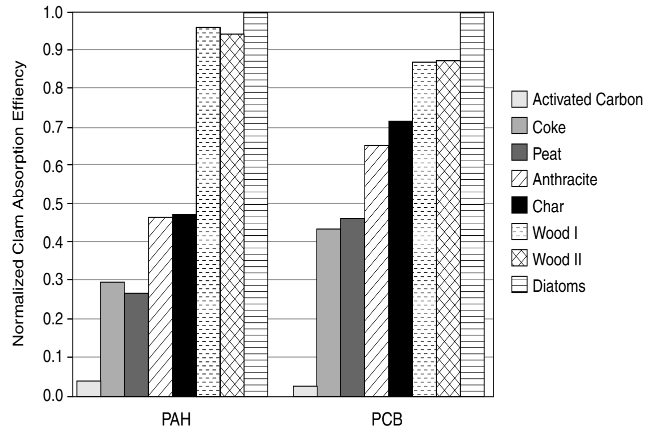


FIGURE 5.4 Clam absorption efficiency.

for one month there was a 69 percent reduction in bioaccumulation of PCBs. This result is quite dramatic and demonstrates that by adding carbon to sediment, PCBs are repartitioned in such a way that they are no longer bioavailable. Similar results were obtained for *Leptocheirus* and *Neanthes*.

In a set of complementary tests, particles with varying amounts of particulate organic carbon were spiked with either benzo[a]pyrene or tetrachloro-PCB and then fed to clams (Figure 5.4). These were short feeding studies in which clams were fed individual particles and then watched to see what was ingested and where the PCB went. That is, the amount of PCB retained versus the amount that passes through the clam is measured. These are called absorption efficiency tests with a PCB or benzo[a]pyrene spiked onto the particle and fed to the clams for eight hours.

In these tests, carbon was ground down to about 20 mm, and clean diatoms were added to mark the start of eating. The clams were fed for eight hours on four separate days. Then a mass balance was calculated to determine how much PCB was retained in the clam and how much appeared in the feces of the clam. When you do that and normalize the data relative to absorption efficiency by diatoms you obtain a relative bioavailability or relevant absorption efficiency. For clams the absolute number was about 90 percent, but diatoms were also measured on every test for consistency from test to test. The results of the benzo[a]pyrene or the tetrachloro-PCB on activated carbon show that when the clam ingested an activated carbon particle with PAH or PCB on it, it passed right through. Only 1-2 percent of the contaminant was retained. This indicates that the bioavailability of the contaminant is negligible.

Aqueous Equilibrium Tests

Figure 5.5 shows the aqueous equilibrium concentrations of PCBs in the presence of sediment from a shipyard in San Francisco that has been either untreated or treated with activated carbon. The results of the study show that after treatment for one month there was about 90 percent reduction in PCB concentration. Thus, the effect seems to be apparent relatively quickly.

A biomimetic device for uptake of contaminants in organism lipids was created from a polyethylene bag filled with fish lipid immersed in a vial containing sediment. The bag was allowed to be in contact with the sediment a period of time. Together with others like it, this is an interesting screening tool and has proven very useful for characterizing

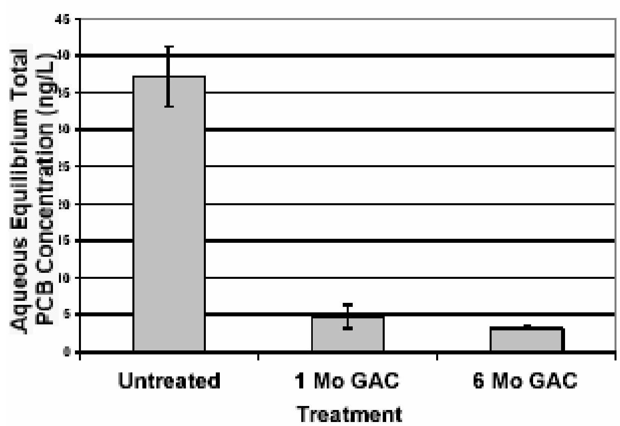


FIGURE 5.5 Aqueous equilibrium tests of PCBs in sediments treated with activated carbon.

TABLE 5.1 Sum of 16 U.S. Environmental Protection Agency Priority Pollutant PAHS, Extractable Oily Matter (Oil and Grease), and Total Organic Carbon Content of Study Lampblack-Impacted Soils and Fisher Lampblack

	Total PAHs (mg/kg)[a]	Oily Matter (wt %)	TOC (wt %)	Lampblack Fraction (wt %)	% of Total PAHs on Lampblack Fraction
Fisher LB	700	0.1		100	100
CA-5	1,410	1.5	14	22	96
CA-2	8,350	4.9	71	65	100
CA-17	12,700	3.9	47[b]	53	95
CA-18	17,600	4.9	50	62	81
CA-10	35,200	9.1	94	84	99

[a]mg/kg soil for the five field soil samples and mg/kg lampblack for the Fisher lampblack.
[b]Reported by Steven B. Hawthorne, University of North Dakota.
SOURCE: Hong et al. (2003).

sediments and natural waters. This study showed that there was a 73-77 percent reduction in the uptake of PCBs with treatment with carbon.

The combined results of all these tests (including some not described here) such as bioaccumulation in three different organisms, aqueous concentration, and absorption efficiency by clams, suggest that it is possible to change the bioavailability of a compound. The next steps are to look at chemistry and bioavailability and the linkages between the microscale (particle) and the macroscale (food web) processes.

LAMPBLACK-IMPACTED SOILS

Another example of contaminant-solid interactions involves recent work (Hong et al., 2003) with California Oil Gas site samples. Before natural gas was distributed in California, gas was made by gasifying oil, and there are many old gas plant sites around the state. The oil would be cracked to obtain methane and a solid residue would remain. Sometimes the residue could be used as fuel and sometimes it was buried on-site.

There are a number of these plants in California, and samples from five different sites were investigated. Large amounts of PAHs were found in this material ranging from thousands to tens of thousands of milligrams per kilogram PAH (Table 5.1).

It was also found that the PAHs vary in their bioavailability. When partitioning studies were done, in looking at what PAHs will be solubilized in water when in contact with some of that material, the lampblack residuals seem to fall into two distinct levels, one high and one low. This is quite interesting because these samples at the low level will pass the California Environmental Protection Agency risk base screening levels for drinking water sources, while the higher level will not.

To determine what was happening, nuclear magnetic resonance (NMR) was used to characterize the lampblack material. NMR data indicated that the material is 100 percent aromatic. It thus will tend to bond PAHs very strongly as long as there is no residual oil. Aromatic oil also comes from this material as long as the concentration is not too high. There thus seems to be a competition between adsorption on the lampblack (high) and absorption on the aromatic oil (low) (Figure 5.6).

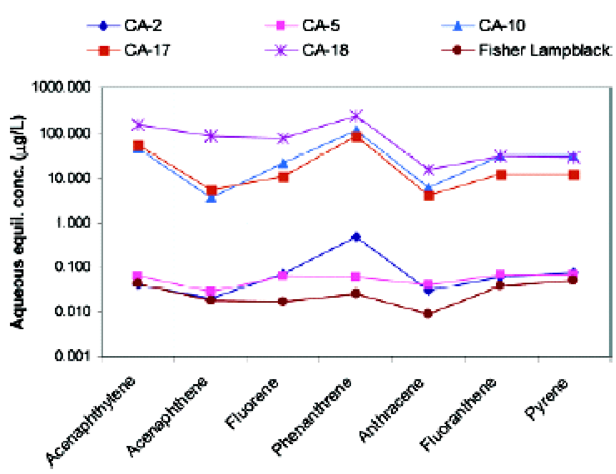


FIGURE 5.6 Aqueous equilibrium concentrations of PAHs for the six study materials as measured by the air-bridge technique. SOURCE: Hong et al. (2003).

BIOAVAILABILITY OF CONTAMINANTS IN SOILS AND SEDIMENTS

To address this bioavailability issue, a committee commissioned by the National Research Council's (NRC's) Water Science and Technology Board undertook a two-year study to understand the bioavailability of contaminants in soils and sediments and released its report entitled *Bioavailability of Contaminants in Soils and Sediments: Processes, Tools, and Applications* (NRC, 2003).

The committee looked at definitions of bioavailability and current use of soil sediment risk management; addressed the physical, chemical, and biological processes comprising the science of bioavailability; assessed measurement tools; and determined how to move forward in regulation.

In terms of the definition of bioavailability, it is thought of as the physical, chemical, and biological processes that affect exposure of organisms to contaminants and uptake of contaminants. Bioavailability processes in soil or sediment include release of a solid-bound contaminant and subsequent transport, direct contact of a bound contaminant, uptake by passage through a membrane, and incorporation into a living system.

One finding from this study was that bioavailability processes are embedded within human health and ecological risk frameworks, but they are often unclear and hidden. These biological processes are physical and chemical and therefore, in principle, can be measured, described, and modeled. This is important because such information leads to mechanistic understanding, and in order to manipulate bioavailability, mechanistic understanding is essential.

Ecological Risk

In order to move the kinds of technologies talked about here for managing sediments into the field, it will be necessary to obtain better mechanistic knowledge at the field scale. This requires expertise of ecologists who know about feeding processes, particle ingestion, and so forth. Quantitative models of fish are also needed to predict the impact of cleaning up at places such as Hunters Point in Alameda, Moffet Field, and Mare Island.

Bioavailability Tools

There are many sophisticated physical, chemical, and biological tools available for the critical analysis of bioavailability. Analytical tools such as X-ray absorption spectroscopy or microscale double laser mass spectrometry have been used to locate and identify PAHs in sediment material. Biological tools are used to evaluate the entry of a contaminant into living organisms without measuring processes A-C. However, the NRC committee's view of this was that there is little consensus about optimal approaches for measuring bioavailability. The absorption efficiency test described earlier is mechanistic and is a controlled experiment. It provides useful information, but it still must be validated with field materials. Thus, each kind of test will have its limitations. In the committee's report (NRC, 2003), a table is provided that specifies generic strengths and limitations of many of the currently available tools. The criteria used to evaluate the tools reflect the committee's opinion that mechanistic approaches (which determine the form and associations of a contaminant) have the greatest potential for ultimately defining bioavailability processes and narrowing uncertainties.

The regulators and industry, on the other hand, tend to prefer simplified operational tests such as extractions which are shortcuts that study mechanistic processes (e.g., equilibrium partitioning) or estimate bioavailability indirectly (e.g., toxicity bioassays). However, these tests lack explanatory capability and have limited applicability. What is needed are mechanistic approaches that will elucidate contaminant form and association.

However, mechanistic approaches are less applicable at present. The way to build consensus on methods to measure reduction of bioavailability, as demonstrated earlier, is to follow multiple lines of evidence that will help us move forward and eventually lead to pilot studies (i.e., adaptive management). The NRC (2003) committee on bioavailability is a proponent of adaptive management, experimenting with tools and models. The committee did not recommend a national policy, but rather recommended that various experiments be tried in the field and those results used to develop a common systematic approach. Investment is necessary to gain this kind of mechanistic understanding and models.

ROLE OF REGULATORS

During the work carried out and presented in this paper, it was very important to work closely with the EPA, the California Department of Toxic Substance Control, and the Regional Water Quality Control Board from the beginning. On the sediment work at Hunters Point, all of these groups are advised on the studies taking place. It is important to ask regulatory agencies what they think about the tests being conducted. Is something being overlooked? Some things might appear interesting to a professor, but one might be missing something that would be a "show stopper."

CONCLUSION

In the end it all comes back to chemistry. Chemistry plays a central role in all that has been described here. Chemistry has to go along with engineering, geosciences, biology, and toxicology. In order to reckon with and make progress on these complex problems such as PCBs in San Francisco Bay, this convergence of disciplines is essential.

ACKNOWLEDGMENT

Stanford University is fortunate to have support from the Department of Defense (DOD) and others who have contributed to this work.

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DISCUSSION

Hudson River Cleanup

Parry Norling, of RAND (now at the Chemical Heritage Foundation), asked if Dr. Luthy's research can be used to reverse the decision or to modify what will be done for cleanup of the Hudson River.

Dr. Luthy thinks that some experiments could certainly be carried out. There will be some hot spots in the Hudson that should be removed, and there is also a lot of sediment with low concentration of PCBs, where his research will probably play a big role. The approach will be to supplement what is done now, remove the hot spots, and then use his strategy afterwards or in conjunction with some capping. He thinks the strategy to dig up the Hudson and put it on the shore nearby communities such as Troy, New York, that do not want it will not achieve a desirable result.

Physical Transport Processes

Tim Shaw, of the University of South Carolina, congratulated Dr. Luthy on his nice work. Mr. Shaw liked the idea of adding the mediating compounds but wondered if physical transport processes have been examined. One of the big potential problems with this would be if the mediating compound was transported separately from the fine-grain sediments that contain the contaminants.

Dr. Luthy agreed and noted that the question is along the lines of what the hydrodynamics are and how one would get the compounds down there and make them work in the field. In a place like Hunters Point, people think that a certain size particle would be needed that would have some hydrodynamic characteristics similar to the material that is present there. It seems plausible that if hydrophobic organic compounds were put in an inch or two of sediment, they would not move. If there was clearly a high-energy site; however, these particles would be flushed away. There are some exceptions such as Seaplain in Alameda, where it is quiescent, in which the compounds could probably just be thrown in there. The behavior of the particles is very important, however, in most cases.

At a sediment conference in San Diego in April, some people from EPA were interested in adding to caps, putting clean sand down on top of the contaminated sediments. Along this line, activated carbon could be added to the sand and then there would not only be a diffusion barrier, but an active trap as well.

Removal of PCBs

Tom Troyer, of King Lee Technologies, said that PCBs are very hard to destroy. Now that it is better known where they are sequestered, he wondered if this leads to any possibility of using in situ destruction.

Dr. Luthy said that PCBs would be attracted to the carbon, and if iron were present it could reduce PCBs through reductive dehalogenation, and perhaps convert them to biphenyl, which would be degraded. He was not sure if the process would work in situ or if other things would compete with the zerovalent iron. He also wondered whether this might affect any really slow process of biological dehalogenation through microbes.

Tom Dillion, of Science Applications International Corporation, stated that he was involved about 25 years ago in a government program to remediate very low level radioactively contaminated sites. The program's issue was removal or stabilization. Typically, the stabilization would cut the health effects by a thousand compared to removal and was somewhere between a hundred thousand and a million times more cost-effective. However, removal was always chosen.

Dr. Luthy responded that this is why it is important to get people like Ned Black and Fred Hetzel from the regulatory agencies engaged early on. Ned Black of the biological technical assistance group at EPA Region 9 has told him that nobody wants the PCBs there and yet they do not want them removed either. Dr. Luthy said that once dredging is started, it can create a big mess and become impossible to deal with.

DDT-Contaminated Sites

Vasilios Manousiouthakis, of the University of California at Los Angeles, asked Dr. Luthy to comment on the effectiveness of similar approaches for DDT-contaminated sites, such as the one in Palos Verdes.

Dr. Luthy did not know about Palos Verdes but stated that his group is now working on the Richmond channel. Richmond is a place where there was dredged DDT-contaminated sediment, new sand, and then new contaminated material on top of that. The chemistries of PCBs and DDT are not very different. DDT will undergo a slight transformation, but basically it is a hydrophobic compound and will probably be affected like PCBs.

Kinetics

Don Phipps, of the Orange County Water District, asked if the kinetics of absorption were relatively rapid and also wondered if one could consider building or using this material in a pillow-type format that could be put in contact with the sediments. The material would take up PCBs slowly and after a period of time could be replaced and recycled.

Dr. Luthy responded that mats can be put down but he has not investigated this area. In the work that his group has done, modeling shows that there are kinetics of uptake by carbon and diffusion through pore water. When things are well mixed, the release from the particles is limiting. There is a rapid release from the mineral fraction, but there is also coal and other material there. It will transfer to the carbon, like a solid-phase diffusion process.

Mr. Phipps pointed out that it may not be really practical to have this diffusion over a large area, but in a fairly small region the contamination is by diffusion into the water. If contamination is over a large area it may be possible to build a renewable cap and then slowly recover it that way. It would be like digging up the sediments without actually digging them up.

Carbon Treatment Concentration

Mark Matsumoto, of the University of California at Riverside, asked why only one concentration of carbon was used and if there is any way to determine the differences in the way the sediment and the activated carbon capture the contaminants..

Dr. Luthy said he started this work with support from DOD and some from Forbes, Stanford, and the Bioex Program. The first part of this work was to show that it is not harmful and that it is effective. For the starting dose of carbon, his group decided to double the total organic content (TOC) of the sediment.

In current work, they are halving and even going to a tenth of what they previously used. What the modeling shows is that if half this dose of carbon is set equal to the TOC, essentially the same results are obtained. When about a tenth of this dose is used with this sediment, higher concentrations result, approximately 1 percent by weight.

Steve Cabaniss, of the University of New Mexico, asked why the modeling shows that going to one-tenth will result in higher aqueous concentration.

Dr. Luthy replied that a higher concentration is being put on the carbon per unit weight. If it is sent to an absorption isotherm, higher concentrations of carbon yield higher aqueous concentrations. The capacity of carbon has not been exceeded, but more is put on the carbon per unit weight.

Fouling

Jay Means, of Western Michigan University, asked if Dr. Luthy had looked at any change in the efficiency of transfer as a function of fouling with biological films.

Dr. Luthy responded that his group has done studies for as long as six months and found that fouling improved with time. There would be other issues if other materials in the sediment could absorb and displace PCBs. This carbon will probably pick up some humic molecules from the sediment and become sticky or gummy, slowing any further uptake as seen in water treatment. He said it takes a long time for this to appear in water treatment.

6

AquaSentinel℠: Biosensors for Rapid Monitoring of Primary-Source Drinking Water

Elias Greenbaum [1]
Oak Ridge National Laboratory

INTRODUCTION

Most of the phytoplankton present in surface waters is composed of algae (Palmer, 1959). The diversity of responses or adaptations to changes in light intensity observed in microalgae suggests that these microorganisms are able to live in a variety of habitats. Seasonal changes in the available light habitats are related to seasonal algal succession patterns (Richardson et al., 1983).

Chlorophyll *a* fluorescence induction curves reflect the efficiency of energy conversion in Photosystem II (PS II) reaction centers (Krause and Weis, 1991). As a result, they can be used as indicators of the physiological state of algal cells. The ratio of variable to maximal fluorescence (F_v/F_{max}), defined as the maximal fluorescence minus the minimal fluorescence divided by the maximal fluoroscence ($(F_{max}-F_s)/F_{max}$), is equal to the quantum yield of Photosystem II. It can be calculated from fluorescence induction curves of photosynthetic tissue that is illuminated by a saturating flash of light (Schreiber et al., 1994; Falkowski and Raven, 1997).

Since the introduction of the pulse amplitude modulation (PAM) measuring technique and the saturation pulse method in 1986 (Schreiber et al., 1986, 2002), chlorophyll fluorescence parameters have been very useful in ecotoxicological studies. Very recently, a dual-channel chlorophyll fluorometer called the ToxY-PAM was introduced for the detection of toxic substances in water (Schreiber et al., 2002). The authors reported detection of the urea-based herbicide Diuron in very small concentrations. The sensitivity was below the 0.1-µg/L detection limit for a single toxic substance in water as specified by the European Commission drinking water regulation.

The purpose of this paper is to describe proof-of-principle experiments that led to AquaSentinel, a continuous water monitoring system in the field of homeland security. The system uses naturally occurring photosynthetic microorganisms as biosensors for the detection of chemical antagonists in primary-source drinking water. Among the toxic compounds tested were potassium cyanide (KCN), methyl parathion (MPt), Diuron (DCMU), and Paraquat. Hydrogen cyanide has an odor characteristic of bitter almonds and is completely miscible in water. In this study, the water-soluble salt KCN was used. The cyanide ion is an extremely toxic and fast-acting poison. MPt is an organophosphorus insecticide and a cholinesterase inhibitor that is structurally and functionally similar to the chemical warfare agents classified as nerve agents. Severe exposure of humans and animals can lead to convulsions, unconsciousness, cardiac arrest, and death. DCMU is a substituted urea-based herbicide. It is a nonionic compound with moderate water solubility. The U.S. Environmental Protection Agency has ranked DCMU fairly high (i.e., as a Priority B chemical) with respect to potential for groundwater contamination. Paraquat is a herbicide that is highly soluble in water. Death is usually due to progressive pulmonary fibrosis and epithelial proliferation in the lungs (Guidelines for Canadian Drinking Water Quality, 1996).

EXPERIMENTAL

Studies were performed using “as-is” freshwater samples and their naturally occurring populations of phytoplankton.

Fluorescence Measurements and Toxic Agents

Figure 6.1 illustrates the successive stages of data acquisition and analysis for fluorescence induction curves by

[1]Contributing authors include: Miguel Rodriguez, Jr., of Oak Ridge National Laboratory (ORNL) and Charlene A. Sanders of ORNL and the Genome Science and Technology Program, Center for Energy and Environmental Biotechnology, University of Tennessee (UT)-Knoxville.

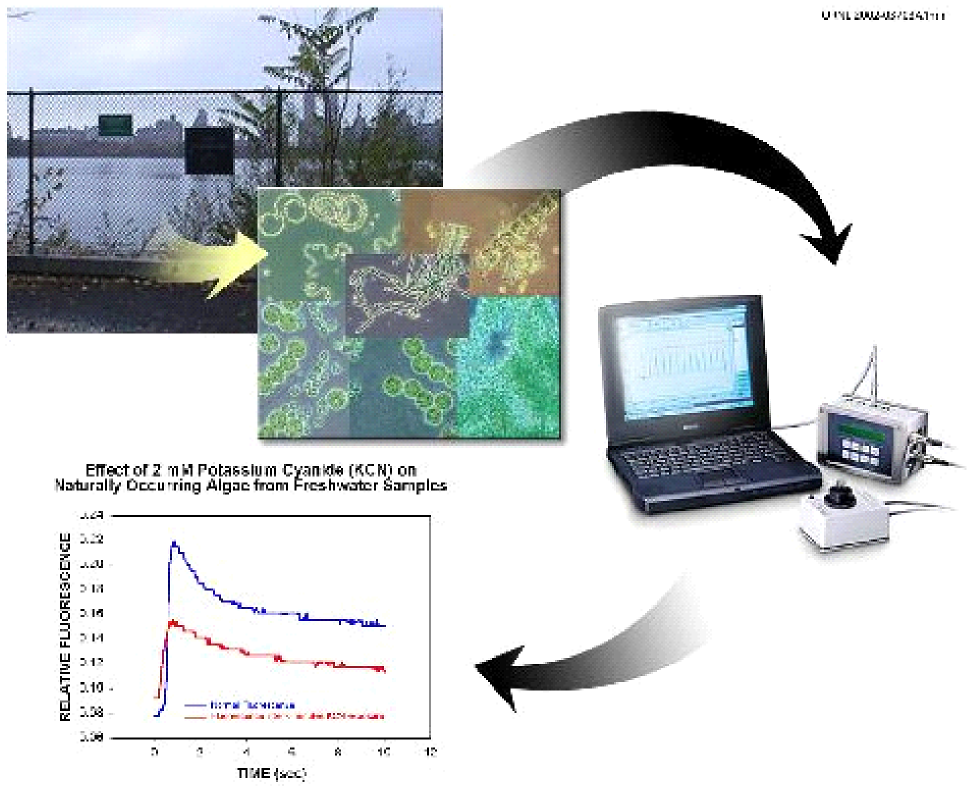

FIGURE 6.1 AquaSentinel: a continuous water monitoring system using naturally occurring algae as biosensors.

AquaSentinel. In a similar laboratory setup with a Walz XE-PAM fluorometer (Heinz Walz GmbH, Effeltrich, Germany), the standard fluorescence cuvette in the fluorometer was replaced with a flow-through model (Hellma Cells, Inc., Model QS-131, Plainview, NY). The cuvette inlet was connected to a glass-bottle reservoir that contained the water samples, and the outlet drained to waste. The system is designed to mimic the flow of river or lake water through the fluorescence detection system. This experimental arrangement allowed continuous monitoring and replacement of water samples in a manner similar to that for the contemplated operation of a real-world biosensor system. Fluorescence induction curves were measured before and during exposure to toxic agents. Fluorescence excitation and emission wavelengths were 660 and 685 nm, respectively. A halogen lamp actinic light source illuminated the cuvette at an intensity of 500 $\mu E \cdot m^{-2} \cdot s^{-1}$ via a fiber-optic cable through direct connection to the cell chamber.

Fluorescence induction curves were recorded every 5 minutes, and data collection for each curve was completed within 10 seconds. Data extracted from the fluorescence induction curves were used to calculate F_s, F_{max}, F_v (variable fluorescence = $F_{max} - F_s$), and the efficiency of PSII photochemistry (F_v/F_{max}). A 200-mL water sample was placed in a jacketed reservoir. The sample was stirred continuously and maintained in darkness with a black cloth. The reservoir was connected to the flow-through fluorescence cell with flexible tubing. To obtain a homogeneous sample before each recording, the volume in the fluorescence cell was replaced three times. After control data were collected, the volume in the reservoir was adjusted to 100 mL and the toxic agent was added. The toxic agents were prepared as stock solutions prior to addition to the reservoir and were injected directly into the top of the vessel and immediately mixed with the sample. Spent samples were drained into a waste bottle. Upon arrival in the laboratory from collection sites at the rivers, the water samples were kept under a fluorescent lamp at an illumination of 50 $\mu E \cdot m^{-2} \cdot s^{-1}$ until use.

RESULTS

Experiments were performed with field samples drawn from the Clinch River at Clark Center Recreation Park in Oak Ridge, Tennessee. The Clinch is the main source of drinking water supply for the city of Oak Ridge. Figures 6.2a through 6.2d show the effect of KCN, MPt, DCMU, and Paraquat, respectively, on naturally occurring algae from the Clinch River.

The results shown here demonstrate that naturally occurring freshwater algae can be used as biosensor material for the detection of toxic agents in sunlight-exposed primary drinking water supplies. These agents block electron transport, impair light energy transfer, or generate toxic secondary photoproducts, all of which provide signals that can trig-

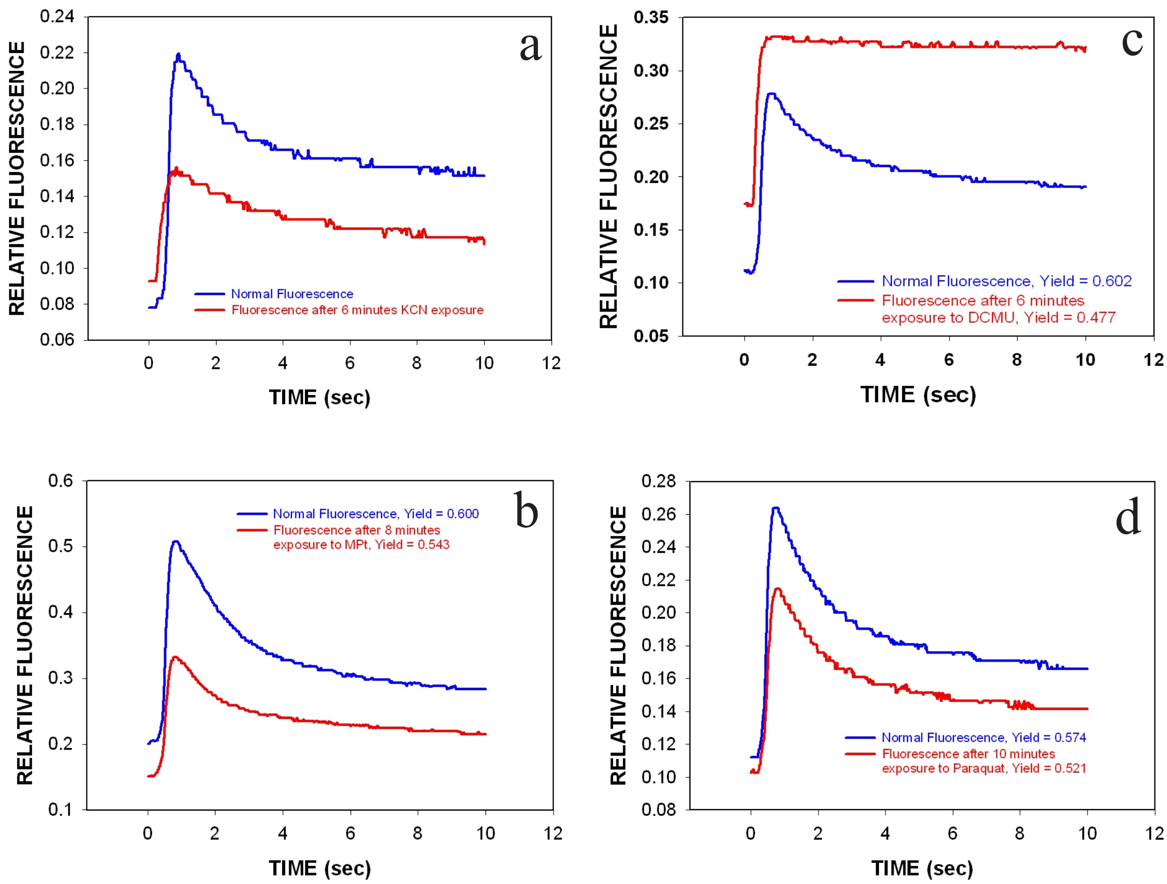

FIGURE 6.2a-d Effect of 2 mM KCN, 20 μM MPt, 10 μM DCMU, and 30 μM Paraquat, respectively, on time-resolved fluorescence signal of naturally occurring algae from the Clinch River. There is a six-minute delay between collection of the two curves in each plot shown. In plots a-c, the top curve shows is the normal fluorescence trace of the water sample, while for plot d it is the bottom curve. Time zero is the initiation of fluorescence excitation of the sample measured.

ger an alarm. Our results showed that the tissue-based biosensors experienced a decrease in photochemical yield when exposed to KCN, MPt, DCMU, and Paraquat. A detectable effect was observed in every freshwater sample tested.

CONCLUSIONS

The data presented in this paper indicate that biosensors based on fluorescence induction curves of naturally occurring freshwater algae can be used to detect cyanide, methyl parathion, DCMU, and Paraquat in primary water supplies under appropriate experimental conditions. In the context of current state-of-the-art biosensor research, they are unique: in the case of sunlight-exposed drinking water, the biosensors occur naturally in the medium to be protected. When combined with encrypted data telecommunication and a database-lookup library containing pertinent data for healthy algae, this approach to the protection of sunlight-exposed primary drinking water supplies may be of practical value under real-world conditions.

ACKNOWLEDGMENTS

The authors thank Dr. K. Thomas Klasson for designing spreadsheets for data analysis and Ms. Beverly S. Mathis for secretarial support. This research was supported by the Tissue-Based Biosensors Program, Defense Advanced Research Projects Agency, under MIPR No. 99-H250 with Oak Ridge National Laboratory. It was also supported by the U.S. Department of Energy Office of Basic Energy Sciences. Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract DE-AC05-00OR22725. The data contained in this paper were collected

as part of the studies published in Rodriguez, M., Jr., Sanders, C.A., and Greenbaum, E. 2002. Biosensors for rapid monitoring of primary-source drinking water using naturally-occurring photosynthesis. *Biosens. Bioelectron.* 17: 843-849.

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DISCUSSION

Fertilizers and Data Interpretation

Parry Norling, of RAND (now with the Chemical Heritage Foundation), began the discussion with a question about fertilizers and whether they might interfere with the fluorescence signal. He thought that high concentrations of fertilizer might stimulate growth of algae and cause a false fluorescence reading.

Dr. Greenbaum responded that while a high concentration of fertilizer could stimulate a bloom of algae, it would be a benign effect. He said that with this technology it is possible to distinguish between changes in fluorescence emissions that are caused by a malicious act and changes caused by benign acts. Dr. Greenbaum said that when dealing with primary-source fresh drinking water, the quality of the water and the quality of the physiological states of the algae should be relatively constant over long periods of time.

Mr. Norling then asked an additional question regarding the fluorescence signal shown earlier for the herbicide Diuron. He noticed that in one chart Dr. Greenbaum showed that the fluorescence signal increased, while in another it decreased (data not shown here).

Dr. Greenbaum clarified that what Mr. Norling noticed was actually a general shift in the line rather than an increase or decrease. The curvature and shape of lines is measured to provide a "fingerprint" by overlaying the data. He said that there are subtle changes that sometimes come from natural variations in the algae. These must be determined by spending time in the river, collecting the data, building a database, and getting a good feel for the natural variance of the algal population in the water. Dr. Greenbaum said that it would then be possible to determine the change in the fingerprint associated with a particular toxin and then determine how large a variance there is between the standard data, the standard curve, and the one that is being collected. He said that how much variance to tolerate before raising a red flag must be determined. Whether changes in the photochemical efficiency are calculated by computing the F_v/F_{max} photochemical efficiency or a point-by-point comparison of the curves, he said that it is possible to determine how large a variance the algae can tolerate. Once that variance exceeds the point of tolerance, the water can be analyzed to determine the cause of the variance.

Measuring Algal Metabolites

Dave Layton, of Lawrence Livermore National Laboratory, brought up how there are often problems associated with algal metabolites (taste and odor) in drinking water. He wondered if this technology could be used to determine the presence of contaminating algae in the water supply

Dr. Greenbaum responded that this is possible.

Applications for Manufacturing or Industrial Processes

Dave Rea, of DuPont (retired), asked whether this technology could be applied to looking at variations in effluents from manufacturing and industrial processes.

Dr. Greenbaum said that depending on the chemical composition or nature of the effluents, they should cause the same types of changes he has demonstrated for the deliberate toxins that might be introduced into water and thus could possibly be used for monitoring industrial waste.

Oligotrophic Systems

Tim Shaw, of the University of South Carolina, commented that a similar technology is used to identify nutrient limitation in coastal marine systems. He wondered whether an oligotrophic system that is already in a state of reduced F_v/F_{max} photochemical efficiency might influence the signal obtained with this technology.

Dr. Greenbaum said that as long as algae are present it does not matter whether they are growing in nutrient-poor or nutrient-rich conditions to obtain the signature fluorescence response. The signal depends on the presence of the chlorophyll and the ability of the algae to undergo photosynthesis. He said that if the algae are growing in the wild, they are undergoing photosynthesis, and if they undergo photosynthesis, there will be a fluorescence signal to measure.

Effects of Sudden Changes

Mark Matsumoto, of the University of California at Riverside, wondered whether sudden nonhazardous changes, such as a spike in salt concentration or temperature, might influence detection of a hazardous substance.

Dr. Greenbaum replied that for most primary-source drinking waters, there would never be any spike in salt concentration or temperature. There are usually only slow diurnal variations. These natural variances are important to investigate in order to utilize naturally occurring biosensors such as the algae. He said that in the data collected so far, the natural diurnal variations occurred with a constant characteristic time that was much slower than the chemical interactions of the toxins with the algae in the water.

Mr. Matsumoto said that he wondered whether such a situation would give a false positive.

Dr. Greenbaum said that the photochemical efficiencies did not change in the measurements obtained. He said that the AquaSentinel technology measures diurnal variation which can affect photochemical efficiency when the sun is very strong, but this is a predictable natural diurnal variation. By looking at the second differential, which departs from the natural diurnal variations, a red flag goes up to indicate that the system has to be investigated further.

Effects of Water Turbidity

David Krabbenhoft, of the U.S. Geological Survey, noted that the rivers discussed in this presentation looked very clear and wondered if more humic or turbid waters would lead to a loss in signal sensitivity.

Dr. Greenbaum said that the water studied was quite clear but that it does have some sediment, including bacteria and other microorganisms. He said that a feature of this technology, however, is that nothing in the water fluoresces at 685 nm or has the characteristic time course. To the extent that particulate matter exists in the water, the signal decreases simply because of scattering. This means that the absolute amount of light would go down but the characteristic signal will not be affected.

Interference from Herbicides

Jay Means, of Western Michigan University, then asked if a background presence of herbicides such as triazines might decrease photosynthetic efficiency and raise the detection limits for the target compounds.

Dr. Greenbaum responded that if a body of water demonstrated a photochemical efficiency of 0.4 for the PS II reaction center, it would be necessary to question whether it should be used as a source of drinking water in the first place. He continued to say that when water is clean, there should be nothing in it that depresses the photochemical efficiency. If herbicides such as triazines are present, then the water should not be used as a primary source of drinking water.

However, Dr. Greenbaum said that this technology is not meant to be used to monitor already-contaminated sources of water. He said that the technology should be used where the assumption is that the water is clean from the start. If a terrorist decides to dump potassium cyanide or methyl parathion into that water, then there will be a point of reference by which to compare the original and current state of the water. He said that in most cases people are not drinking water that is so heavily contaminated that the photochemical efficiencies of the algae that live in the water are already suppressed. If the water is really bad, algae would not even be able to grow.

Mr. Means followed up with a comment that two-thirds of the surface water and probably a third of the groundwater supplies in the United States are contaminated with triazines.

Dr. Greenbaum responded that if that was true, the rivers studied would have indicated this. However, at the concentrations present in the rivers, he did not see any adverse effects of such compounds on the algae.

Application as an Air Sensor

Don Phipps, of Orange County Water District, asked if this technology might be used in the form of a biofilm of algae. He said that it should be possible to improve the signal-to-noise ratio because of the higher concentration of algae. He also said that this would be much simpler and would make it possible to utilize the technology in both air and water.

Dr. Greenbaum replied that there is already a company that makes a kit for culturing algae to produce biofilms. He did not agree that it would be simpler, however, because making a biofilm requires more labor. Using algae that occur naturally in the water renders the technology discussed in this paper non-labor intensive and reagentless. He noted that conventional biosensor technology is typically single use, but with this technology the biosensors are already present in the water and are a part of the environment being studied. He added that the important aspects of this technology are that it is non-labor intensive, can easily be automated, and monitors continuously in real time.

With respect to making a film for use as an air sensor, Dr. Greenbaum agreed that it would be very useful. He said that algae can be entrapped on a filter paper and then used to measure airborne gases such as mustard gases, tabun, or sarin. The algae in this form can then be used for measuring toxic agents in air and water. Work done in measuring airborne contaminants with entrapped algae on filter paper was published two years ago in the journal *Biosensors and Bioelectronics*. In fact, he said that this was the original application for the algal biosensor technology discussed here, but that during the course of that program water protection became a high-priority issue so the technology was applied to water and not air.

System Cost

Tom Dillion, of Science Applications International Corporation, asked about the cost of the AquaSentinel system.

Dr. Greenbaum responded that the system could be built for less than $20,000 per unit, perhaps even less than $10,000, based on the price of the components of the system. A fluorometer is also needed but the one used here was more sophisticated than necessary for these special measurements. He said that the entire system could actually be put on a chip. Estimating that 500 to 1,000 of these units would sell around the world, the price would probably be less than $10,000.

System Location

Mr. Dillion followed up by saying that it would be good to utilize this technology in individual buildings. He said that in terms of protecting a water supply, dilution phenomena make it unlikely that attacks will happen at a water supply area.

Dr. Greenbaum replied that this technology only works for primary-source drinking waters because once that water has been filtered and disinfected, the algae are removed. Without algae, the fluorescence signal one would want to monitor would not exist.

Purposeful Nutrient Enhancement

Vasilios Manousiouthakis, of the University of California at Los Angeles, wondered if there might be compounds that could be mixed with the maliciously placed toxin so that it would help the algae grow, and therefore have some kind of compensatory effect on the sensors and prevent the needed detection level being reached.

Dr. Greenbaum responded that it would not be possible to do this because the presence of the nutrients needed to grow the algae would not change the sensing signal of toxins such as cyanide, methyl parathion, or DCMU. He said that the chemistry and specific action of these toxins are independent of the nutrients present in the system in this case. However, he said that the kinetics of fluorescence decay is the difference between algae grown in a nutrient-rich lab environment versus the more nutrient-poor field conditions. He said that in the lab the kinetics of decay are slower because the algae are much healthier than those living in the river, but that even when they are very healthy the algae are still susceptible to the harmful effects of the toxins.

Business Opportunities and Responsibilities

7

Some New Approaches at the Orange County Water District

Virginia Grebbien
Orange County Water District

Since chemists and water industry scientists approach water quality and chemistry-related issues from different perspectives, an exchange of views is important for mutual understanding. Here, the water supply situation in the world and the current challenges that numerous chemicals pose for water districts are discussed.

GLOBAL WATER

There is not enough water worldwide to meet future needs and population demands. Both the United Nations and the World Bank have announced that the world is facing a water shortage. Unfortunately, 2 million people a year die due to lack of water or contaminated water. Disinfection is a very easy cure, but it does not always occur. As the global population increased from 2.5 billion to 6 billion, the water available per person dropped 58 percent.

WATER IN CALIFORNIA

In entering the global economy with increasing technology, more water is being used because technology requires it. Dams, reservoirs, and concrete canals have been built, but more has to be done to change the existing infrastructure. Since the 1960s nothing has been built in California even though the State Water Project was initiated. Since that time, the demand for water has increased 38 percent and new water supplies have increased by only 2 percent (which is actually a significant number). The State Water Project serves a little over 3 million acre-feet a year, all of which has come from local water supply development. Most likely, more water will not be available from state water project-type facilities. Consequently, conservation, water recycling, conjunctive use, brackish water desalting, ocean desalination, and water resource management programs will be needed.

Southern California

Southern California is a leader in water conservation programs. Even with an increasing population, Los Angeles (LA) has kept water demand flat over the last 12 years through extensive conservation programs including education in the schools, programs in which toilets are replaced with ultralow-flow models, water audits, xeriscape (conservation of water and energy through landscaping), low-flow irrigation, and various conservation incentives.

Southern California has housing cost, infrastructure, transportation, and water supply problems. Colorado River cutbacks are impacting the area because water is being purchased from the Metropolitan Water District that has two sources of supply, the State Water Project and the Colorado River. There are problems in the distribution system so Colorado River water cannot be purchased from the Metropolitan Water District to replenish the groundwater basin. As a result, alternative sources of supply must be found, or there will be shortages of about 120,000 acre-feet a year in 2020.

As water districts face shortages, they must take water out of storage to meet the demand and turn off all surplus deliveries. Fortunately, Metropolitan's state project allocation increased to 90 percent due to rain in April.

The population in California will increase by 15 million by 2020, and the state department of water resources predicts that there will be annual shortages of 2 million to 4 million acre-feet per year by that time. Since people continue to move into California, alternative sources must be found. Built with state resources in the 1960s, the State Water Project moves water from San Francisco into Southern California. Twenty-seven different agencies have participated in this facility, which is located from the San Joaquin Valley to Southern California. Southern California uses 2 million acre-feet of water from the bay delta in Northern California. The river and the system have to be managed better for environmental considerations, yet people also want to drink the water. Farmers would like to use it to irrigate crops, and agriculture is one of the largest economies or businesses in California. Groups are fighting over this unresolved and unfunded issue. There was one major lawsuit on the environmental documentation surrounding this issue, and it was resolved about a year ago, but the process continues. There is no new operating plan or plan to implement environmental restoration. Additionally, there is no plan for dividing up agricultural use versus urban use for one of the largest projects in the state.

In addition to the State Water Project, there is a federal program called the Central Valley Project (CVP). Built by the Bureau of Reclamation, this series of dams, reservoirs, and canals moves water from the same delta area to San Joaquin Valley and then down to Kern County in Bakersfield. Taking more than a million acre-feet from the same watershed, the CVP delivers water solely for agriculture. There are recent court rulings and governmental rulings that environmental due diligence be paid on the CVP. Additionally, there is the Environmental Water Restoration Account for which the agricultural community has to give up water so that it can be used for environmental purposes. This represents a shift of water away from consumptive purposes back to the environment. Rather than creating more supply, it is used for consumption.

Los Angeles

The LA Aqueduct comes from this same area and crosses over down into Southern California to the city of Los Angeles, moving a couple of hundred acre-feet of water from Mono Basin into the city of Los Angeles. The environmentalists around Mono Basin in the 1970s created the Mono Lake committee. In the late 1980s the city of Los Angeles had to use less water, and the level of Mono Lake had to stay at a prescribed elevation. Again, water was moved away from the urban environment. A well system was developed in Los Angles and water was pumped out of the Owens Valley area, turning it into a dry lake bed. This resulted in a loss of up 60,000 acre-feet of water a year—enough water to support 120,000 families. When the water supply from the LA Aqueduct is low, the city turns to the State Water Project and the Metropolitan Water District.

The Colorado River

California has been fighting over Colorado River water since the 1930s, and the Quantification Settlement Agreement involves the county of San Diego, the Imperial Irrigation District, and the Metropolitan Water District. The Department of the Interior has reduced by almost half the amount of water that Metropolitan can import from the Colorado River through the Colorado River Aqueduct, which comes across from the Colorado River to the LA Basin. The fight is over who has priority in terms of the water, and San Diego wants to take water from the Imperial Irrigation District area. Because of the driest couple of years on record, Lake Powell is down to less than 50 percent of its volume and 50 percent of the supply from the Colorado River Aqueduct has been lost.

THE ORANGE COUNTY WATER DISTRICT (OCWD)

Background

In Orange County, OCWD's mission is to provide safe water at a low cost while being sensitive to the environment. The OCWD is unique in that it was established in 1933 by a special act of the state legislature and has its own enabling legislation that governs everything it does. Primarily, like most water districts, Orange County was an agricultural community that had to find sustainable water supplies in a new political environment as it converted from an agricultural to an urban setting.

To ensure rights to the Santa Ana River, the groundwater basin has to be managed in a sustainable fashion so that this precious resource will be here for generations to come. The OCWD has 350 square miles in its district. Two mountains geologically divide the upper watershed from the lower watershed along the Santa Ana River. The Chino Groundwater Basin flows into the Orange County Groundwater Basin, and it is hydraulically connected through the Santa Ana River. Prado Dam goes up into Riverside and Big Bear.

Near the University of California at Irvine, the OCWD is at the tail end of the groundwater basin. It is contained within the Santa Ana River watershed, which goes north to the San Gabriel Mountains and Big Bear. It is the largest watershed in Southern California, and the OCWD is the proud owner of the Santa Ana River, which the state health department considers the second most impaired water body in California.

In Orange County, there are approximately 2.2 million people in about 20 cities, with a current demand of 510,000 acre-feet and growing to about 610,000 acre-feet. In this area, 66 to 75 percent of the water comes from the groundwater basin. For the last 11 years, 75 percent of demand comes from the groundwater basin, while the remainder has been imported from the Metropolitan Water District. However, in 7 out of the last 11 years, the OCWD pulled more water out of the basin than it put back in. This year, people are going to be able to pump only 66 percent of what they demand out of the groundwater basin. In Orange County, there is a socialized, managed groundwater basin where people learn how it can perform so that if they pump over a certain level they are fined.

Projects and Research

The Santa Ana River is 54 percent of OCWD's water supply. In the 1940s the Corps of Engineers fixed the main channel of the Santa Ana River, but it is hydraulically connected to the groundwater basin which is along the bottom of the river and gets a lot of recharge. Water is pulled from the Santa Ana River into artificial recharge basins; there are approximately 14 recharge basins and 20,000 acre-feet of storage. A tremendous amount of research on the fate and transport of water through the geology has been done to date.

Time, energy, and research have been devoted not only to water quality but also to physical operation of the facilities. Because there is so much silt in the Santa Ana River, a hardened crust forms and blocks the percolation capacity. A basin cleaning vehicle has been developed to keep up the percolation rate.

Over the last 30 years, the OCWD has heavily monitored and doubled the yield out of the groundwater basin, a feat that no other basin in California has been able to achieve. Because it is managed and not adjudicated, it has been able to get a lot out of this basin and to help Orange County grow.

The OCWD has also been involved with a number of research institutes, supporting them with financial, technical, and staffing resources. The OCWD has conducted a number of different projects and programs to increase its own replenishment supplies. There is limited Santa Ana River water, and the OCWD cannot buy anything from Metropolitan at the moment, but it is in the process of creating a project that will make its own replenishment water. However, the OCWD has outstripped its supply, has a limited capacity to recharge the groundwater basin, and needs to buy more recharge basins. It has to figure out other ways to get water into the basin besides creating open pits. An additional problem is an accelerated rate of seawater intrusion. Membrane treatment is the wave of the future. Much work has been done in the last decade, but more can be done. What kind of pretreatment and energy options can be created that reduce the cost of this treatment? The OCWD's research found that advanced oxidation processes are interesting because these catalysts reduce not only energy but also chemical requirements.

The Orange County Water District has done a lot of research on reverse osmosis fouling, cleaning the water factory, membranes, and ultraviolet (UV) irradiation. It was also able to characterize the total organic carbon in water; however, the health department has taken and replicated the characterization as a regulatory requirement for all recycled water projects. Additionally, it just spent $10 million in eight years on the Santa Ana River water quality and health study. A source water characterization study of the Santa Ana River was also conducted covering its fate, transport, interactions, and interrelation with the geology of the basin. No other agency in California has done such an exhaustive analysis of its source water supply. The agency wanted to know how it could improve operations and provide a safer, more reliable, more sustainable product its consumers.

Now that this research is complete, the OCWD is building a project called the Groundwater Replenishment (GWR) System, in which it is going to take secondary treated effluent domestic wastewater from the Orange County Sanitation District. The OCWD will treat the water and build a 14-mile pipeline; half of the water will go to the top of the county into the spreading basins and be recharged into the groundwater basin, the other half will be injected into the seawater intrusion barrier, a project comprising 72,000 acre-feet a year.

The seawater barrier will improve so that there will be no seawater intrusion. Modeling shows that we have to be up around 30,000 acre-feet a year of injection. For the same price as buying water from the Metropolitan Water District, 70,000 acre-feet of water is being put into the groundwater basin, so at the same time the water supply issue is being solved. This new supply is contained within Orange Country and is environmentally benign and beneficial. The amount of discharge into the ocean is being reduced.

In the treatment train processes for the project, the OCWD has to perform source control, microfiltration, reverse osmosis, and UV disinfection. With all of the different chemical constituents that businesses discharge into the sewer system, it is very important to make sure that some of the chemicals do not go in but are dealt with through point source and onsite treatment.

CHALLENGES FROM THE CHEMICAL SCIENCES

The chemical sciences have created challenges for the water supply industry. New industrial and household chemicals introduced into society, such as hair care products, contaminate rivers, lakes, and groundwater basins. Chemicals are commonly detected in ultratrace quantities by increasingly sensitive tests. Since only the level of a chemical and not its consequences are reported, the public has become increasingly skeptical. As a result, the water industry and the regulatory community face challenges to provide accurate information to the public.

For example, there is a debate about whether the arsenic standard should be set at 5 or 10 parts per billion (ppb). The water district can handle 10 ppb, but if the standard is set at 5 ppb, Santa Ana River water cannot be used because it has naturally occurring arsenic levels of 6 ppb. In that case, 300,000 acre-feet of water could be lost. Is this level of arsenic really a risk? The issue has to be presented in a health risk information context. Because the information is not available, establishing appropriate risk-based monitoring requirements and regulatory limits is difficult.

Local water supply projects are at risk of not being implemented, and water sources have been removed from service. The levels are well below the maximum containment levels, but the sources have been closed due to public perception and political fear about the safety of the water supply.

The Whittier Narrows Montebello Forebay Project in LA County recharges tertiary treated effluent from domestic wastewater into the groundwater basin. The OCWD cannot conduct tertiary treatment, but instead is doing source control, microfiltration, reverse osmosis, and UV oxidation. The processes are very expensive, and a $100 million project has become a $450 million project. There is a certain amount of risk in the chemistry of the water that people must be willing to live with, because this money is probably better spent on urban housing, transportation, and social issues.

Therefore, multiple scientific disciplines must be integrated into the research and applied methodology to determine what is safe, sustainable, and acceptable. The chemistry of these contaminants must be understood, such as what they are, how they interact with other chemicals and other constituents, what their fate and transport are, and what the health-based aspects are. In this way, chemists and water scientists can work together to achieve a safe, lasting water supply.

DISCUSSION

Water Retailers

David Layton, of Lawrence Livermore National Laboratory, noted that Orange County should be commended for its innovative research in these areas and sets a great example for many water agencies across California and throughout the country. He asked what retailers are going to do now that they are being cut back and whether Metropolitan can meet the water needs of Southern California for 20 years as planned.

In her response Ms. Grebbien said that retail agencies were unhappy that groundwater production had been cut back. The total cost to them was more than $10 million because they had to buy Metropolitan water instead. As a result, the OCWD developed a collaborative process in which information about the status of the water supply was shared and suggestions were discussed. The group's suggestion was to continue pumping the water. Ms. Grebbien approached her Board about the issue, which said it did not want to be known as the Board that let the basin get overdrafted to the point at which it would be harmed. The OCWD eventually took the blame for increasing rates. Orange County residents knew they had a duty to protect and preserve the groundwater and were willing to pay the price. This experience showed that the water levels will eventually go back up, so a problem and a solution exist.

Southern California's Future Water Needs

In response to the second part of Mr. Layton's question, Ms. Grebbien said that one must look past the headline of the Metropolitan (Met) report and into the body of the report and its assumptions. The Met is reliable, not because its supplies are increasing but because all of the local agencies are increasing theirs. This is all based on local water supply development. According to the Met report, 320,000 acre-feet will be pumped out of the groundwater basin. It is reported that in 2020 the value will be 465,000 acre-feet. The Met is reliable because it has the water district pumping 465,000 acre-feet, doing the GWR project, and doubling the GWR project. There is state bond money to go toward local supply development, and the water district needs Met's help with the regulatory community in order to succeed.

OCWD Water Rates

Dennis Hjeresen, of the Green Chemistry Institute, pointed out that the *Albuquerque Journal* in New Mexico started a series on New Mexico water issues. The first lead story was looking to the successes and featured Orange County and Southern California. He asked how the OCWD compares water rates to others for average citizens; what the water districts do for local companies, particularly with regard to chemical contamination; and what tools are provided to help reduce that source contamination.

Ms. Grebbien replied that the rates were significantly increased by 18 percent, corresponding to a 4-5 percent increase on average at the retail level, or less than an additional $2 a month on the average homeowner's bill. In Orange County, the average cost of water is less than a typical cable TV bill of $30 a month. In the overall scheme of things, water is inexpensive. Water is heavily subsidized through an ad valorem property tax, and the Metropolitan Water District has a huge amount of taxing capability; a lot of its revenue comes from assessed valuation tax. These subsidies keep the cost of water artificially low. On the other hand, Disneyland, the city of Anaheim's largest water customer, had an annual cost increase of a little over $100,000.

Alternative water supplies are necessary, but they cost money. The groundwater basin has a huge financial advantage. The water rate was just increased $149, and an acre-foot costs about $50 in energy to pump out. A little more than $200 is needed to produce an acre-foot of groundwater. If you buy that acre-foot from the Metropolitan Water District you will pay $440, and it just implemented a tiered rate structure. The only kind of water that Orange County can now buy is tier two water, which is $480 an acre-foot. Therefore, there is still a huge financial advantage in taking water from the groundwater basin.

Contamination

In response to the second part of Dr. Hjeresen's question, Ms. Grebbien said that the OCWD works primarily with the Orange County Sanitation District on source control. The OCWD's challenge in working with the sanitation district has been to keep from using chemicals that are interesting for their discharge requirements and from a water regulatory perspective. As a result, the sanitation district has started to add to the list of chemicals that it regulates. In addition, she said the OCWD works very closely with the regional water quality control board, actively monitoring and coordinating with industries within the basin. For example, a membrane manufacturer in Orange County was using dioxane that was detected in OCWD's wells. The OCWD went to the sanitation district, which looked in its inventory of companies to find the "culprit" who then terminated operations and is now using a safer chemical.

Population Growth in California

Jeffrey Perl, of the Chicago Chem Consultants Corporation, questioned the ability to control the influx of some subdevelopments through real estate zoning laws.

Ms. Grebbien replied that Orange County is actually fortunate because most of the population growth is going to occur in what is called the inland empire and San Bernardino and Riverside Counties. Historically, however, the water industry has said that planning and growth issues are not its responsibility and that the industry is there to serve a demand. In all of its environmental documentation, such as the California Environmental Quality Act or the National Environmental Protection Act, it is the planning commissions and land use planning agencies must deal with growth. However, those days are gone. A bill was passed a couple of years ago in the state legislature called the Khuel Bill, which said for every 500 or more home developments, homes can be built only if there is an identified water supply to go along with the development. Prior to this bill, the Urban Water Management Planning Act required water agencies to put together a plan every five years explaining where their water will come from. The new Khuel Bill has actually been used to stop or slow down some projects in LA County. This year, another bill in the state legislature would reduce the 500-home requirement to 50 homes. Prior to this workshop, the city of Irvine and the Irvine Company were working on a small home development. The Irvine Ranch Water District put together a report that said it has sustainable water coming from the groundwater basin and the Metropolitan Water District and that there was sufficient water for this development. The OCWD does not have a report that addresses the Khuel Bill, but it is currently doing the planning work in order to be able to put it together. In the Southern California area, the antigrowth advocates are starting to use water as their weapon and the water industry is paralyzed and unprepared for this.

Effect of Chemistry on the Water Industry

Vasilios Manousiouthakis, of the University of California at Los Angeles, wanted to address the comment made about the chemical sciences and their adverse impact on the water industry and others in business. A remark was made in the morning about how there is a serious adverse impact in the chemistry and chemical engineering areas, resulting from the negative connotation of "chemicals." It must be realized that the United States is prosperous today because there has been a very healthy chemical industry contributing to the gross national product since the 1940s. Now, the delayed adverse impact that this industry has had on our environment is being seen. If any group of people can slow this adverse impact it is chemists and chemical engineers. Mr. Manousiouthakis wanted to caution Ms. Grebbien that remarks about the chemical sciences' impact on the water industry may have unintended consequences.

Ms. Grebbien agreed and said she understands that products made from chemicals benefit society. The general public has to realize, however, that it cannot have these things without adverse effects. If there are going to be consequences, they should be managed from a holistic approach. The water industry would like to work with the chemical sciences to tackle this issue.

8

A Perspective from a Water Company

Floyd Wicks
American Water Company of California

INTRODUCTION

In the United States the water industry is quite fragmented. There are 60,000 water utilities throughout the country, half of which are privately owned, and many serve very small communities. About 33 million people are served by the investor-owned water industry in this country, representing one out of seven people population-wise. The American Water Company of California (AWC) is a member of the National Association of Water Companies (NAWC), which is located in Washington, D.C. There are 42 states represented by this NAWC group. There are 330 investor-owned water utility members of NAWC.

In total, the NAWC member companies represent about $3 billion in revenues annually and around 15,000 employees. Of that, AWC has about 520 employees and $0.2 billion of annual revenues, relatively small by comparison. However, it is the third largest publicly traded company in the United States, because some of the larger companies have been purchased by foreign companies. It is traded on the New York Stock Exchange, provides water service to 75 cities in California and two Arizona communities, and was incorporated in 1929. Water utilities, public or private, in the United States all must meet the regulations for contaminants as determined by the states and U.S. Environmental Protection Agency (EPA).

Water Quality Issues: Historical Perspectives

Prior to 1974, U.S. Public Health Service Standards were met by the water utility industry, but they were voluntary. They were not mandated by federal or state agencies. Of course, if they were not met, consequences would result. In 1974, the Safe Drinking Water Act made that compliance mandatory.

In 1975, interim primary drinking water regulations were promulgated. Trihalomethanes are chlorinated organic compounds that can cause problems and were introduced in 1979. They have been around a lot longer, but a certain maximum contaminant level had not been set.

Growth in Regulated Contaminants

There are two major amendments to the Safe Drinking Water Act (SDWA), one in 1986 and one in 1996. Figure 8.1 shows that the impact of the 1986 amendment was dramatic.

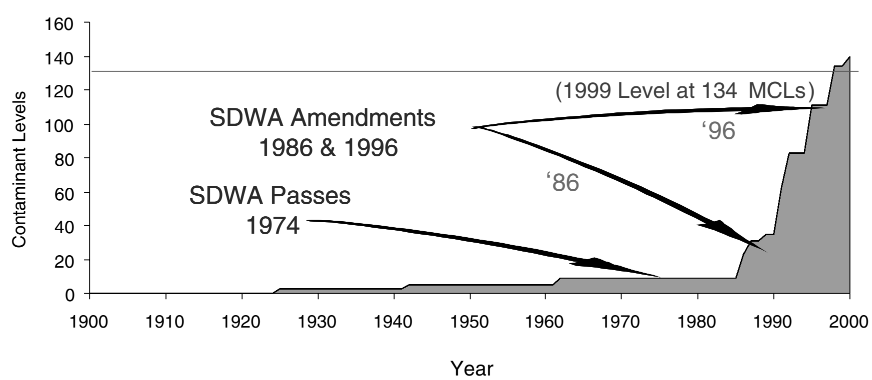

FIGURE 8.1 Growth in regulated contaminants.

Up to that time the number of contaminants was reasonable, but then in 1986, Congress actually mandated that EPA add 25 new contaminants every three years, regardless of the cost to remove these constituents from water. The 1996 amendment added more to the equation.

The 1996 amendment incorporated a cost-benefit rationale. In California there are a number of lawsuits against water utilities for providing water that is contaminated. The question is to what degree the contaminants are present. Even though all standards have been met since they were put in place, some customers have been prompted by attorneys to file lawsuits against the AWC and other water utilities in California.

Impact on American Water Company

The AWC has the distinction of serving in many parts of the state and has 300 production wells of its own. It pumps from contaminated groundwater sources, and treatment facilities remove those constituents. However, there are 22 lawsuits against the company. A number of county water systems and other private water companies have been sued as well.

The issue brought to court by the company was whether the court or the Public Utilities Commission (PUC) should regulate these standards. What level of treatment should be provided to make sure that people have a safe, good feeling about drinking their tap water?

The AWC has spent in excess of $7 million to date to defend itself against these lawsuits. The PUC conducted an investigation into the lawsuits, and AWC had to go back into its records for 25 years to provide the PUC with all the analyses of water distribution and treatment plant samples, in excess of 2 million samples. In those samples, contaminants were outside the range of the maximum contaminant level only 16 times. Therefore, the PUC found AWC to be in compliance with the law. In the Hartwell decision, the Supreme Court upheld the jurisdiction of the PUC over private utilities. The decision left all the public agencies in the lawsuit, but pulled the private agencies out. Only if plaintiffs can prove that EPA standards were violated can private companies be sued in court.

The fairness of imposing these kinds of costs on utilities and their customers has to be assessed, and the legislators, not the courts, should be urged to address these issues of responsibility. The companies are all also responsible when it comes to providing good-quality, sustainable water at affordable prices.

Number of Regulated Contaminants Versus Research Investment

Figure 8.2, although outdated, shows the number of contaminants increasing and the research investment trailing downward rather than upward. Our legislators should be asked to authorize more investment in the research side of the water utility industry. The other alternative is to label the product to caution that it may be harmful to your health (see Figure 8.3).

INVESTMENT

More than 2 million people, mostly children, die every year due to water-related diseases. More than 6,000 people die each day from waterborne disease or lack of water; put into perspective, half of that number died in the September 11, 2001, tragedy in New York.

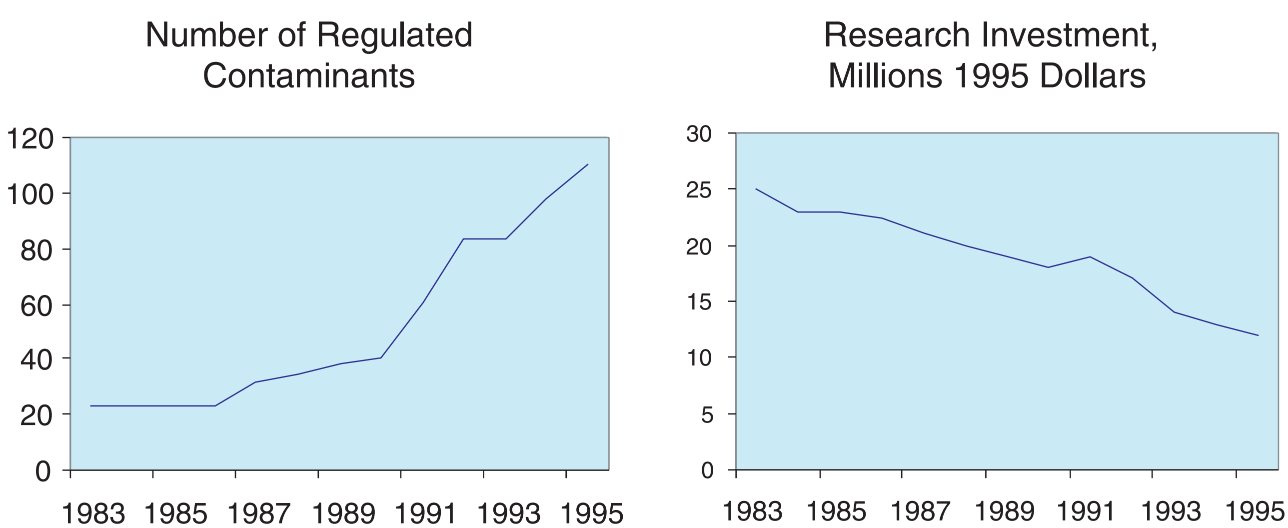

FIGURE 8.2 Number of regulated contaminants versus EPA research investment.

FIGURE 8.3 Labeling the water supply.

So the question regarding water quality is whether the contaminant list should be expanded when less than 0.5 percent of all the water delivered to a home is actually ingested. More than 99.5 percent is used elsewhere, either for flushing toilets, irrigating lawns, or washing cars. Why should all of that water have to be treated to such a high standard? Should a different way to treat water that ends up in your kitchen tap be considered? Perhaps "point-of-use" filtration or other chemical means to satisfy that concern could be performed.

WATER DISTRIBUTION PROBLEMS

In terms of California's water supply, there is great production in the northern part of the state, but poor distribution. About 75 percent of available water in California is in the northern third of the state, yet 75 percent of the actual demand is in the southern two-thirds. Approximately 50 percent of all water in California gets redirected one way or the other.

Water comes to Southern California from a great distance: 600 miles of the state aqueduct system from Lake Oroville in the northern part of the state down to Los Angeles and further down to San Diego. From the Colorado River there are 242 miles of aqueduct.

States' Activities

In Colorado, a 100 year supply is required for a new development in an attempt to have sustainable water for the future. A way around the requirement is drilling in some areas of Colorado to depths of more than 1,000 feet to get water that has been there for thousands of years, knowing that the recharge is not there. This may not be considered sustainable water for development unless in the interim the opportunity is there to pump back down into the aquifer for future use. However, this is not part of the current legislation in Colorado. A 100-year supply is also required in Nevada. In California the recent Kuehl legislation requires a 20-year sustainable supply.

Long-Term Challenges (2050)

In the year 2050, there will be 3 billion more people than there are today, with most expected to settle in semiarid regions. Using current farming technology, there will be 60 percent more water required just to grow the crops to feed 3 billion more people. This is a tremendous pressure on the resource. However, most of the soils today that are suited for agriculture are already in use.

OPTIONS

One option is demand-side management; in other words, the more water people use, the more they pay for that water. Another option is for people to change their diets. Virtual water could also be used; simply take the water, clean it, and put it back below ground for future use.

Desalination

Approximately 97 percent of the water in the earth is in the oceans. Of the remaining 3 percent, only a third is drink-able water. The rest of it is tied up in glaciers or in areas that are just not able to be tapped.

About 70 percent of the world's population lives within 50 miles of an ocean, so desalination could have advantages, including a sustainable supply. Desalination should be considered drought proof, which is justification for the higher cost to treat the water. The cost is about $900 per acre-foot; an acre-foot is about 326,000 gallons. For $900, that is a reasonable cost.

The Metropolitan Water District (MWD) recently built a reservoir to store water in Riverside that cost in excess of $2 billion. There is a great storage reservoir in the ocean. Why would a reservoir be built inland when there is a population center so close to the ocean? Given the cost avoided by not building reservoirs, the cost of $900 an acre-foot is inexpensive for a drought-proof source such as the ocean.

There are currently five sites under investigation in California alone for putting desalination into play. AWC has signed a contract with Poseidon Resources, the company that is building a 25-million-gallon-a-day plant in Tampa right now. The plant that AWC signed up to be part of is going to be about a 100-million-gallon-a-day treatment plant in Southern California. Of that, about 80,000 acre-feet, or 20 percent of the volume of water purchased from the MWD, will be replaced annually. The AWC's portion of the treatment plant would be a capacity of about 20,000 acre-feet per year, which is projected to be on-line in about five years. There are others in Orange County that are looking at tapping into that plant's capacity as well.

Education

American Water really wants to be a part of the bigger picture in California. In the early 1990s the organization was redesigned. An in-house university was created to reshape the organization into a more forward-thinking team.

The employees and customers are the beneficiaries. Employees are provided with the option of seven different "tracks" of learning. There is a water quality track that leads to certification by the State of California in either treatment or water distribution. The employees can actually get continuing education units they can transfer to the local university. This is a tremendous program and an interesting part of the water company's business now. It not only trains people but develops them.

SUMMARY

In summary, desalination is really nothing new. Clouds contain water that is desalinated ocean water. Lake water is desalinated from those clouds. The environmental cycle provides water to everyone on Earth at zero cost per acre-foot. People have made the water supply imperfect and now have to spend $900 per acre-foot to clean it up and put it back on the land.

DISCUSSION

Bottled Water

Parry Norling, of RAND (now with the Chemical Heritage Foundation), asked how bottled water would compare to the American Water Company's water if it was analyzed for some of the contaminants.

Mr. Wicks responded that if tap water is put into a bottle and put in a refrigerator, the chlorine taste that people find objectionable would be dissipated. The water is also healthier because it has been disinfected. Bottled water was taken directly off the shelves in various stores and tested primarily for bacteria because it has similar constituents for total dissolved solids (TDS), calcium, and magnesium. In many cases, a fairly substantial background count of bacteria was found. Considering that water is on the shelf at room temperature, it is alarming to find any bacteria at all.

Eli Greenbaum, of Oak Ridge National Laboratory, stated that if bacteria can be detected easily in bottled water, there should be a reduced carbon source in there as well. He wondered if Mr. Wicks has examined that.

Mr. Wicks answered that he has not, but that it sounds like a good idea. However, he is not familiar with it.

Tim Shaw, of the University of South Carolina, answered that plasticizers in a plastic bottle can leach out at a pretty high rate.

Mr. Wicks added that most of the bottles are made from polyvinyl chloride (PVC) materials. His customers use about 560 gallons a day, which is a lot of water, for which they pay about a $1.30 per day. Compared to bottled water in the store, this water is really cheap.

An unidentified speaker stated that he thinks most bottles are now polyethylene terephthalate (PET) rather than PVC. In that case, there is no plasticizer (often dioctylphthalate) to leach out. There might be, although unlikely, lower-molecular-weight cyclic esters that potentially can leach out.

Desalination

Debbie Elcock, of Argonne National Laboratory, wondered if Mr. Wicks had any thoughts in terms of desalination or had any information about looking at the front end for pollution prevention and life cycle cost. She also asked if Mr. Wicks knows what the by-products are and what usually happens with them.

Mr. Wicks responded that the location with which he is involved is right at a power plant site. There are no transmission costs involved due to the proximity to the plant. The load is basically constant once the plant is on-line. There is not a lot of peaking in this kind of a treatment plant. It is envisioned that the peaking would be provided to customers by the various groundwater basins. The plant runs year-round, and when the demands are low, the excess water goes into the groundwater basins below the ground where it does not evaporate and is simply pumped back out when needed.

Additionally, Mr. Wicks stated that the by-products of desalination certainly are a concern to environmentalists and to the American Water Company. By locating the process near a power plant, water from the ocean is being used for cooling. A tremendous stream of water is pulled out of the ocean, probably in excess of 500 million gallons per day.

When the tap is taken off that line to go directly to the treatment plant and the process involves removal of the salts and everything else in the water, it is a reverse osmosis process. The water can be taken down to 200 parts per million of TDS, but the rest of it has to go back into the receiving stream. The waste is discharged back into the ocean from the power plant; however, on the basis of volume, the amount is incidental. The volume is far less damaging to the environment than building another dam or the other alternatives that are required to add to the water supply. Another dam cannot be built in California.

Indoor Water Demand

David Layton, of Lawrence Livermore National Laboratory, noted that the minimum demand usually seemed to be in January, which represents primarily indoor water use. To assure customers that they are being providing a secure and reliable water supply, it would seem important, from a company standpoint, to meet that indoor demand.

Mr. Wicks responded that his customers use on average 0.6 acre-foot annually. In some areas they use a lot more water because of the desert, but that averages about a full acre-foot per customer. The wintertime demand is certainly something to consider.

Cost of Water

Bruce Macler, of the U.S. Environmental Protection Agency, was interested in the definition of water—whether it should be considered a product or a service. He pointed out that if it is a product, then product liability comes into play; otherwise it does not. Dr. Macler said that if you have a service, then the SDWA may not really apply. He wanted to know how to protect the public if water is a service rather than a product.

Mr. Wicks responded that AWC does not charge for water, only for delivery. Water is a natural resource that is modified to some extent to meet certain standards and delivered through a series of pipes and reservoirs. He tells people that they are charged for service and it had better be the best service available. Given this fact, the water company is regulated by the utilities commission, so it does not earn on the labor that goes into providing that service. The only way a private water utility makes money for its shareholders is through the investment in pipelines, reservoirs, and wells. When the water comes out of a tap it must meet certain minimum standards as set by the EPA, and the water company is successful at that but is still getting sued.

An unidentified speaker was interested in knowing the actual cost of producing an acre-foot of water in California from the available sources of supply.

Mr. Wicks answered that the service costs roughly $2.50 per 1,000 gallons. Multiplying that by 326 (the number of thousand gallons in an acre-foot), the cost to the customer is approximately $1,000 an acre-foot.

The water company has no authority to tax people. The city wants to take the company over because it says the bills are the highest in 10 surrounding cities. However, revenue that comes in from the individual taxpayer in those cities with municipal water systems is not considered in the analysis of water bills. If only the water bill is examined, the company is second highest in terms of actual cost of water, but if all the other sources of revenue for those other cities with municipal water systems are examined, the company is second lowest.

Contamination

Mark Matsumoto, of the University of California at Riverside, asked why the problems are treated if very little water is for direct human consumption.

Mr. Wicks stated that there are a lot of experiments under way, such as the Irvine Ranch Water District that has portions of its water system piped in two different ways. One is for water that goes inside the building; the other is for irrigation water outdoors and is reclaimed water used in a separate pipeline. He said that this is very expensive to do. In Barstow, every customer uses 1 acre-foot of water, most of which is outside and cheaper. The current standard concentration for arsenic is 10 parts per billion (ppb) though it used to be 50 ppb, and decreasing it to 2 ppb was considered. At 2 ppb, every well in Barstow would need treatment, and it would have been cheaper to put 100 miles of pipeline in to parallel every pipeline in the streets in Barstow and then simply provide treatment for the small amount of water that goes into a home. The final number came in at 10 ppb, and only 2 out of more than 20 wells reflected concentrations greater than that.

Don Phipps, of the Orange County Water District, made a comment about microbial contamination. He said that if you follow water and other sources, the organisms that live in some of these waters can actually survive under incredibly oligotrophic conditions or low parts-per-billion concentrations of carbon. However, the microbes present are not necessarily harmful. Mr. Phipps mentioned that bottled water is also not sterile or particle free. He said that in fact, no commercial product other than certified particle-free water would be particle free. No commercial water system is going to produce a water of that quality.

Mr. Wicks agreed with Mr. Phipps's comments and replied that his company has to send out a consumer confidence report every year. He said that in some samples, bacterial contamination will be found. For example, the company had a situation in the greater metropolitan area with part of its water coming from the Metropolitan Water District, which changed its disinfection to chloramines. Free chlorine was going in from the company's wells, and part of the system ended up without chlorine, leading to bacterial problems. Planning activities are going on underground, yet nobody knows exactly what the cause is.

Dr. Macler explained that the problem is that the Food and Drug Administration does not have the resources to ensure that standards are being met. It is behind EPA in terms of regulations actually on the books. He pointed out that the requirement is for pathogenic microorganisms, not bacteria or other microorganisms that are nonpathogens. Pasteurized milk and water have organisms in them that will grow but are not considered pathogenic.

9

Sustainable Development: Role of Industrial Water Management

Bhasker Davé
Ondeo Nalco

INTRODUCTION

Sustainable development is a development path that can be maintained indefinitely because it is socially desirable, economically viable, and ecologically sustainable. Economically viable sits at the top of the pyramid in Figure 9.1 because it a very important factor in an industrial environment. Highly sustainable development in industry works only if the company can still make a profit. In other words, there is no such thing as a "golden subsidy."

Key Drivers for Sustainability

Global freshwater consumption quadrupled in the last 50 years. In 2000, there were 5,000 km^3 of fresh water used. Sector withdrawals are shown in Figure 9.2, with 70 percent going to agriculture, 20 percent to industry, and 10 percent to domestic uses.

However, in looking more closely, water usage varies considerably between developed countries and developing countries. The water demand for the top four industrialized countries (United States, France, Germany, and Canada) shown in Table 9.1 is significantly higher for industrial than agricultural use. In India, China, and Brazil, large centers of development, water use varies considerably from that in the industrialized countries. For India and China, respectively, 93 percent and 87 percent of the fresh water used is in agriculture, whereas industrial uses are very small, with 4 percent for India and 7 percent for China. However, these countries are now going through an explosion of industrial growth. The gross domestic product (GDP) of China is growing 8-9 percent a year and India's GDP is growing 7 percent a year. Such growth will no doubt have a significant impact on water use. If world water use doubles, where is the fresh water going to come from? As the rest of the world is striving to be "developed," how will the increased freshwater demand for industrial use be satisfied? Industrial water management is going to be a very critical issue in making development sustainable.

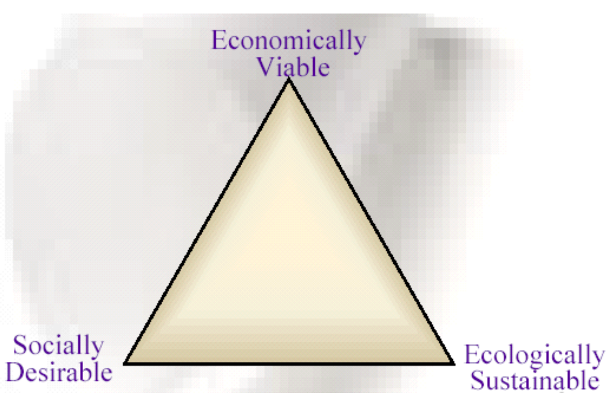

FIGURE 9.1 The three points of sustainable development.

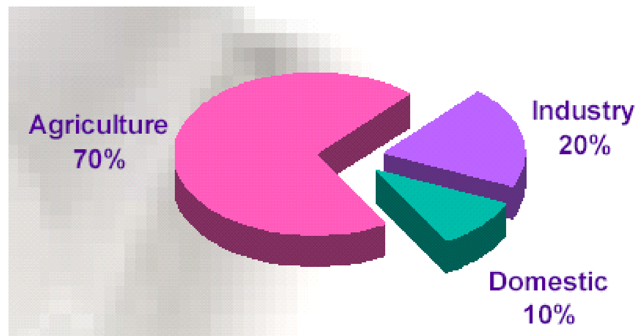

FIGURE 9.2 Global water withdrawal by sector. SOURCE: Igor A. Shiklomanov, State Hydrological Institute, St. Petersburg, Russia, and UNESCO, Paris (1999).

TABLE 9.1 Comparison of Water Usage for Developed and Developing Nations

	Domestic Use (%)	Industrial Use (%)	Agricultural Use (%)
Canada	11	80	8
United States of America	12	46	42
France	16	69	15
Germany	14	68	18
Brazil	43	17	40
China	6	7	87
India	3	4	93

SOURCE: Food and Agriculture Organization (1999) AQUASTAT estimates.

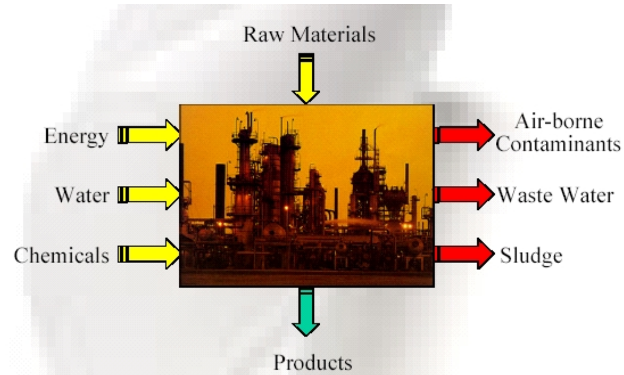

FIGURE 9.3 Industrial inputs and outputs.

Industrial Perspective

Figure 9.3 shows some very generic input-output for a given industrial site. The three major imported resources are energy, water, and chemical entities, and the undesirable outputs are airborne contaminants, wastewater, and sludge. Therefore, from an industrial perspective sustainable growth goals include reducing both resource consumption (e.g., water) and harmful environmental impacts, while increasing profitable growth.

In looking at the economic intensity of water and energy for different industries, pulp and paper and petroleum refining are the largest users of water and energy in the manufacturing sector (Figure 9.4). The numbers shown represent cubic meters of water used per dollar value of the product output. For energy, the units are megajoules (MJ) of energy used for every dollar of product made.

Integrated Water Management

It is important to look at the manufacturing system in its entirety to address water resource management issues (Figure 9.5). Water is typically used in three main areas: manu-

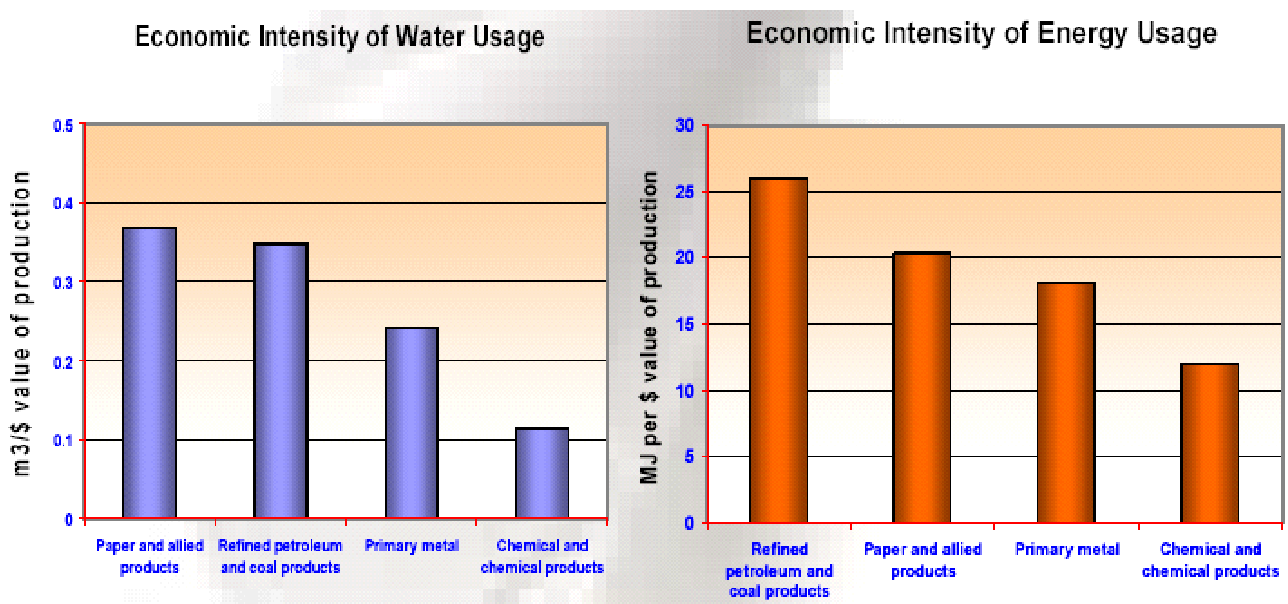

FIGURE 9.4 Water and energy use.

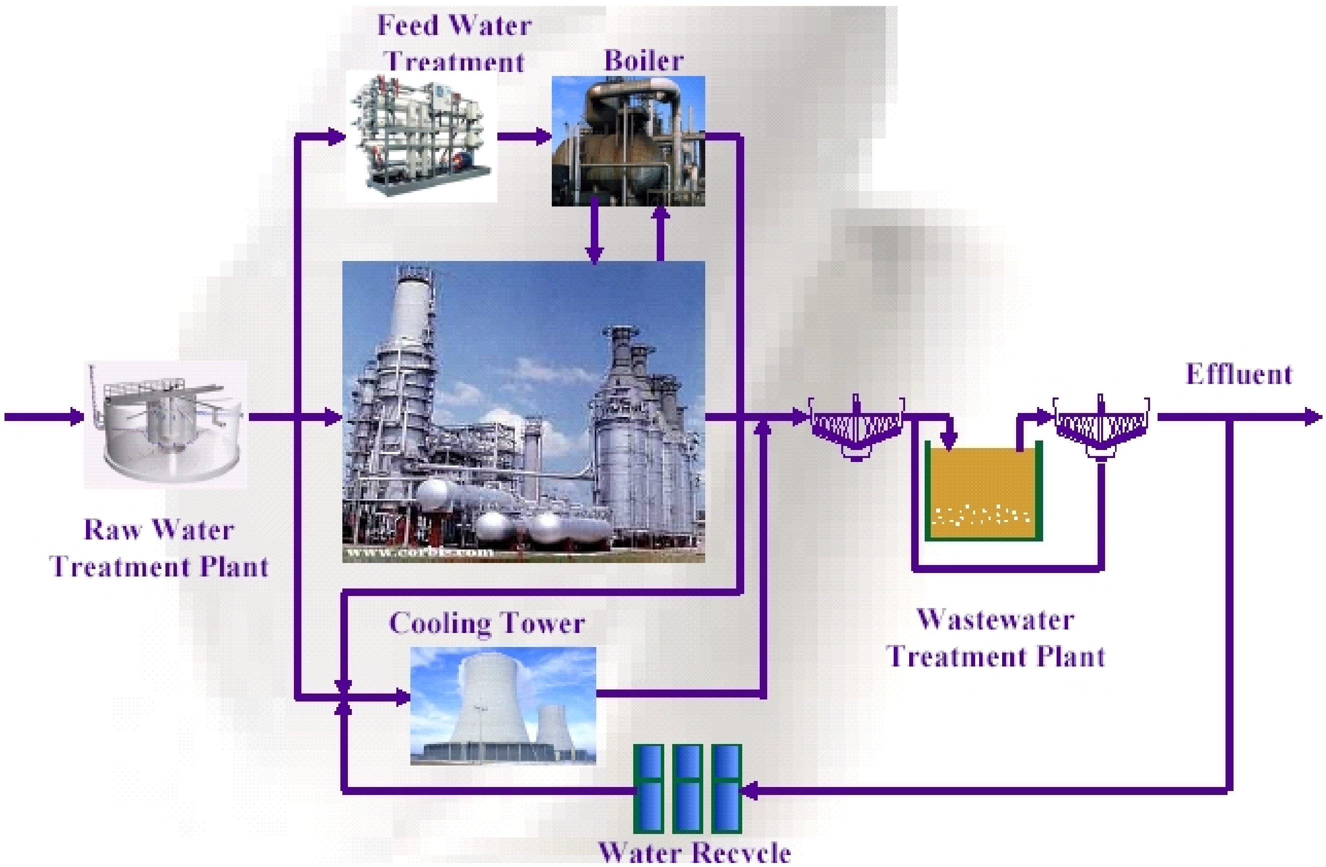

FIGURE 9.5 Integrated water management.

facturing process, cooling water, and feedwater for the boiler system to generate steam. Typically, there is also raw water treatment, especially when surface water is being used; wastewater treatment, which includes removing solids; and biological treatment.

Integrated water management entails evaluating and optimizing all of the resources used for an entire site. Some of the water flows are shown in Figure 9.5. For example, the condensate from the process flows back into the boiler for the recovery of heat and water. The boiler blowdown or the effluent of the whole plant could also be used as a cooling tower.

WATER RESOURCE MANAGEMENT

Figure 9.6 shows the hierarchical approach that Ondeo Nalco has developed to address water resource management. The foundation of this approach is conservation, or reducing water use through improved operation of existing equipment and processes. This could mean understanding and preventing scale, corrosion, and microbial formation. Reuse deals with understanding the water quality requirements for the water demand and matching the wastewater from one area as makeup for another area. For example, boiler blowdown could potentially be used as a cooling tower makeup. On top of the pyramid is the recycle option, where chemical sciences currently make a significant capital investment. There is a high level of resource utilization and risk of contamination, but the risk decreases any impact on the environment.

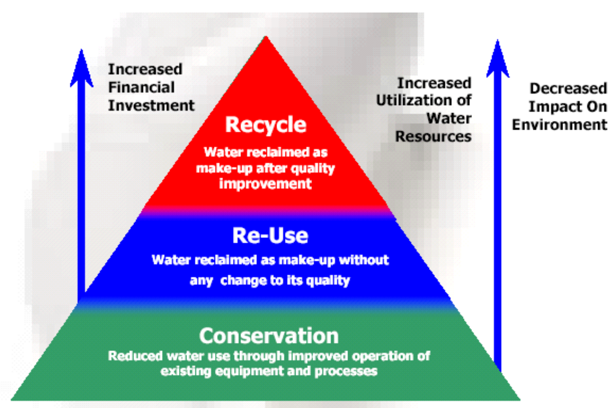

FIGURE 9.6 Water resource management and the Advanced Recycle Technology (ART™) services pyramid.

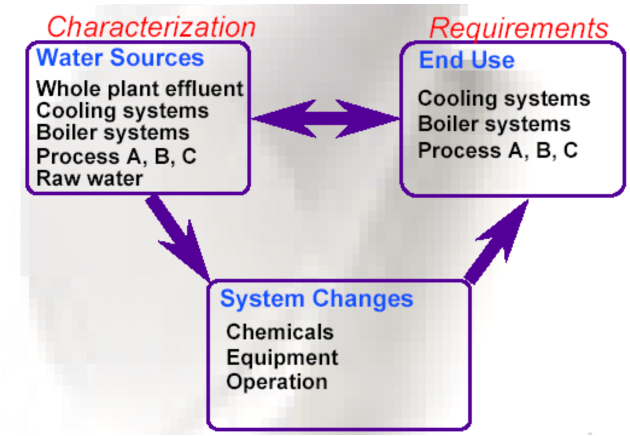

FIGURE 9.7 Water process management.

Water Process Management

A key part of water process management is characterization from a chemical science point of view (Figure 9.7). For example, efforts are being made to recycle centric water from polyvinyl chloride (PVC) manufacturing. PVC manufacturing actually uses deionized water in the suspension polymerization process. In fact, for every pound of PVC produced, a pound of deionized water is used only once and then discharged.

One of the greatest concerns about recycling this water is the presence of residual chemicals left over from various stages of the production process. Typically, a free-radical scavenger called a "shortstop" is used to increase the polymerization reaction. If the shortstop remains in the water and ends up in the front of the batch reaction, it can potentially cause problems. Concentrations as low as 50 parts per billion (ppb) of shortstop in water used for the suspension polymerization process can have a detrimental effect on product quality and productivity.

Another example comes from the pulp and paper industry where, during the pulping process (especially mechanical pulping), a significant amount of organics from wood goes into the water and can potentially cause a problem in the papermaking process. It is difficult to measure these contaminants and to know whether they will be harmful to other processes.

Water quality requirements are important for the cooling water system, the boiler feedwater, and the manufacturing process. The water quality requirements, however, are not very clear, and even the people who manufacture do not know the exact quality requirements. Identifying water quality requirements is very important for the manufacturing process since matching them utilizes conservation and reuse approaches that end up being very cost-effective for managing water on an industrial site.

However, when the water system changes, three major components have to be addressed: chemicals, equipment, and operation. By changing the chemistry it is possible to handle the chemical contaminants. For example, a trash-resistant polymer has been developed so that more organics can be handled in the papermaking process and still produce high-quality product. The other important aspects of the system are the equipment and the operation. For example, bringing in sensor technology and automating water treatment will make the process more viable because it will improve the reuse and recycling of the water and decrease the amount of harmful contaminants produced.

Figure 9.8 shows a five-step approach developed by Ondeo Nalco for site-wide integration of the water resources. The first step is scope development, which involves clearly defined goals and a detailed project plan, including a time line and the resources required. Then a plant audit is conducted to identify best practices. This is where first principles of chemical engineering are applied such as mass and energy balance for the water resources and contaminants. Technical and economic evaluation is then carried out to evaluate different options that might be available. The next step is the pilot study evaluation where the most economically and technically best solution is determined for a given site. Finally, there is process implementation. This is not an additional capital requirement at the site, but often rather the implementation of good ideas.

Advanced Water Chemistry Modeling

To model a system, a steady-state simulation is assumed. Any given mode will consist of three major components for evaluation: (1) chemical and physical properties, (2) unit operations models, and (3) economic correlation (Figure 9.9). Chemical and physical properties such as mass balance,

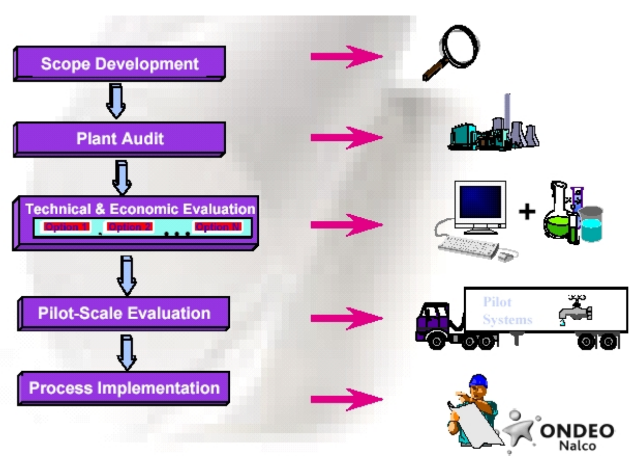

FIGURE 9.8 Advanced Recycle Technology services.

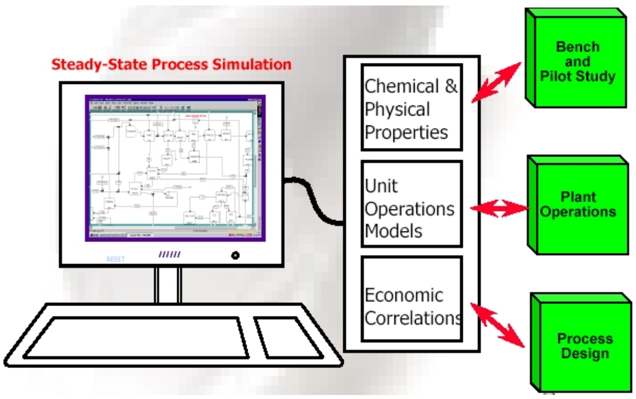

FIGURE 9.9 Advanced water chemistry modeling.

air versus water discharges, and effects of pH and temperature, are evaluated. For unit and plant operation, cooling towers, boilers and membrane separations, ion exchange and clarification, and the manufacturing process have to be reviewed. It is necessary to look at the site-wide water management and every place that water plays a critical role. Finally, economic correlations are carried out. Ideally, flow sheeting is performed to utilize available technical merits. Factoring in capital expenditures for the new water treatment equipment and operating expenses also helps the economic evaluation, not just the technical merits.

WATER RESOURCE MANAGEMENT EXAMPLES

Virtual Paper Mill

In this simulation of an integrated mill, a very small part of the pulp and paper process involving only the paper machine is examined (Figure 9.10). It is a very fairly complex stream or flow sheet that helps to optimize water use in the mill. Typically in the paper machine, the starting rate is for water to be used about 17-25 times before it is discharged. Each component is analyzed for the potential to build up mineral deposits (form scale). Computer modeling is a very good tool because it helps to look at situations under varying conditions.

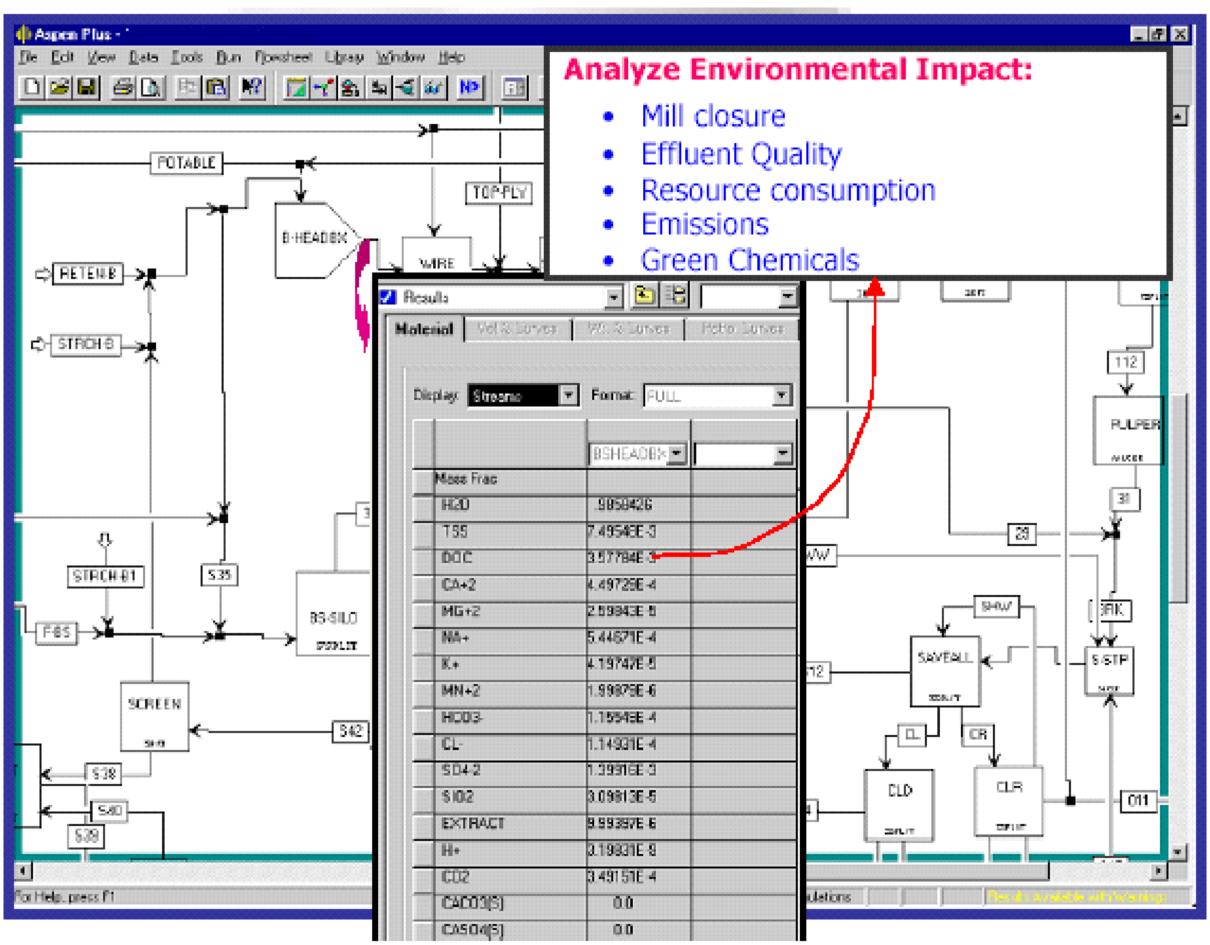

FIGURE 9.10 Virtual paper machine model.

From a manufacturing point of view, the virtual paper machine is not enough because it cannot determine how water chemistry will affect the product quality. It cannot predict whether the machine will still run at 60 miles per hour or will have to slow down. Therefore, Ondeo Nalco research plays a very important role in helping to better understand the manufacturing process and the role played by water, energy, and fiber. The most critical part here is the ability to look at the impact of this water in different arenas. Equipment, not just chemistry, is also important. It is necessary to look at what equipment can be used.

Recycled Newsprint Facility: Integrated Water Resource Management

At a North American newsprint site the goal was to reduce water demand by 25 percent of the 12 million gallons used per day and to improve fiber recovery. A key aspect of water recovery is that it often leads to improved recovery of other resources. This site also considered using municipally treated wastewater. Contaminant buildup in the system was also an issue. Ondeo Nalco used an integrated approach to look at resource management including the mass and energy balance using computer simulation to evaluate the conceptual designs.

The site discovered it was possible to reduce the water usage in the plant by 33 percent by taking higher-yield fibers. Each percentage on the fiber yield is worth a million dollars per year. The implementation cost is about $2.5 million, with an annual savings of $5.3 million a year. This case shows that it is possible to achieve sustainable development at a reasonable savings.

U.K. Petroleum Refinery: Water Audit Uncovers Saving Potentials

The next example is from the petroleum refinery industry. The goal here was to look at reducing the total cost of operation especially from a water resource point of view. In looking at benchmarking, almost two times as much water is used in the processing of crude compared to the industry standard. By applying the integrated resource approach at the site, the best practice alone saved 450 m^3 per hour, which resulted in a savings of about 2,000 gallons of water per minute. This is a good example of what can be achieved by implementing best practices. Overall, saving 1,000 m^3 per hour brings the refinery close to the industry average. It will save about $2.7 million just by preventing a leak and doing the blowdown control. Looking at the alternative source for makeup water can provide another 1 million dollars in condensate return, and returning condensate to the boiler leads to energy and water savings worth $1.2 million. By implementing a site-wide approach of water and energy resource management, it is possible to give money back to the manufacturing sector.

Green Chemistry: ULTIMER® Coagulants and Flocculants

The better reuse of wastewater involves removal of suspended solids, which typically requires coagulation and flocculation. These processes are often used in a variety of industrial and municipal wastewater areas. Water-soluble polymers are used for flocculation in sludge water, and Nalco is one of the largest manufacturers of this liquid water-soluble polymer.

When liquid water-soluble polymer is used, the liquid part is typically oil. The polymer is a discontinuous phase made in the continuous phase of oil. When this liquid is used in wastewater treatment, the oil is actually there to carry the polymer, after that it has no use. Oil is there only to control viscosity. It is thus a manufacturing issue. Nalco has built a patented technology of liquid dispersion polymers, so that now the polymer is actually in a solution of ammonium sulfate that is also surfactant free. In fact, the salt used is the by-product of other manufacturing processes. Thus, waste is being taken from one industry used for Nalco raw material. There is complete elimination of oil and the surfactants, which makes transportation easier because the product is also free of volatile organic compounds, environmentally benign, and easier to handle. This product won a Presidential Green Chemistry Challenge Award in 1999.

Green Chemistry: Lazon® Biocides

Microbial activity in recycled water is a critical issue. Using chlorine as a biocide often leads to formation of potentially harmful by-products. Green biocides, based on hydrogen peroxide and other nonhalogenated compounds, have been created that can maintain residual toxicity for bacteria, but do not create any organic by-product contamination The environmentally friendly end products are listed in Table 9.2. The green biocides have also shown improved control of microbes.

Automation and Cooling Water

The Erin Brockovich, Pacific Gas & Electric, story helped bring to light the issue of chromate use in industry cooling towers. Using chromate at pH 6 inhibits corrosion, scale, and microbial buildup. Chromate has many benefits, but it is

TABLE 9.2 Green Chemistry and Lazon Biocides

Green Biocide	End Products
Glutaraldehyde	Carbon dioxide and water
Hyrdrogen peroxide	Oxygen and water
Ondeo Nalcon Lazon® technology—multicomponent, nonhalogenated, oxidizing biocide	Carbon dioxide, water, and oxygen

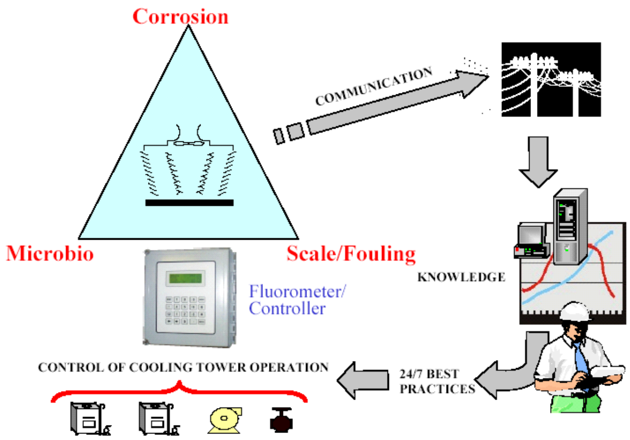

FIGURE 9.11 Automating the cooling water "triangle."

not a sustainable solution. Chromate has been found to be very harmful to humans exposed to air emissions from cooling towers. The blowdown from the cooling tower is supposed to be a zero liquid discharge, but the rubber linings can give out and this is what led to the aquifer contamination that Erin Brockovich identified.

Since chromate cannot be used now, new solutions are needed. Automation today plays a key role (Figure 9.11). For example, a fluorometer can be utilized to monitor microbial activity in cooling towers. If microbial activity is found, as signaled by a change in fluorescence, a biocide will be used on an "as-needed" basis. The system can also measure corrosion and scaling in real time. Therefore, if people use more dirty water in the cooling tower, they are taking more risk, but by bringing the right chemistry and automation, they can manage the risk more effectively.

TRASAR® for Reverse Osmosis (RO) Scale Control

The TRASAR system (Figure 9.12) accurately measures the concentration of antiscalant in either the feed or the concentrate streams. The system utilizes fluorescence technology to enable the scale inhibitor chemical feed to be maintained at the prescribed dosage. The RO TRASAR technology ensures that the desired dosage is maintained at all times.

TWENTY-FIRST CENTURY INDUSTRIAL WATER MANAGEMENT

Figure 9.13 shows what industrial water management will look like in the twenty-first century. Some of the items shown are already happening; for example, RO is the main choice for the boiler feedwater system. Also, microfiltration (MF) and ultrafiltration (UF) clarification membranes are used in the manufacturing process.

FIGURE 9.12 TRASAR for RO scale control.

In wastewater treatment, a membrane bioreactor is combined with the clarification membrane. This produces half the amount of sludge and more than 95 percent removal of the biological oxygen demand (BOD). High BOD is typical of polluted water. Very high quality water is generated that can be recycled back to the cooling tower or to the RO system.

For surface water, 50 percent of the new industrial water treatment in Europe is now based on membrane technology. The total growth in the industrial segment this year is about $2.5 billion in capital sales of membrane technology in industrial water, excluding municipal use. The operating cost to the customer in the manufacturing sector is $7 billion, and the growth rate is about 10 percent annually. In looking at industrial needs, it is important to reduce the total cost of operation, improve the liability, and improve the performance.

SUMMARY

Industrial water management is a very critical component of sustainable development. An integrated approach to industrial water management can actually provide a cost-effective solution; chemistry, equipment, and operations, especially automation, play a significant role. Chemical

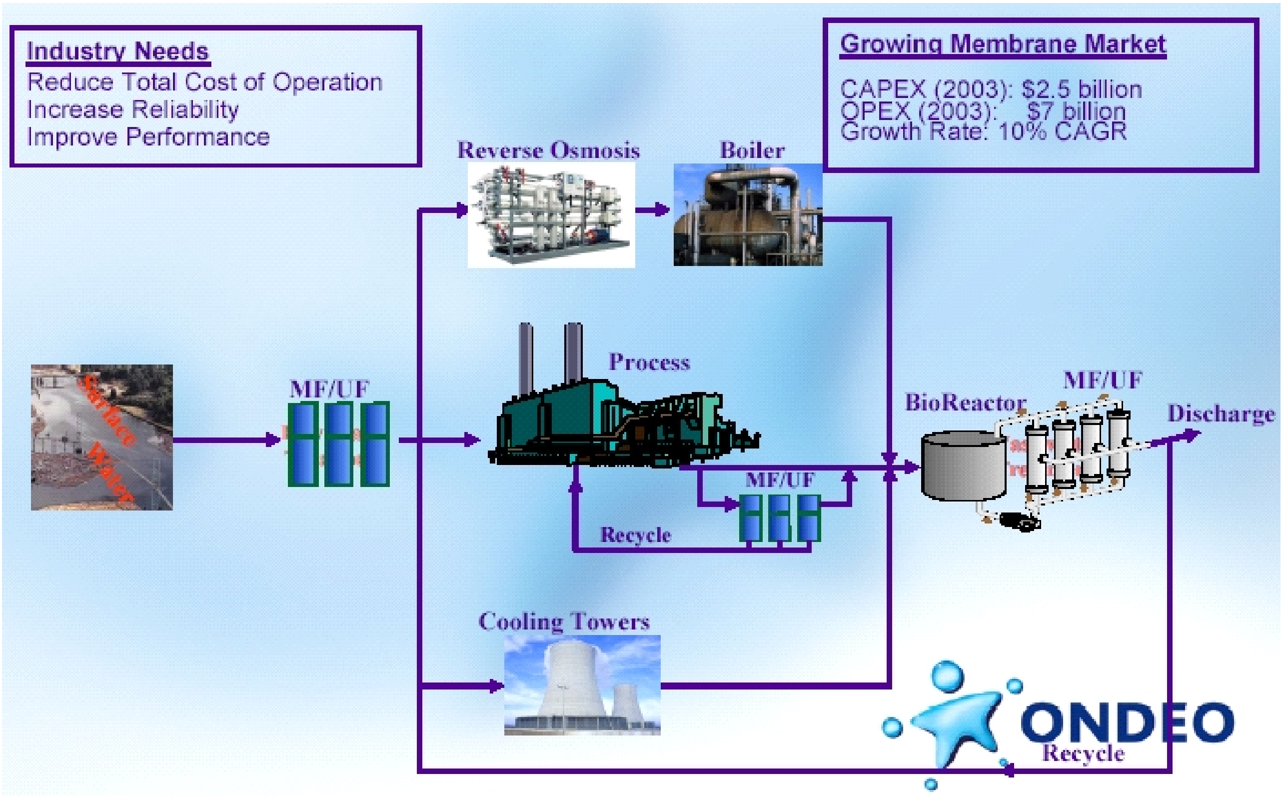

FIGURE 9.13 Twenty-first century industrial water management and the role of membrane separations technology.

sciences should look at this tier as an opportunity for new business, especially the membrane separations equipment area. There is tremendous growth to be made here, and it will play a very critical role going forward in industrial water management.

DISCUSSION

Microbial Monitoring

Dick Carlson, of San Diego County, was looking at the use of recycled water for cooling towers. He said that one of the concerns of recycled water is the growth of bacteria that lead to Legionnaires' disease. He wanted Dr. Davé to discuss more about using the Ondeo Nalco technology to monitor biological contaminants in real time.

Dr. Davé responded that they can monitor on-line microbial activity in the cooling water system, but the process does not distinguish between *Legionella* and other organisms. It measures total microbial activity in the system through a technology based on fluorescence. There is a fluorescence moiety that reacts with enzymes in the bacteria by oxidizing and changing the fluorescence properties.

Industrial Reuse of Water

Vasilios Manousiouthakis, of the University of California at Los Angeles, stated that it is important to have some metrics for the source water, whether it is renewable or nonrenewable. This may not be a concern here in the United States, but it is a concern in many parts of the world where fossil water is being extracted at very high rates. This water is not renewable, and it is important that industry is aware of this particular issue and is not tapping into nonrenewable water. He asked about the rate of reuse in the United States. It was mentioned that industrial use is around 46 percent, and he wondered how much of that water is being reused today by industry.

Dr. Davé replied that a significant part of that water is not being reused because the largest consumers in the industrial segment (power generation, manufacturing, and mining) are actually the power generation segment. Most of the power generation uses water once through the system. Of the 46 percent, a significant portion is actually power generation.

He continued to explain that the world is very connected. For instance, the outbreak of severe acute respiratory syndrome (SARS) is not a Chinese problem but a world problem affecting our economy. There is interconnectedness and it is necessary to take a more global view of the total cost and impact on the environment.

Integrated Source Approach for New Facilities

Dan Askenaizer, of Montgomery, Watson, and Harza, was curious about whether industrial clients building new facilities are requesting that an integrated resource approach be incorporated up front in the design of this new facility.

Dr. Davé said that it is not the normal or standard practice. It occurs more on a sporadic basis, especially by the people who are putting in a new desalination plant in a refinery. In one case, resource management was implemented from the design phase because the cost of water was very high. They actually built a desalination plant along with the refinery so they had an integrated approach.

10

Water Solutions and Strategies in the Chemical Industry

*Carol R. Jensen**
The Dow Chemical Company

Large technology-driven companies have both responsibilities and opportunities to use water resources wisely. This involves careful use of water (conservation), as well as responsible control of contaminants in discharge streams (pollution control). In addition, there may be opportunities to leverage technology and knowledge to opportunities outside these companies as products or services. The Dow Chemical Company is an example of a company that actively participates in each of these water-related activities.

The purpose of this paper is to review examples of Dow's activities in each of these areas. It will cover two aspects: (1) Dow as a water user and (2) Dow as a supplier of clean water technology. It is hoped that Dow's experiences will enable and encourage other companies and organizations to enhance their water-related activities.

DOW—A WATER USER

Overall, Dow is a significant user of water. Globally it uses about 900 billion pounds of fresh water per year (~300 million gallons per day). Approximately 90 percent of this water is pre-treated before use, and 70 percent is post-treated and discharged after being used only once. From a financial standpoint, Dow invests about $100 million annually for water acquisition, pre-treatment, post-treatment, and disposal. Overall, about $1.2 billion of capital infrastructure is employed for water treatment and disposal. The water demand at its major sites is increasing by 6 percent each year. Over the next 10 years, Dow expects to make water-related capital investments of $1 billion and increase its annual water-related operating costs by $100 million. Water is clearly a significant economic issue for Dow. Management of water resources and assets across the company is recognized as a critical activity.

World-class companies, however, need to manage more than just resources or assets. They also need to manage public perception, particularly in the communities where they are located. In 1996 Dow announced 10-year public goals related to its environmental, health, and safety activities. These goals were voluntarily proposed. Dow's annual progress toward these goals can be tracked on its public web site, *www.dow.com*. These goals include the following reductions in emissions to air and water for Dow's global operations.

- Reduce chemical emissions by 50 percent.
- Reduce priority compounds by 75 percent.
- Reduce the amount of waste and wastewater generated per pound of production by 50 percent.
- Reduce dioxin emissions by 90 percent.
- Reduce energy use per pound of production by 20 percent.

Figure 10.1 shows Dow's progress toward its wastewater reduction goal. In 2002, Dow produced 2.85 pounds of wastewater for each pound of product. This reduction has occurred as Dow's total production has increased.

Dow's chemical processes also produce waste chemicals, some of which are released to the air or water in small quantities. Figure 10.2 shows Dow's progress toward its global public goal for dioxin emission. In this figure, dioxin is defined as the totality of 7 dioxins and 10 furans, and "TEQ" denotes "toxic equivalent," a quantitative measure of the combined toxicity of a mixture of dioxin-like chemicals. Dow released a total of 8.68 g of dioxin (TEQ) in 2002. It is on target to meet its public 2005 goal of 4.05 g. These small amounts are dispersed in literally trillions of gallons of water, resulting in concentrations on the order of a few parts per

*Contributing author David J. Moll, Ph.D., is a research scientist in Performance Chemicals Research and Development, the Dow Chemical Company.

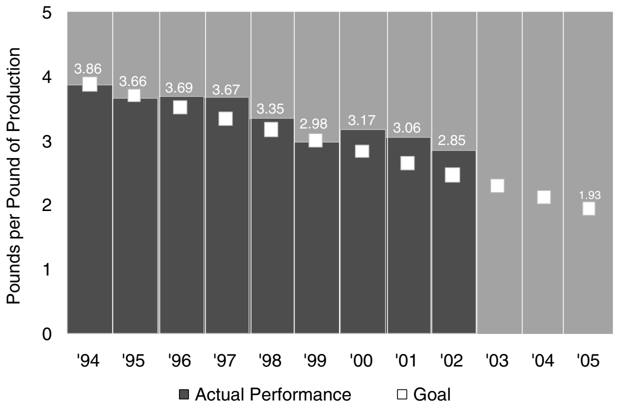

FIGURE 10.1 Dow's progress toward its public 10-year wastewater reduction goal.

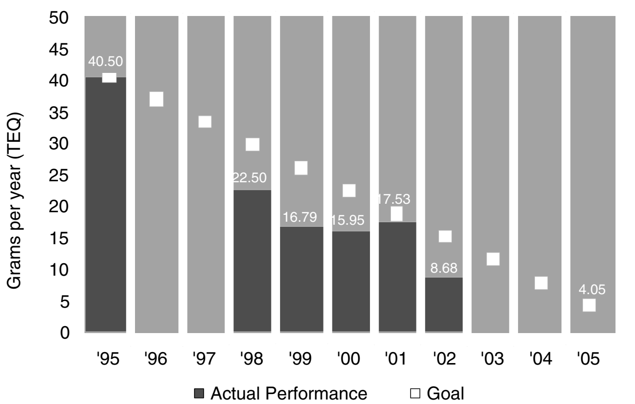

FIGURE 10.2 Dow's progress toward its 10-year public dioxin emission goal.

quadrillion (10^{15}) or less. Developing the sampling and analytical technology to detect these concentrations has been a formidable challenge for Dow.

The magnitude of cost and complexity of Dow's water-related activities prompted it to create an Environmental Operations Business in 1998. One of the goals of this business was to integrate Dow's best practices in water, manage resources and technology, and optimize supplier relationships globally across the entire company. Pragmatically, creating a "business" or "profit-and-loss" entity in a company elevates the importance of its activities by making it financially accountable.

The Environmental Operations Business is responsible for managing Dow's water envelope globally. It also manages water rights, conveyance, quality, use, and treatment for discharge. It is responsible for $3 billion of water-related assets, and consists of about 700 employees. It has the goal of reducing costs of all environmental operations by $1 billion dollars over the next 50 years. During its first year of operation it achieved a 3-5 percent reduction in water use across the entire company. Several specific examples follow.

Example 1

To meet expansion needs and to meet Dow's long-term environmental objectives, the Terneuzen site in Netherlands completely restructured its water infrastructure. The site now recycles 80 percent of its treated fresh wastewater and has reduced energy consumption for producing boiler feedwater by 90 percent. This is equivalent to reduced production of 55,000 tons of CO_2 per year (or saving 930,000 million Btu per year).

Other significant results of this project include the following:

- annual savings of U.S. $1.2 million for the cooling tower water supply as a result of recycling treated fresh wastewater, instead of importing fresh water;
- by replacing multistage flash evaporation of seawater with reverse osmosis technology, 50 tons of low pressure steam is made available per hour for alternative uses on-site; and
- long-term availability of fresh water in the region made possible by the significant increase in recycling.

The Terneuzen case demonstrated clearly that conservation and growth *are* compatible. In fact, in many cases, it makes excellent business sense to pursue water conservation and recycling.

Example 2

In Freeport, Texas, home of Dow's largest site, an initial goal of 30 percent reduction in freshwater use was set. By simply looking closely at water use, Dow found that it was losing 13,000 gallons per minute, merely through the inefficiency of water flow control within the system. This problem was remedied through simple enhancements to water management protocols, resulting in an annual savings of $135,000 per year in water and electricity.

This example demonstrated that saving water often comes not from new technologies but from better management of water transmission from one point to another. This success was the result of a Six Sigma project. Six Sigma methodology is playing a major role at Dow in providing a consistent, thorough methodology for evaluating water envelope management issues.

Example 3

A cooling tower optimization project that is under way at Dow's operations site in Midland will reduce freshwater

FIGURE 10.3 Dow's recently developed internal slogan to encourage wise use of water resources.

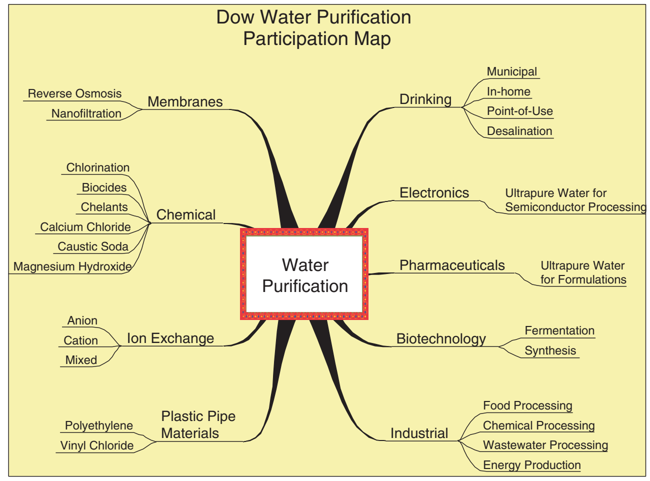

FIGURE 10.4 Examples of Dow's activities in water purification technology.

consumption by 37 million gallons a year. What was learned from this project is being replicated at four other Dow sites. One of the clear advantages of a global Environmental Operations Business (EOB) approach is that successes at one location can be effectively leveraged across the entire global corporation.

Dow's Environmental Operations Business is also responsible for creating a mind-set and culture for good water management. Figure 10.3 shows Dow's recently developed slogan to keep a cultural awareness of the importance of good water management prominent.

DOW—A SUPPLIER OF CLEAN WATER TECHNOLOGY

The second half of this overview of Dow's water-related activities deals with extensions of Dow's technologies to external applications. Dow has a rich and extensive history of developing and supplying water purification and handling technologies. Figure 10.4 highlights some of the major categories of Dow's participation. These include a variety of chemical treatment approaches: (1) ion exchange; (2) specific technologies for the electronics, pharmaceutical, and biotechnology industries; and (3) separation membranes, among others. In many cases, technology developed for Dow internal needs is now being supplied to satisfy external needs and applications.

Separation membranes, in particular, are a class of technologies with diverse and rapidly growing uses. Dow began research on membrane technology in the mid-1950s. Early research focused on developing microporous hollow-fiber technology that led to kidney dialysis membranes, reverse osmosis (RO) membranes, and gas separation membranes.

This overview highlights Dow's activities in reverse osmosis and nanofiltration. In 1986, Dow acquired the FilmTec Corporation, a small company located in Minnesota. This accelerated Dow's participation in the RO and nanofiltration market.

FilmTec's standard membrane family is based on an interfacial reaction that forms an aromatic polyamide thin film at the surface of a microporous support layer. This ultrathin film is a cross-linked polymer network that serves as the discriminating layer that does the separation. Depending on cross-link density and other factors, this layer can selectively reject various salt ions, organics, or other contaminants while allowing essentially pure water to pass through. This membrane structure is "wound" into a spiral configuration, forming a modular element that is easily installed into a cylindrical pressure vessel.

The total cost of operation of a typical RO membrane plant has been estimated to include 5 percent as membrane replacement cost and 44 percent as electrical power. One of the contributions to society that large corporations such as Dow make is to continually lower technology costs, thus enabling more widespread use of those technologies. Figure 10.5 shows the historical decrease in feed pressure required to yield a constant water production rate from Dow's brackish water elements. This reduction in pressure has significantly decreased the cost of power for reverse osmosis plants.

Feed pressure reductions, element cost decreases, increased salt rejection (selectivity), and other performance enhancements have significantly lowered the historical RO processing cost. Figure 10.6 depicts this decline graphically for both brackish water and seawater desalination. The steady decline in power requirements and capital investment has enabled larger and larger RO plants to be built. Figure 10.7 shows the historical progression of increased capacity for the world's largest reverse osmosis membrane plants, including future plants that are expected to be built. Over a period of 15 years the world's largest plants have grown from 1 million or 2 million gallons a day to more than 100 million gallons a day.

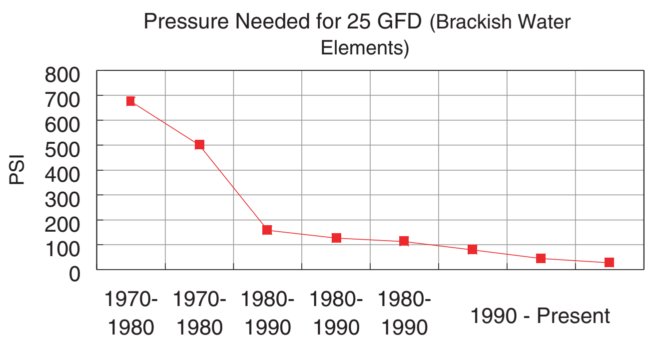

FIGURE 10.5 Historical reduction in operating pressure for Dow's reverse osmosis membranes.

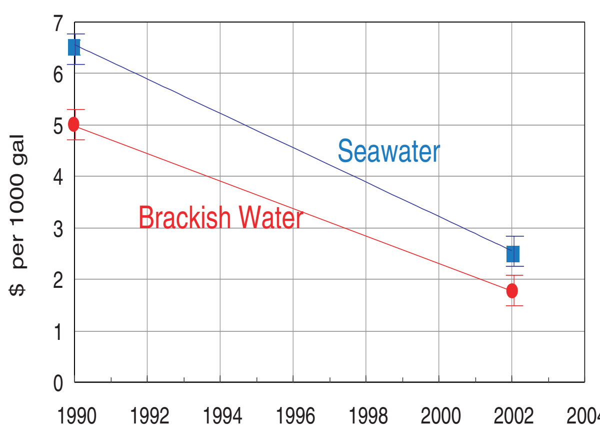

FIGURE 10.6 Historical cost reduction trends for seawater and brackish water reverse osmosis processes.

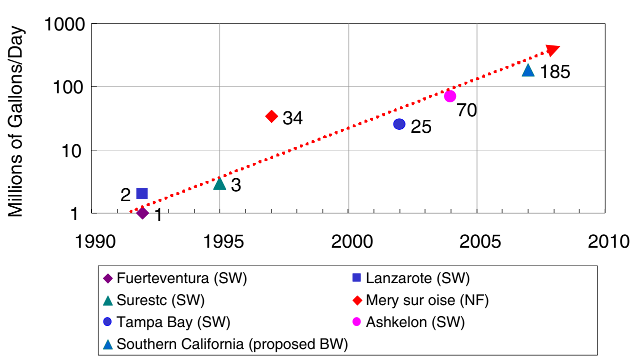

FIGURE 10.7 Reverse osmosis membrane facilities—largest plants as a function of time, with nanofiltration (NF), seawater (SW), and brackish water (BW).

The Mery sur Oise nanofiltration plant in a suburb of Paris, France, illustrates some of the unique capabilities of Dow's membrane science. This plant supplies water for 500,000 residents. Water from the Oise River, over time, has experienced increasing amounts of agricultural runoff, particularly pesticides and herbicides. The local water authority wanted to remove these agricultural contaminants while maintaining the naturally occurring calcium and magnesium ions. Water quality, particularly taste, was a critical driver for this technology.

Dow designed a specific membrane chemistry and structure to meet these requirements. A plant containing 9,100 nanofiltration modules was built based on this technology. It has been in successful operation since 1999.

Figure 10.8 illustrates another application of nanofiltration membrane technology. Dow and Marathon Oil of Houston, Texas, developed a nanofiltration membrane process to remove sulfate from the seawater used for injection into offshore oil field reservoirs. On an offshore oil platform, the only water available for injection is seawater. Barium sulfate scale results when sulfate ions in seawater come in contact with barium in the reservoir rock commonly found in the North Sea and West African oil fields. This scale plugs the pores in the reservoir rock, preventing the flow of oil and thus jeopardizing subsequent oil production. In the past, the problem of sulfate scale formation was tackled by chemical dosing. Nanofiltration enables production of offshore reservoirs where chemical dosing is not adequate or feasible. This example again illustrates the link between energy and water purification. A cost-effective reduced-energy process for sulfate removal actually enables the production of oil in offshore reservoirs that could not normally be produced.

Jurong Island, Singapore, provides a final example of Dow's membrane separation capabilities. This island is one of seven southern islands off Singapore. A modern, integrated petrochemical complex is located there that is a key element of Singapore's strategy to develop Jurong Island into a world-class chemicals hub in the Asia-Pacific Region.

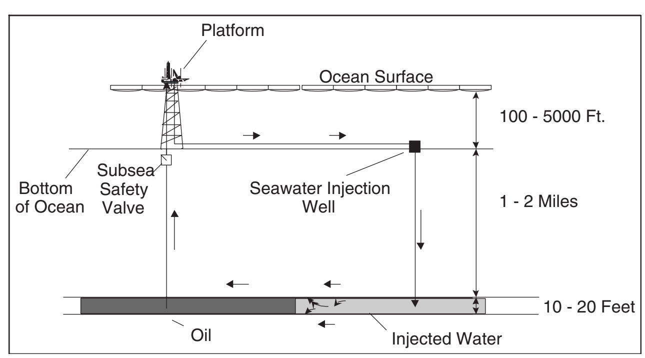

FIGURE 10.8 Nanofiltration membranes remove sulfate ions that could precipitate from water injected into oil reservoirs from offshore platforms.

About half of Singapore's potable water comes from neighboring Malaysia under supply agreements scheduled to expire in 2016 and 2036. Jurong Island's booming petrochemical industry represents a rapidly increasing demand for high-grade industrial water.

In January 2000, SembCorp Utilities & Terminal started a high-capacity reverse osmosis plant designed to treat 6 million gallons per day. This plant will recover up to 86 percent of the tertiary treated sewage water and turn it into reusable high-grade industrial water. The inlet water is biologically active such that conventional membranes would rapidly lose productivity through fouling. Dow installed recently developed, fouling-resistant membrane elements to meet the challenge. This example illustrates how technology developments such as fouling-resistant membrane elements are expanding the role of reverse osmosis technology to applications where it formerly could not be used.

SUMMARY

Large chemical companies such as the Dow Chemical Company are playing critical roles as both users and suppliers of water technology. Dow, in particular, has proactively formed a global Environmental Operations Business with a mission to elevate the importance of water management and standardize best practices worldwide. Using tools such as Six Sigma, this business has established a track record of successes in water conservation and economic savings.

Dow has also embarked on a strategy of public accountability. It has voluntarily created long-term goals related to water use and dioxin-related releases to the environment. These goals were announced publicly. Progress toward achieving these goals is reported annually to the public.

Finally, Dow has a rich portfolio of water-related product technologies. Reverse osmosis and nanofiltration membrane technologies are highlighted in this paper because of their growing use in a broad spectrum of new water purification applications.

The authors hope that these examples of Dow Chemical's water-related activities will enhance the industry's awareness and commitment to proactive and intelligent management of water. There is immense value in the exchange of information between users and producers of water-related technologies. Chemical companies are uniquely positioned to impact the water industry because of their dual roles as water technology users and providers.

ACKNOWLEDGMENT

The authors thank the following Dow colleagues for contributing much of the information and perspective contained in this paper: Ian Barbour, Marvin Bourelle, Roy Davis, Paul Dean II, Peter Dulcamara, Tammy Falardeau, Karl Fennessey, Matt Hallan, Chuck Martz, Bill Mickols, John Osborne, George Quarderer, Lanny Robbins, Kristina Schnepf, Tracy Taylor, and Kelli Walsh.

DISCUSSION

Tertiary Wastewater of Singapore

Dick Carlson, of San Diego County, stated that he had understood that Singapore was moving toward performing reverse osmosis on tertiary wastewater for drinking water rather than just for industrial purposes.

Dr. Jensen responded that it may very well be. Although she has no direct knowledge of the reverse osmosis project, she has met a couple of times with the Economic Development Board, and she knows that it is focused heavily on desalination processes for drinking water. If people think about the industrial consumption there, they will realize how extensive it is.

Nanofiltration Technology

Vasilios Manousiouthakis, of the University of California at Los Angeles, asked if Dr. Jensen could provide some information on the nanofiltration technology and how it compares in terms of salt removal.

Dr. Jensen said that the nanofiltration technology is actually a derivative of Dow's reverse osmosis technology. Nanofiltration is essentially designed on a case-by-case basis to selectively pass, so it is actually designed with different levels of cross-linking and different levels of free amine and free carboxylic acid. The technology can be designed so that it has different porosities and different affinities for separate ions. In terms of salt removal, it depends on the particular application, but generally there is less salt removal and higher water permeability for nanofiltration than for reverse osmosis.

Dow's Environmental Operations

Frankie Wood-Black, of ConocoPhillips, was interested in how well Dow's establishment of its environmental operations is working.

Dr. Jensen responded that it is working well. In the first couple of years, there has actually been some tremendous success at being able to identify some fairly large opportunities for cost reduction just by getting control of the envelope. There has also been the opportunity to have a strategic goal-targeted approach rather than a reactive approach. It has been around for five years, and has had some good success, and time will tell as to whether the success can be sustained.

Dennis Hjeresen, of the Green Chemistry Institute, asked for an idea as to how far that envelope extends. From the discussion it sounds as though it extends to the company, but what about the impact of Dow products on the environment? How far does the thinking extend that there are a lot of developments in terms of pesticides, herbicides, and other products?

In her response, Dr. Jensen said the thinking does extend beyond the company. There is clearly a very focused effort on the subject of sustainable development. As new products are being developed, there is a tremendous sensitivity to what the ultimate outcome of these products will be.

Debbie Elcock, of Argonne National Laboratory, commented that waste and water reduction goals were set prior to the establishment of the EOB and asked what the driver was at that point, because it did not sound as though it was necessarily tied to profits.

Dr. Jensen replied that the goals were set in the early to mid-1990s before the establishment of the EOB and that they were not tied to profits, but to a sense of social responsibility. Once a company gets to be fairly large such as Dow, a lot of attention can be drawn to its environmentally related activities. It was originally set up to be sensitive to important issues and drive the organization to take action. The opportunity to look at someplace where one can actually save money and do something smart is a very high priority.

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Classifying Drinking Water Contamination for Regulatory Consideration

Bruce A. Macler
U.S. Environmental Protection Agency

INTRODUCTION

The bottom line of the U.S. Environmental Protection Agency (EPA) Drinking Water Program is to provide safe water that everyone can drink and remain healthy. Technological applications are necessary to do this, but they must be as vigorous and solid as possible. The majority of the current water treatment needs are day-to-day operations at the local level, specifically at a small system level. Southern California Water and the Orange County Water District are among the top 400 utilities in the United States in size and sophistication. There are 55,000 public water systems in the country that are community water systems. There are more than 100,000 transient water systems. There may be 20,000 more systems that serve places such as schools or factories. These are not as sophisticated, and thus they need very vigorous and robust treatment technologies and approaches.

There is a general misunderstanding as to what regulations are about, what they are aimed to achieve, and how they are developed. The EPA does oversee assessment of wastewater; however, the primary area covered in this paper is drinking water treatment and distribution. Both problems and opportunities are considered.

REGULATORY CONTEXT

The primary goal of regulation is protection of public health. The aim is to have water that is safe to drink, water that is swimmable, and water that provides fish that are safe to eat.

Clean Water Act

Ecosystems are considered particularly under the Clean Water Act. For instance, protecting fish is an issue because there need to be enough fish available that are safe for human consumption.

The Precautionary Principle and Safety

The biggest component is the precautionary principle, embedded in the water laws that lead to water regulations. Applying the precautionary principle means that you want to be as protective as possible. If the risk is unknown, there must be a conservative estimate, and the worst must be assumed. There is also a big consideration of cost-benefit and the appropriateness of matching costs against public health return.

How safe is safe? Perceptions of safety are politically, socially, and economically important.

The federal laws and the regulations are means to ends. The Clean Water Act, the Safe Drinking Water Act, and all of the environmental acts involving other media are like paints on a palette, used to paint a picture of improving public health. For water utilities, the regulations are an end in themselves, because most utilities are not proactive. The top 400 can be proactive because they have the resources and the mind-set. They will deal with contaminants at a much lower level than they actually have to. Many utilities, however, are just trying to meet standards, which mean that the standards have to provide the needed level of protection.

The Clean Water Act rules are fairly simple: water should be fishable and swimmable. It is fishable in the sense that there are enough fish to catch, and from a public health standpoint, they must be edible and nontoxic. Swimmable means that the water is nontoxic. You can swim in it and you can get a little water in your mouth and it will not hurt you.

Safe Drinking Water Act

Ambient water quality criteria have been set up by toxicologists and risk assessors in the EPA and give end points for what is safe. Those end points are developed strictly on a precautionary principle basis and without any regard for whether they are achievable. The health effects of a contaminant are evaluated based on viability and how solid the information basis is. If the information is based on adult exposure, the results are extrapolated to be protective of everyone, and a benchmark is set on a reference dose or cancer level. The value may be well below detection or treatability, but it will stand as the criterion for the contaminant.

Similarly, under the Safe Drinking Water Act, there is also a maximum contaminant level goal for oral ingestion set with respect to risk and conservativeness. There is no consideration of practicality. The goals are essentially zero risk, but zero risk is not achievable. There must be a consideration of what passes or what can be achieved.

From a risk assessment standpoint, this causes problems because the value cannot be detected epidemiologically. Some people have said that people are not getting sick from arsenic; therefore, there should not be a regulation, or the regulation should be set at a level where people do get sick. Epidemiology does not have that resolution. The bottom line is that these goals are below what can be detected in the real world.

As a result, it is not possible to backtrack to determine success. It is hoped that the risk assessments are legitimate.

NEW APPROACHES

Congress essentially said in the 1986 Safe Drinking Water Act Amendment that there would have to be more regulations. The EPA then had the task of trying to find additional chemicals to regulate that it had not already given Congress.

Now it is necessary to take a look from a systems standpoint. Hazard assessment via a critical control point process, such as that used in the food industry, could also be applied to drinking water. In that case, a system-wide examination from source to tap is done in order to identify problem areas and move forward.

Improved Analytical Methods

There is a need for straightforward and reliable analytical methods that are relatively cheap. For many of the small utilities, the cost of monitoring is the major cost, particularly with small groundwater systems for which they really do not have surface infrastructure or big treatment plants. They basically have a well, a storage tank, and the lines that go out from them. Methods exist for nearly every contaminant, but sometimes they are expensive. Working toward cheaper methods that serve our purpose is necessary.

Improved Treatment Technologies

Another important need is low-maintenance treatment technologies. It is very hard to find operators that are well trained to run sophisticated treatment hardware. We need stand-alone equipment that will run automatically, a necessity if we are to move forward.

Point-of-use devices and point of entry devices have been suggested as a means to beat the problem of highly treated water being used to water lawns or wash cars while a small percentage is used for drinking. The idea would be good if every homeowner could be trusted to run a device reliably to remove all contaminants on the list, and this is a daunting task.

WATER USE PROBLEMS: FROM SOURCE TO TAP

Contaminants removed from water have to be disposed. Clean Water Act activities focus primarily on contaminant control—point control through National Pollutant Discharge Elimination Systems (NPDES) permits, the permits on discharge from manufacturing or from point sources and nonpoint sources such as agricultural or water runoff. The parameters (e.g., pH, temperature) are very broad and are largely there to protect fish and other aquatic life from degradation.

There are controls on specific pollutants obviously, but in general, there are broad parameters. There is an increasing worry over the persistent organics or chemicals that have been created and are somehow getting into wastewater. There are some worries, but there is no way to know right now if they are dangerous, because too little is known.

Drinking Water Resources

With regard to drinking water source and resource issues, neither the Clean Water Act nor the Safe Drinking Water Act deals with resources directly. These acts were written that way specifically; Congress did not want to interfere with state's rights in water resources. However, they have been used to deal with resources to some degree, and they certainly come to play in desalination, recycling, and reuse.

There are source water protection provisions in the Safe Drinking Water Act and the Clean Water Act that are aimed at prevention and control of contaminant releases. The Safe Drinking Water Act and the earlier versions really dealt with treatment plant operations.

One potential drinking water resource is obtained through desalination of salt water. In desalination, the main issue is brine disposal, particularly in inland areas. Desalination in coastal areas works well because the brines can be disposed by running them back into the ocean and, to a first approximation, they are relatively benign. To a certain extent this also works inland, as in the Los Angeles area where there are brine drains.

On the other hand, in agricultural areas in the Central Valley of Northern California, there are problems from agricultural drainage, which are essentially brines. The political and technical aspects of this prevent sending the brines down through the delta and into the ocean or creating a pipeline from the inland areas out to the ocean. In order to keep the lands in production there have to be better ways to dispose of the brines.

Reuse of wastewater is another potential source of drinking water. The current problem with reuse is that there is not much information about the health effects of persistent organics. There are enough persistent organics in the water for some concern, which may or may not be legitimate. It will be some time before there is adequate health information to go forward. Unfortunately, there may well be pressure to regulate before there is a good handle on the associated risks.

In terms of needs, wastewater and reuse treatment technologies are certainly needed to control these persistent organics. The Orange County Water District and others are doing some very interesting work on this. Ideally it would be good to get away from a chemical and biochemical approach to this problem and instead try to remove all organics regardless of their potential for harm.

Another problem with wastewater reuse is contamination by disinfection by-products. Water disinfection technologies are needed to minimize these by-products, especially with the growing concern about nitroso-containing chemicals. The work on membranes is impressive but could improve. The reliability of membranes is great, but lowering the energy costs will make a difference, particularly for applications to smaller systems.

Drinking Water Treatment

The main issue with drinking water treatment has always been dealing with microbial pathogens in a multiple-barrier approach. The laws from the Safe Drinking Water Act, the Surface Water Treatment Rule and its variations, prescribe a physical removal basis and a disinfection basis. Source water protection now presents an additional barrier, and physical removal has many steps: coagulation, flocculation, precipitation, and filtration.

Waste minimization of sludge is still an issue. Dealing with and minimizing sludge and finding other types of coagulants that do not produce as many tons of sludge would be great. Removal of the problematic chemical contaminants is also important; if they cannot be kept out of the sources, then they must be removed through treatment.

All surface water systems and any groundwater system will have multiple contaminants. Until regulating contaminants one by one stops, utilities are going to have to work with multiple contaminants that may be quite distinct chemically.

Water Treatment Needs

The immediate needs for water treatment include improvement in the membrane technology, such as pretreatment, resistance to fouling, durability, ease of use, and breadth of contaminant removal.

There are some oxidized metals and metalloids and other chemicals on the horizon. Of the chemicals dealt with in drinking water on a national basis, from a public health side, arsenic is the biggest issue and is worse than most contaminants except for the microbials and disinfection by-products. Treatment needs lie in the area of "-ate" control: arsenate, chromate, nitrate, perchlorate, phosphate, silicate, and others.

Utilities are looking at their distribution systems, many of which have been in the ground for a hundred years and are finding that the systems are starting to fall apart. The systems have to be replaced at a rate of more than a million dollars per mile. Many larger systems are thousands of miles in length.

Most utilities deal with physical failure on a when-it-happens basis. If a main blows causing a sinkhole in the middle of the street, they go out and fix it. Most utilities have a replacement rate of around 1 percent a year.

Options are needed that would minimize corrosion and damage. Infiltration and intrusion of contaminants, particularly microbials, have to be prevented. In the urban setting, drinking water transmission lines run in the same areas as sewer lines. Sewer lines leak and the area in soil around sewer lines has a lot of contaminants that are not wanted in drinking water. The problem is particularly bad in cities that use wells; as wells are kicked on and off, there are pressure fluxes through the distribution. There can be zones of zero or negative pressure moving through. Siphoning also occurs.

There is a cross-connection from different types of intrusions to worry about. About a third of waterborne disease outbreaks are associated with distribution system failures. There are going to be regulations on distribution system protection in the next four to six years.

There may be ways of lining the distribution system pipes with polymers or membranes that would help harden the system. Methods exist but more are needed. Furthermore, in-place pipeline rehabilitation materials and the methods for putting them in without digging up streets would be beneficial.

Systems must maintain disinfection and the disinfectant residual in distribution because of potential intrusions and to some extent because of the potential for bioterrorism. However, increased disinfection boosts disinfection by-products, but these are currently regulated. Additionally, there is a need to have residual and to control biofilms that can sequester materials.

What are the needs for distribution systems? A broad-spectrum disinfection agent that can persist in the distribution system and does not create problematic by-products is critical. Chlorine works well but its use has downsides. It creates halogenated by-products and a taste that people do not like.

BIOTERRORISM

Water systems are incredibly vulnerable to bioterrorism, from both the chemical side and the biological side. It is pretty remarkable that to date there is no evidence of attacks on water systems, because it is essentially impossible to prevent an attack. There have been a couple of attempts that did not work, but there have been no thought-through attacks by individuals or groups such as state-supported bioterrorists or local militia types.

Monitoring Tools

Multiple barriers to attack have limited effectiveness in the likelihood that an attack spread beyond a few people; the goals are to minimize the damage. If there was a bioterrorism attack, it would be a unique event, so water systems are not going to put a lot of effort into preventing an attack. Monitoring tools are being worked on as a means of response.

Not many people will have access to weapon contaminants, so there is not a need for very many labs to be able to analyze those. False positives are bad, because we do not want to scare the public, but a false negative is much worse. Current technologies for analysis are crude and include very broad parameters. It would be useful to be able to have some technologies that could be performed on a real-time basis.

Cleanup and Disposal

Technologies are becoming available now for cleanup and disposal, such as thin film-type technologies for specific contaminants, but more technologies would be better. They can start being distributed, but there is not a huge need for that. If contaminants get into a distribution system, there will be miles of system to clean up. A small consideration is that some of those agents will be fairly persistent at times.

NEEDS FOR THE FUTURE

Near Term

Over the next five years, simple removal technologies utilizing disposable media are needed for small utilities. Control of arsenate, perchlorate, *n*-nitrosodimethylamine, and methyl *tert*-butyl ether is needed. Ion exchange is great if it can be done. There are large-scale applications in the perchlorate area. The Colorado River has a chlorate concentration of 4-5 parts per billion (ppb), and it is conceivable to have a future regulation in that range.

The best way to work on water quality is to go upstream to Henderson, Nevada, where the contamination originates and try to eliminate the problems there. However, that feat would take some work. As mentioned previously, a better distribution system disinfectant would be helpful.

Long Term

For 10 or more years from now, it would be ideal to have the technologies ahead of the regulations. Control of persistent organics in the brine and sludge disposal technologies is needed. The long-term trends should be to control the organics and clean up the water to customer satisfaction because there is more to water quality that meeting standards. There is a persistent pressure to control things that people worry about, and the health information is not available for backup.

DISCUSSION

Limiting the Proliferation of Biocides

Don Phipps, of the Orange County Water District, stated that on the control side of biofilms, some interesting technologies have recently been getting the attention of the media. There are also new surface-active biocides, chemicals that can be covalently bound to surfaces and will limit the proliferation or attachment of bacteria. He mentioned that he thought it might be an interesting process to try to develop pipe liners that are coated with these compounds and see if someone can gauge a test to determine if this would help limit the proliferation of biocides in the pipes. Mr. Phipps said that limiting the proliferation of biocides has a couple of advantages, including the reduction of the disinfection load required to maintain a residual. If the proliferation could be limited, the efficiency would be increased for the standard liner, and the total microbial load distribution system could be lowered.

Dr. Macler said this would reduce the demand on the residual. However, he said the real issue would be the stability of the biocide on the surface. How would you get the residual on the surface to begin with?

Mr. Phipps thinks the way these biocides really operate is that they are bound to the surface. They are not an exchangeable biosynthetic.

Water Regulation of American Indian Casinos

Dick Carlson, of San Diego County, commented that in his county there are a number of American Indian casinos using recycled water because they need waste distribution as a result of the waste load. They actually have anecdotal evidence of recycled water being used inside one of the casinos for toilet flushing, which is not a problem. However, this has been connected to the drinking water system in the same casino. He wanted to know who regulates this kind of activity.

Dr. Macler explained that the EPA is responsible for regulating those activities. He said that under the Safe Drinking Water Act, EPA develops and promulgates these drinking water regulations and the states can take on the authority to implement them to gain primacy. American Indian tribes have some sovereignty, but EPA deals with their lands. The agency has direct implementation authority and handles the situation with the tribes. He said that more tribes are running these casinos in California and they are growing from small-scale operations of about 200 people drinking from a system, to a large scale where thousands to tens of thousands of people are being exposed.

Environmental Management System for Local Municipal Government Entities

Dan Askenaizer, of Montgomery Watson and Harza Engineering Company, asked whether EPA regional offices or headquarters are involved in the effort to encourage the use of an environmental management system for local municipal government entities.

Dr. Macler answered that the programs are not really on the drinking water side. There are plans for hazardous materials. He thinks some of the utilities were looking to the effort to be relieved of regulatory burden.

The federal level in Washington, D.C., has not really embraced the drinking water program. Therefore, he is unsure what the likelihood of persistence for the program will be.

Research Funding

Mark Matsumoto, of the University of California at Riverside, acknowledged the discussions about the amount of dollars available for R&D going down in drinking water areas as well as the fact that few impacted agencies are able to provide the funds or have the funding to do the R&D necessary for their own research needs. He asked Dr. Macler what he sees as the near-term and long-term funding picture for government research.

Dr. Macler affirmed the interesting situation in R&D. Looking at just EPA's budget and the money that goes to the laboratories in Cincinnati for drinking water R&D, he said it goes down. At the same time, there are congressional line items where a congressman in Glendale provides $900,000 to the city for R&D, $750,000 for more R&D, and $2 million for still more R&D; it becomes evident where a lot of R&D is getting done. Dr. Macler said that the Metropolitan Water District has received a federal line item of $3.5 million for desalination research that he is overseeing. The district has to match it. EPA has about $6 million in desalination membranes, brine disposal, and pretreatment. There is money in other places, but no one is trying to bring the pieces together to make sure everyone is trying to reach one main goal. Money is available. In looking at the congressional line item, three or four years ago it was a few million dollars and now it is hundreds of millions. He added that there are a lot of $0.5 million to $2 million R&D projects that are supposed to go out for bid.

Perchlorates

Mr. Matsumoto next mentioned the perchlorate debate as an example of the role of science with regard to setting limits.

Dr. Macler referred to the Safe Drinking Water Act in which Congress said that water should essentially be without risk. This essentially means that if the risk is unknown, the worst case should be assumed. Often the data being used come from both human and animal studies.

For example, for perchlorate, the studies are at the 200- to 300-ppb exposure level. That is the lowest observed adverse effect level. He said the study on humans was very short term in adults. The study on rats used multiple generations of rats and looked at the pups, fetuses, and pregnant mice. The data then have to be extrapolated to make some judgment for humans. A sensitive subpopulation for humans is pregnant women and infants, but studies cannot be done on these populations. Therefore, a conservative extrapolation must be made. For cancer, a linear approach is used to extrapolate downwards. For noncancer end points, uncertainty factors are used.

Dr. Macler continued that if the limit is moved up an order of magnitude, the unknown risk is greater. The level might be legitimate, but the comfort level is reduced. He said that science can only go so far, and the risk assessment world has to make a determination. Risk assessors must be willing to take uncertainties into account. Eventually there is a management decision that takes into account the social aspect of the situation.

Dr. Macler said that a possible reason for a perchlorate drinking water regulation is the Colorado River and the 34 million people that drink its water. If the risk is one in a million, this is equivalent to 34 people, which is unacceptable from the Safe Drinking Water Act standpoint. It would have been best if cleanup of the Colorado River had started five years ago. He said that some methodologies are being developed for cleanup of such sites that are not too expensive.

Different Levels of Treatment for Different Uses

Debbie Elcock, of Argonne National Laboratory, raised questions about having different levels of treatment for different uses. Based on the statutes and legislation, we know what the level should be for drinking water. Do we know what the level would be for different industrial uses or for agriculture? Water for these purposes would not have to be as treated. It might be economical to actually treat for the different levels for different uses. Is there the legislative authority to do that?

Dr. Macler replied that treatment for industrial use would depend on the process and on whether the regulations were for environmental or occupational safety and health purposes. For agricultural purposes in California there are different watering requirements depending on the vegetation. Median strips along freeways are watered with different water than golf courses. If human exposure is more likely, the water quality must be better. Another consideration is whether plants can tolerate the water.

Bhaskar Davé, of Ondeo Nalco, added that he thinks the safety of people working in an industrial environment should be first and foremost. He said that according to Title 22 for California, there is a minimum residue of chlorine allowed to ensure that pathogens are killed before coming to an industrial site. As to different treatment levels for different uses, the industry at a given site would have to make a decision about where the water is being used, because different water could be used in a cooling tower than in the boiler. Dr. Davé said that the treatment would be very application specific and not very cost-effective.

Mr. Phipps added that for industrial use, the constraints of the process will probably be more stringent on the quality of the water than the regulatory environment.

Dr. Macler responded that the true value of water often is the cost. He likes to think of water having values in different ways; that is, industrial water is ultrapure and very valuable. There are quantifiable values for water that is used for certain applications in industry, and other applications do not require that high water value. Domestic drinking water is valuable because it is to be protective of public health, but water for lawns should not be valued as heavily.

The National Water Research Institute has had some projects to determine values of waters to be able to have a decent economic approach. California would benefit from giving some consideration to the value for different uses.

Fareed Salem, of ConocoPhillips, commented that in principle for maximizing reuse, water should be treated to the maximum quality affordable. The difficulty in assessing the value to each industry or each application is where the struggle is. He thinks most industries are beginning to think defensively by determining the minimum that can be done to get by the regulation. He asked how we can change the mind-set or the culture in the business community to think proactively about water quality and to adopt an offensive rather than a defensive strategy. Fundamentally, if we were to really think of water sustainability and long-term solutions, we have to change the mind-set of the culture into one that thinks differently about this resource.

Dr. Macler did not know if that was feasible. His experience is that usually an economic situation is being attacked. If you can make these technologies in a way that is more profitable and get the benefit of risk reduction or better environmental qualities, then it will happen. Additionally, the small systems do not have a lot of money to be able to adopt a proactive outlook. They can barely be reactive.

Maximum Contaminant Level Goal

An unidentified speaker mentioned some studies on recyclable water where a risk level of 1 in 10,000 infections per year on the drinking water side was used. That value is then compared to the safety of the recycled water. The speaker wondered where such a value might have originated.

Dr. Macler stated that he believes whoever came up with the value "pulled it out of the air." The concept of acceptable risk came up in the 1980s during the 1986 revision of the Safe Drinking Water Act, in which Congress set up the maximum contaminant level goal (MCLG) and a level of no known health consequence with an adequate margin of safety. He said that traditionally the MCLG has been set at zero for carcinogens, meaning there is no acceptable level. That was a decision not a regulation or a law. The real wording is that the risk is one in a million, an upper-bound determination of the worst that could possibly happen. The real risk is quite likely to be much less than that and could actually be zero. Dr. Macler continued that the percentage of deaths due to gastrointestinal problems from microbials is near 0.01 percent. The risk is then 1 in 10,000. He asked whether this was a reasonable number. He said that it turned out to be a feasible number with respect to the Surface Water Treatment Rule and the regulation for *Giardia*. The regulation manager investigating microbial risk assessments presented this number at a conference, the value got printed, and finally it showed up in the preamble to the regulation. The background rate of infection is about 1.5 gastrointestinal illnesses per person per year.

Appendix A

Workshop Participants

Paul Anastas, Office of Science and Technology Policy, Washington, DC
Dan Askenaizer, Montgomery Watson and Harza Engineering Company, Pasadena, CA
Ellyn S. Beary, National Institute of Standards and Technology, Gaithersburg, MD
Mark Bernstein, Rand, Santa Monica, CA
Donald M. Burland, National Science Foundation, Arlington, VA
Steve Cabaniss, University of New Mexico, Albuquerque, NM
Richard Carlson, County of San Diego Department of Environmental Health, San Diego, CA
C.K. Chou, Lawrence Livermore National Laboratory, Livermore, CA
Jeannie L. Darby, University of California, Davis, CA
Bhasker Davé, Ondeo Nalco Company, Naperville, IL
Jan Dell, CH2M Hill, Santa Ana, CA
Thomas A. Dillion, Science Applications International Corporation, San Diego, CA
Derek Dormedy, California State University, Fresno, CA
Lawrence Duffy, University of Alaska, Fairbanks, AK
Debbie Elcock, Argonne National Laboratory, San Diego, CA
Jean H. Futrell, Pacific Northwest National Laboratory, Richland, WA
Ann Marie Gebhart, Underwriters Laboratories Incorporated, Northbrook, IL
Virginia Grebbien, Orange County Water District, Fountain Valley, CA
Elias Greenbaum, Oak Ridge National Laboratory, Oak Ridge, TN
David Groves, RAND, Santa Monica, CA
Evelyn Hartzell, U.S. Environmental Protection Agency, Cincinnati, OH
Patrick G. Hatcher, Ohio State University, Columbus, OH
Alan D. Hecht, White House Council on Environmental Quality (now at the U.S. Environmental Protection Agency), Washington, DC
Thomas E. Hinkebein, Sandia National Laboratories, Albuquerque, NM
Dennis J. Hjeresen, Green Chemistry Institute, Washington, DC
Carol Jensen, The Dow Chemical Company, Midland, MI
Aaron Kofner, RAND, Santa Monica, CA
David P. Krabbenhoft, U.S. Geological Survey, Middleton, WI
David Layton, Lawrence Livermore National Laboratory, Livermore, CA
Richard G. Luthy, Stanford University, Stanford, CA
Bruce A. Macler, U.S. Environmental Protection Agency, San Francisco, CA
Vasilios Manousiouthakis, University of California, Los Angeles, CA
Mark R. Matsumoto, University of California, Riverside, CA
Jay C. Means, Western Michigan University, Kalamazoo, MI
Robin L. Newmark, Lawrence Livermore National Laboratory, Livermore, CA
Parry M. Norling, DuPont (retired) and RAND, Arlington, VA (now with Chemical Heritage Foundation, Wilmington, DE)
Jeffery P. Perl, Chicago Chem Consultants Corporation, Chicago, IL
Donald W. Phipps, Jr., Orange County Water District, Fountain Valley, CA
David R. Rea, DuPont Company (retired), Wilmington, DE
Fareed A. Salem, ConocoPhillips, Houston, TX
David Schubert, Salk Institute for Biological Studies, La Jolla, CA
Tim Shaw, University of South Carolina, Columbia, SC

Jeffrey J. Siirola, Eastman Chemical Company, Kingsport, TN
Richard Skaggs, Pacific Northwest National Laboratory, Richland, WA
Mark A. Smith, University of Arizona, Tucson, AZ
Tom Troyer, King Lee Technologies, San Diego, CA
Jim Van Vooren, Underwriters Laboratories Incorporated, South Bend, IN
Mark Wang, RAND, Santa Monica, CA
Floyd E. Wicks, American States Water Company, San Dimas, CA
Eric Wood, Weyerhaeuser Company, Federal Way, WA
Frankie Wood-Black, ConocoPhillips, Ponca City, OK

Appendix B

Biographical Sketches of Workshop Speakers

Bhasker Davé is currently R&D manager of advanced recycle technology (industrial water management) and membrane separations technology at Ondeo Nalco Technical Center located in Naperville, Illinois. Dr. Davé has more than 12 years of experience in design and evaluation of water recycle processes in the chemical processing, pulp and paper, and primary metals industries. Dr. Davé has a B.S. in chemical engineering (First Class with Distinction) from the University of Madras (India), a M.S. in thermal and environmental engineering from Southern Illinois University, and a Ph.D. in chemical engineering from Texas A&M University.

Virginia Grebbien was appointed general manager of the Orange County Water District (OCWD) in April 2002. With more than 16 years of experience, Ms. Grebbien is well known in the field of water resources management and planning both in Southern California and throughout the state. Ms. Grebbien came to OCWD from Poseidon Resources where she was senior vice president of project development. Her career includes holding several management positions, including principal engineer for Bookman Edmonston Engineering, general manager of Central and West Basin Municipal Water Districts, and manager of local resource development for Metropolitan Water District of Southern California. Ms. Grebbien is a professional engineer with a B.S. degree in civil engineering from California State Polytechnic University in Pomona. She is a former board member and past president of the WateReuse Association and founding president of the California WateReuse Research Foundation. Currently, Ms. Grebbien is a member of the WateReuse Federal Legislative Committee and serves on the Department of Water Resources Recycled Water Task Force.

Elias Greenbaum, is a corporate fellow and research group leader, Oak Ridge National Laboratory, and professor of biological physics, University of Tennessee (UT). He received the B.S. degree from Brooklyn College and Ph.D. in physics from Columbia University under the guidance of Professor Chien-Shiung Wu. Dr. Greenbaum's main area of research is the field of photosynthesis and its application to nanoscale science and technology, biosensor development, and renewable hydrogen production. He was named 2000 Oak Ridge National Laboratory Scientist-of-the-Year and received the 1995 Department of Energy's (DOE's) Biological and Chemical Technologies Research Program Award and several Lockheed Martin Energy Research Corporation and UT-Battelle, LLC awards. Dr. Greenbaum is a fellow of the American Physical Society and the American Association for the Advancement of Science. He holds 10 patents and is the author of more than 100 publications in peer-reviewed scientific journals. He is editor-in-chief of the Springer-AIP Biological and Medical Physics Series and served as associate editor of the *Biophysical Journal*.

Alan D. Hecht is currently director for sustainable development in the Office of Research and Development at the U.S. Environmental Protection Agency (EPA). Previously, Dr. Hecht was associate director for sustainable development at the White House Council on Environmental Quality. In the White House, he also served as director of international environmental affairs for both the National Security Council and the Council on Environmental Quality (October 2001-May 2002). Dr. Hecht was the White House coordinator for the 2002 World Summit on Sustainable Development. Spanning a federal career of 26 years, Dr. Hecht previously served as the principal deputy and deputy assistant administrator for international activities at the U.S. EPA (1989-2001). He was the acting assistant administrator for international activities from 1992 to 1994. Dr. Hecht has also served in science and policy positions with the National Oceanographic Administration (1982-1989) and the National Science Foundation (NSF; 1976-1982). He was director of the National Climate Program from 1981 to 1989, and director of the Climate Dynamics Program at NSF from 1976 to 1981. Dr. Hecht has a B.S. in geology from Brooklyn College and a Ph.D. in geochemistry and paleoclimatology from Case Western Reserve.

Thomas E. Hinkebein is a distinguished member of the technical staff at Sandia National Laboratories in Albuquerque, New Mexico. He received his Ph.D. in chemical engineering from the University of Washington, Seattle. Dr. Hinkebein currently manages the Geochemistry Department, which is responsible for a number of fundamental science studies as well as the development of novel arsenic water treatment processes. He also currently manages several lab-directed research and development programs that explore novel concepts in water supply enhancement and desalination. Additionally, Dr. Hinkebein is responsible for coordinating the development of a technology roadmap for future research in desalination technology.

Dennis L. Hjeresen currently serves on the Board of Directors of the Green Chemistry Institute (GCI) and as GCI director. He is on partial loan from the Risk Reduction and Environmental Stewardship Program at Los Alamos National Laboratory. He has a long history of creating pollution prevention programs and catalyzing partnerships. Dr. Hjeresen established Los Alamos as the lead DOE laboratory for EPA Green Chemistry Programs. He has lectured and given presentations in this area all over the world and established significant international interest in green chemistry. Dr. Hjeresen serves as a member of the editorial or advisory boards for the *Journal of Green Chemistry*, the *Journal of Environmental Science and Technology,* and the *Journal of Clean Products and Environmental Policy*. He serves as a member of the U.S. delegation to the Organization for Economic Cooperation and Development (OECD) Joint Meeting of the Chemicals Committee and Working Party on Chemicals, Pesticides and Biotechnology: Working Group on Research and Development in the Context of Sustainable Chemistry. Dr. Hjeresen received a M.S. in neuroscience in 1982 and a Ph.D. in neuroscience (minor in ecology) in 1984 from the University of Washington in Seattle. His research career has focused on biological effects of environmental pollutants and includes an extensive list of peer-reviewed publications and a history of professional service.

Carol Jensen is vice president of global research and development for performance chemicals, the Dow Chemical Company. Dr. Jensen joined the company in 2001 from the 3M Corporation where she was the executive director of the corporate technology and electronics and communications markets. She started her career in 1979 with IBM in San Jose, California, as a group leader in electronic materials. In 1990, Dr. Jensen joined 3M Corporation in Austin, Texas. As technical director for electronic products, she led technology development and platform launches for various electronic connection and microcircuit products. In 1998, Dr. Jensen was named managing director for 3M Denmark A/S, in Copenhagen. She had responsibility for sales, marketing, customer relationships, technical service, and supply chain for the total portfolio of 3M products for Denmark, Iceland, and other Scandinavian countries. Dr. Jensen returned to the United States in 2000, based in St. Paul, Minnesota, where she had direct responsibility for several corporate R&D laboratories and oversight of the electronic and telecommunications business laboratories engaged in materials, process, and new product development covering much of 3M worldwide sales. Dr. Jensen has authored 7 patents and 25 trade secrets. She received a B.S. in chemistry from Douglass College, Rutgers University, and a Ph.D. in physical organic chemistry from the California Institute of Technology.

David Krabbenhoft is a research scientist with the U.S. Geological Survey (USGS). He has general research interests in geochemistry and hydrogeology of aquatic ecosystems. Dr. Krabbenhoft began working on environmental mercury cycling, transformations, and fluxes in aquatic ecosystems after completing his Ph.D. in 1988, and the topic has consumed him since. His work on mercury started with the Mercury in Temperate Lakes project in 1988, which served as the springboard for other environmental mercury research in the United States and around the world. In 1994, Dr. Krabbenhoft established the USGS Mercury Research Laboratory and has since assembled a team of multidisciplinary mercury investigators in Wisconsin. The laboratory is a state-of-the-art, analytical facility strictly dedicated to the analysis of mercury, with low-level speciation. In 1995, he initiated the multi-agency Aquatic Cycling of Mercury in the Everglades (ACME) project, and in 1998, he organized and conducted a national synoptic sampling of mercury in sport fish, sediment, and water from 122 sites across the United States for the USGS. More recently, Dr. Krabbenhoft has been a primary investigator on the internationally conducted Mercury Experiment to Assess Atmospheric Loading in Canada and the United States (METAALICUS) project, which is a novel effort to examine the ecosystem-level response to loading an entire watershed with mercury. The Wisconsin Mercury Research Team is currently active in projects from Alaska to Florida, and from California to New England. Since 1990, Dr. Krabbenhoft has authored or coauthored about 50 papers on mercury in the environment. In 2006, he will serve as cohost for the Eighth International Conference on Mercury as a Global Pollutant in Madison, Wisconsin.

Richard G. Luthy is the Silas H. Palmer Professor of Civil and Environmental Engineering at Stanford University. His B.S. in chemical engineering and his M.S. and Ph.D. in environmental engineering are from the University of California at Berkeley. Dr. Luthy's area of teaching and research is environmental engineering and water quality. His research interests include physicochemical and microbial processes and applied aquatic chemistry with application to waste reduction and treatment, and remediation of contaminated soil and sediment. He is noted for work on phase partitioning and the treatment and fate of hydrophobic organic compounds. Dr. Luthy's research emphasizes interdisciplinary approaches to understand the behavior and availability of organic contaminants and the application of these approaches to bioavialability and environmental quality criteria. His current work includes the in situ control of PCBs (polychlorinated biphenyls) and DDT (dichlorodiphenyltrichloroethane) in contaminated sediments, and the environmental fate and behavior of perfluorinated organic compounds and nitromusks in the aquatic environment. Dr. Luthy chairs the National Research Council's (NRC's) Water Science and Technology Board and was a member of the NRC Committees on Innovative Remediation Technologies and on Intrinsic Remediation. He chaired the recently completed NRC study on the bioavailability of contaminants in soils and sediments. He is a past president of the Association of Environmental Engineering and Science Professors. He is a registered professional engineer, a diplomate of the American Academy of Environmental Engineers, and a member of the National Academy of Engineering.

Bruce A. Macler is national microbial risk assessment expert in the Water Division of the U.S. Environmental Protection Agency (Region 9). As national expert for microbial risk assessment for EPA, Dr. Macler provides guidance and assists in developing agency policies and programs in human health and ecosystem risk assessment and risk management. Prior to his current assignment, he served as national drinking water regulations manager from 1993 to 1997. Before joining the EPA in 1989, he was an assistant research botanist and lecturer at the University of California, Berkeley (1982-1987) and as assistant research professor in the Marine Sciences Research Center at the State University of New York at Stony Brook (1981-1982). Dr. Macler earned his A.B. (1974) and his Ph.D. (1981) in biochemistry from the University of California, Berkeley. His current research interests center on determining the magnitude and causes of waterborne microbial disease. This work has included several studies on the occurrence of fecal pathogens in groundwater, their fate and transport in the subsurface environment, and approaches to assessing public health impacts from these contaminants. Associated research interests include public perceptions on the safety of drinking water and their implications for regulatory water policy. Major current activities involve characterization of vulnerability to bioterrorism attacks on drinking water and development of a risk assessment paradigm for indoor molds. As national drinking water regulation coordinator for EPA Region 9, Dr. Macler participates actively in the development and implementation of all national primary drinking water regulations.

Floyd E. Wicks is president and chief executive officer (CEO) of American States Water Company. Mr. Wicks is also president and CEO of Southern California Water Company (SCWC), the principal operating subsidiary of American States Water Company, and president and CEO of American States Utility Services Company and Chaparral City Water Company in Arizona. A registered professional engineer in California, Ohio, and Pennsylvania, Wicks' professional career spans the past 30+ years. He received both his B.S. in civil engineering and his M.S. in water resources engineering from Ohio State University. Mr. Wicks is a member of various professional organizations, including the National Association of Water Companies (NAWC) for which he served an 18-month term as president. Mr. Wicks continues to serve on the NAWC Nominating Committee and currently serves on the Board of Trustees of the American Water Works Association Research Foundation. Mr. Wicks is also a past member of the Advisory Committee to the President's Commission on Critical Infrastructure Protection.

Appendix C

Origin of and Information on the Chemical Sciences Roundtable

In April 1994, the American Chemical Society (ACS) held an Interactive Presidential Colloquium entitled "Shaping the Future: The Chemical Research Environment in the Next Century."[1] The report from this colloquium identified several objectives, including the need to ensure communication on key issues among government, industry, and university representatives. The rapidly changing environment in the United States for science and technology has created a number of stresses on the chemical enterprise. The stresses are particularly important with regard to the chemical industry, which is a major segment of U.S. industry; makes a strong, positive contribution to the U.S. balance of trade; and provides major employment opportunities for a technical work force. A neutral and credible forum for communication among all segments of the enterprise could enhance the future well-being of chemical science and technology.

After the report was issued, a formal request for such a roundtable activity was transmitted to Dr. Bruce M. Alberts, chairman of the National Research Council (NRC), by the Federal Interagency Chemistry Representatives, an informal organization of representatives from the various federal agencies that support chemical research. As part of the NRC, the Board on Chemical Sciences and Technology (BCST) can provide an intellectual focus on issues and fundamentals of science and technology across the broad fields of chemistry and chemical engineering. In the winter of 1996, Dr. Alberts asked BCST to establish the Chemical Sciences Roundtable to provide a mechanism for initiating and maintaining the dialogue envisioned in the ACS report.

The mission of the Chemical Sciences Roundtable is to provide a science-oriented, apolitical forum to enhance understanding of the critical issues in chemical science and technology affecting the government, industrial, and academic sectors. To support this mission, the Chemical Sciences Roundtable will do the following:

- Identify topics of importance to the chemical science and technology community by holding periodic discussions and presentations, and gathering input from the broadest possible set of constituencies involved in chemical science and technology.
- Organize workshops and symposia and publish reports on topics important to the continuing health and advancement of chemical science and technology.
- Disseminate the information and knowledge gained in the workshops and reports to the chemical science and technology community through discussions with, presentations to, and engagement of other forums and organizations.
- Bring topics deserving further, in-depth study to the attention of the NRC's Board on Chemical Sciences and Technology. The roundtable itself will not attempt to resolve the issues and problems that it identifies—it will make no recommendations, nor provide any specific guidance. Rather, the goal of the roundtable is to ensure a full and meaningful discussion of the identified topics so that the participants in the workshops and the community as a whole can determine the best courses of action.

[1] *Shaping the Future: The Chemical Research Environment in the Next Century,* American Chemical Society Report from the Interactive Presidential Colloquium, April 7-9, 1994, Washington, DC.

Appendix D

For Further Reading

International Environmental Technology Centre (United Nations Environmental Programme). Fresh Water Issues (see http://www.unep.or.jp/ietc/issues/freshwater.asp).

This provides information on freshwater augmentation, pollution in lakes and reservoirs, wastewater and storm water, sewage, and links to other references and resources.

Organizing Committee for the Workshop on the Environment. 2003. *Challenges for the Chemical Sciences in the 21st Century: The Environment,* Washington, DC: The National Academies Press.

This workshop report has relevant sections on drinking water disinfection and disinfection by-products, water and sediment chemistry, green chemistry and water, examples of reduced industrial uses of water, and biogeochemical controls on the mobility of trace metals in groundwater.

Postel, Sandra. 1992. *Last Oasis: Facing Water Scarcity,* New York: W.W. Norton. (see http://www.worldwatch.org/press/news/1999/07/17/).

This is an examination of the limits—ecological, economic, and political—of water, maintaining that the technologies and know-how exist to make every drop go further; agricultural use could be cut by 10-50% (drip irrigation), industrial use by 40-90% (extensive recycling), and cities by 30% without major expense.

Simon, Paul. 1998. *Tapped Out: The Coming World Crisis in Water and What We Can Do About It.* New York: Welcome Rain (see http://www.horizonmag.com/2/simon.htm).

Former Senator Paul Simon outlines the problems we face with the lack of adequate water supplies and suggests specific things the average citizen can do to help. He makes a strong case for an increase in desalination research and urges citizens to ask Congress to appropriate funds for this research and for water conservation.

Somerville, Chris, and Johan Briscoe. 200l. Editorial: genetic engineering and water. *Science* 292:2217.

Although many innovations in modifying plant water use are theoretically possible, one opportunity is related to the focus of this special issue of *Science,* on plant pathology. It has been estimated that up to 40% of plant productivity in Africa and Asia, and about 20% in the developed world is lost to pests and pathogens. Approximately one-third of the losses are due to viral, fungal, and bacterial pathogens, and the remainder is due to insects and nematodes. Much of the loss occurs after the plants are fully grown: a point at which most of all of the water required to grow a crop has been invested. Thus reducing losses to pests and pathogens is equivalent to creating more land and more water.

Tullo, Alexander. 2002. Turning on the tap: The world's growing concern about water supply is making the water treatment market more attractive for chemical suppliers. *Chemical & Engineering News,* 80(46): 7-42.

This article describes the activities of Ciba Specialty Chemicals, Ondeo Nalco, SNF Floerger, GE Betz, Drew International, Great Lakes Chemical, and US Filter; related articles in the same issue: "Basic Materials Keep a Technology Edge: Innovation and Symbiosis Catalyze Growth of Filter-Stage Chemicals for Water Treatment" and "China Changes Gear: China Wants Cleaner Water, It Wants It Yesterday, and it's Spending Billion on Treatment Plants" (see http://pubs.acs.org/cen/coverstory/8046/8046water.html).

Water Science and Technology Board (WSTB), National Research Council. 2002. *Annual Report 2001-2002* (see http://www7.nationalacademies.org/wstb/1WSTB_Annual_Report.html).

The web site includes a list of relevant publications and studies by the WSTB.

WSTB. 2002. *Envisioning the Agenda for Water Resources Research in Twenty-first Century*. Washington, DC: National Academies Press (copies available from the Water Science and Technology Board, National Research Council, 2101 Constitution Avenue, N.W., Washington, DC 20418; telephone: (202) 334-3422, fax: (202) 334-1961, or see http://www.nap.edu/catalog/10140.html).

Concerns have grown among the public and water resources professionals about the adequacy of future water supplies, the sustainability and restoration of aquatic ecosystems, and the viability of our current water resource research programs and our institutional and physical water resource infrastructures. This report summarizes discussions about the future of the nation's water resources and the appropriate research needed to achieve their long-term sustainability.