ON CONTROLLING THE CHEMICAL CONTAMINATION OF GROUNDWATER

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Keywords: chemical contamination, public policy issues, environmental behavior, chemical transport, chemical properties, contaminants, toxicology assessment, groundwater sampling, contaminant reduction

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Summary

During the past two decades water resources research programs have increasingly focused on groundwater. It is now obvious that serious gaps exist in our knowledge of: a) the characteristics of the quality and quantity of the groundwater resource; b) the ways in which groundwater becomes contaminated; c) techniques to minimize impacts of contamination; d) the realistic magnitude of public health problems that arise from contaminated drinking water; and e) cost-effective management methods to protect

groundwater from contamination. The research discussed here will provide scientific information to minimize water quality deterioration resulting from chemical use and misuse. The eventual aim is to ensure a rational protocol to establish water quality standards for ground and drinking waters.

This article explains the complexity of components needed to resolve major water contamination issues on a broad geographical basis, especially when strong public input in the decision-making process is demanded. The process described here is costly and time-consuming, and the author is fully aware that only nations with "luxury economies" are capable of expending such time, effort, and money on resolving chemical contamination issues. Other, more urgent programs likely demand the use of many nations' scarce financial resources. However, much of the background work has already been completed—as shown in this document—and is readily transferable to other countries and regions which are less opulent than the USA. Certainly gross contamination of a nation's water supply can be averted at much lower costs than the complex program described here would indicate. For those nations who cannot afford the expenditures to curtail gross contamination they must be helped by the wealthier nations or through the United Nations to obtain innovative low-cost financing for these endeavors. Nothing is more basic to a nation's well-being than a reliable and plentiful supply of high quality water. The highest quality of water should be reserved for human and other animal consumption. In cases where demand exceeds supply, water of lower quality can be used for irrigation and manufacturing.

The unavailability of a constant (quantity and quality) supply of clean water is a scourge in many countries which—in turn—affects overall global well-being. With the vastly increased transoceanic movement of people worldwide, both the threat and actuality of transmission of waterborne diseases will in the end bear greater costs (financial, demand for medical care, lowered life expectancy, family and community dislocation, etc.) than the costs required to ensure the provision of high quality water on a global basis.

1. Public Policy Issues

The public policy issues embraced here are of concern to the general public and their political representatives. Nations must provide a plentiful supply of high-quality water for all uses. Future decisions on groundwater use and its preservation are likely to have profound impacts on land use and national economies. Vital questions include: a) Where can agriculture be conducted and how will farmland be managed? b) How can predictions be made to determine which lands are overly susceptible to movement of chemicals to groundwater? c) What health risks can be tolerated when establishing drinking water and other groundwater standards? d) How can land (agricultural, landfill sites, urban) be managed to minimize use of chemicals and protect water resources from degradation?

Groundwater investigations should pursue three early initiatives: a) evaluate existing information and repackage it in a format and language readily understandable for use in policy evaluations; b) establish priorities for research utilizing the inputs of top decision-makers, remembering that some decisions have to be made quickly and decision-making deadlines should be an important consideration in setting priorities;

and c) evaluate information distribution systems to provide decision-makers with the best techniques for quickly accessing relevant information and policy alternatives.

2. Information Gathering

2.1. Environmental Behavior Predicted from Chemical Properties

Experience has shown that it is too expensive and time-consuming to study individual chemicals in the variety of soils, landscapes, climates, crop rotations in which they are used. Short cuts must be sought. Fortunately, the transport, fate, and effects of chemicals in the environment are linked to their molecular structures. This interdependence exists because chemical reactivity, mobility, and toxicity are controlled by chemical properties determined by molecular structure. Quantitative structure-activity relationships form linkages to chemical properties that provide a basis for predicting the fate and effects of chemicals in the environment. The overall number of chemicals of environmental concern is immense (>50 000); the number and classes of pesticides is about 300 active ingredients. Rapid, cost-effective methods for predicting chemical properties are vital. Most rapid and least costly are those methods requiring information only on chemical structure.

While related to the chemical properties of the compound, chemical behavior is determined by environmental interactions. For example, sorption to soil and sediment components modifies transport and degradation rates. Thus, an understanding of the linkages between chemical properties and the interactions and transformations occurring in the environment is essential in predicting chemical residue transport and fate. Information on chemical properties is vital for predicting the toxicology of chemicals. Acquisition of available information on chemical properties, reliable methods for measuring them, and valid models for predicting fate and effects using this information are urgently needed.

Chemical properties cannot be incorporated into models of transport, fate, and effects without taking into account the chemical property-dependent interactions occurring in natural systems. These interactions include partitioning between air–water, air–soil/sediment, and water–soil/sediment phases, and chemical and biochemical transformations. Predictive methods for some physicochemical interactions have been developed.

2.2 Transformation of Chemicals

The fate of toxic organic chemicals is governed largely by the rate and extent to which they degrade in the environment. Consequently, determining the degradability of chemicals to nontoxic metabolites is of major importance in evaluating environmental hazards associated with their use. Transformations may occur through biological and/or nonbiological mechanisms. Some compounds undergo relatively rapid chemical degradation mainly through hydrolysis, oxidation or reduction while others undergo photodegradation or conjugation. Some chemical and photolytic reaction rates are enhanced by sorption of the chemicals on particle surfaces. However, microbial metabolism is considered to be the major pathway of degradation in soil and aquatic environments. Its efficiency depends on the composition of the microbial population as affected by soil, limnological, and hydrogeological factors. Similar types of metabolic processes may be found in soils, sediments, and groundwater but degradation rates and products vary widely because of differences in environmental conditions.

Chemicals differ in their resistance to microbial degradation. Some are highly resistant, others are easily biodegraded. This varying degree of resistance is attributed to: a) the chemical's inherent resistance or susceptibility to microbial attack; and b) the biodegradable chemicals becoming largely or totally unavailable for microbial degradation due to environmental factors and interactions. For example, some biodegradable compounds become resistant when adsorbed by clay minerals and organic constituents of soils and sediments, especially at sites where microorganisms cannot penetrate.

Little is known about biodegradation of organic compounds in the soil's subsurface (vadose zone) and in groundwater (phreatic zone). Potential for biodegradation of chemicals below the root zone exists, but the rate at which it proceeds is unknown. The subsurface environment differs considerably from microbial habitats found in surface soils and waters.

To clarify the fate of chemicals it is essential to identify major metabolites in various environments so that their toxicological significance can be assessed. Degradation products of organic chemicals may be as toxic, more toxic or less toxic than the parent, and each metabolite may have a different effect on human health. Analytical methodologies for identifying parent compounds and metabolites and confirming their composition are desperately needed, as well as cost-effective assays for them in complex media. To date, most degradation studies have involved only the disappearance of the parent compound from the environment. Unless all-important toxic products that appear in the degradation pathway are taken into consideration, this approach will lead to underestimation of the residence times of hazardous residues. Accurate degradation pathways and rate data are needed to develop dependable mathematical models for predicting transport and fate of chemicals and their metabolites in surface- and groundwater.

2.3 Chemical Transport

Transport of chemicals from point of formation, emission, application, or storage into surface- and groundwaters, and their reactions en route are key aspects of the toxic pollutant problem. A thorough understanding of the transport-reaction chain is essential for effective and economic control of chemical pollutants.

Overall objectives are:

- to establish the factors controlling water and chemical movement in and through the root and vadose zones of soils to groundwater; and
- to measure and model the transport and dispersion of chemicals in groundwater.

Although numerical models have been developed to predict contaminant transport in the vadose zone and groundwater, indications are that the models are considerably more reliable in predicting water flow than in their ability to simulate the transport of organic contaminants. Present models are inadequate in simulating dispersion and the interactions and transformation affecting contaminant solute transport in soil and groundwater systems. Problems arise in part from dealing with aqueous-solid phase interactions, particularly adsorption, and chemical and biological transformations during transport. Some models have incorporated dispersion, adsorption-desorption, and first-order degradation rate information on the associated equilibrium and kinetic parameters applicable under field conditions, but to date the models are insufficiently refined to allow site-specific decisions to be made about the susceptibility of particular soils to contaminate groundwater. A three-tier approach is needed to assess chemical transport: a) data should be obtained from representative field sites to provide ground-truth information; b) the rate and extent of transformations and adsorption-desorption must be determined under conditions similar to those in the field; and c) transport models should be modified and/or developed to accommodate information on flow path, interactions with solids, and transformations occurring during transport.

A quantitative understanding of the influence of solid-solution interactions and transformations is perhaps the greatest impediment to predicting transport and distribution of chemicals in soil and groundwater systems; adsorption-desorption reactions are the main form of solid-solution interaction. To model the attenuation of chemicals, information on adsorption-desorption kinetics and equilibrium relationships is essential. Another key process affecting transport involves chemical and microbial transformations occurring in the system. A principal goal is to predict degradation based on structure-susceptibility relationships and incorporate this information into transport models.

In addition to contaminant transport from surface soils and waste disposal sites, the mobility of chemicals in sediments associated with surface waters may also be a problem. Surface and groundwater systems are interconnected, and polluted sites are potential sources of groundwater and subsequent surface water contamination. Consequently, more data on the factors controlling the mobility of contaminants associated with bottom sediments is needed, including dispersion into surface water through diffusion, particle-mediated transport, and advective transport into aquifers. In addition to the chemical and biological interactions affecting transport, important problems must be addressed concerning the movement of water in the unsaturated and saturated zones including the influence of heterogeneity in porous media, modeling unsaturated flow and gas-phase transport, and assessing such important physical parameters as hydraulic conductivity. Mathematical models should be tested to evaluate movement of landfill leachate to describe the fate of chemicals in the root and vadose zones, and to estimate their potential for predicting groundwater quality for a variety of management schemes.

2.4 Innovative Management Practices

2.4.1 Agricultural Management Practices

Continued field-scale investigations are needed to develop so-called "best" management practices for agriculture. In the past decade numerous investigations have been made on no-till and conservation tillage practices. It is widely reported that most of agriculture will be under some form of conservation tillage in the near future. Minimum tillage practices have been designed in large measure to reduce fuel consumption, runoff, and soil erosion; and certainly these practices reduce the threat of nonpoint pollution to surface waters. However, the impact of the processes on transmission of pesticidal and fertilizer chemicals to groundwater is little understood. Some investigations show that leaving stubble and other plant residues at the soil surface can enhance some disease vectors, particularly fungal diseases. Also, increased use of herbicides is often associated with these cultivation practices. After a few years of minimum tillage, earthworm populations rise dramatically and worm holes short-circuit water and associated pollutants to greater depths in the soil profile. By reducing runoff, particularly during heavy storms, more water is available for transport through the soil to carry pollutants to groundwater. Information on water movement in soils—at the field-scale level is urgently needed particularly with reference to macropore infiltration, e.g. down cracks or worm holes in fine-textured soils.

Farmers who use pesticides must understand that it is not essential to remove every vestige of weeds, nematodes, insects, etc. from a field to assure high crop yields. Prior to the use of herbicides, the mechanism for curtailing growth of grasses in cornfields was to allow the rapid growth of the corn to shade out the grasses. Investigations need to be made to see if production can be maintained while using very low amounts of herbicide in the early phases of growth and allowing the crop canopy to eliminate weeds by shading.

Some simple methods that might be investigated for retaining pesticides in the root zone are to modify the surface hydraulics of the soil so that under rainfall or irrigation conditions excess water is diverted around the main sites of chemical placement. Only enough water need reach the chemical to allow it to perform its function. Minor surface landforming on susceptible soils (particularly sandy soils) can provide this water diversion with little mechanical energy input. A second possibility is to localize placement of chemicals to reduce the amount of water coming in contact with them. Successful procedures have been developed to do this with nitrate. Slow-release formulations allow plants to take up plant nutrients as they are released. A similar concept might be applied to pesticides, especially those taken up systemically. A third possibility is that some of the new biodegradable plastics could be used to form temporary barriers around pesticides to shield them from percolating waters. Some, but not excessive, redesign of farm equipment may be needed to apply some of these proposed techniques.

2.4.2 Waste Containment Technology

A major problem in industrialized societies is the proper, safe and long-term handling of wastes. Waste disposal in landfills impacts everyone because all are direct or indirect waste generators and many suffer from the economic and health impacts of improper waste disposal. Clearly, waste minimization, reduction and beneficiation should be actively pursued. Therefore, construction of secure waste disposal sites with containment of waste effluent that cannot be treated or until it can be treated immediately is an important issue in evolving management tactics. Waste containment systems currently include bottom liners, sideslope liners, covers and vertical barriers, and utilize earthen materials and geosynthetics. The barriers must control water seepage and restrict the escape of such hazardous substances as pesticides or volatile organic compounds in solution or vapor phase. Laboratory and field experience shows that some chemicals can affect the structural integrity of soil. The susceptibility of hydraulic conductivity to change with time or exposure to chemicals, impacts the use of clay in waste containment barriers. Test results are only available for simple monochemical systems or for short time periods relative to the active life and post-closure security periods of waste containment and storage facilities. Even in field situations involving little or no fluid flow, chemical flux through a barrier may be controlled by chemical concentration gradients. Diffusion and its importance as both a transport and an attenuation mechanism have been recognized. An acute shortage of long-term field data exists with regard to performance of barriers to waste leakage.

Waste containment technology is in need of innovative approaches to develop another generation of barriers. Economic and construction factors often are limiting. The feasibility of using improved designs and new materials as a substitute or amendment for soils needs investigation. For instance, pozzolanic fly ash is a relatively inexpensive material shown to have favorable hydraulic characteristics and interesting properties for removing certain contaminants. Its attractive physical properties such as resistance to damage by freeze/thaw and wet/dry exposures and superior strength and mechanical characteristics suggest development of barriers liners and covers) using pozzolanic fly ash as a substitute for clay, as an additive to clay, or as a material interlayered with clay. For instance, the superior strength of pozzolanic fly ash could allow construction of steeper sideslope liners resulting in increased waste disposal volumes over the same area. The constructibility of liners, their cost-effectiveness, their interaction with mixed chemical systems, their performance under field conditions, and their longevity are important information needs. Furthermore, development of technologies for rapid detection of leakage and the use of reverse- or electro-osmosis to concentrate contaminants or control solute transport across barriers are items of immediate concern.

2.5 Contaminant Reduction and Conversion

Methods to cleanup hazardous organic wastes suffer from many problems, making management a pressing scientific and social issue. Annually, many new compounds are synthesized, potentially contributing to water pollution. Techniques such as landfilling for disposal of byproducts, expended major products, and waste products formed in chemical manufacture are inadequate. Analytical advances allow detection of lower and lower trace levels of pollutants in water, but treatment methods remain archaic. New, efficient and economic methods are needed for reduction and conversion of chemical wastes and byproducts. Two innovative strategies for degradation of contaminants reaching aquatic systems are: a) photodegradation catalyzed by hydrous oxide surfaces; and b) development of mixed microbial populations capable of degrading target compounds under natural or modified environmental conditions.

The photocatalytic approach involves use of energy from light (possibly sunlight) to promote oxidation of organic compounds on the surfaces of oxide particles. The metal oxides serve first as adsorbants to concentrate the organic compounds and then as catalysts to degrade them. Ceramic membranes constructed of hydrous oxides may serve the same purpose and provide a means for separating the products from the liquid waste. Research is underway and pilot plant testing is warranted. Technology transfer should involve communicating the results to government agencies and industry.

Bioremediation, the controlled biodegradation of toxic chemicals, has long been used to remove petroleum contaminants from soil. Recent biotechnology advances in microbial ecology and genetic engineering suggest that bioremediation has a broader applicability and may provide a practical, cost-effective system for clean-up of a variety of organic contaminants from soils, sediments, and groundwaters. A problem encountered in microbial degradation of organic contaminants is the formation of highly recalcitrant intermediates. In fact, biological conversion of organic pollutants to metabolic "dead-end" products is a common phenomenon. An alternative to the use of pure cultures is to exploit the diversification achievable with microbial consortia to accomplish complete mineralization of pollutants. Construction of consortia to exclude "dead-end" products may be achievable by maintaining pollutant concentrations at very low levels. Pesticide-contaminated soils or sediments should be used as starter sources for developing pollutant-degrading microbial consortia. For successful consortia, the effects of environmental factors should be evaluated, loading rate limits should be established, and microbial inoculants should be tested on a variety of soil types. In the final stage, successful systems should be evaluated under field conditions.

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Bibliography

Orloff N. (1984). We scoff at big risks and scotch small ones. *Wall Street Journal*, 3 December, 34. [A newspaper article discussing the public's understanding of voluntary and involuntary risk and suggesting that the public is not well-informed on technical issues and provide a reaction rather than an informed opinion.]

Zaki M., Moran D., and Harris D. (1982). Pesticides in groundwater: the aldicarb story in Suffolk County, New York (USA). *American Journal of Public Health*, 72, 1391–1395. [A journal article, written by health administrators that discusses major risks that the public is willing to accept and their intolerance of some risks that are comparatively minor and often immeasurable such as food additives, pesticides, air pollutants, and water contaminants.]

Biographical Sketch

Gordon Chesters was born in Lancashire, England in 1932, and is marred with three children. He holds a B.Sc. degree in Chemistry and Agricultural Chemistry from the University of Wales, United Kingdom; he earned M.S. and Ph.D. degrees in Bacteriology and Soil Science from the University of Wisconsin, USA; he was granted a D.Sc. degree for Research from the University of Wales. He is an elected Fellow of the

Agronomy Society of America and the Soil Science Society of America. He was employed at the University of Wisconsin, Madison from 1954 until his retirement in 1998. Positions he held include: Professor (and Department Chair) of Soil Science; Professor and Chair of the Water Chemistry Graduate Degree Program; Professor of Environmental Studies in the Land Resources and in the Water Resources Graduate Degree Programs; Professor of Environmental Toxicology; and Director of the University of Wisconsin's Water Resources Research Institute. From 1969–1998 he held all of these positions concurrently. Professor Chesters has also served as major professor and research thesis director for over 250 research papers in peer reviewed journals, and has prepared several hundred research project proposals and research reports. His principal areas of research are: determining the rates and pathways of chemical and biological degradation of pesticides; evaluating their transport through the environment, particularly through soils to groundwater and through groundwater; establishing their toxicological significance; and transferring scientific analysis of pesticide contamination to state and federal agencies responsible for setting environmental standards. He chaired a large research program conducted through the Pollution from Land Use Activities Reference Group of the U.S./Canada International Joint Commission on the impact of land-use on the water quality of the Great Lakes. He was also instrumental in evaluating the water quality and other natural resources of the Upper Mississippi River Basin. He led an effort to determine the environmental impact of a large coal-fired electric power generating plant located in an environmentally pristine area. He has had continued interest in dissemination of scientific information, not only to scientists and the general public, but also to agency administrators and elected decision-makers.