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Ground Water Contamination: What You Need To Know

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**Uncovering the Hidden Resource: Groundwater Law,
Hydrology and Policy in the 1990s**

**University of Colorado at Boulder
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I. Introduction

This presentation is an overview of selected technical aspects of ground water contamination problems. The intent is to highlight and focus a few of the more important aspects, particularly as they may relate to regulatory and litigation issues. It is my opinion that all too often the demands imposed directly or indirectly by regulation and litigation are incommensurate with the state-of-the-art as we now understand and practice it. Specific examples are 1) travel time calculation, 2) prediction of low level concentrations, and 3) ground water remediation. The limitations of the science-art with respect to these aspects is developed and discussed.

The presentation begins with a brief discussion of some of the more important sources of ground water contamination and of the contaminants themselves. Emphasis is placed on organic contamination with subsurface nonaqueous phase liquids as the source. Such problems are widespread and constitute a particularly challenging technical problem. Selected aspects of contaminant transport are presented. The importance of advection and dispersion and the uncertainties in the parameters describing these processes is briefly developed from a conceptual point of view. Consequence of these uncertainties is described. The role of models is touched on. Finally, a source remediation is discussed in the context of proven and emerging technologies and their effectiveness.

II. Sources of Ground Water Contamination

The range of processes and activities that can cause contamination of ground waters is remarkably large. The Office of Technology Assessment (1984) has categorized potential sources of ground water contamination as follows:

CATEGORY I. - Sources Designed to Discharge Substances.

This category of sources includes septic tanks, injections wells, and on-land disposal of waste waters and sludges.

CATEGORY II. - Sources Designed to Store, Treat, and/or Dispose of Substances; Discharge Through Unplanned Release.

List of potential sources of this type is very long. Examples include landfills, waste impoundments, mine tailings and waste rock, storage tanks, and radioactive disposal sites.

CATEGORY III. - Sources Designed to Retain Substances

During Transport or Transmission.

Obvious examples in this category are pipelines, trucks, and transport by rail.

CATEGORY IV. - Sources Discharging Substances As Consequence of Other Planned Activities.

Mine discharge, percolation through surface mine backfill, irrigation return flows, fertilizer and pesticide applications, and urban runoff are examples of sources falling into this category.

CATEGORY V. - Sources Providing Conduit or Inducing Discharge Through Altered Flow Patterns.

Here, the outstanding example is cross-contamination of aquifers through oil, water, exploration, and monitoring wells.

CATEGORY VI. - Naturally Occurring Sources Whose Discharge is Created or Exacerbated by Human Activity.

Perhaps the most common example in this category is salt water intrusion into coastal aquifers induced by ground water use.

Perusal of the above list makes it clear that potential sources range from local, focused releases (e.g., a storage tank leak) to diffuse sources that may cover large areas (e.g., percolation of waters through surface mine backfill). Also, contaminant releases to ground water vary tremendously with respect to time; ranging from a practically instantaneous, one-time spill to essentially continuous influx of contaminants over long time periods. Furthermore, the input rarely is constant. The variability of contaminant sources with respect to areal extent, duration, and loading rate is an important characteristic that influences all considerations of ground water contamination, whether they be technical, economic, or legal.

III. Ground Water Contaminants

The substances that might constitute a contaminant in any given situation number in the thousands, perhaps tens of thousands. When viewed in detail, there exists a corresponding large number of individual behaviors with respect to movement in the subsurface and potential

consequences to ground waters. In this summary presentation it is possible to mention only a few of the most pervasive and problematical ones.

A. Nitrates

Nitrates in ground water is, perhaps, the most widespread of ground water contamination problems. While there exist several sources of nitrates in ground water, the most important source is fertilizer application in production agricultural. Water applied to the land is not completely returned to the atmosphere by the evapotranspiration process in either rain-fed or irrigated agriculture. The excess water percolates into underlying aquifers and carries with it nitrates in excess of that utilized by the crop.

Between 10 and 15 million tons of nitrogen fertilizer is used in the United States each year. Application rates range between 100 and 400 pounds of nitrogen per acre per year. Experiments indicate that from 10 to more than 50 percent of the nitrogen added may be lost to ground waters. Wide ranging studies in the "corn belt" show nitrate concentrations in drainage waters to vary between 10 and 80 mg/l of nitrogen as nitrate. The generally accepted drinking water limit is 10 mg/l of nitrogen as nitrate.

The nitrate ion is an anion and, therefore, highly mobile in the subsurface.

B. Trace Metals

Trace metals is the name given to a large group of metals that occur naturally in ground water at very low concentrations, for the most part. Some common ones frequently associated with ground water contamination are arsenic, lead, cadmium, zinc, copper, and selenium. Again, there are several sources of trace-metal contamination of ground waters, ranging from industrial waste waters to fossil fuels.

It is probably not surprising that mine effluents and percolation of precipitation through mine tailings and waste rock is among the most significant sources. Reduced sulfur minerals, most commonly pyrite, undergo oxidation in the presence of appropriate combinations of water and oxygen. A product of the oxidation process is sulfuric acid. In the absence of sufficient buffering capacity, the pH of the water is reduced and trace metals that would otherwise be immobile are produced into the subsurface waters. The common name given to these processes is acid mine drainage. Examples abound in Colorado and in other states and countries.

C. Organic Chemicals

Organic chemicals number in the thousands as do their various uses. Given the widespread production, transportation, use, and disposal of organic chemicals, it is hardly surprising that they constitute one of the most ubiquitous of ground water contaminants.

Organic chemicals may be introduced into the ground water system already dissolved in water. More commonly, the dissolution into ground water is subsequent to entry into the subsurface as a nonaqueous phase liquid (NAPL). Organic liquids less dense than water are referred to as LNAPL while those more dense than water are called DNAPL. This broad division has significance primarily for the hydrogeologist or engineer charged with site investigation and problem diagnoses. However, these two categories have some chemical significance as well because LNAPLs are most commonly petroleum hydrocarbons (gasoline, jet fuel, etc.) containing soluble aromatics while DNAPLs are almost always chlorinated solvents, wood treating oils, and coal tars.

While nonaqueous phase liquids are immiscible with water from the point of view of fluid mechanics, their constituents always have some finite solubility in water. The nonaqueous phase liquid functions as a continuing source for dissolved contaminants in the subsurface water as it passes through the zone where NAPL is present. The solubilities of constituents in NAPL are often thousands of times greater than the concentrations for which there is concern for human health.

Practically everyone is at least passingly familiar with petroleum spills or leaks. It has been estimated that 20 percent of the nation's 2 million underground storage tanks leak and have contaminated subsurface waters. Perhaps less obvious to the public are contamination problems associated with chlorinated solvents. Over 15 billion pounds of dense chlorinated solvents were produced in the United States in 1986. These solvents are utilized in a wide variety of industries and it is hardly surprising that there exists a correspondingly large number of sites contaminated by these chemicals. Plumb and Pitchford (1985) surveyed 183 waste disposal sites in the United States and found that four of the top five most frequently identified organic chemical contaminants were chlorinated solvents. Widespread presence of chlorinated solvents in European ground waters has been identified.

Nonaqueous phase liquids in the subsurface function as a persistent source for dissolved organic contamination. Organic liquids less dense than water tend to sink through the vadose zone and accumulate in the vicinity of the water table. A trail of residual NAPL exists virtually everywhere along the migration path, both in the vadose and in the saturated zones of the subsurface. The residual slowly dissolves into soil gas and subsurface waters. In some cases, the LNAPL will manifest itself as floating product in observation or monitoring wells, giving rise to the concept of LNAPL floating as a distinct layer in the aquifer, much as oil would float on the surface of a pond. This concept of how LNAPL is distributed in the aquifer is largely incorrect, however, due to the effects of interfacial tension and wettability interacting with the solid materials comprising the aquifer (Farr et al., 1990). Instead, the distribution is characterized by a gradually varying content of LNAPL with a significant portion below the water table and some held at pressures less than atmospheric pressure.

In contrast DNAPL tend to sink toward the bottom of the aquifer. Again a trail of residual marks the path of migration. DNAPL in excess of residual may exist as thin lenses or pools formed on the surface of fine-grained strata or at the base of the aquifer. Reduction of DNAPL mass by dissolution into the passing ground water is a slow process and is generally insufficient to remove the source DNAPL in any reasonable time period.

Contamination of ground waters by DNAPL is a special problem requiring special site investigation and remedial techniques (EPA, 1991). Unfortunately, it is not always easy to establish the presence of DNAPL; often the presence must be inferred from indirect evidence. Conventional site investigation techniques have the potential for promoting further and deeper penetration of DNAPL. Cross contamination by movement along a well bore during or subsequent to drilling is a particularly prevalent problem. Even pumping for dissolved-plume control may remobilize DNAPL that had come to rest under the pre-existing conditions.

IV. Contaminant Transport

Contamination of ground water is usually manifest by the presence of dissolved substances in well waters. The areal and vertical distribution of contaminants defines the "contaminant plume". This plume is often depicted as an isopleth map of equal concentrations. The geometry of a contaminant plume and the magnitude of the concentrations within the plume

depend upon source geometry, concentration, and loading history and upon the way the contaminant is transported in the aquifer.

The dominant transport mechanism for dissolved contamination is advection. This is simply the tendency for the chemical to be carried along by the water in which it is dissolved. Advection is characterized by the magnitude and direction of ground water flow which, in turn, is dependent upon the hydraulic gradient, the hydraulic conductivity, and the porosity in the aquifer. Some solutes move along essentially at the same rate as the ground water, but others experience interactions with the solid aquifer materials or undergo chemical reactions that greatly modify their distribution and apparent rate of motion.

Hydrodynamic dispersion is a second-order process that is a manifestation of the variation of ground water velocity around the mean advective velocity. Solute mixing by hydrodynamic dispersion is a reflection of the heterogeneity of the aquifer at a scale smaller than the scale associated with the measurement or analysis of advection.

A. Advection and Solute Travel Times

The concept of solute transport by advection is very simple. The mean advective velocity of ground water is the product of the hydraulic conductivity and the hydraulic gradient divided by the aquifer porosity. The direction of the flow is colinear with the hydraulic gradient (unless the aquifer is anisotropic, a feature that is beyond the scope of this summary presentation). The path along which solute is advected is known as a streamline. The time required for solute to move between two points of interest along a streamline (e.g., from the source to the property boundary) is called the travel time.

Computation of advective velocity and, hence, travel time is simple in principle. However, variations of hydraulic conductivity, porosity, and hydraulic gradient at scales below the measurement scale induce a great deal of uncertainty into the estimation of advective velocity and travel time. The usual procedure is to measure hydraulic head in widely spaced wells with rather long well screens. The result is a map of hydraulic head that provides little or no information about the hydraulic gradient at scales below that defined by the well spacing.

Hydraulic conductivity, a measure of the ease with which water moves through porous media, is a strong function of size of the opening (pores) through which the water must pass. Geologic heterogeneity can cause the hydraulic conductivity to be remarkably different from

point to point, even over short distances. It is virtually impossible to determine in detail the areal and vertical distribution of hydraulic conductivity in an aquifer. One must always resort to use of averages applicable to large blocks of the aquifer or to a statistical description of the spatial variability of hydraulic conductivity.

Solute travel times play an important role in the analysis of plume development with respect to both prediction of future behavior and inference of plume history. This is particularly true in litigation, where the arrival time of contamination at a particular point, location and time of release, and etc., often are of critical importance. Because of the uncertainty in the estimation of hydraulic conductivity and the hydraulic gradient, solute travel times cannot be reliably estimated with the precision required for resolution of these kind of legal issues.

It has been my experience and that of others that advective transport of solutes in heterogeneous aquifers is almost always more rapid than estimated based on block-averaged hydraulic conductivities. Some solute finds a relatively fast path through the aquifer while some moves more slowly. The hydrologist, hydrogeologist or engineer is usually obliged to report travel times as being within some broad time range or as a probability that the travel time was less than some specified value.

B. Hydrodynamic Dispersion

The coefficient of hydrodynamic dispersion is sort of an ignorance factor introduced to account for our inability to measure or calculate the solute mixing that occurs due to pore-scale processes. Introduction of "ignorance" factors at one scale of observation or analysis to account for processes occurring at a scale below the observable is a time honored and generally successful technique in science and engineering (e.g., thermal conductivity, fluid viscosity, hydraulic conductivity). And the concept of hydrodynamic dispersion as a Fickian process has proven adequate in solute transport studies carried out at what might be characterized as the "local" scale (e.g., laboratory columns).

Extension of the Fickian concept of hydrodynamic dispersion to field scale problems has been much less successful. The size, shape and concentration distribution within a contaminant plume reflects mixing processes that occur at scales equal to or smaller than that of the plume itself. As the plume grows and moves, mixing processes at increasingly greater scale are

reflected. No single value for the coefficient of hydrodynamic dispersion appropriately characterizes the evolution of the plume, therefore.

The evolution of solute plumes in the field is not a Fickian process in most cases. Nevertheless, the overwhelming majority of contaminant transport analyses assume that it is and assign values for the dispersion coefficient that are large enough to account for solute spreading caused by unobserved advection (i.e., advection at scales below the scale of the analysis or measurement). In this way, the coefficient of hydrodynamic dispersion is made to account for the probability of some solute finding a path along which it can travel much faster than the mean advective velocity. Large coefficients of dispersion, thus, account for the very gradual spatial changes in solute concentration often observed in the field.

There are at least two dilemmas with this approach:

- 1) How does one rationally estimate the coefficient of dispersion when there exists no plume to "calibrate" against?
- 2) How does one estimate the increase of dispersion as the plume continues to grow and experience increasing scales of heterogeneity?

Again, it is within the context of regulation and litigation where these technical dilemmas take on their greatest significance. While the technical community can do a pretty good job of predicting the first-order features of a solute plume (e.g., the direction of migration, mean velocity, general shape and extent), it is not capable of accurately predicting when a particular well will achieve a concentration of 5 ppb, for example. Yet regulatory compliance and legal determination of harm or damage may turn on just such an issue.

V. Contaminant Attenuation

Some solutes do not significantly interact with other solutes nor the water and solids comprising the aquifer. Such contaminants are referred to as conservative or ideal because their mass in solution as a species is conserved. The concentration of such solutes may decline by dilution but the actual contaminant mass is not reduced.

Fortunately, many contaminants of health concern are not conservative. That is, their mass in aqueous solution is reduced by one or more attenuation mechanisms. The common practice outside the research arena is to account only for certain equilibrium and first-order time dependent attenuation processes. These are commonly known as linear equilibrium adsorption

and first-order decay. These processes are characterized by simple algebraic expressions and amenable to inclusion in transport and fate models.

The actual physical, chemical, or biological process is largely ignored once it has been determined that the attenuation can be algebraically described by the equation for linear adsorption or first-order decay. Thus, we speak of a half-life for benzene, just as we do for radioactive decay, even though the degradation in the first instance is a biological process.

Chemicals with short half-lives and large adsorption coefficients do not create large contaminant plumes. Conversely, chemicals that undergo only mild degradation and adsorption are those that result in very large plumes. As a general rule, dissolved organic contaminants from petroleum hydrocarbons form much smaller plumes than do chlorinated hydrocarbons. Being LNAPLs, petroleum hydrocarbons reside primarily in the vicinity of the water table where organic matter (for adsorption) and oxygen (for degradation) are more abundant than far below the water table where DNAPL plumes are often initiated. Furthermore, the constituents of petroleum hydrocarbons are much more amenable to biologic degradation than are chlorinated solvents. Dissolved plumes from petroleum hydrocarbons usually exist at a scale of a few to several hundreds of feet, while chlorinated solvent plumes sometimes stretch for a few miles.

VI. Use of Models

Models that quantify the ground-water flow and contaminant transport processes are a tremendous aid to site investigation, diagnoses, and management. They are not, however, capable of being all things to all people. With few exceptions the contaminant transport is based on the advection-dispersion equation. This equation includes the effect of advection by incorporating the ground-water flow distribution calculated from the solution of the relevant flow equation. Advection is, therefore, included at a scale dictated by the degree of detail with which the hydraulic conductivity distribution is known or designated. In practice this almost always means that average values over large blocks are used.

The use of large blocks with average values for hydraulic head and conductivity dictate that the values assigned for the coefficient of dispersion must account for nonuniform advection at scales smaller than the block size. As we have seen, there is a great deal of uncertainty in both the advection and dispersion components of the calculation when large blocks are used.

Also, we have noted that the advection-dispersion equation itself must be questioned for large scale problems.

The above factors combine to result in a great deal of uncertainty in the calculated time and space distribution of contaminant concentrations. Such uncertainty is of little practical consequence in some problems (e.g., prediction of performance of a pump and treat system) but is a major shortcoming in others. For example, the maximum contaminant level for many organic compounds is five or six orders of magnitude less than the solubility limit. To predict the locations and times of occurrence of the MCL requires that the prediction be accurate over five or six decades of relative concentration. This is simply too much to ask of a model based on shaky theoretical ground and subject to large uncertainty in the input parameters. Predictions of concentrations at the 5 ppb level from sources at the 100s or 1000s ppb level is little more than an educated guess.

VII. Remediation

Hundreds of millions of dollars are spent annually in the United States in attempts to remediate ground waters. In the regulatory context, remediation often means a return to drinking water standards or pre-contamination levels. Few, if any, remediation projects have been successful by that measure. Here again, I see a fundamental conflict between the capabilities of technology and the requirements imposed by society.

Pump and treat is the obvious approach to control and reduction of dissolved plumes. However, this technology has no significant chance for success unless the source is removed. Particularly for DNAPL sites, this may be tremendously difficult and, perhaps, impossible to successfully accomplish. If the DNAPL has not penetrated too deep, it may be possible to isolate the source area through use of sheet-pile or slurry walls. To my knowledge there exists no proven technology or combination of technologies that will remove DNAPL to the extent that it is eliminated as a source.

In-situ vapor extraction is thought to be a successful source removal technology when the NAPL is a volatile and occurs in the vadose zone. Even then, it appears to be effective only in rather permeable, homogeneous media. It has been used in conjunction with ground water pumping to attempt to remove NAPL from below the water table. Again, success appears to be limited to rather permeable, homogeneous media.

In-situ air sparging is a technique that is becoming popular. I can find no hard evidence of its effectiveness. Conceptual models, relating to the mechanisms, that have appeared in the literature are largely erroneous and there is at least one fundamental scientific reason on which to question the potential of the method.

There exist several other emerging technologies that may prove useful in the future. Among them are surfactant washes and stream flooding. These technologies and several others must be regarded as being in the developmental stage.

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