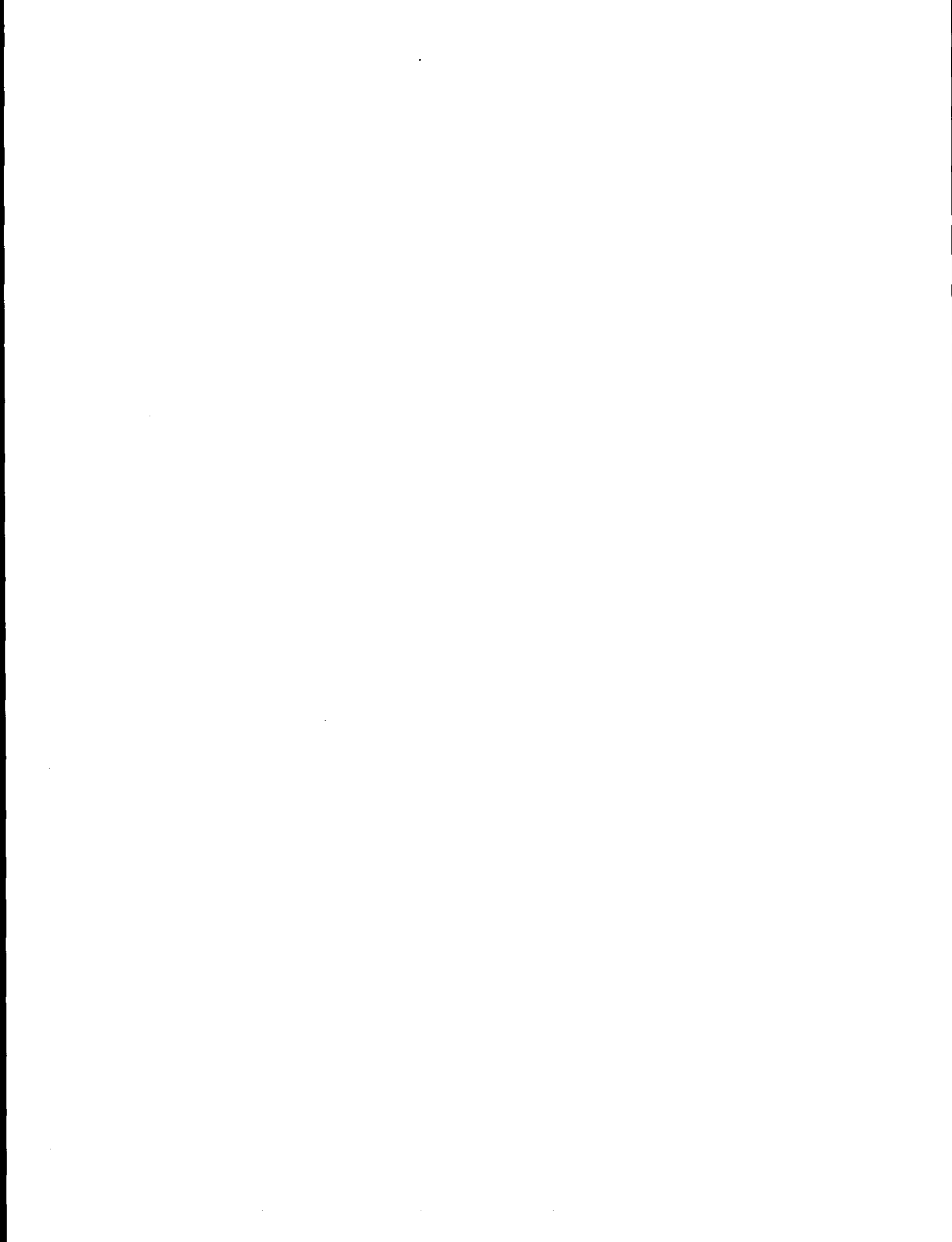


Assessment and Management of Toxics in the Watershed



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Foreword

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threatens human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

This publication has been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

Hugh W. McKinnon, Director
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Abstract

The demand for water is beginning to outstrip the available supply of water. The truly insidious insult to freshwater supplies comes from anthropogenic impacts that pollute freshwater supplies and the surrounding watersheds, making even less water available for use.

Watersheds are impacted by a variety of toxic substances. Some of these toxic pollutants enter the watershed through direct introduction but by far the most serious problems of toxics found in the nation's water supplies are created through indirect means. Many toxics are introduced into the water supply through their movement through the biosphere. The more ubiquitous of these toxic substances are mercury and pesticides. Challenges to managing the numerous risks posed by mercury in the environment include: alternative treatment options for mercury contaminated wastes; in situ treatment of mercury in sediments; identification and control of diffusive sources of mercury; and the fate and transport of mercury in the watershed environment. Challenges to managing the numerous risks posed by pesticides in the environment include: pesticide degradate and mixture characterization and behavior; pesticide application and transport data; and reliability and effectiveness of pesticide occurrence modeling and pesticide management practices.

This paper summarizes the current state of knowledge on the toxic sources, their impact on ecosystem and human health, discusses challenges to the successful management of toxics, and presents an outline of suggested management-related research for watersheds.

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I. Introduction

As part of EPA's mission to protect human health and the environment, the National Risk Management Research Laboratory's Watershed Management Team embarked upon the development of information on key issues impacting the health and viability of the nation's watersheds. As a result of examining environmental impacts at the watershed level, the watershed management team amassed a daunting list of impacts to watersheds. It was determined that the list of impacts could be categorized under five major issues: flow, nutrients, toxics, sediments, and pathogens. Each of these issues has been addressed by an individual document that examines the human health and ecological impacts, management and control activities, and research needs regarding the issue at the watershed level.

One of the major issues impacting watersheds is the subject of toxic substances or "toxics". Watersheds are impacted by a variety of toxic substances. Some of these toxic pollutants enter the watershed through direct introduction but by far the most serious problems of toxics found in the Nation's water supplies are created through indirect means. Many toxics are introduced into the water supply through its movement through the biosphere. Some of the main contributors of contamination to watersheds are:

- Contaminated sediments
- Pathogens

- Mercury
- Disinfection By-Products
- Pesticides
- MTBE
- Metals
- Endocrine Disrupting Chemicals
- Synthetic Organic Chemicals
- Perchlorates
- Nitrates/Nitrites

Coverage of all of these toxic substances under one document would be cumbersome. Also, EPA has well developed research programs on many of these substances and the Watershed Management Team is addressing contaminated sediments, nutrients, and pathogens under separate papers. As a result of these factors, this paper has been narrowed in scope to cover the toxic substances mercury and pesticides. Each toxic substance is examined according to the impact that the pollutant has on aquatic and terrestrial systems and the source of the pollutant. The human health effects of the pollutant are also summarized. Following the discussion of the sources and impacts of the pollutant, the management controls that have been or can be deployed to remediate and control the impact of the pollutant are described. Finally, future research needs of the pollutant are addressed.

II. Mercury

Mercury: Background

There is general agreement among researchers that the amount of mercury being released into the atmosphere has increased steadily since the dawn of the industrial era (U.S. EPA, 1997). According to one estimate, approximately two-thirds of the total world's yield of Hg has been produced during the twentieth century, and anthropogenic inputs of Hg to the environment have increased about 3-fold since 1900 (Fitzgerald, 1991).

The sources of the mercury emissions are broadly categorized as natural mercury emissions and anthropogenic mercury emissions (U.S. EPA, 1997). The emissions of mercury that are not specifically from current human activity nor from truly natural sources are referred to as "recycled," or "re-emitted," anthropogenic emissions.

Current theory suggests that a large part of the current atmospheric mercury burden is in the form of a worldwide background concentration composed almost entirely of elemental mercury (HgO) in gaseous form. Deposition from the atmosphere to the earth's surface, however, involves oxidized mercury. Natural and recycled anthropogenic emissions are thought to be mostly in the form of HgO (Bullock, 1999). Anthropogenically emitted mercury is deposited (to the oceans) as Hg(II) and then reduced to volatile HgO and re-emitted (U.S. EPA, 1997).

The primary sources of natural mercury emissions are volcanic eruptions and volatilization or solubilization of mercury from rocks, soils, and sediments; anthropogenic mercury releases are thought to be dominated by industrial processes such as chlorine alkali processing and metal processing, and combustion sources that release mercury into the atmosphere, including coal-fired power plants and municipal and medical waste incinerators. The Expert Panel on Mercury Atmospheric Processes (1994) estimated that the anthropogenic emissions may account for 50-75 percent of the total annual input to the global atmosphere (Expert Panel on Mercury Atmospheric Processes, 1994). The estimates of the panel are corroborated by Lindqvist et al., (1991), and Porcella (1994) (U.S. EPA, 1997).

The re-emission of deposited mercury results most significantly from the evasion of elemental mercury from the oceans. This process could account for approximately 30% of total mercury flux to the atmosphere (U.S. EPA, 1997).

Mercury also can contaminate land and water when it is directly released in industrial waste waters, or when waste containing batteries and other sources of mercury are disposed of (U.S. EPA, 1997).

Given the present understanding of the mercury cycle, the flux of mercury from the atmosphere to land or water at any one location is comprised of contributions from the natu-

ral global cycle, the global cycle perturbed by human activities, regional sources, and local sources (U.S. EPA, 1997); however, the knowledge of where mercury settles in the environment is incomplete; its source attribution and the deposited mercury's origin have proven difficult to quantify (Hanisch, 1998). Ultimately, mercury ends up in the sediments, fish and wildlife, or evades back to the atmosphere by volatilization (U.S. Geological Survey, 1995).

The effective risk management of mercury in watersheds requires extensive knowledge about deposition and source attribution within and among watersheds, atmospheric and ground transport mechanisms, and the influence of the environment on chemical transformations. As one of several research arms of the United States Environmental Protection Agency's (U.S. EPA) Office of Research and Development (ORD), the National Risk Management Research Laboratory (NRMRL) strives to conduct and direct research that will further the understanding of mercury contamination and management and provide to regulators and watershed managers the information that can be used to make informed risk reduction and management decisions.

Mercury: Aquatic Ecosystem Effects

The greatest concern with mercury pollution is methylmercury (CH_3Hg^+), an organic form of mercury produced by sulfate-reducing bacteria from inorganic mercury in both sediments and waters. The formation of methylmercury is the most significant transformation because methylmercury is far more toxic and bioavailable than any other form of mercury. Methylmercury accumulates in the food chain and reaches humans, other mammals, and birds through methylmercury-tainted fish (Rouhi, 2001), the consumption of which is known to be the dominant pathway for exposure (U.S. EPA, 2001). The biological effects of exposure to mercury at levels realistically found in ecosystems remain uncertain; however, the pattern of mercury deposition nationwide influences which eco-regions and eco-systems will be more highly exposed.

Methylmercury contamination now accounts for 78 percent of the fish-consumption advisories in the United States. Forty-one states had advisories attributed to mercury as of 1999, and the number of statewide fish-consumption advisories issued for lakes, rivers, and coastal waters has increased substantially in the last decade. Many waters with contemporary fish-consumption advisories can be characterized as lightly contaminated systems, and seemingly small inventories or inputs of mercury can cause significant contamination of fish (Wiener, 2001).

The factors that contribute to methylmercury bioaccumulation in fish have been the topic of extensive

research. Previously, it was suggested that a low pH and relatively large amounts of dissolved organic carbon in the water would increase the buildup in fish. More recently, this suggestion has been challenged. Research conducted by the Electric Power Research Institute (EPRI) found that although there is some correlation between the concentration of dissolved methylmercury in the water and increased levels in the fish, it was not possible to explain the differences in bioaccumulation solely on the basis of pH and dissolved organic carbon. Other factors, such as the presence of chlorophyll, sulfate, chloride, and calcium also appear to be at least partly responsible for the differences in bioaccumulation (Douglas, 1994). Also, the disturbance of wetland sediments could facilitate mercury transport by changing oxidation states, lowering pH, and resuspending sediment-bound mercury complexes in the water column.

Mercury: Atmospheric Transport and Fate

The atmospheric pathway of the global mercury cycle is known to be the key source of mercury contamination to most threaten aquatic systems (Bullock, 1999), and although much uncertainty still exists, several studies indicate that the relative contribution of mercury loadings to land and water from atmospheric deposition can be substantial.

Numerous studies of elevated mercury levels in remote locations, where atmospheric transport and deposition appears to be the principal mechanism for contamination, provide further evidence of the importance of the atmospheric pathway. It is also thought that any contributions from soils also originate from the atmosphere (Sorensen et al., 1990).

The air transport and deposition patterns in the United States for mercury emissions depend on various factors, including the form of mercury emitted, the location of the emissions source, the stack height of the source, the topography near the source, and the prevailing air circulation patterns.

An understanding of the transport and oxidation of mercury in the atmosphere is essential for predicting the impact of emissions on deposition (Douglas, 1994), but despite decades of research, the transformations of mercury in the environment or when mercury is released directly to land or water bodies are not fully understood (Rouhi, 2001; U.S. EPA, 2000). A significant barrier to this understanding is the difficulty of separating current mercury concentrations by origin because of the continuous cycling of the element in the environment. For example, anthropogenic releases of elemental mercury may be oxidized and deposit as divalent mercury far from the source; the deposited mercury may be reduced and re-emitted as elemental mercury only to be deposited again continents away.

It is also difficult to make a direct connection between emissions of any pollutant at one location and deposition at another. Emissions from a particular source may spread over a wide area and deposit in several watersheds. Several studies suggest links between atmospheric deposition and environmental impacts; however, it is difficult to actually trace most atmospheric pollutants into the food web because pollutants that have been deposited through air deposition are difficult to distinguish from those that entered the food chain

through other pathways. Modeling is typically used to make these links (U.S. EPA, 2001).

These uncertainties have caused controversy over how to control mercury emissions. Although the U.S. EPA accepts a plausible relationship between emissions from industrial sources and deposition, there is still a need for more quantitative certainty about the amounts of mercury that are locally deposited rather than globally dispersed (Hanisch, 1998). There is also a lack of reliable data about the speciation of mercury, which contributes further to assessment.

Mercury: Terrestrial Transport and Fate

The atmospheric input of mercury to soil is thought to exceed greatly the amount leached from soil, and the amount of mercury partitioning to runoff is considered to be a small fraction of the amount of mercury stored in soil. The affinity of mercury species for soil results in soil acting as a large reservoir for anthropogenic mercury emissions. Even if anthropogenic emissions were to stop entirely, leaching of mercury from soil would not be expected to diminish for many years (U.S. EPA, 1997), and according to a modeled scenario that was constructed as part of a research effort on northern Wisconsin lakes, it would take eight years before any change in fish concentrations would be observed, and the decrease would be small (U.S. Geological Survey, 1995).

An accurate assessment of the fate and transport of mercury after it has been deposited on the land's surface is inherently a complex task, owing to a vast number of interaction possibilities that can occur. Watersheds characterized by various land uses and soil types make it difficult to delineate individual transport processes.

Once deposited, the Hg(II) species are subject to a wide array of chemical and biological reactions. Soil conditions (e.g., pH, temperature and soil humic content) are typically favorable for the formation of inorganic Hg(II) compounds such as $HgCl_2$, $Hg(OH)_2$ and inorganic Hg(II) compounds complexed with organic anions. Although inorganic Hg(II) compounds are quite soluble (and, thus, theoretically mobile) they form complexes with soil organic matter (mainly fulvic and humic acids) and mineral colloids; the former is the dominating process. This complexing behavior greatly limits the mobility of mercury in soil.

Much of the mercury in soil is bound to bulk organic matter and is susceptible to elution in runoff only by being attached to suspended soil or humus. Some Hg(II), however, will be adsorbed onto dissolvable organic ligands and other forms of dissolved organic carbon and may then partition to runoff in the dissolved phase (U.S. EPA, 1997).

Sediments also serve as a major repository for persistent and toxic chemical pollutants, including mercury, released into the environment. In the aquatic environment, chemical waste products of anthropogenic origin that do not easily degrade can eventually accumulate in sediments (Salomons et al., 1987). In most aquatic systems, the rapid and efficient processes of sorption and settling scavenge hydrophobic organic contaminants from the water column, with the result that the largest fraction of persistent trace contaminant inventories presently reside in sediments (Eadie). The concentration of the contaminant in the sediments will be highly site specific and dependent on the physical, chemi-

cal, and biological factors affecting sediment-water exchange (Medine, 1989).

Mercury: Management

The development of a variety of tools has led to better understanding of mercury in the environment (Porcella, 2001). For instance, models can be used to answer questions about deposition rates and source attribution of mercury. And, although models can be useful tools, the information derived from them is reliant on the quality of the data and reasonableness of the assumptions that go into making them. Therefore, the limitations and sensitivity of a model must be clearly understood, and the model must be based on reasonable data with known error margins and reasonable assumptions.

Other mercury management strategies have been implemented as a result of regulations that have been enacted. These strategies have stemmed the release of mercury from primary sources during the past decade. It is estimated that the eventual outcome of the regulations will reduce mercury emissions from anthropogenic sources by more than 50%, as compared to 1990 levels.

Actions for which impacts have been, or should be, realized include:

EPA issued emission standards for medical waste incinerators

- EPA issued emission standards for hazardous waste combustors, including incinerators, cement kilns, and light weight aggregate kilns
- EPA Draft Action Plan which prescribes actions to respond to the public's right to know about sources of mercury emissions, integrate EPA's actions under its various programs to address mercury, emphasize pollution prevention and efficient use of resources to control mercury emissions, and foster communication and cooperation among all stakeholders in developing strategies to control mercury.

Actions to control air emissions of other pollutants will also reduce mercury emissions. The implementation of the National Ambient Air Quality Standards for fine particulate matter and ozone, and the second phase of the acid rain program could result in a reduction of mercury emissions from utility boilers. Similarly, actions to reduce emissions of the greenhouse gases could also reduce mercury emissions from utilities and other industrial boilers, whereas the Land Disposal Restrictions for Mercury-bearing Hazardous Wastes will re-evaluate land disposal restrictions on mercury to consider alternatives to mercury recovery and incineration (U.S. EPA, 1997; U.S. EPA, 2000).

Although these actions affect mercury emissions from the major sources, the scope of the impact will be limited in that they apply only to facilities that operate within the continental United States. To stem the release of mercury nationwide will require a focused and concerted effort among the affected nations.

A number of bilateral and multilateral programs offer the United States an opportunity to promote and engage in co-

operative mercury efforts (U.S. EPA, 2000). Examples include:

- The Great Lakes Binational Toxics Strategy, signed by the United States and Canada seeks a 50 percent reduction in the deliberate use of mercury and a 50 percent reduction in the release of mercury caused by human activity by 2006.
- The United Nations Economic Commission for Europe negotiated a legally binding protocol on mercury and other metals, which includes obligations to control mercury emissions from stationary sources and to establish, update, and report mercury emission inventories.
- The Arctic Environmental Protection Strategy, which is implemented through five working groups, is responsible for monitoring the levels and assessing the effects of selected anthropogenic pollutants in all compartments of the Arctic.

Mercury: Research Needs

Mercury-related research, as it applies to watersheds, can be broadly grouped into the following categories: risk characterization, fate and transport, management, and restoration; as well as implementation of TMDLs.

Within the ORD, several laboratories are actively pursuing mercury research, each with a different focus. The National Exposure Research Laboratory (NERL) provides research information on stressor sources; pollutant transport, transformations and exposure; and source-to receptor predictive exposure models applicable to the appropriate temporal scales and to site, watershed/regional and global scales. The National Center for Environmental Assessment (NCEA) research activities are focused on developing and evaluating model-based methodologies and techniques to improve the risk assessor's ability to synthesize, put into context and use exposure and effects data in risk assessment. The National Health and Environmental Effects Research Laboratory (NHEERL) provides scientific research on the effects of contaminants and environmental stressors on human health and ecosystem integrity. The National Risk Management Research Laboratory conducts research to reduce risks from pollution that threaten human health and the environment.

To contribute to the further advancement of mercury research and to improve the fundamental understanding of the behavior of mercury in the watershed environment, future research efforts should build upon the existing database of knowledge, leverage resources where applicable, and be conducted cooperatively when feasible.

The mercury transformations that occur in air, water, and on land and methylmercury's accumulation in fish, wildlife, and humans (based on the fish ingestion exposure pathway) present a set of scientific and technical challenges for both regulators and researchers. The priority mercury research efforts, which will address some of the current challenges, include developing methods that accurately characterize mercury sources and the species of mercury released from those sources; understanding mercury transport and the transformations that occur in the air and water and on land;

assessing mercury exposures to and effects on humans and ecosystems; developing cost-effective ways to manage risks from mercury sources and sinks; and understanding mercury cycling through air and water so that it is possible to predict how quickly changes in mercury sources emissions can appear in receiving waters and fish (U.S. EPA, 2000; Shick, 2000).

In addition, it is important to establish whether or not a reduction in mercury emissions directly corresponds to a reduction of methylmercury in fish. As noted by the U.S. EPA in its 1998 Report to Congress, the quantitative nature of the relationship between power plant emissions and fish methylmercury remains a key uncertainty that must be resolved before the United States can adopt mercury management practices with predictable outcomes.

The prioritized research needs on the transport, transformation, and fate of mercury include enhanced monitoring of atmospheric mercury deposition for model application, improved understanding of the transport, transformation, and fate of mercury in the aquatic and terrestrial media, and enhanced monitoring of mercury and methylmercury in the aquatic and terrestrial media for improved risk management. There is also a clear need for atmospheric models to be used in the development of emissions limits to protect water quality, human health, and ecological health (U.S. EPA, 2000).

Research activities are also needed that will bolster the current mercury management strategies have been planned and implemented by the U.S. EPA and other interested organizations. The scope of these research activities include 1) evaluation of control technologies, 2) development of prediction models to estimate stack-emitted mercury concentrations in the air, water, and soil, and 3) assessments to examine the health and environmental effects of mercury exposure (U.S. EPA, 1997).

Mercury: NRMRL Research Objectives

NRMRL has current research activities in various aspects of the environmental impacts of mercury.

Whereas other research activities are more focused on command and control or accounting, emphasis here is on risk management related research that is within the scope of the mission of NRMRL and part of the Laboratory's research plan for watershed management.

Based on the current needs and data gaps, priority research areas for the NRMRL should include the evaluation of alternative treatment options for mercury contaminated wastes, in situ treatment of mercury in sediments, identification and control of diffusive sources of mercury, and the fate and transport of mercury in the watershed environment. Critical areas of research involving mercury impaired waters and watersheds yield research questions such as those outlined in this section.

- Can available models accurately predict the fate and transport of mercury in a watershed? If not, to what extent do the models fail to predict the impacts of mercury-contaminated sediments and mercury in mixed land-use watersheds?

- To what extent can the existing watershed models be modified to better serve the needs of water quality planners, specifically for the implementation of mercury-related total maximum daily loads (TMDL)?

As the U.S. EPA and state pollution control agencies have increasingly emphasized watershed-based assessment and integrated analysis of point and non-point sources, modeling has been used extensively to evaluate a wider range of pollutant transport and environmental response issues. The models are applied to answer a variety of questions, support watershed planning and analysis, and develop TMDLs.

One challenge faced by water quality managers is the lack of integrated, scientifically sound approaches to identify problems in watersheds and to predict the results of potential control actions on receiving water quality and aquatic habitat. Developing a TMDL implies establishing a known cause-and-effect relationship. The relationship between cause and effect is often complex, and involves the interaction of point and non-point sources, hydraulics, sediment transport, and water quality. The mathematical models can provide a predictive capability which aids in determining TMDLs based on establishing cause-and-effect relationships and addressing multiple stressors and interrelation within watersheds.

The focus of this research should be on the determination of the state-of-science for watershed modeling as it pertains to the assessment of mixed land-use watersheds, development of modeling tools, improvement of modeling capabilities, and to provide technical support and training.

The critical risk management areas for which there is currently no modeling capability should also be determined and areas for which additional research would be beneficial should be identified.

- What is the effectiveness and efficacy of the management alternatives for the control of diffusive sources of mercury?
- Can a plausible correlation between the reduction of mercury through the alternative management options and the reduction of methylmercury production?

Metals and mercury, in particular, are a major cause for impairment of surface water bodies. The top four causes of impairments include sediments, pathogens, nutrients, and metals. These four sources of impairment result in half the impairments nationwide, with metals comprising about a fourth of these impairments. Mercury is the primary metal of concern.

Three areas should be researched: an evaluation of existing best management practices, and, as necessary, the modification of available models, landscape characterization methods, or classifications schemes, and field evaluations of mercury control techniques.

A comprehensive review of best management practices (BMP) available for mercury reduction and/or control should be conducted. These practices can include the evaluation of waste disposal methods to riparian control techniques. Subsequently, an evaluation of existing models, landscape char-

acterization methods, and classification schemes for assessment of mercury from diffuse sources. Afterwards, modifications might be made to the models/methods to address risk management approaches in controlling mercury.

- What is the effectiveness and efficacy of the management alternatives for both the treatment of mercury-contaminated wastes and sediments?

The U.S. EPA Office of Solid Waste has deemed alternative technology research and demonstration as one of its priorities. Also of concern is the ultimate disposal of mercury stockpiles and the approaches for the management of mercury in sediments.

Data show that the solubility of mercury can increase under certain landfill conditions. Currently, there is not an acceptable stabilization process that can permanently immobilize mercury for disposal. The U.S. EPA is considering the feasibility of requiring a macroencapsulation step in addition to a stabilization process, prior to landfill. The performance

of macroencapsulation methods, including long term performance, should be evaluated for selected mercury-bearing wastes.

Thousands of tons of stockpiled excess mercury and mercury-bearing wastes remain as a legacy of its industrial production. The long term management of these sources remains a major challenge to environmental risk managers. Also, the decommissioning of mercury cell chlor-alkali plants remain a significant source of secondary mercury. NRMRL will assess the alternatives for mercury storage and retirement.

With regard to the management of mercury in sediments, three approaches are available: capping, in-situ methods, and dredging followed by confinement or treatment. NRMRL has an established contaminated sediments research program and many of its research findings for metals are applicable to mercury. However, research is needed on in-place management of mercury-contaminated sediments that focuses understanding and enhancement of processes that sequester mercury from the food web.

III. Pesticides

Pesticides: Background

A pesticide is any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest. Pests can be insects, mice and other animals, unwanted plants (weeds), fungi, or microorganisms like bacteria and viruses. Though often misunderstood to refer only to insecticides, the term pesticide also applies to herbicides, fungicides, and various other substances used to control pests. Under United States law, a pesticide is also any substance or mixture of substances intended for use as a plant regulator, defoliant, or desiccant.

By their very nature, most pesticides create some risk of harm to humans, animals, or the environment because they are designed to kill or otherwise adversely affect living organisms. At the same time, pesticides are useful to society because of their ability to kill potential disease-causing organisms and control insects, weeds, and other pests. In the United States, the Office of Pesticide Programs of the U.S. EPA is chiefly responsible for regulating pesticides.

In the United States in a typical year, about 4.5 billion pounds of chemicals are used as pesticides (measured on the basis of active ingredient). For 1997, the quantities used are estimated, by type of pesticide, as shown in Table 1.

Conventional pesticides and "other pesticide chemicals" (e.g., sulfur, petroleum, etc.) account for about one-fourth of the total pesticide active ingredient used in the United States (1.23 billion pounds or 27 percent of the total). A majority of these pesticides are used in agriculture to produce food and fiber (77 percent or 944 million pounds of active ingredient in

1997), with the remainder used in industry/government applications and by homeowners. With usage of 1.23 billion pounds (for conventional pesticides plus other pesticide chemicals), the United States accounts for about one-fourth of such usage world wide. Chlorine/hypochlorites are the leading type of pesticides in the United States, with half of the United States total usage. Wood preservatives and specialty biocides make up the remainder of the United States total of 4.63 billion pounds in 1997. The above quantities equal 4.6 pounds per capita in the United States for conventional pesticides plus sulfur, etc., and 17.0 pounds per capita for the total of all types. The most widely used pesticide in United States agricultural crop production by volume is the herbicide atrazine. The herbicide 2,4-D has the largest volume of usage in the nonagricultural sectors. (U.S. EPA, 1999)

Urban/suburban pesticide sources may include maintenance of residential yards, cemeteries, golf courses, construction sites, schoolyards, and roadsides, as well as extermination of cockroaches and termites. For example, atrazine and simazine have been used for controlling weeds along roadways (Pitt et al., 1996) In particular, lawn applications by residential homeowners are a major concern. Usage of conventional pesticides by homeowners is estimated at 76 million pounds for 1997 (U.S. EPA, 1999).

According to a U.S. EPA fact sheet (Wild Ones Handbook: Today's Lawns), the National Academy of Sciences (NAS) believes that lawn use is "a significant component of the total pesticide program." Although usage estimates from the U.S. EPA Office of Pesticide Programs show that the overwhelming majority of pesticide use is for agricultural purposes, the NAS states that homeowners use "...10 times more per acre than do farmers", suggesting a potential for high pesticide impacts in streams drained by urban areas.

Pesticides: Atmospheric Transport

The atmosphere is an important part of the hydrologic cycle that can transport pesticides from their point of application and deposit them outside the area or basin of interest. Nearly every pesticide that has been investigated has been detected in air, rain, snow, or fog throughout the country at different times of year. Annual average concentrations in air and rain are generally low, although elevated concentrations can occur during periods of high use, usually in spring and summer months. Several instances have been recorded in which concentrations in rain have exceeded drinking-water standards for atrazine, alachlor, and 2,4-D. Atmospheric contributions are most likely to affect stream quality during periods when direct precipitation and surface runoff are the major sources of streamflow.

Table 1. Estimated Pesticide Usage in the United States

Type	Lbs (billions)	%
Conventional pesticides	.97	21
Other pesticide chemicals (sulfur, petroleum, etc.)	.26	6
Subtotal	1.23	27
Wood preservatives	.66	14
Specialty biocides	.27	6
Chlorine/hypochlorites	2.46	53
TOTAL	4.62	100

Finding agricultural herbicides like alachlor, atrazine and cyanazine in urban stormwater may seem surprising since these herbicides are not used in lawn and garden compounds. However, U.S. Midwest studies suggest that concentrations of atrazine in urban stormwater are consistent with concentrations found in rainfall. Both atrazine and alachlor easily evaporate from treated farm fields and later end up in rainfall or snow. Atrazine contamination of rainfall is more widespread than alachlor contamination because atrazine is more widely used and more persistent in the environment.

The detections in urban areas of alachlor (albeit at a concentration of less than 0.01 $\mu\text{g/L}$) and cyanazine, herbicides with no known uses in nonagricultural settings, may have been the result of historical use, atmospheric deposition, or transport of the herbicides from nearby application areas, either in the air (through spray drift) or in ground water. The other three agricultural herbicides detected in the urban areas (atrazine, simazine, and metolachlor) may also have entered the shallow ground water by atmospheric or subsurface transport from nearby agricultural applications. Indeed, recent detections of alachlor, atrazine, cyanazine, and metolachlor in rainfall and stormwater runoff in a small urban watershed in Minneapolis, Minnesota, where none of these compounds had been applied (Capel et. al, 1998), demonstrate that agricultural pesticides may be carried by atmospheric transport from nearby application areas into a watershed where they have not been used. However, because atrazine, simazine, and metolachlor are also used for nonagricultural purposes, the possibility that some of the detections of these compounds in the urban areas during the USGS National Water Quality Association Land Use studies (NAWQA LUS) could have resulted from their nonagricultural use near the sampled areas cannot be ruled out.

Pesticides: Terrestrial Transport

Intensive pesticide use appears to be a necessary but not a sufficient condition for encountering high frequencies of pesticide detection in groundwater. The wider ranges in pesticide detection frequencies observed at higher use are presumed to reflect the varying influence of other factors in addition to use in governing pesticide detection rates among different areas (e.g., soil properties, hydrogeology, and recharge rates). Soil permeability and intensive irrigation are two factors known to facilitate the movement of pesticides to groundwater. Pesticide application spray drift is another method by which pesticides may contaminate surface water.

The soil organic carbon partition coefficient (K_{oc}), a measure of the tendency of a compound to partition into soil organic carbon from aqueous solution, provides a quantitative, inverse indication of its anticipated mobility in ground water. Water solubility is often invoked as a measure of the relative likelihood of pesticides to be detected in ground water. Water solubility is less appropriate for this purpose than K_{oc} , however, because unlike the latter parameter, water solubility does not account for sorptive interactions between the compound and solid-phase organic matter in the subsurface (Barbash and Resek, 1996). Henry's law constant quantifies

the relative degree of partitioning between gas and aqueous phases in the unsaturated zone.

As is the case for other surface-derived contaminants, the hydrogeologic factors that influence the movement of pesticides to ground water are primarily those that control the movement of water. Thus, pesticide detections in shallow ground water tend to be more common in areas with permeable soils than in areas covered by glacial tills, clays, and other low-permeability geologic materials. In addition, higher levels of organic carbon in soils and other subsurface materials may diminish the likelihood of pesticide contamination of ground water by slowing pesticide migration (through sorption) and, for compounds susceptible to biotransformation, by enhancing microbial activity. Pesticide detections generally are more common in unconsolidated and solution-weathered (karst) aquifers than in relatively unweathered bedrock aquifers. Unconfined aquifers are more susceptible to contamination than those that are confined. In general, pesticide contamination tends to be more likely, and more temporally variable, in shallow ground water than in deep ground water (Barbash and Resek, 1996). Ground water in alluvial aquifers associated with rivers carrying substantial pesticide loads often contains detectable levels of pesticides particularly where the infiltration of the river water is enhanced by the pumping of nearby wells.

Pesticides: Fate

Pesticide contamination of groundwater is an issue of national importance in the United States because groundwater is used for drinking water by about 50% of the population (Kolpin, et. al., 1998). Pesticides rank 12th on the list of top 16 causes of impairments to waterbodies based on the 1998 Clean Water Act 303(d) List.

The highest concentrations of pesticides in groundwater are expected to be present at the water table. Pesticide concentrations may be undesirable because of (i) contamination of downstream public water supplies such as reservoirs; (ii) the economic loss suffered by farmers who lose fertilizer and pesticides to the stream; (iii) potential stresses on fish communities; and (iv) eutrophication of downstream surface waters. Tile drains and surface runoff have been shown to be important pathways for migration of pesticides from agricultural fields to surface waters. High concentrations of herbicides may occur in surface runoff during spring rains following herbicide application.

Physical and chemical properties of pesticides have been used to examine their relations to the detection of these compounds in groundwater. The four parameters that have been used most frequently for this purpose are K_{oc} , which describes the partitioning of organic compounds between water and soil organic carbon; Henry's law constant, which characterizes the partitioning between the aqueous and gas phases; water solubility, which provides an estimate of the maximum aqueous concentration likely to be encountered; and soil dissipation half-life, which serves as a rough indicator of persistence in situ.

All other factors being equal, the likelihood of detecting one pesticide in ground water compared to another is directly related to the degree of partitioning into the aqueous

phase, relative to soil organic matter or soil gas (which, in turn, affects relative mobility in the aqueous phase), and the relative resistance to chemical transformation in soil, with or without mediation by microorganisms.

Pesticides break down to other compounds over time in the natural environment. Little is known about the occurrence of breakdown products, or their possible health and environmental effects. Frequent detections of some breakdown products, however, indicate the need for their consideration in the development of water-quality standards and monitoring strategies.

The parameter used most commonly to quantify the environmental persistence of pesticides in soil is the field dissipation half-life, which represents the amount of time required for the concentration of a compound measured in a field soil to decrease to half of its initial value. Despite its widespread use, however, this parameter is of only limited utility for understanding the rates and mechanisms of the underlying processes responsible for dissipation in soil because it does not distinguish between decreases in concentration caused by the actual transformation of the parent compound and those caused by its transport away from the site of measurement in air, ground water, or surface water (Barbash and Resek, 1996). Aerobic soil half-lives are measured in a laboratory and, thus, are less representative of field conditions than the field dissipation half-life. However, because aerobic soil half-lives are measured under conditions that are considerably more controlled and standardized and unaffected by offsite transport comparisons among different compounds and different studies are more reliable for aerobic soil half-lives than for field dissipation half-lives, the time scales of transformation of these herbicides in aerobic soil may vary from weeks to years.

According to Gilliom et al. (1999), pesticides were commonly found in low-level mixtures. Stream water annual averages seldom exceeded drinking water criteria (nor did samples from wells). But the criteria only covers 43 compounds and a limited range of effects. Most studies of pesticides in surface water and groundwater have focused on pesticide detection. But degradation products of pesticides may be as toxic as the parent compound if not more so. A study in Iowa (Kolpin et al., 1998) examined municipal wells for agricultural pesticides and their degradates. If the degradates were included in determining the pesticide concentrations, the authors found that the degradates can make up a large (up to 90%) percentage of the total concentration. Thus, the absence of a pesticide in the groundwater does not guarantee that the compound is gone if the degradation products have not been analyzed.

It is reasonable to suppose that the more intensively a pesticide is used in a given area, the more likely it is to be detected in groundwater, but the evidence in support of this hypothesis is remarkably sparse (for example, Barbash and Resek, 1996; Kolpin et al., 1998). This may, in part, be a consequence of the limitations in the spatial and temporal resolution of the data currently available on pesticide use in the U.S. At present, the finest scale at which pesticide use information can be obtained across the Nation is on a countywide basis, and only for their applications within agricultural settings. Data on nonagricultural pesticide use are

considerably more limited and are available only at a national scale.

The predominance of atrazine relative to prometon in shallow ground water beneath agricultural areas is consistent with the primarily agricultural use of atrazine, whereas the predominance of prometon relative to atrazine in the urban areas reflects the primarily nonagricultural use of prometon. The relatively common occurrence of prometon in agricultural settings, however, suggests that pesticide applications for nonagricultural purposes such as for treating pavement, fence rows, rights-of-way, and other commercial and residential areas may still be relatively extensive in agricultural areas. The similarity in simazine detection frequencies between the agricultural and urban areas is consistent with the fact that the nationwide use of this herbicide in nonagricultural settings is nearly as high as in agricultural locations.

Atrazine residues were detected more frequently than any other pesticide compounds. The widespread detections of atrazine residues in groundwater were likely to have been the combined result of the comparatively slow rate of atrazine transformation under environmental conditions and the extensive long term use of the herbicide in both agricultural and nonagricultural settings in this country. Indeed, atrazine has been the pesticide used most extensively in the United States since the early 1970s (Kolpin, et al, 1998).

Prometon is used primarily for nonagricultural purposes; such as domestic and commercial applications to driveways, fence lines, lawns, and gardens and as an asphalt additive (Kolpin, et al, 1998). Prometon was the pesticide most frequently detected in urban settings and third most detected parent compound overall. Research has documented a direct relationship between urban-residential land use and prometon detections in groundwater as well as in surface water (Kolpin, et al, 1998).

Pesticide results from 41 land use studies conducted during 1993-1995 indicate that pesticides were commonly detected in shallow groundwater, having been found in 54.4% of the 1034 sites sampled in agricultural and urban settings across the United States. Pesticide concentrations were generally low with over 95% of the detections at concentrations less than 1ug/l. The compounds detected most frequently were atrazine (38.2%), deethylatrazine (34.2%), simazine (18.0%), metolachlor (14.6%), and prometon (13.9%).

Pesticides were commonly detected in both agricultural and urban settings. Urban and suburban pesticide use significantly contribute to pesticide occurrence in shallow groundwater.

Pesticides: Environmental Impacts

Common lawn and garden insecticides such as diazinon and malathion may not be persistent in the environment, but they are toxic to bees, fish, aquatic insects, and other wildlife. Diazinon is especially toxic to birds. It has been banned from golf courses because there are documented cases of waterfowl dying while feeding on areas treated with diazinon.

There is a continuum in the movement of water, solids, and solutes (e.g., atrazine) from a terrestrial environment, such as an agricultural field, through a surface water system and eventually to the marine environment. In 1996, 2,193

fish consumption advisories were issued in 48 states. Mercury, PCBs, chlordane, dioxin, and DDT were responsible for almost all fish consumption advisories in 1996 (U.S. EPA, 1998).

Evidence has accumulated to demonstrate that pesticides are routinely present in streamwater and groundwater associated with urban/suburban settings. A synthesis of National Water-Quality Association (NAWQA) results from across the United States (Gilliom et al., 1999) details pesticide findings. The authors report the unsettling results that pesticides were found in almost every stream sampled, and in 50% of wells sampled; the study sites included urban land-use areas. It found that herbicide concentrations are highest in agricultural areas and insecticides are highest in urban areas. The common herbicides in urban areas are simazine, prometon, 2,4-D, diuron, and tebuthiuron. The most common insecticides in urban locales are diazinon, chlorpyrifos, carbaryl, and malathion.

Maximum Contaminant Levels (MCLs) established by the U.S. EPA do not cover pesticide degradates, and at present do not take into account additive or synergistic effects of combinations of pesticide compounds or potential effects on nearby aquatic ecosystems.

Pesticides: Human Health Impacts

Laboratory studies show that pesticides can cause health problems, such as birth defects, nerve damage, cancer, and other effects that might occur over a long period of time. However, these effects depend on how toxic the pesticide is and how much of it is consumed. Some pesticides also pose unique health risks to children.

For these reasons, the Federal Government, in cooperation with the States, carefully regulates pesticides to ensure that their use does not pose unreasonable risks to human health or the environment. In particular, the Federal pesticide program is designed to ensure that these products can be used with a reasonable certainty that they will pose no harm to infants, children, and adults (U.S. EPA, 2000).

Pesticides: Management

Prevention

For many pests, alternatives to the use of traditional chemical products are available that are equally effective and are cost-competitive with chemical control methods. Integrated Pest Management programs have been put in place in some cases, using natural biological predators to keep pests under control without using pesticides. The need for chemical pesticides can be reduced through careful selection of pest resistant vegetation, plant and hardware selection to minimize requirements for irrigation, best mowing practices, and planned elimination of pest habitats (e.g., standing water that may attract mosquitoes, cracks and crevices in structures that will admit and harbor cockroaches). Best management practices have been developed to utilize less toxic pesticide alternatives wherever possible. Facility design and operational procedures are developed to accommodate pest management practices that are less susceptible to offsite transport of chemicals, such as pesticides and fertilizers,

thereby reducing the potential for groundwater contamination. Less persistent pesticides are used in concert with spot application techniques and minimum application levels. Biologically-based pesticides, such as pheromones and microbial pesticides, are becoming increasingly popular and often are safer than traditional chemical pesticides.

Control

The storage, handling, and use of pesticides can lead to environmental degradation through the interaction of incompatible chemicals due to improper storage, expiration of materials (which subsequently become wastes), spills and other uncontrolled releases, employee exposure to toxic chemicals, and pesticide runoff into environmentally sensitive areas. Pesticide inventory and control practices have been implemented to avoid the need to handle pesticides as waste and to limit uncontrolled releases of pesticides. Safe mixing techniques include ensuring that pesticides are mixed in clear and open areas that can be easily cleaned and avoiding mixing upstream from waterbodies (including drains leading to surface water bodies and groundwater aquifers). Other techniques include mixing the least amount of pesticide possible and using closed mixing systems that reduce the potential for release and exposure. Facilities are advised to have a pesticide spill prevention and control plan. Employee education and awareness programs are being developed to ensure employees understand the optimal situations for pesticide use.

There are technologies in place that minimize the amount of pesticide applied by using proper orifice spray nozzles at the correct pressure to minimize the amount of pesticide needed to treat a given area. The technologies also control pesticide droplet size and deposition. Pesticide runoff can be reduced by using row banding application techniques to limit the amount of pesticides applied, using contact pesticides that do not have to be incorporated into the sod, and not spraying in potentially sensitive areas.

The residuals resulting from the use of pesticides, such as wastewater and empty pesticide containers, must be properly managed to ensure that the environment is not negatively affected. Options to reduce the volume of this waste stream include purchasing products in bulk, refillable or returnable containers, and products with water soluble packaging. Federal regulations require rinsing empty pesticide containers at least three times before disposal. Pesticide containers must not be buried or burned, even after triple-rinsing. Rinsed containers can be disposed of at a sanitary landfill or often may be returned to the supplier for reuse. Reusable containers reduce the need for rinsing and disposal. Pesticide-contaminated rinse waters can be used in future pesticide mixing and application as an alternative to disposal, or can be applied in onsite landscape applications.

Pesticides: Research Needs

Significant advances in pesticide-related research have been made. The research, which has been conducted by the U.S. EPA Office of Pesticide Programs, ORD, universities, the private sector, and other federal organizations, has covered a variety of topics.

Within ORD, several laboratories are currently involved in pesticide research. NCEA is currently researching a spatial approach to non-point sources of pesticides in surface waters as part of its pesticide research efforts. NERL is focusing on pesticide exposure assessment, surface water hydrology, and constituent transport. NHEERL is conducting research investigating the impact of pesticide exposure on children and the laboratory is also investigating the ecosystem effects of pesticide contamination. NRMRL is involved in collaborative pesticide research efforts with the other laboratories and also is investigating the improvement of pesticide spray application technology to reduce spray drift of pesticides during application.

To contribute to the further advancement of pesticides research and to improve the fundamental understanding of the behavior of pesticides in the watershed environment, future research efforts should build upon the existing database of knowledge, leverage resources where applicable, and be conducted cooperatively when feasible.

As a result of a review of current research activities in the area of pesticide impacts on watersheds, it was discovered that the pesticides of most concern in the contamination of watersheds are atrazine, simazine, cyanazine, metalochlor, alachlor, 2,4 D (2,4 Dichlorophenoxy Acetic Acid), diazinon, chlorpyrifos, prometon. Research focused on these pesticides would address the impacts they have on both surface and groundwater. They would also address the impacts of pesticides on agricultural watersheds and urban/suburban watersheds.

For pesticide degradate and mixture characterization and behavior, not enough is known about additive or synergistic effects when more than one pesticide is present. Also, not much is known about low-level long-term exposure with pulses. Pesticide degradation products present an additional concern. The National Research Council (NRC) echoes this sentiment in its 1998 book *Identifying Future Drinking Water Contaminants* by concluding that "polar degradates of herbicides are increasingly important." Research questions include:

- What are the degradation products of pesticides?
- What are the effects of low-level long term exposure to pesticides?
- What are the synergistic effects when more than one pesticide is present in water?

Research in this area would improve our understanding of the impacts of mixtures of pesticides on human health and the environment by generating sound scientific data on health and environmental effects of degradation products of pesticides. This data should seek to delineate the transformation process that results in the creation of degradates. The data should also provide information on the toxicity of degradates and various pesticide mixtures to ecosystems and human health.

Mixtures of contaminants also require special consideration in assessing possible health and environmental effects, and thus in developing and improving water-quality standards. More than one-half of all stream samples contained five or

more pesticides, and nearly one-quarter of groundwater samples contained two or more. These mixtures of pesticide parent compounds also occur with breakdown products and other contaminants, such as nitrate. Continued research is needed to help reduce the current uncertainty in estimating risks from commonly occurring mixtures. As improved information is accumulated, the occurrence of contaminant mixtures should be considered when developing water-quality standards and monitoring requirements.

For pesticide application and transport data, improved data is needed on the amounts of pesticides applied and areas treated particularly in the case of pesticides used in urban/nonagricultural settings. Understanding the mechanisms of pesticide and N transport is crucial to understanding the occurrence, distribution, and concentrations of agrichemicals in the water resources. Research in this area should collect data to better understand the air deposition of pesticides within watersheds. Also, more comprehensive monitoring is needed of pesticides during hydrologic events. Without monitoring information during major hydrologic events, a full accounting of nutrients and pesticides transported by streams is incomplete, and a full understanding of the effects of these contaminants on the health and living resources of receiving waters is restricted.

NRMRL research should focus in three areas:

- Control of Pesticides in watersheds as an alternative to drinking water treatment
- Pesticide Application/Transport Data
- Reliability and Effectiveness of Pesticide Occurrence Modeling and Pesticide Management Practices

For reliability and effectiveness of pesticide occurrence modeling and pesticide management practices, quantifying nonpoint pollutant sources is challenging because they are diffuse, transient, and highly variable site to site, within a runoff event and among different events. Therefore, there is a need to rely on estimation techniques and models to quantify these pesticide sources. Improvement in the science on the mechanisms of degradation, fate, and transport of pesticides into surface waters and groundwater and their impacts on the watershed and its and the ecosystems should provide supportive data for the development of improved watershed models. The U.S. EPA, for example, is using NAWQA pesticide data to test the reliability of models now being used to predict possible pesticide occurrence in streams and reservoirs. Water-quality models have been in use for many years, but their utility depends on their reliability for representing actual conditions. Without demonstrated reliability based on comparisons to measured conditions, confidence in a model is difficult to attain, and the usefulness of the model in decision making, especially in controversial situations, is limited.

Development of data on the impact and effectiveness of pesticide best management practices such as pollution prevention and treatment alternatives for contaminated drinking water and sediments along with quantifying sources of pesticide and their impacts on water quality improve models for movement of pesticides through the watershed.

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