Water Quality Aspects of Incidental and Enhanced Groundwater Recharge of Domestic and Industrial Wastewaters

Published in: Proc. Symposium on Effluent Use Management, TPS-93-3, pp. 111-120,
American Water Resources Association, Bethesda, MD (1993)

G. Fred Lee, Ph.D., P.E., D.E.E. and Anne Jones-Lee, Ph.D.
G. Fred Lee & Associates
El Macero, California

1993

ABSTRACT: An important source of water for groundwater recharge in some areas is river water that passes through the river bed. In many areas, especially the arid West, domestic and industrial wastewaters comprise a large part of the dry-weather flow of rivers. This can result in significant incidental recharge of groundwaters by domestic and industrial wastewaters. Associated with such recharge is the potential for transport of contaminants in the wastewaters to the groundwater aquifer system. Some regulatory agencies are becoming sufficiently concerned about the incidental recharge of groundwaters by wastewaters discharged to rivers that drinking water standards are being incorporated as NPDES discharge limits on wastewaters discharged to rivers and tributaries. Other regulatory agencies are not considering incidental recharge in establishing NPDES discharge limits. If groundwater quality is to be protected, there is need to consider the potential impacts of contaminants in point- and non-point-source discharge-runoff on groundwater quality through incidental recharge. This paper presents an overview of issues that should be considered in protecting groundwater aquifer systems from the recharge of contaminants in wastewaters discharged to river systems that recharge groundwaters.

KEY TERMS: groundwater; recharge; wastewaters; aquifer; hazard assessment; water supply

INTRODUCTION

Groundwaters provide about 50% of this country's domestic water supplies. Many groundwater basins are used at such rates that the groundwaters are being mined. This contributes to the growing interest in enhanced ("artificial") groundwater recharge to stabilize the position of the watertable, and in some instances to return the watertable to levels existing before the overdraft. In addition, water development projects that had been focused largely on the development of surface water reservoirs for water storage are being refocused on water conservation and the development of groundwater storage of surface waters (conjunctive use) owing to difficulties in constructing new surface water reservoirs. Water utilities and districts in many areas of the country are participating in and/or planning for conjunctive use projects in which surplus surface waters obtained during wet periods are recharged to the aquifer for use during dry periods/droughts.

There is considerable discussion today about the potential impact of contaminants in waters used for enhanced recharge on groundwater and aquifer quality (i.e., the ability of the aquifer to serve as a reliable water supply source or conjunctive use aquifer). The widespread finding that many groundwater basins have been polluted by contaminants derived from industrial, municipal, and agricultural activities, coupled with the conclusion that once a groundwater and aquifer area are polluted it is difficult (if not impossible at least in the near-term) to restore the aquifer to unrestricted use, provides justification for concern about the potential impacts of contaminants in recharge waters on groundwater and aquifer quality. Regulatory agencies at the federal and state levels are establishing concentration limits for contaminants in waters used for enhanced recharge, that are designed to protect groundwater and aquifer quality. In addition there is growing concern about the quality of "incidental recharge" waters such as river waters that pass to the groundwater aquifer through the riverbed. Wastewater discharges to rivers are not typically being evaluated and regulated with regard to potential impacts of contaminants on groundwater and aquifer quality. This paper reviews the water quality aspects of groundwater recharge associated with enhanced and incidental recharge.

OVERVIEW OF WATER QUALITY ISSUES

In evaluating the potential impacts of chemical and biological contaminants in recharge waters it is necessary to determine whether the contaminants in such waters could:

- pollute an aquifer to impair its use for water supply,
- lead to the pollution of waters recovered from the aquifer due to contaminants already present in the aquifer from natural and anthropogenic sources,
- limit the ability to recharge and recover water from the aquifer - impact aquifer hydraulic quality.

There is a variety of physical, chemical, and biological reactions and processes that take place in aquifers that can cause contaminants in incidental and enhanced recharge waters to have undesirable impacts on the conjunctive use of aquifers. At this time the general characteristics of these reactions and processes and their impacts are recognized but only poorly quantified. Because of the relatively poor quantitative understanding of the aqueous environmental chemistry (chemical thermodynamics and chemical kinetics) and transport of chemical contaminants in aquifers it is essentially impossible to reliably and quantitatively predict the impact of contaminants in recharge waters on the quality of the water that can be recovered from the aquifer. Inadequate quantitative and predictive capabilities leads to either over-regulation or under-regulation of enhanced and incidental groundwater recharge waters.

Surface waters that recharge aquifers include relatively poorly treated domestic and industrial wastewaters, agricultural waters, and urban and rural stormwaters. Each of those sources contains a wide variety of chemical contaminants that can be adverse to groundwater and aquifer quality. However, the quality of waters that recharge groundwater tends not to be formally addressed; recharge is allowed to take place until problems are discovered. In some instances regulatory agencies have developed treatment requirements for treated domestic wastewater used for enhanced recharge, although those requirements tend to be somewhat arbitrary. Reverse osmosis and/or activated carbon bed treatment is being required in some areas for domestic wastewaters that are recharged to an aquifer. At other locations the aquifer is relied upon to provide the additional treatment of partially treated domestic wastewaters, for protection of groundwater quality. Discharges of partially (secondarily) treated wastewaters commonly serve as sources of incidental groundwater recharge. Insufficient attention is being given today to developing the information needed to reliably assess before the fact, whether contaminants in a particular recharge water will adversely affect an aquifer system.

OVERALL APPROACH

The impacts of contaminants associated with an existing or proposed source of incidental or enhanced groundwater recharge water on the quality of an aquifer or of the recovered waters, under plausible worst-case conditions, should be evaluated in a hazard assessment framework of the type described by Lee and Jones (1982). While the focus of the risk assessment described by Lee and Jones was the evaluation of environmental risk associated with a particular waste management operation such as a landfill, the overall approach is the same. There are basically two components to such a hazard assessment, the environmental chemistry and fate of contaminants, and the impacts of those contaminants.

The aqueous environmental chemistry of the contaminant(s) in a particular aquifer system is controlled and described by the hydraulics (transport) of water and small particles, including colloids, and the nature and rates of chemical and biochemical transformations of the chemical constituents in the recharge waters, in the aquifer water, and in association with aquifer solids. The quantitative description of the aqueous environmental chemistry in such systems requires the development of a mathematical model to describe the hydraulics and chemical thermodynamics/kinetics. While at this time it is not possible to construct reliable quantitative predictive models of this type, the modelling exercise is extremely important in developing a systematic, organized approach toward the evaluation of the fate and behavior of chemical contaminants in recharge projects. It is also important for defining those aspects in which there is need for site-specific investigations to determine whether a particular contaminant or group of contaminants in recharge waters will be adverse to the aquifer or recovered water quality.

The assessment of potential impacts of contaminants associated with incidental and enhanced recharge water must consider the impacts of the known and uncharacterized components of the recharge water, and their transformation products on beneficial uses of the groundwaters and aquifer. The evaluation must extend beyond "carcinogens" to all contaminants that could adversely affect beneficial uses, including conventional and non-conventional pollutants, as well as conservative tracer components.

Those responsible for organized enhanced groundwater recharge projects, and for discharge-release of waters that incidentally recharge groundwaters should be required to conduct detailed monitoring programs to reliably determine the fate and effects of contaminants present in the recharge waters that could be adverse to the quality/use of the groundwater and aquifer. Such monitoring is necessary to properly conduct recharge operations and can be extremely valuable in the anticipation of problems caused by enhanced or incidental groundwater recharge.

REGULATING CONTAMINANTS IN RECHARGE WATERS

Because of the importance of groundwater and aquifers to the future development of the country, a significantly stronger approach needs to be taken to regulating incidental and enhanced recharge of surface water to aquifers. PL 92-500, the 1972 amendments to the Clean Water Act and its subsequent amendments established as a goal "zero pollutant discharge" for the protection of surface waters of this country. Groundwater aquifer systems do not at this time receive the same degree of protection under federal law. In fact US EPA RCRA Subtitle D regulations for solid waste management provide for only postponement of groundwater pollution by a few potentially hazardous chemicals. The degree of groundwater quality protection provided by implementation of California regulation is also significantly less than that afforded surface waters. This discrepancy in protection afforded by the regulations is exacerbated by the fact that once contaminated, groundwaters are in generally substantially more difficult than surface waters to restore to usable condition. In many cases, it is essentially impossible to make such restoration. There is need to amend the Clean Water Act to include control of those activities that can contribute to impairment of uses of groundwaters and aquifers. All dischargers (sources) of contaminants that can impair groundwater or aquifer quality should be required to demonstrate that the discharge/runoff of contaminants, and management of wastes (both liquid and solid) can be done without significant potential for impairment of groundwater quality for any anticipated use or hydraulic characteristics, *ad infinitum*.

Agricultural interests should not be allowed to apply chemicals in crop production without first convincingly demonstrating on a site-specific basis that such use represents little threat to groundwater and aquifer quality. Municipalities, industries, and others should be required to "manage" their solid wastes in ways that do, in fact, ensure prevention of groundwater and aquifer pollution for as long as the wastes represent a threat. Municipal and industrial dischargers of wastewater and urban and rural sources of non-point source discharge/runoff should be required to determine whether any potentially significant amounts of chemical or microbial contaminants in the discharge/runoff could be recharged to groundwaters downgradient of the discharge/source. Upstream dischargers/sources of contaminants to incidental recharge should be subject to the same restrictions as those responsible for organized and enhanced recharge projects.

The US EPA has initiated efforts to control contaminants in stormwaters from urban areas through the development of stormwater detention basins. In some areas dry wells in parking lots and other areas, and stormwater evaporation/recharge basins are used to manage stormwaters and their associated contaminants. These systems are ostensibly designed to remove contaminants that could otherwise adversely affect aquatic life in the receiving water. Concern must be directed toward evaluation of whether the management of stormwaters with such methods could lead to groundwater pollution. As discussed by Lee and Jones-Lee (1993) stormwater management approaches involving detention basins designed to remove contaminants potentially adverse to aquatic life, are only effective in removing large particles that contain contaminants in non-toxic forms. Therefore, not only are detention basins largely ineffective for protecting beneficial uses of surface waters (since the contaminants of concern pass through them without removal), but they are also becoming of concern because of their potential to contribute to groundwater pollution.

If groundwater recharge occurs either incidentally or via enhanced recharge activities, those responsible for the contaminants should have to demonstrate in a reliable and convincing manner that such a discharge will not impair groundwater or aquifer quality. A true long-term perspective should be required in developing a plausible worst-case scenario evaluation for potential impacts of contaminants derived from any source. Every discharger/source of contaminants to groundwater should also be required to fund the necessary monitoring studies capable of detecting incipient impacts under plausible worst-case conditions before significant damage to the aquifer occurs, and a response and remediation approach for those incipient impacts.

In response to concern about impacts of contaminants in recharge waters, some regulatory agencies have established NPDES limits at drinking water standard levels because of downstream enhanced groundwater recharge projects. In order to avoid significant over-regulation and waste of funds for unjustified contaminant control, the source of the chemicals (discharger) should be allowed to demonstrate that under plausible worst-case conditions, the chemicals present in the discharge, either alone or in combination with other sources, will not reach a point of incidental or enhanced groundwater recharge, to adversely affect groundwater or aquifer quality. Together with those responsible for the enhanced recharge project, a discharger should be provided an opportunity to conduct the necessary site-specific studies to demonstrate the reliability of a more cost-effective approach toward contaminant management without significant risk to groundwater or aquifer quality under plausible worst-case scenario conditions. If those responsible for the contaminants/discharge do not wish to conduct the necessary site-specific studies to develop site-specific limitations, worst-case limitations should be established. In situations where there are questions about the need for or level of control of a particular contaminant(s) in a recharge water, the policy should be to err on the side of protection. Such an approach is justified based on the importance of aquifers to current and future water resources and the inability to correct errors that result in groundwater contamination/aquifer utility loss, once they are made.

Specific Contaminants

Presented below is a discussion of a number of specific types of contaminants that need to be considered in regulating incidental and enhanced groundwater recharge.

Specific Organics

There is a wide variety of specific organic chemicals that must be regulated in recharge water in order to protect groundwater quality. These range from low-molecular-weight solvents classified as volatile organic compounds (VOC's) to high-molecular-weight organics, such as polynuclear aromatics (PAH's), PCB's, and dioxins. Of greatest concern for groundwater contamination are the low-molecular-weight solvents such as trichloroethylene (TCE) and its transformation product, vinyl chloride. The VOC's tend to be highly mobile in groundwaters due to their low tendency to sorb on aquifer solids and their resistance to biotransformation. They are the organic chemicals of greatest concern at most "Superfund" sites. Because of their volatility (high Henry's constant), the VOC's typically do not persist in surface waters for long distances; they are therefore rarely a problem in incidental groundwater recharge unless significant recharge occurs very near the source of these chemicals.

A group of VOC's that is of concern in domestic wastewater recharge is the trihalomethanes (THM's). THM's are formed in the chlorination of domestic water supplies; chlorine reacts with natural and some pollution-derived organic matter in the raw water to produce THM's. Chloroform is the THM of greatest concern at this time, although in some situations where bromide is present in the water that is chlorinated, brominated THM's may also be of concern. THM's persist through the distribution system and are present in domestic wastewaters.

It is unclear whether there is significant THM formation in the chlorination of domestic wastewaters. Typically THM's are not formed to a significant extent in the chlorination of organics in the presence of ammonia such as would be found in domestic wastewaters. The chlorine reacts with ammonia to form chloramines faster than it reacts with the organics to form THM's. It is for this reason that many water utilities across the country have been able to reduce the total THM content of treated water by adding ammonia to the water to encourage the preferential formation of chloramines. Normally domestic wastewaters contain sufficient amounts of ammonia so that the chlorine added for disinfection is rapidly converted to chloramines. While some THM's are formed in the presence of chloramines in domestic water treatment, the ammonia in the domestic wastewater should minimize their production. Independent of how the THM's are formed, they are present in domestic wastewater effluents. While they will be rapidly lost to the atmosphere when the wastewaters are discharged to surface waters, they can be of significant concern to groundwater quality when the domestic wastewaters directly recharge groundwater without adequate opportunity for volatilization of the THM's.

The concern about THM's and other VOC's is that they have been found to be "rodent carcinogens," i.e., they have been found to cause cancer in rats or mice exposed to high concentrations; pursuant to the Delaney clause, there is concern about chemicals shown to cause cancer at any concentration. One of the VOC's, vinyl chloride, is a known human carcinogen - it has been found to cause cancer in man - and therefore deserves special recognition. At this time there is considerable controversy about the appropriateness of regulating those VOC's that have been found to cause cancer only in rodents exposed to high concentrations. Bruce Ames and his co-workers (Gold *et al.,* 1992a,b) noted that approximately 50% of the foods commonly eaten today contain natural carcinogens in greater potency concentration than the VOC's as tested under the Delaney testing procedure. There is considerable justification to question whether many of the VOC's should be regulated as they are as carcinogens. However, from a groundwater recharge perspective, until the regulatory authorities change the regulatory approach to recognize that many of these so-called rodent carcinogens do have threshold concentrations below which the risk of cancer is very small to non-existent, it will be necessary to control the VOC input to groundwaters in recharge projects in order to limit the amount of VOC's in the recovered waters.

It is being found that some of the VOC's, such as the THM's, are apparently transformed within the aquifer system. This transformation may reflect dilution between the point at which the treated wastewaters are added to the aquifer and the waters already in the aquifer. Conroy *et al.* (1991) found a significant reduction in the concentration of THM's and other chlorinated organics in their study of a number of test basins into which secondary and tertiary wastewater effluents were added. They reported that microbial activity appeared to be the mechanism responsible for a significant part of the decrease in concentration. While the test systems investigated by Conroy *et al.* would have tended to have much higher biological activity due to the presence of the organics derived from the wastewaters, some of the work done at Superfund sites at various locations also indicates some microbial transformation of some VOC's in groundwaters. It also would be expected, however, that some of the VOC's in recharge waters would be present in the recovered waters, and therefore be subject to regulation as potential carcinogens.

In addition to concern about VOC's, such as THM's, there is also need for concern about the behavior of THM precursors (organics) in recharge recovery projects. The level of THM precursors is very low in most groundwaters because of the sorption of such organics on the aquifer solids and because of biotransformation. In groundwater recharge projects with domestic wastewaters, however, the wastewaters could be expected to add greater amounts of organics to the aquifer; some of those THM precursors would be sorbed on aquifer solids and biotransformed, but some would be expected to be present in the recovered water. Chlorination of those recovered waters could create elevated levels of THM's in the treated recovered water. Ordinarily it would not be expected that the concentrations of THM's formed from chlorination of water from recharge recovery operations would reach critical concentrations. However, with the US EPA in the process of reviewing the THM standard (MCL) for drinking water, it is possible that increased attention will have to be given to THM precursors in the recharge water that could lead to THM's in the recovered water upon disinfection with chlorine.

Many of the higher-molecular-weight organic Priority Pollutants frequently considered to be of concern in domestic water supplies would not be expected to be significant problems in either incidental or enhanced groundwater recharge projects. High-molecular-weight organics, such as PCB's, dioxins, and PAH's, tend to be highly sorbed on aquifer solids and on organic mats commonly formed in the upper layers of the soil column at recharge sites. The binding of the organics within the mat or on the surfaces of aquifer solids is sufficiently strong that normally insignificant amounts of them would be released in the water recovery operations. Those operating recharge and recovery projects, however, should verify that their particular system is effective in removing the high-molecular-weight Priority Pollutant organics.

Other Organics

One of the most significant unknowns about both incidental and enhanced groundwater recharge projects is the behavior and effects of the myriad unidentified/uncharacterized "non-conventional pollutant" organics that are present in municipal and industrial wastewaters and surface waters. There are approximately 60,000 chemicals used in the US today; fewer than 200 of those are analyzed in water quality investigations. The total amount of organics present is commonly determined by measurement of total organic carbon (TOC) and dissolved organic carbon (DOC); the typical Priority Pollutant scan analysis identifies only a few percent of the total organics present. The behavior and potential effects of the unidentified organics, the "non-conventional pollutants," are unknown. Of particular concern are those chemicals that are of moderate molecular weight; such organics would tend to be poorly sorbed on aquifer solids and resistant to biological transformations that typically occur in aquifers. Enhanced recharge of groundwaters with surface waters that contain a variety of organics, such as municipal and industrial wastewaters and urban and rural stormwater runoff, could introduce non-conventional pollutants to water supplies that are hazardous to public health. Surface waters downstream of urban/industrial areas that serve as incidental recharge water can also be of concern to municipal and individual waterwells that draw water immediately adjacent to rivers with only the aquifer between the river and the wells available as a filtering media/treatment zone. Because of the short treatment zone, the non-conventional pollutants in the river water could be of greater concern than they would typically be in normal incidental river water recharge.

Septic tank wastewater disposal systems are widely used throughout the US for wastewater disposal. Use of septic tanks has been an accepted practice as long as all of the wastewater infiltrates or evapotranspires, and none surfaces. In general, little attention has been given to the potential significance of contaminants in septic tank systems to groundwater quality beyond an after-the-fact concern for nitrate. However, as discussed by Canter and Knox (1985) household wastewaters contain a wide variety of organic and inorganic chemical contaminants and microbial contaminants that can render a groundwater unusable for domestic purposes without treatment.

In some areas such as California, separate management of "grey water" from sinks, laundry, etc., is being allowed and encouraged by regulatory agencies for water conservation. As with septic tanks, a successful grey water disposal operation is one that provides moisture for yard plants and causes no surface water pollution. However, grey water disposal operations, like septic tanks, can pollute groundwater with non-conventional organics as well as with conventional pollutants. Greater attention needs to be given to groundwater pollution caused by septic tank and grey water wastewater disposal operations.

In order to limit the concentrations of non-conventional organics that could be recovered in a recharge recovery project, the California Department of Health Services (DHS) Office of Drinking Water (Hultquist *et al.*, 1991) has proposed to limit the TOC in treated municipal wastewaters that are recharged to groundwaters. While Hultquist *et al.* stated that TOC was chosen as a surrogate to represent unregulated organics of concern, use of that surrogate could cause significant errors in assessment. How the bulk of the organics (TOC) behave in a recharge recovery project will likely have little relationship to how specific, highly hazardous chemicals behave. It is known, for example, that TOC is not a reliable indicator of the behavior of the VOC's.

The California DHS's proposed approach, based on limiting TOC in wastewaters recharged to groundwaters, is arbitrary and without significant technical foundation. Large amounts of funds are now being programmed to be spent to remove TOC from wastewaters to be used in recharge projects, by reverse osmosis treatment at a cost of several hundred dollars per acre-foot, in order to achieve the DHS guideline. This could be either over-regulation or under-regulation since the bulk of the TOC-DOC certainly has significantly different chemical properties that affect its behavior in aquifers than a large number of the organic chemicals of greatest concern in domestic water supplies.

Extensive work has been done over many years to try to characterize dissolved organic carbon compounds in various aquatic systems and wastewaters. While a few specific compounds have been identified, the bulk of the organics that comprise the dominant portions of DOC, are "humic" and other related largely uncharacterized polymeric compounds of natural plant origin. In that organic matrix could readily be various hazardous chemicals that have not yet been identified and whose hazards to public health and water quality are largely unknown. The attempts to characterize humics have been of limited value in providing information that can be used to determine the hazards that wastewaters represent to aquifer and water quality in recharge/recovery projects.

Rather than trying to determine the characteristics of each of the myriad non-conventional pollutant organics in a recharge or recovered water, it would be far more cost-effective to examine their potential impacts. Work needs to be done to develop for routine use appropriate testing protocols for testing treated effluents and surface waters, such as stormwater runoff from urban areas, for carcinogenic, mutagenic, and teratogenic activity. Tests of this type at the cellular level or simple organism level, such as the Ames test, have been available for a number of years and are now listed as proposed (approved) standard methods by APHA *et al.* (1992).

It has been known for many years that treated domestic wastewaters show positive responses in such testing, indicating that there are chemicals in those wastewaters that, at least under the conditions of the test, are of potential human health concern. The basic problem that needs to be resolved is how to translate the results of the enzymatic, bacterial, and other such tests to risk levels for humans. This is an area that needs urgent attention. Until technically valid approaches are developed for testing for potential impacts of the non-conventional pollutants, the approach that should be followed is to limit the organic content of all recharged waters, both incidental and enhanced to the maximum extent readily possible. The focus should be on controlling the dissolved organic carbon fraction that is mobile in the aquifer below the surface layer of the recharge location.

Natural Carcinogens

Increasing attention is being given to the presence of natural carcinogens, such as radon and arsenic, in domestic water supplies. The finding that many groundwater supplies in the US contain arsenic and/or radon at concentrations associated with upper-bound cancer risks on the order of 1 in 1,000 to 1 in 10,000 additional cancers for those individuals who are exposed to the water (either through consumption or inhalation in the case of radon) is causing the domestic water supply industry considerable concern. While billions of dollars are being spent at Superfund sites to reduce cancer risks from rodent carcinogens, such as the VOC's, to 1 in 1,000,000 in order to protect drinking water quality, the public is allowed to be exposed to cancer risks 100 to 1000-times greater from the known human carcinogens radon and arsenic.

Because of its volatility, radon is rarely present in surface water supplies in concentrations of concern. However, there are situations in which a surface water could recharge an aquifer where, due to natural processes, the water would absorb sufficient radon in the aquifer to be considered to be adverse to public health. Any recharge recovery project should consider and evaluate this possibility, especially in light of the US EPA's proposed drinking water standards for radon.

Arsenic is ubiquitous in surface and groundwaters at naturally occurring concentrations of about 1 g/L. Further, arsenic has been widely used as a pesticide in orchards and on other crops, as a herbicide for control of weeds along roadways, in fields, and in residential areas (lawns), and as a defoliant for cotton. Such uses have led to concentration of residual arsenic of hundreds to a thousands or more mg/kg in soils. Careful evaluation should be made of the potential for water quality problems in recovered water due to arsenic that may be in the incidental or enhanced recharge water and that which could be derived from the aquifer due to dissolution of arsenic chemicals. While the US EPA has not yet established a new MCL for arsenic in drinking water, the proposed values include concentrations below the normal background concentrations that are found in both surface and groundwaters in many parts of the US. It is conceivable that recharge waters could contain arsenic in concentrations below the new MCL, but when those waters are recovered, the concentration of arsenic could be above the MCL and require treatment before the water could be used for domestic purposes. The costs of arsenic removal, based on current technology, are expected to be quite high and would certainly limit recharge recovery projects in those areas where the aquifer contains sufficient arsenic to cause the water to exceed the new MCL's.

Nitrate and Other Nitrogen Species

The chemical often of greatest concern in both incidental and enhanced groundwater recharge projects is nitrate. The concentrations of total nitrogen in recharge waters are often sufficient to lead to concentrations of nitrate in groundwaters in excess of the drinking water MCL of 10 mg N/L. While the overall aqueous environmental chemistry of nitrogen in groundwaters is fairly well-understood, it is difficult to predict the nitrate concentration that will occur in the groundwater given a certain total nitrogen concentration in the recharge water. This is because it is difficult to predict the rates of the nitrification and especially the denitrification reactions that will occur in an aquifer. The rates of those reactions depend to a large extent on the oxygen status of the aquifer. Not only are the bulk dissolved oxygen properties of the aquifer that can be determined by conventional sampling techniques, important, but also the microzone properties such as associated with microbial growth and slime layers can be very important in affecting the ultimate nitrate content of a groundwater for a given initial total nitrogen input. Additional work needs to be done to determine how to optimize the conversion of nitrogen species to nitrogen gas within the recharge zone. Such efforts will likely be highly cost-effective in managing excessive concentrations of nitrate in both enhanced and incidental recharge projects.

Pathogens

Increasing concern is being raised about the fact that secondarily treated domestic wastewater still contains virus and some other types of human pathogens that represent public health hazards to those who use waters for domestic water supply and contact recreation. Concern is also being voiced about viruses in surface waters derived from domestic wastewater-containing groundwaters in areas of incidental groundwater recharge. This situation is similar to virus transport from wastewater infiltration basins used as part of enhanced groundwater recharge.

Gerba and his associates have published extensively on the transport of viruses, bacteria, and other pathogens in groundwaters associated with enhanced recharge projects (e.g., see Powelson and Gerba, 1993; Gerba and Goyal, 1985). They and others have found that there is transport of pathogens in groundwater systems; of particular public health concern is the transport of viruses.

While there is virus inactivation ("kill") in aquifer systems, especially within the vadose zone, there is concern about viruses' appearing in recovered water to represent a threat to public health. Hultquist *et al.* (1991) reported on DHS-proposed guidelines for the manner of enhanced groundwater recharge and recovery to minimize public health risks from pathogens and chemical contaminants. The California DHS is expected to formally propose guidelines this summer or fall for public comment, governing enhanced groundwater recharge with reclaimed wastewaters (Hultquist, 1993). DHS has not developed proposed regulations covering incidental groundwater recharge by wastewaters.

Acceptable Concentrations of Contaminants in Recharge Waters

Hagemann and Sabol (1993) discussed current US EPA Region IX and X policy governing enhanced groundwater recharge demonstration projects that are being conducted as part of the 1983 High Plains States Groundwater Demonstration Program Act of the Bureau of Reclamation; according to that policy, the concentration limits for contaminants in the recharge waters are the drinking water MCL's. While this may seem to be appropriate, there are situations in which this approach can lead to significant problems. As discussed above in the case of arsenic, even where the recharge waters meet the MCL for arsenic, the aquifer could add sufficient arsenic to the waters to render the recovered water unusable for domestic purposes without extensive, highly expensive treatment. Universally allowing the concentrations of contaminants in the recharge waters to equal MCL's, is not technically valid. Site-specific evaluations should be made of the type discussed above to evaluate the plausible worst-case-scenario problems that could occur at a specific site. Particular attention should be given to assessing whether the recharge waters could acquire sufficient additional contaminants from the aquifer to render the water unsuitable without treatment for domestic or other use.

Another significant problem with using the MCL for a contaminant as the concentration limit in recharge water is that the MCL values for a number of contaminants are being decreased. What is acceptable today for use for domestic water supply will not necessarily be acceptable in the future. As mentioned above, the MCL's for THM's, arsenic, and radon are in the process of being evaluated and will likely be decreased. Recently, the US EPA decreased the action level for lead in drinking water. Those who work in the area of water quality standards development know that the promulgation of new standards often lags behind knowledge in the field by many years, often decades, and is subject to a variety of considerations beyond public health protection, including political and economic issues.

Further, as discussed above, MCL's exist for only a limited number of chemicals. Many chemicals of potential public health and water quality concern do not have MCL's. Therefore, what appears to be a successful recharge project today may become a significant liability due to changes in or development of new MCL's; groundwater resources could be lost and millions of dollars could have to be spent trying to clean up an aquifer as a result of changes in the acceptable concentrations in the recovered water. In the establishment of acceptable concentrations of contaminants in incidental or enhanced recharge waters, consideration should be given not only to the current standards, but also to the potential for reduction in the standard levels and the addition of new regulations.

AQUIFER COMPATIBILITY

One of the major areas of importance in evaluating enhanced as well as incidental groundwater recharge is the compatibility of the recharged water constituents with the aquifer. Vandemoer (1985), Hem and Robertson (1987), and more recently DeBoer *et al.* (1993) discussed various kinds of chemical reactions that can occur within an aquifer that could affect its hydraulic performance (water transport). Of particular concern is the potential for chemical reactions to cause creation of insoluble species that plug the aquifer, such as the formation of calcium carbonate precipitates. In addition, there is a variety of other reactions such as cation exchange, dissolution of mineral phases, and the formation of clays that can occur in an aquifer that can significantly change the transport properties of the aquifer.

Precipitates of some chemicals can be dense and cause little hindrance to water transport. Other precipitates can be amorphous bulky solid phases that can clog the aquifer. Such clogging is manifested as changes in the hydraulic characteristics of the recharge wells. A common problem in enhanced recharged projects is the plugging of the well slots and/or gravel pack. While the constituents in the aquifer and those in the recharge water may not be incompatible, reactions can occur in the recharge wells as well as in the recovery wells which could alter well hydraulics. In addition to chemical reactions, consideration must be given to biological clogging of the wells and the aquifer. Nutrient-rich and organic-rich media such as occurs in some recharge waters, can readily promote luxuriant biological growths that can plug well screens and aquifers. The ability to predict such problems based on the chemical characteristics of recharge waters is highly limited at this time.

Many chemicals of concern such as heavy metals, have multiple oxidation states; the chemical reactions and thus the transport of those chemicals therefore depend on the redox (oxidation/reduction) conditions of the aquifer. The redox condition of an aquifer is largely controlled by the presence of dissolved oxygen (D.O.) in the recharge waters. Uncontaminated groundwater typically contains a few mg/L of dissolved oxygen. Recharge waters normally contain several mg/L D.O., but also several mg/L BOD (biochemical oxygen demand). The amount of BOD in recharge waters is typically sufficient to consume the oxygen in those waters with the result that the recharge waters become anoxic (without oxygen) once they are in the aquifer. This condition, in turn, causes a variety of reactions that are detrimental to water quality such as those that result in the formation of ferrous iron, manganous manganese, and hydrogen sulfide. The iron and manganese are typically derived from aquifer solids, although some can be contributed from recharge waters. Sulfide is largely derived from recharge water and in some aquifers from gypsum ($CaSO_4$) in aquifer solids. The anoxic conditions also control a large number of biochemical reactions such as the conversion of nitrate to nitrogen gas.

While various types of equilibrium-based models, such as the US EPA MINTEQ models (Allison *et al.*, 1991), are available and can be used to calculate whether particular reactions could occur, the ability to reliably predict whether the reactions do, in fact, occur is at this time minimal. Great caution must be exercised in the use of the thermodynamic equilibrium models for predicting chemical reactions that occur in the environment. The modelling effort is only as good as the ability to predict the chemical species that can be formed. Failure to consider a particular species that would be present in a aquifer can readily cause the model results to be unreliable.

Further, and most important, the models are based on thermodynamic equilibrium which is rarely achieved under environmental conditions. Chemical thermodynamic models only predict the direction and potential extent of a reaction; they provide no reliable information on the rate at which the reactions occur. There is a wide variety of factors that influence the rates of chemical reactions, especially precipitation reactions, which are poorly characterized at this time as they would apply to groundwater aquifer systems. The coupling of chemical reactions to hydraulic properties of aquifers is very poorly understood.

Thermodynamic models should be used to provide **insight** into possible chemical reactions of concern; they should never be used to predict what will occur in the aquifer. By providing this insight they can guide monitoring programs to look for specific points of concern that could affect the overall performance of the aquifer and chemical contaminants of potential concern. It is important to try to the maximum extent readily possible to tie the hydraulic characteristics of the aquifer to the predicted chemistry of the recharge and aquifer water and solids. It is important to note that the term "chemistry" refers to the chemical reactions that can occur, not simply the chemical composition of the waters. By carefully monitoring the performance of the aquifer relative to the chemical reactions and biological growths that are, in fact, occurring within it, it may be possible to gain insight into potential problem areas that need to be addressed before they significantly adversely impact the recharge project.

While not primarily a groundwater quality problem groundwater tables are causing ground fissures that damage structures on the surface. Ground cracking also occurs in some areas with overdraft of a groundwater basin associated with subsidence. Fissures and cracks in the soil can serve as conduits that enhance groundwater recharge and the potential for groundwater contamination by surface water-associated contaminants.

FIELD EVALUATIONS

A number of investigations associated with enhanced recharge projects have conducted limited-scale laboratory to large-scale field studies in which waters of the type that are proposed to be recharged and recovered are added to the test system. Such an approach can yield useful information, but it is very important that the relationship between the test system and the real-world aquifer are understood and evaluated. The authors are aware of a number of field studies that do not properly simulate the chemical environment and hydraulics that will occur in the aquifer system. Unless test systems are reliably developed and evaluated and incorporate appropriate scaling factors, the limited-scope laboratory or field studies may have little reliability in predicting the behavior of the aquifer under full-scale operations. At this time there is an urgent need to conduct studies of the actual conditions that exist within the aquifer where incidental and enhanced groundwater recharge has occurred, over a number of years.

Two characteristics of paramount importance in any laboratory and field testing program of the potential behavior of contaminants in recharge projects are the moisture content and oxygen content. The typical aquifer system prior to recharge consists of an unsaturated "vadose" zone above the watertable. However, during periods of recharge that normally unsaturated area becomes saturated with water. Description of contaminant (chemical or microbial) transport under unsaturated conditions in the laboratory or field will not properly predict their behavior under the saturated conditions associated with recharge operations. Powelson and Gerba (1993) reported that viruses are deactivated to a much greater extent in the unsaturated zone of an aquifer than in the saturated zone. Such a finding should not be interpreted to mean that the rates of deactivation found in such studies will be found in the normally unsaturated zone when saturated during recharge.

Because of the importance of dissolved oxygen in controlling redox reactions in an aquifer, D.O. should always be measured in groundwater. This is easily done with down-borehole instruments such as Hydrolab equipment.

By examining the chemical, biological, and hydraulic characteristics of the aquifer at various locations relative to the characteristics of the waters that are recharged and removed from it, it will be possible to begin to better predict how to establish new enhanced recharge projects, and more reliably establish guidelines for the degree of contaminant control that must be achieved at the sources of contaminants in incidental recharge. Eventually, this empirical work, coupled with good hydrodynamic and aquatic chemistry (thermodynamics and kinetics) evaluations, will lead to more reliable standards for the degree of contaminant control that need to be established for the recharge waters to protect the near-term and long-term use of the aquifer as a water supply source, and its hydraulic quality.

CONCLUSIONS

It is clear that the planning of a successful recharge project requires far more sophistication than is typically undertaken today in evaluating the significance of contaminants in the recharge waters as they may affect the quality of the recovered water and the aquifer performance. The brute force approach that has been used in developing groundwater recharge projects should be abandoned in favor of a more sophisticated, enlightened approach in which the current state of aquifer hydraulics, aquatic chemistry and water quality are used to design, monitor, and maintain both incidental and enhanced groundwater recharge.

REFERENCES

Allison, J., D. Brown, and K. Novo-Gradac, 1991. MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.0 User's Manual, EPA/600/3-91/021, US EPA Athens, GA.

APHA, AWWA, WEF, 1992. Standard Methods for the Examination of Water and Wastewater, 18th ed, American Public Health Association, Washington, D.C.

Canter, L., and R. Knox, 1985. Septic Tank System Effects on Ground Water Quality, Lewis Publishers, Chelsea, MI.

Conroy, A., J. Chahbandour, G. Amy, L. Wilson, and B. Johnson, 1991. Fate of Chlorination By-Products during Soil Aquifer Treatment, Fifth Biennial Symposium on Artificial Recharge of Groundwater Proceedings, Challenges of the 1990s, University of Arizona, Water Resources Research Center, Tucson, AZ, pp. 37-47.

DeBoer, D., D. Peters, V. Schaefer, 1993. Injectate/Ground Water Chemical and Geochemical Interactions at the Huron Artificial Recharge Project, Proc. Sixth Biennial Symposium on Artificial Recharge of Groundwater, Water Resources Research Center, University of Arizona, Tucson, AZ, pp. 189-200.

Gerba, C. and S. Goyal, 1985. Pathogen Removal from Wastewater during Groundwater Recharge, Artificial Recharge of Groundwater, Butterworth Publishers, Boston, pp. 283-317.

Gold, L., T. Stone, B. Stern, N. Manley, and B. Ames, 1992a. Rodent Carcinogens: Setting Priorities, Science 258:261-265.

Gold, L., N. Manley, N., and B. Ames, 1992b. Extrapolation of Carcinogenicity Between Species: Qualitative and Quantitative Factors, Risk Analysis 12(4):579-588.

Hagemann, M., and M. Sabol, 1993. The Role of the United States Environmental Protection Agency in the High Plains States Groundwater Recharge Demonstration Program, Proc. Sixth Biennial Symposium on Artificial Recharge of Groundwater Symposium, Water Resources Research Center, University of Arizona, Tucson, AZ, pp. 325-343.

Hem, J., and F. Robertson, 1987. Hydrogeochemistry of Ground Water Recharge in Alluvial Aquifers, Southern Arizona, Proc. Third Symposium on Artificial Recharge of Groundwater in Arizona, Water Resources Research Center, University of Arizona, Tucson, AZ, pp. 30-51.

Hultquist, R., 1993. California Department of Health Services, Office of Drinking Water, Berkeley, CA. Personal communication.

Hultquist, R., R. Sakaji, and T. Asano, 1991. Proposed California Regulations for Groundwater Recharge with Reclaimed Municipal Wastewater, Environmental Engineering, Proc. Specialty Conference, American Society of Civil Engineers, NY, pp. 759-764.

Lee, G. F., and R. A. Jones, 1982. A Risk Assessment Approach for Evaluating the Environmental Significance of Chemical Contaminants in Solid Wastes, Environmental Risk Analysis for Chemicals, Van Nostrand, New, York, pp. 529-549.

Lee, G. F., and A. Jones-Lee, 1993. Water Quality Impacts of Stormwater-Associated Contaminants: Focus on Real Problems - Condensed Version, Proc. First International IWQA Specialized Conference on Diffuse Pollution: Sources, Prevention, Impact and Abatement, Chicago, IL, September.

National Research Council, 1984. Groundwater Contamination, Geophysics Study Committee, National Academy Press, Washington D.C.

Powelson, D., and C. Gerba, 1993. Comparative Removal of Viruses by Sandy Alluvium during Infiltration of Wastewater, Purpose, Problems, and Progress, Proc. Sixth Biennial Symposium on Artificial Recharge of Groundwater, Water Resources Research Center, University of Arizona, Tucson, AZ, pp. 87-100.

Vandemoer, C., 1985. Water Quality Impacts of Recharging Cap Supplies, Proc. Second Symposium on Artificial Recharge in Arizona, Water Resources Research Center, University of Arizona, Tucson, AZ, pp. 36-52.

~~~~~~~~~

Reference as: "Lee, G. F. and Jones-Lee, A., 'Water Quality Aspects of Incidental and Enhanced Groundwater Recharge of Domestic and Industrial Wastewaters,' Proc. Symposium on Effluent Use Management, TPS-93-3, pp. 111-120, American Water Resources Association, Bethesda, MD (1993)."
~~~~~~~~~