Limiting factors in ground water remediation*

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Abstract

If one is charged with restoring a contaminated aquifer today, the procedure of pumping contaminated water to the surface for treatment and discharge is most often the state-of-practice technology. The perceived success of pump-and-treat technology can be misleading if the hydrology and contaminant characteristics at the site are not adequately understood. A failure to understand the processes controlling contaminant transport can result in extremely long pumping periods and, consequently, costly and inefficient remediation. Effects of tailing, sorption, and residual immiscible fluids on time required for pump-and-treat remediation of ground water are discussed.

Introduction

The remediation of ground water contamination is one of the most challenging problems that faces the environmental field today. In the past ground water contamination was resolved by simply leaving the problem in place and moving water supply wells to a new location. Today, the use of ground water resources as well as the number of potential contaminant sources coupled with the contemporary environmental ethic has made this approach unacceptable.

Ground water is one of our most important resources. Everyday in the United States the ground water resource is utilized by over 50% of the population and approximately 220 million gallons (0.84 km^3) of ground water are extracted for use. Furthermore, ground water development is increasing; on the average over 40 new wells are drilled every hour to produce additional supplies. Clearly, ground water is a resource that should be properly managed and understood.

Although the supply of clean water is abundant, it is under constant assault by both past and present land use and waste disposal practices. The Congressional Office of Technology Assessment (OTA) has identified over three dozen categories of ground water contamination. Of these industrial landfills, surface

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impoundments, septic tanks and cesspools, disposal wells, fertilizers, oil and gas wells and underground storage tanks pose the greatest threats. More specifically, there are over 1,400 hazardous waste disposal sites covered under the Resource Conservation and Recovery Act (RCRA), and according to the General Accounting Office over 70% may be leaking [1]. In addition, the U.S. Environmental Protection Agency (EPA) has documented over 180,000 surface impoundments – pits, ponds, and lagoons – for waste disposal. More than 98% of these are located within one mile of a drinking water well or potential drinking water source [2]. One of the most prevalent threats to clean ground water is leaking underground storage tanks. The EPA estimates that over 75,000 tanks are annually releasing 11 million gallons of gasoline to the subsurface. Furthermore, over 1,000 locations have been placed on the National Priorities List of hazardous waste sites by the EPA, and it is estimated that this number could potentially rise to 30,000 [3].

The most widely used approach for remediation of ground water contamination is the extraction of the contaminated water followed by treatment at the surface. This method is commonly referred to as pump-and-treat remediation. An ideal pump-and-treat remediation project would involve the installation of extraction wells at defined locations, the pumping of these wells to contain and remove the contaminant plume, treating the extracted water at the surface via carbon adsorption or other means, and then discharging the clean water at the surface or recharging it back to the subsurface. Although successful pump-and-treat projects have occurred, for the most part, pump-and-treat is not the simple solution once envisioned. Specifically, the complexities of the subsurface environment coupled with the diverse nature of the contaminants make the extraction of the contaminants difficult and costly.

Transport effects

The interaction of the processes affecting the transport of contaminants significantly influences the effectiveness and efficiency of pump-and-treat technology. In particular, these processes hinder the removal of contaminants from the subsurface. The resultant effect is the slow, gradual decrease in contaminant levels as water is pumped from an aquifer. This effect is termed tailing. Tailing acts to prolong the expected time of extraction, increase the volume of water necessary for treatment, and, thus, increase the cost of remediation [4].

Numerous mechanisms control the movement of contaminants through porous media. The transport processes associated with even the simplest forms of contamination, conservative, non-reactive dissolved constituents, involve advection, dispersion, and molecular diffusion. Advection is the primary process of contaminant transport and is the movement of the contaminant in the ground water flow system. Dispersion involves the movement of contaminants

via fluid mixing that results from heterogeneities within the pore spaces of the aquifer. In general, dispersion acts to attenuate the contaminant concentration while increasing the size and rate of transport of the contaminant plume (Fig. 1). Diffusion is the slow movement of ions or molecules in response to concentration gradients. Because molecular diffusion is time dependent, its effect on the overall transport is more significant at low velocities. As a result, diffusion is an important process in finer grained aquifer materials and can significantly affect pump-and-treat remediation.

Thus, the migration of dissolved contaminants through aquifers is controlled to a great degree by the permeability of aquifer material. In homogeneous strata of high to moderate hydraulic conductivity, such as in sand and gravel aquifers, advection is the predominant process of transport while in
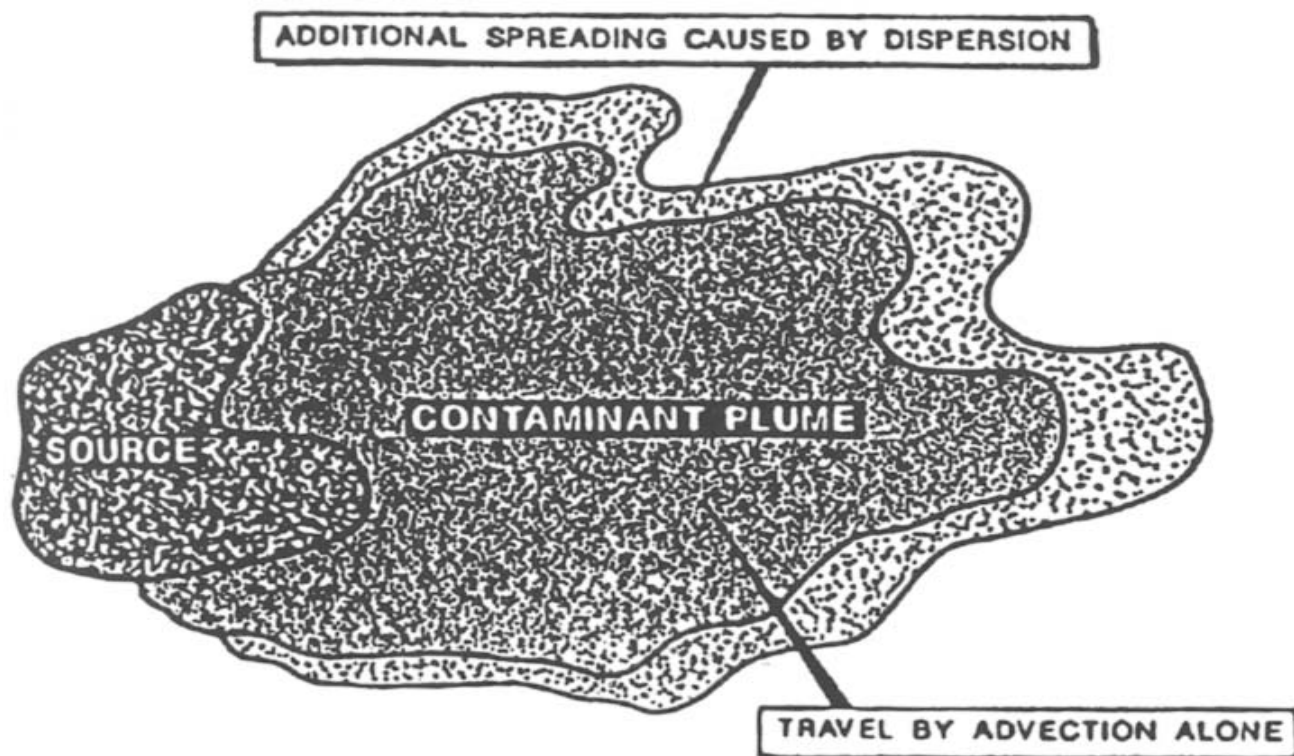

Fig. 1. Plan view of contaminant migration by advection and dispersion.
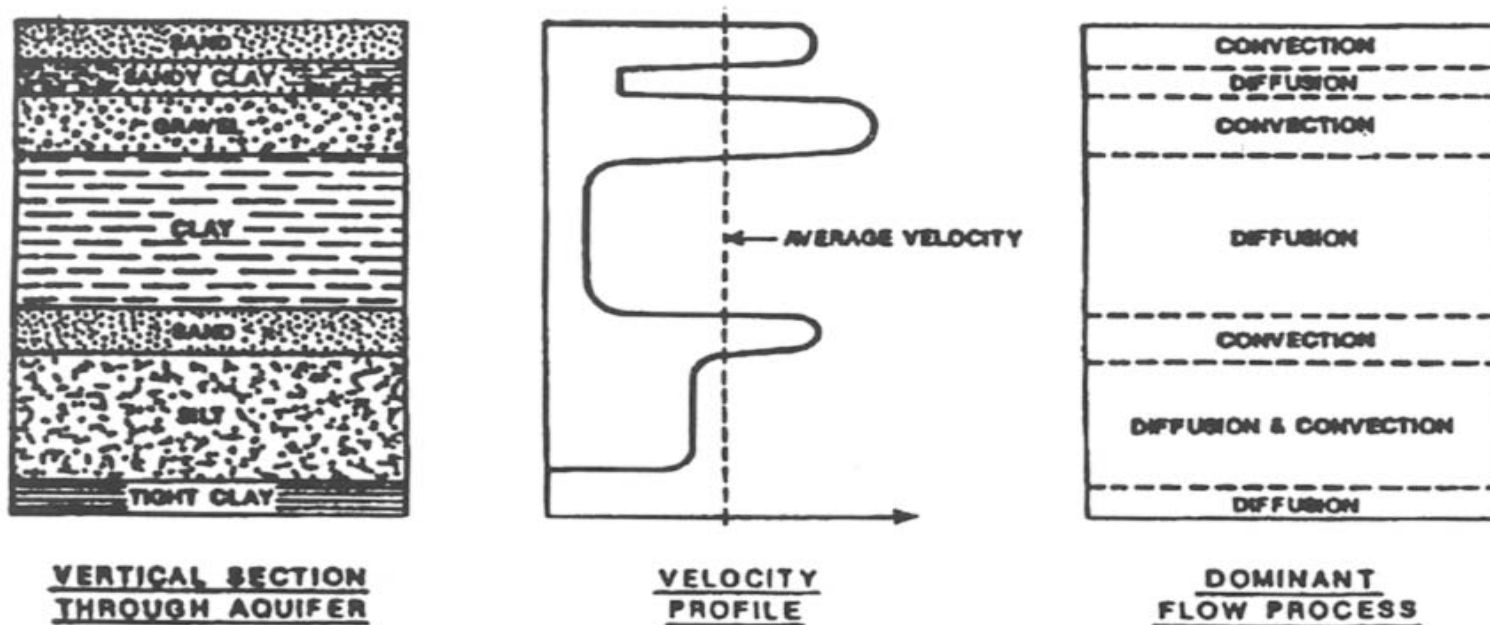

Fig. 2. Effects of geologic heterogeneity on contaminant transport.

heterogeneous strata of low hydraulic conductivity contaminants migrate slowly, primarily by diffusion (Fig. 2). Over time, greater volumes of the contaminants migrate into areas of low permeability — those zones containing the smallest pores. As a result, when pumping is initiated to extract the contaminants, the fluids in the aquifer are not uniformly mobilized. Fluids in the larger, open pores move more readily while the fluids in the smaller, closed pores are retained. In short, pumping creates preferential movement of the contaminants in the larger pores. Given time, the contaminants present in the finer pores eventually migrate by diffusion to the larger open pores. However, this preferential migration resulting from heterogeneities in hydraulic conductivity increases the time required to extract all the contaminants, and thus, creates a tailing effect.

Chemical effects

Additional complexities develop when the contaminants react with the aquifer materials via sorption and/or chemical and biochemical reactions. Sorption is the transfer of contaminants between ground water and mineral and organic surfaces. Several processes act to remove contaminants from the ground water to the solid phase: adsorption, the attraction of a contaminant to the solid surface; absorption, the incorporation of the contaminant into the interior of the solid; and ion exchange, adsorption with a charge-for-charge replacement of the ionic species in solution with ionic species in the solid. The overall effect of sorption is to retard the migration of the contaminant plume. Although this behavior reduces the size of the plume, it increases the difficulty in extracting the contaminant from the aquifer. Most of the sorption reactions processes are completely or partially reversible; as a result, contaminants are not permanently removed from the aquifer by sorption, rather these constituents are simply stored in the solid phase. Desorption adds contaminants to the fluid phase from the solid phase by reversing the reactions.

As water is pumped from the aquifer during pump-and-treat remediation, the dissolved portion is removed and replaced by clean water drawn in from outside the contaminate plume. This situation alters the previously existing equilibrium, and the contaminant continues to partition from the solid phase to the aqueous phase to establish an equilibrium. As a result, the contaminant levels will initially decrease upon migration of the clean water into the aquifer but will eventually increase as a new equilibrium condition develops. Hence, an aquifer may have to be flushed several times to successfully redissolve all the contaminant from the solid surfaces. Furthermore, if the velocities developed by the pumping are too rapid to allow contaminant levels to establish equilibrium conditions, the affected water may be removed before allowing maximum contaminant dissolution. This results in a low contaminant removal

efficiency, increased pumping time, and larger volumes of water requiring treatment.

Sorption and desorption are complex processes and are a function of the type of contaminant, the composition of the solid, the chemistry of the aqueous phase and the distribution of contaminant between the solid and fluid phases. Petroleum hydrocarbons, chlorinated solvents, and PCBs are examples of common contaminants that have a high affinity to sorb. Likewise, clay minerals, because of their large surface areas that carry an overall negative charge, are aquifer materials that have a strong tendency to sorb chemicals from the fluid phase. The pH of the ground water can also influence sorption reactions. Since sorption reactions are reversible, the distribution of the contaminant between the fluid phase and solid is important; this distribution is described by the linear partition coefficient, K_d. The parameter K_d is the ratio of the mass concentration in the aqueous phase to the mass concentration sorbed on the solid phase.

$$K_d = C_s/C_a \tag{1}$$

where C_a denotes the mass concentration in the aqueous phase, and C_s is the mass concentration sorbed in the solid phase. A large K_d value indicates strong sorption while a small K_d value indicates the constituent is retained with the aqueous phase.

By determining the linear partition coefficient, it is possible to define the retardation, R, of the contaminant resulting from sorption.

$$R = 1 + (K_d P_s/(P_a \times \epsilon) \tag{2}$$

where P_s is the soil bulk density, P_a the density of water, and ϵ the porosity.

More importantly in the design of pump-and-treat systems is the velocity of the contaminant (V_c), which can be described as the ratio of the water velocity to the retardation factor.

$$V_c = V_w/R \tag{3}$$

Hence, an estimate of the time required to extract a contaminant can be determined. The following example is a simple scenario illustrating the time required to extract a contaminant from an aquifer [5]. Given a relatively homogeneous, uniform sand aquifer with a thickness of 55 feet (17.5 m) and having a porosity of 30%, assume approximately 10 acres (4 ha) of the aquifer are contaminated by chloride from a salt storage area. The volume of contaminated ground water is approximately 55 million gallons or 210 000 m^3 (10 acres$\times$43560 ft^2/acre$\times$55 feet$\times$0.3 void space per acre$\times$7.5 gal/ ft^3=53,905,500 gal). Under these ideal conditions, it would be possible to exchange the water in the ten-acre plume in about a year by pumping at a rate of 100 gallons per minute (365 days/y$\times$24 h/day$\times$60 min/h$\times$103 gal/min = 54,136,800 gallons). Assuming that the extraction well is at the center of a

radial plume, the velocity of the ground water from the periphery of the plume to the well is about 370 feet per year or approximately 1 foot per day.

However, assuming that sorption is an active process, a more realistic condition, the time required to extract the contaminant increases. For example, given the conditions previously described with a linear partition coefficient of 0.5, a soil bulk density of 100 lb/ft^3, and a ground water density of 62.4 lb/ft^3, then the contaminant velocity would be approximately 75 percent slower than the water velocity ($V_c = 372$ ft/y/$1+0.5(100$ lb/ft^3/$(62.4$ lb/ft$^3 \times 0.3))$) $V_c = 101$ ft/y).

This slower velocity could prolong the pumping time to over three years. It is evident from this illustration that sorption and heterogeneities in the aquifer material can pose significant difficulties in pump-and-treat technology.

NAPL Effects

The existence of non-aqueous phase liquid (NAPL) contaminants present additional difficulties in pump-and-treat remediation. These water-immiscible phases are of two general forms: lighter-than-water non-aqueous phase liquids, termed L-NAPLs, such as gasoline and oil; and denser-than-water non-aqueous phase liquids, termed D-NAPLs, such as halogenated solvents and creosote/coal tars. L-NAPLs float on the ground-water table and are generally contained within the capillary fringe. In contrast, D-NAPLs sink downward through the aquifer and can migrate independently of the ground water direction. Pump-and-treat remediation is relatively successful in extracting floating product. Current methods can remove over 90% of the floating L-NAPL source [6]. The extraction of D-NAPLs has not been effective simply because these contaminants are rarely located within the aquifer. As a result, the D-NAPL contaminant source remains slowly dissolving in the aquifer for time periods ranging from decades to hundreds of years.

When dealing with NAPLs, remediation is further complicated by their affinity for sorption to aquifer materials. This creates a major problem as even after the product is removed surface tension forces retain this fluid phase. As a result, after the removal of the free product by pumping an L-NAPL can occupy up to 50% of the soil pore space — primarily in the finer pores [7] (Fig. 3). This trapped immiscible fluid is termed the residual saturation or residual phase and cannot be removed in any substantial quantity by pumping.

When the residual phase is a contaminant such as gasoline, its benzene, toluene, and xylene components can partition into the passing ground water. The rate of transfer and the concentration within the aqueous phase depends on the contaminant characteristics and the location of the residual phase with respect to the flowing water. In the case of gasoline and other complex fluids, the rate of contaminant transfer into water will change as the gasoline ages, or
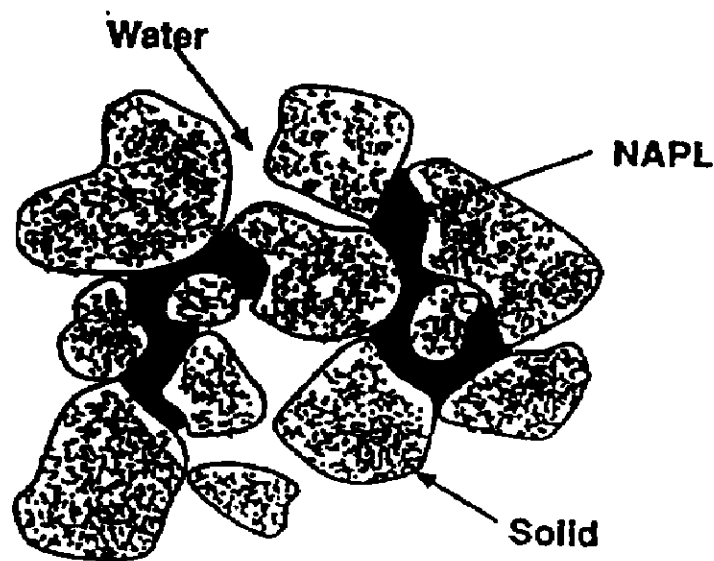
Fig. 3. Residual saturation within aquifer voids.

as its composition changes. Thus, the residual phase may act as a source for future contamination.

It is this relatively slow rate of contaminant transfer which is deceiving when attempting to remove contaminants using increasingly higher pumping rates. The concentration may initially appear to be reduced or even eliminated due to dilution as large amounts of uncontaminated water enter this area of the aquifer, or by lowering the water table below the source of contamination, or both. In any event, when pumping ceases, the residual phase water soluble components will again dissolve into the ground water, and the contaminant concentration will return to the previous level. To place this in perspective, assuming similar contaminant conditions as the previous scenario and only a 10% residual saturation of toluene, it would take about 1,500 years' pumping at 100 gallons per minute to reduce the initial amount of toluene by 80% if no other processes of transformation were active.

Summary

Although pump-and-treat is not the quick fix once envisioned, it is still a viable remediation method. In particular, it is useful when the contaminants are mobile, and the aquifer is homogeneous and has a high hydraulic conductivity. Conversely, pump-and-treat is not extremely useful under the opposite conditions — when the contaminants are NAPLs, have a high sorption affinity, and when the aquifer is heterogeneous and has a low hydraulic conductivity (Fig. 4).

The design of pump-and-treat remediation systems is improving to increase the effectiveness of the technology. For example, pulsed pumping may improve the efficiency of this technology by allowing contaminants located in low permeability zones to diffuse outward into areas of higher hydraulic conductivity during nonpumping times. Likewise, this non-pumping time allows sorbed contaminants and residual NAPLs to reequilibrate with the ground water.

Favorable Conditions	Unfavorable Conditions
SOURCE TERM	
Source Removed	NAPLs at Residual Saturation
CHEMICAL PROPERTIES	
Mobile chemicals	Chemicals sorbed or precipitated
HYDROGEOLOGY	
High hydraulic conductivity (e.g., K > 10^{-6}cm/s)	Very low hydraulic conductivity (e.g., K < 10^{-7}cm/s
Homogeneous	Highly heterogeneous

Fig. 4. Conditions favorable and unfavorable to pump-and-treat remediation.

Hence, during the subsequent pumping cycle the minimum volume of contaminated ground water is removed at a maximum contaminant concentration. In addition, low permeable barriers can be constructed along the periphery of the plume to minimize the movement of the contaminants, to reduce the volume of fresh water being contaminated by remediation, and to ultimately lower the volume of water requiring treatment.

Continuing research in the complexities of subsurface transport and transformation of contaminants will further increase the effectiveness and efficiency of pump-and-treat remediation. However, since the understanding of subsurface processes is currently fragmented and not complete, it is important to appreciate the conditions in which a remediation method, such as pump-and-treat, is effective so that successful remediation can be achieved at minimal cost.

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