3

(

CONTAMINATED LAND TREATMENT TECHNOLOGIES

Edited by

JOHN F. REES Celtic Technologies Ltd, Cardiff, UK

<u> </u>			
. TECHNICAL 1 (Please read Instructions on I	REPORT DATA the reverse before complet		
1. REPORT NO. EPA/600/A-92/224	3.		
4. TITLE AND SUBTITLE	5. REPORT	/	
CRITICAL EVALUATION OF TREATMENT TECHNOLOGIES	WITH S BEBEOR	MING ORGANIZATION CODE	
TARTICOLAR RELEASE TO TOPIC AND TREAT STSTEP			
7 AUTHOR(S)	8. PERFOR	MING ORGANIZATION REPORT NO.	
¹ Carl G. Enfield			
PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGR	AM ELEMENT NO	
P.O. Box 1198. Ada. OK 74820	TD1Y1A	1	
² Dymamac Inc. R.S. Kerr Environmental Resea	rch Lab	ACT/GRANT NO.	
P.O. Box 1198, Ada, OK 74820	In-Hou	ISE	
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE O Sympos	F REPORT AND PERIOD COVERED	
U.S. Environmental Research Laboratory	14. SPONSC	DRING AGENCY CODE	
P.O. Box 1198	EPA/60	00/15	
Ada; OK /4820			
Published: ELSEVIER APPLIED SCIENCE, London	and New York, for SCI	WATER AND ENVIRONMENTAL	
GROUP. Proceedings of Contaminat	ed Land Treatment Tech	nnologies, pp 220-234.	
16. ABSTRACT			
Ground-water extraction and treatment, or pump and treat, is the most commonly used			
States. There are major limitations to using	this technology for r	restoration of aquifers	
to drinking-water quality in a reasonable tim	e frame. The major li	initations to pump-and-	
treat technology, which are connected with th	e difficulty in extrac	ting of contaminants	
from the subsurface, can be explained in term	s of the basic process	ses controlling sub-	
surface, can be explained in terms of the basic processes controlling subsurface			
contaminant transport and rate. Ine same pro	cesses that limit the	effectiveness of pump	
understand and account for these processes when designing aquifer remediation projects			
Research is being carried out by the United S	tates Environmetnal Pr	otection Agency and	
other organizations to reduce some of the limitations and improve the efficiency of			
pump-and-treat.			
<i>X</i>			
17. KEY WORDS AND DO	CUMENT ANALYSIS	FRMS C. COSATI Field Group	
Pump-and-Treat			
Ground-water remediation		}	
Subsurface Processes			
18. DISTRIBUTION STATEMENT	19. SECURITY CLASS ITHIS Repo	Det) 21 NO. OF PAGES	
	UNCLASSIFIED	19	
	20. SECURITY CLASS (This page INCLASSIFTED	ZZ. PRICE	
FPA Form 2220_1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE			

Contents

Foreword by The Earl of Cranbrook	`
Preface	vii
Risk Analysis as a Guide to Soil Remediation Strategies M. Loxham	I
An Approach Being Developed in ICI for the Assessment of Soil and Groundwater Contamination: <i>K. J. Potter</i>	12
On Site and In Situ Treatment of Contaminated Sites	30
Containment and Remediation of Contaminated Sites by Extraction of Vapour or Groundwater G. A. M. van Meurs	47
Remedial Barriers and Containment	58
Solvent Extraction for the Treatment of Contaminated Soil H. Eccles and C. P. Holroyd	83
Theory and Practice of Clean Cover Reclamation	97
Principles and Application of Physical Particle Separation for Treatment of Contaminated Land K. P. Williams	113
Treatment of Acidic Industrial Lagoons	129
Vitrification of Contaminated Soils	143

ix

;

Organic Stabilization/Solidification: Theory and Practice	160
The Role of Planning Authorities in Influencing Design of Land Treatment R. Turner	180
A Thermal Method for Cleaning Contaminated Soil	195
Critical Evaluation of Treatment Technologies with Particular Reference to Pump-and-Treat Systems S. G. Schmelling, J. W. Keeley and C. G. Enfield	220
Experience Acquired with the Oecotec High-Pressure Soil Washing Plant 2000 in Cleaning Contaminated Soil HJ. Heimhard	235
Land Reclamation and Redevelopment at Blekholmstorget	252
Bioremediation of Contaminated Ground	270
Technology to Application in Recycling Contaminated Land	285
Index of Contributors	309

x

• • •

;

CRITICAL EVALUATION OF TREATMENT TECHNOLOGIES WITH PARTICULAR REFERENCE TO PUMP-AND-TREAT SYSTEMS

STEPHEN G. SCHMELLING¹, JACK W. KEELEY², AND CARL G. ENFIELD¹ 1) United States Environmental Protection Agency, 2) Dynamac, Inc. Robert S. Kerr Environmental Research Laboratory P. O. Box 1198, Ada, Oklahoma, 74820, USA

ABSTRACT

Ground-water extraction and treatment, or pump and treat. is the most commonly used technology for remediating contaminated ground water at hazardous waste sites in the United States. There are major limitations to using this technology for restoration of aquifers to drinking-water quality in a reasonable time frame. The major limitations to pump-and-treat technology, which are connected with the difficulty in extracting of contaminants from the subsurface, can be explained in terms of the basic processes controlling subsurface contaminant transport and fate. The same processes that limit the effectiveness of pump and treat limit most other aquifer remediation technologies, as well. It is important to understand and account for these processes when designing aquifer remediation projects. Research is being carried out by the United States Environmental Protection Agency and other organizations to reduce some of the limitations and improve the efficiency of pump-and-treat.

INTRODUCTION

Slightly over a decade ago there were relatively few detive efforts to rectify known cases of ground-water contamination. Indeed, it was only at this time that early efforts were being made to estimate the extent and magnitude of ground-water contamination problems. By now, the number of hazardous waste sites on the United States Environmental Protection Agency (EPA) National Priorities List (NPL) exceeds 1,000, and estimates have been made that the number could grow to 2,000. The United States Congressional Office of Technology Assessment (OTA) estimated that the list could reach 10,000, requiring remediation activities well into the 21st century [1]. The most common area of concern at sites on the EPA Superfund list is ground-water contamination [2].

During the early days of ground-water remediation, pump-and-treat systems were the leading, if not the only, technology available. Pump and treat was based on a common-sense idea. If, as a result of aqueous samples from monitoring wells, the ground water was known to be contaminated, all that had to be done was to pump the contaminated water from the

aquifer and treat it. However, the results of the typical pump-and-treat remediation project were often discouraging. The system would initially remove a large mass of contaminant with a concomitant decrease in the concentration of the contaminant. However, after a relatively short time, the concentration of the contaminant leveled off at a value well above the design goal of the system. The system kept pumping and treating, but the contamination lingered, even with continued pumping. It was much like Lady Macbeth trying to wash the blood from her hands -- "Out, damned spot! Out, I say!" [3]. Pumping at a higher rate caused the concentration of the contaminant in the extracted water to diminish, but, if the pumps were turned off for some period of time, the water being brought to the surface would once again have increased levels of contaminants.

As a result of such field experience, and concurrent laboratory studies, scientists and engineers began to question the effectiveness and efficiency of such systems. During the last several years They also began to examine the causes of the problems and to look for ways to improve the situation.

The major difficulties with pump and treat are related to the "pump", or extraction, portion of the process. There are fundamental reasons why it is difficult to extract contaminants from the subsurface. These fundamental reasons, which are discussed in detail below, also limit the efficiency of many other aquifer remediation technologies. Surface treatment of the extracted water, the "treat" portion of pump and treat, has its own set of engineering problems, but in general, surface treatment is a much more mature technology and is not the limiting factor in the successful use of pump and treat.

The purpose of this paper is to briefly discuss: (1) some of the reasons why the removal of ground water for remediation does not always lead to the desired results, (2) the contaminant-transport processes responsible for this behavior, and (3) possible schemes to help overcome some of these problems. There is also a brief discussion of ground-water extraction systems in concert with other technologies.

Keely [4] identified four factors which affect the efficiency by which ground-water extraction removes contaminants from the saturated subsurface. These are:

1) diffusion of contaminants into low permeability sediments,

- 2) hydrodynamic isolation (dead spots) within well fields,
- 3) desorption of contaminants from sediment surfaces, and

C

 liquid-liquid partitioning of an immiscible contaminant as a result of the presence of a separate non-aqueous phase liquid (NAPL)

The first two factors might be combined under the general heading of hydraulic inefficiencies. Equally important to the success of any aquifer remediation is the need to adequately characterize the site and the contaminant characteristics. Without an adequate site characterization it will be highly unlikely that the remedial action will be well designed, and it will be almost impossible to determine whether or not it is actually cleaning up the site.

In order to better understand the influence of these factors in pump-and-treat systems, it may be helpful to define a simple hydrologic scenario against which each can be tested. This scenario, depicted in Figure 1, consists of a 4 hectare area of ground-water contamination with a saturated thickness of 17 meters and an effective porosity of 30 percent of the aquifer volume. The example includes the assumptions that the aquifer has sufficient hydraulic conductivity to allow pumping at any reasonable rate without adjusting the hydraulic gradient, the aquifer boundaries are constant, and there is an infinite source of water.





13

Under these ideal conditions, and with an ideal extraction well system, it ought to be possible, pumping at 400 L/min, to exchange the water in this 4-hectare plume in about one year and remove the contamination from a soluble contaminant (e.g. chloride) at low concentration. In reality, however, it may be necessary to pump for two or three or more years to reach an acceptable contaminant concentration due to the "tailing" effect often observed under even these simple conditions.

HYDRAULIC INEFFICIENCIES

As shown in Figure 2, tailing is the slow, almost asymptotic decrease in contaminant concentration as contaminated water is extracted from the aquifer and fresh water takes its place. When compared to the theoretical or more ideal concepts of removal, tailing can require

significantly longer pumping times even when dealing with the simple conditions outlined in this scenario.





Subsurface heterogeneity, as shown in Figure 3, is one cause of tailing. In the simplest case of a highly soluble contaminant such as chloride, tailing results when the contaminants



Figure 3. Example of subsurface heterogeneity

1.5

diffuse into low permeability sediments over a long period of contamination and slowly diffuse back out during a pump-and-treat remediation. Under a uniform hydraulic gradient, the velocity of water varies directly with the hydraulic conductivity of individual layers, and field measurements have demonstrated that, even in relatively homogeneous aquifers, the hydraulic conductivity can vary by a factor of 10, or more, over distances on the order of tens of centimeters. When water is pumped through the aquifer, contaminants in the regions of high permeability are removed relatively efficiently. Contaminants in the zones of low permeability are only slowly removed by diffusion to the bulk of the flowing water in the zones of high permeability or by advection at much slower velocities through the zones of low permeability. A rule of thumb suggests that the longer a site has been contaminated and the more layered the geologic material, the longer the effects of tailing will be present. Even when these zones of low permeability are stressed by pumping wells, the time required to purge contaminants is likely to be extensive.

A simple example can demonstrate the effect of the variability of hydraulic conductivity on the removal of a soluble contaminant, such as chloride. The example assumes an aquifer with two equally thick layers --- one layer having 10 times the hydraulic conductivity of the other, and both having an effective porosity of 30 percent. If it is assumed that the initial chloride concentration is the same in both layers, and that there is no diffusion between the layers, the time of remediation using chloride free ground water can be estimated.

Figure 4a shows a curve of relative concentration (concentration relative to the initial concentration) at the extraction point versus time for an assumed flow rate. The relative



Figure 4a. Effect of variability of hydraulic conductivity on removal of a miscible contaminant concentration remains at unity for a short period of time then drops off and reestablishes a new concentration where it remains for a considerable period of time. The shape of the curve is typical of field observations and has also been demonstrated in the laboratory.

If the pumping rate is increased by 50 percent (Figure 4b), the concentration drops off more rapidly and stabilizes at the same plateau. The net result of the higher pumping rate is to reduce the overall time required for remediation while the plateau concentration is dependent on the relative hydraulic conductivities of the sediment layers and the portion each of the layers contributes to flow through the system. However, for a surficial aquifer, increasing the

<u>ج</u> . _

pumping rate will change the shape of the free water surface, often isolating a portion of the contamination from the flow path. When the pumps are turned off and the aquifer is allowed to stabilize, the concentration of contaminants in the ground water may return to the original level.



Figure 4b. Effect of variability of bydraulic conductivity at higher flow rate

Zones of hydrodynamic isolation (dead spots) within well fields both down gradient of extraction wells and up gradient of injection wells [4], are an inevitable consequence of the natural hydraulic gradient and the gradients created by the pumping and injection wells. Like zones of low permeability, the movement of contaminants from these zones occurs primarily by diffusion, and the removal of contaminants from these zones will be inefficient during remediation using pump-and-treat systems.

SORPTION

As discussed earlier, highly soluble contaminants such as chloride are dissolved in the liquid phase and, at low concentrations, are essentially transported along with the moving ground water in most soils. Most other contaminants, however, tend to partition, or be distributed, between the liquid, solid, and vapor phases which comprise the subsurface matrix. In the ground-water zone of the subsurface, the relationship between the concentration of the contaminant in solution and the mass sorbed on the aquifer solids depends on the chemical characteristics of the contaminant, the chemical properties of the ground water, and the properties of the geologic matrix. In many cases, the relationship between the mass of contaminant sorbed and the concentration in solution is approximately linear. In such cases the extent of sorption can be describe in terms of a partition coefficient which is the ratio between the amount on the solid phase and the amount in the liquid phase. As a general rule, highly hydrophobic organic compounds are much more strongly sorbed than more soluble organic

compounds. Sorption of metals and other ionizable contaminants is a more complex phenomenon and is dependent on pH and other system parameters that may be highly variable [5].

Sorption must be accounted for when estimating the contaminant mass to be removed. Because of sorption, the mass of the contaminant adsorbed onto the aquifer solids may be as great or greater than the mass in solution. When there is significant sorption, estimates of contaminant mass based only on water samples will seriously underestimate the mass to be removed. When dealing with highly insoluble compounds like DDT, PCBs, or dioxin, almost all of the material will normally be associated with the solid phase and very little will be associated with the water phase. The best way to estimate the mass of sorbed contaminants is by collecting cores of the aquifer material and measuring a partition coefficient

Sorption reduces the efficiency of pump and treat. Sorbed contaminants can only be extracted if they are desorbed and in solution. When contaminants are strongly sorbed, only a small fraction of the total contaminant mass is removed with each pore volume pumped. Alternatively, the average velocity of the sorbed contaminant may be viewed as retarded relative to the average velocity of the ground water or highly soluble contaminants. In either case, additional pore volumes will have to be pumped to remove the sorbed contaminants. The increase can be from a factor of slightly greater than one to 10 or more. This can increase the time required to remediate the aquifer from a few years to tens of years.

Research has shown that the release of many contaminants from the solid phase can be exceedingly slow [6]. This slow desorptive release acts much like diffusion from zone of low permeability. Acting together, these two processes greatly accentuate the tailing effect. Depending upon the nature of the compounds, the slow desorption of contaminants from sediment surfaces often results in a profound tailing effect when attempting to remediate



Figure 5. The effect of sorption, in addition to subsurface heterogeneity, on the removal of a soluble contaminant

ground-water by pumping. The more a contaminant preferentially associates with the solid phase, the more difficult that contaminant is to remove.

The partitioning of a contaminant between water and aquifer material is commonly proportional to the amount of organic material present in the aquifer sediments. Frequently there is more organic carbon and therefore greater partitioning to the finer sediments. If the example discussed in Figure 4a were altered to include a partition coefficient of unity in the layer of high hydraulic conductivity (the amount associated with the solid phase is equal to that associated with the liquid phase), and a partition coefficient of 5 in the layer of low hydraulic conductivity, it would take longer before the initial decline in relative concentration (Figure 5) and much longer before complete remediation could be realized. The relative concentration at the plateau remains the same as in the example of Figure 4a. It can be seen that the magnitude of this plateau or tail is independent of the partition coefficients of the individual layers and that the effect of partitioning is to increase the amount of time required to achieve remediation goals.

IMMISCIBLE FLUID PHASES

When an immiscible fluid, or non-aqueous phase liquid (NAPL) is released into the unsaturated zone a fraction of it will volatilize and be released to the atmosphere, and the remainder will start to move downward toward the water table under the influence of the force of gravity as shown in Figure 6. If the original source of contamination is removed, capillary forces will immobilize part of the separate phase liquid as discontinuous blobs trapped within the pore spaces as shown in Figure 7. This immobile material, which can occupy from five to



Figure 6. Release of a NAPL from an underground storage tank

`3'



40 percent of the pore space [6], is referred to as "residual saturation" or "residual phase" and cannot be removed in any substantial quantity by pumping.

Figure 7. Residual saturation remaining after removal of original source of contamination

Gasoline is an example of an immiscible fluid with a specific gravity less than one, commonly referred to as a light non-aqueous phase liquid or (LNAPL). Because they are less dense than water, LNAPLs remain near the water table. The soluble components of the LNAPL will partition into the moving ground water and contaminate it. This partitioning appears to be greatly enhanced if the water table fluctuates. LNAPLS, primarily gasoline from leaking underground storage tanks, are a leading cause of ground water contamination in the United States.

Of even greater concern, from a remediation standpoint, are dense nonaqueous phase liquids (DNAPLs) such as coal tars or chlorinated solvents which have specific gravities greater than one. If enough DNAPL volume is released to the subsurface to overcome capillary forces, the DNAPL will continue to migrate vertically through the saturated zone until it encounters a relatively impermeable layer where it may form a perched DNAPL pool. In addition to accumulating in DNAPL pools, residual DNAPL will be trapped in pore spaces within the saturated zone as well as in the vadose zone, dissolve into passing ground water, and be transported in the direction of ground-water flow.

The rate of contaminant partitioning from NAPLs into ground water, and the eventual concentration reached is dependent on the characteristics of the contaminant and the location of the residual phase with respect to the flowing ground water. If the residual phase is a complex fluid such as gasoline, the rate of contaminant partitioning from the NAPL into water will be different for the individual constituents of the non-aqueous fluid. As a result the composition of the non-aqueous fluid will change with time.

ſ,

It is apparent that if remediation is dependent on allowing the DNAPL to dissolve into ground water and pumping the aqueous phase contamination to the surface, the remediation process will require a very, very long time. To remove one liter of a common and relatively soluble contaminant such as trichloroethylene (TCE) from the ground water would require pumping 1,400 liters of ground water contaminated at 1,100 mg/l, the aqueous solubility level of TCE.

If the immiscible phase can be located it should, as a rule, be pumped directly and removed. However, the relative importance of forces that control the rate, direction, and ultimate fate of DNAPLs is different than for the distribution of dissolved phase plumes. DNAPL movement is more strongly controlled by both large and small scale geologic heterogeneities than by the movement of ground water. As a result, the distribution and movement of DNAPLs is difficult to determine, even at sites of relatively homogeneous geology with a well understood DNAPL source. Even if the free-phase DNAPL can be located and pumped, residual saturation will remain and continue to contaminate ground water as the contaminants partition into it. The kinetics of this partitioning, whether from free product DNAPL or from residual saturation. can prove deceptive when attempting to remove contaminants using pump and treat.

The contaminant cannot be removed faster than it is released from residual saturation or pools of immiscible fluids, or than it can diffuse from regions of immobile water into the passing ground water. The result is similar to that described earlier for the kinetics of diffusion from zones of low permeability or desorption. The concentration may initially appear to be reduced, or even eliminated, by dilution when bringing larger amounts of uncontaminated water into play, or by dropping the water table below the source of contamination, or both. However, if the pumps are stopped for a period of time, the contaminants will again partition or diffuse into the moving ground water and their concentrations will return to their previous levels. Without an understanding of these processes pump-and-treat systems will probably be poorly designed and will likely contaminate more fresh water than would be the case if no pump-and-treat remediation were attempted.

Nonetheless, pump and treat can be of considerable use in reducing the extent of the dissolved phase plume, and this action can be of considerable value in the overall plan of site remediation. Control of the aqueous phase plume by pumping can prevent further contamination of down-gradient ground water. It can also reduce the mass of contaminant to be dealt with in further remedial activities. It should also be noted that there is a great deal of research underway to enhance the effectiveness of pump and treat in dealing with DNAPLs.

Some insight into the effect of NAPLs on remediation time can be gained by returning to the scenario developed for the removal of chloride in Figure 1. If, rather than chloride, the constituent is toluene dissolved in the residual saturation of a gasoline plume, it would be necessary to pump at a rate of 400 L/min for about 1,500 years to reduce the initial amount of

toluene by 80 percent if the residual saturation amounted to only 10 percent of the aquifer voids and no other processes of transformation were occurring. Even if the configuration of the plume and the hydrology of the aquifer would allow increasing the pumping rate to 4,000 L/min without dewatering the contaminant plume, it would still require 150 years to reduce toluene by 80 percent. Almost certainly a system such as this would result in the contamination of a great deal of fresh ground water by moving it through the area of contamination. Even if the aquifer would allow unlimited pumping, it is important to realize that there is a point beyond which the removal of contaminants would not increase because of the limitations imposed by partitioning and diffusion rates.

IMPROVING THE SITUATION

The acknowledged problems with pump and treat, along with the recognition that it is often the only available aquifer remediation technology for many situations, have led to considerable discussion and research on ways to make it more effective. Moreover, since many of the problems of pump and treat also limit the effectiveness of other aquifer remediation technologies, steps taken to improve pump and treat will have benefits for other technologies as well. There are steps that can be taken to use existing knowledge to improve pump and treat, and steps for which research and new knowledge are required.

Site Characterization

^{رې} ک

There is general agreement that one of the most important parts of any pump-and-treat remedial action is a good site characterization. The subsurface can be an extremely complex environment whose characteristics change dramatically over small horizontal and vertical distances. The ability to design remediation systems and make an estimate of their effectiveness is proportional to the amount of information available about a number of factors including:

- 1) the location and distribution of contaminants,
- 2) the identity and quantitative values of hydrogeologic parameters, flow paths, and other influences such as pumping wells and streams,
- 3) quantitative measurements of contaminant partitioning between liquid, solid, vapor, and NAPL phases,
- 4) the effect of remediation activities on flow paths and interactions between contaminants and subsurface solids.

Obviously, the more complex a site, the more intense the effort required to obtain these types of information. In some cases the technology required to obtain the information is available, in other cases it is theoretically available but its use is not routine, even for relatively homogeneous sites, and in other cases the technology is still the subject of research. Among the tools which are available and being used by experienced ground-water scientists are depth-specific clusters of monitoring wells which can be used to locate areas of water miscible

contaminants and can sometimes be used to suggest the locations of immiscible contaminants. Extensive core sampling can (a) assist in the determination of permeability distributions and therefore predominant flow paths; (b) provide information concerning the location, distribution, and total amount of contaminants; and (c) allow estimates to be made of contaminant partitioning between the liquid, solid, vapor, and immiscible phases. Standard hydrologic tests are required to provide information on the hydrogeology of the system, while geophysical techniques can sometimes be used to reduce the number of samples required.

It is not always apparent where to locate sampling points or how many points will be required to adequately characterize a site. As the geology and the parameters discussed above become more complex, the more sample points are required for characterization, and the more difficult the interpretation of information becomes. As the hydrology of a site and the nature of the contaminants becomes more complex, the confidence in any remediation technology is decreased. In fractured and karst media, which underlie many hazardous waste sites, the technology available to characterize water and contaminant movement is largely undeveloped. Slurry Walls

The use of slurry of cut-off walls in conjunction with pump and treat can be used to improve the effectiveness of pump and treat. A slurry wall placed in front of an advancing plume can greatly reduce the amount of water extracted and requiring treatment. This will also reduce the amount of uncontaminated water that would otherwise become contaminated using an extraction system alone. If a slurry wall surrounds a contaminant source and plume, groundwater extraction could maintain a negative head at the site. The slurry wall will reduce the amount of fresh water being contaminated by the remediation, and reduce the amount of water requiring treatment to the leakage rate of the barrier wall, plus that due to infiltration and any water applied at the site to accelerate the remediation.

Research

The US EPA and other organizations are conducting research to improve the effectiveness of pump and treat. One effort is the EPA's Subsurface Cleanup and Mobilization Processes (SCAMP) research program which is looking at ways to enhance the effectiveness of pump and treat and for sites contaminated by DNAPLs. SCAMP research is focusing on two major applied research areas: (1) improved site characterization, and development and (2) evaluation of means to enhance the effectiveness of pump and treat. SCAMP is also funding some of the necessary basic research on the fundamental transport and fate processes needed to support the two applied areas.

Research on site characterization that is being carried out under SCAMP is presently composed of two activities. The first is to develop a manual for use by practitioners for characterizing sites contaminated by DNAPLs. This document is expected to: (a)summarize the current state-of-the-art for characterizing sites suspected of DNAPL contamination; (b) summarize likely near-term improvements; and guide further EPA research on site

characterization. SCAMP research is also investigating methods which combine field measurements and modeling to characterize fractured rock sites, keeping in mind a realistic estimate of the resources available for site characterization at a typical hazardous waste site. Future work will be aimed at direct methods for the detection and quantification of DNAPLs and measurement of multiphase parameters such as relative permeabilities.

SCAMP research on the development and evaluation of technologies to improve pump and treat is aimed at overcoming the problems identified earlier. A modeling study, using the opportunity for more realistic simulations offered by supercomputers, is investigating the benefits to be expected from novel pumping schemes. These include vertical pumping to force water through layers of low permeability, and pulse pumping to potentially reduce the amount of water to be treated. In theory pulse pumping can be useful in breaking up zones of stagnation discussed earlier and changing the direction of flow to improve the efficiency of removal when contaminants must enter ground water through slow partitioning or diffusion. However, there has been little field work or other evidence to evaluate the effects of pulse pumping.

Other work under the SCAMP research initiative is investigating the use of chemical additives in an attempt to improve pump and treat. Chemical additives such as surfactants and solvents are among the most promising short-term approaches for enhancing the effectiveness of pump and treat. Surfactants have the potential to improve the effectiveness of pump and treat in two ways. The first is by increasing the solubility of hydrophobic contaminants in ground water. Increasing the solubility will generally reduce the extent of sorption to the aquifer solids, and has the potential to reduce the number of pore volumes, and time, required to remove sorbed contaminants. The effect of surfactants on sorption kinetics is less clear and is part of the research. Increasing the solubility could also increase the extent of dissolution of residual or free-phase NAPL. The second way that the use of surfactants can potentially enhance the effectiveness of pump and treat for NAPLs is by reducing the interfacial tension between the NAPL and water, making it possible to mobilize the residual saturation.

SCAMP research on the use of surfactants for increasing the effectiveness of pump and treat is being carried out at the laboratory-bench scale and through the use of a large physical model aquifer at RSKERL. The large physical model will be used to simulate an enhanced pump-and-treat scenario to remediate a DNAPL spill. In addition to investigating the effectiveness of surfactants for enhancing pump and treat, the research is also paying close attention to the characteristics of surfactants that will make them acceptable to the public for injection into potential or actual sources of public drinking water.

Extensive laboratory work at RSKERL, and other institutions, has shown that miscible solvents such as ethanol can increase the solubility of hydrophobic contaminants in water [9]. Ethanol has relatively low toxicity and probably would be acceptable for addition to the subsurface. Work is currently underway on a small field project to test the effectiveness of

ethanol in improving the efficiency of extracting a mixture of aviation gasoline and tetrachlorethane (PCE) from a shallow aquifer in the state of Michigan.

Additional research, sponsored by the EPA and other US federal agencies, is concentrating on the use of physical agents such as steam or hot water to increase the effectiveness of DNAPL removal. This technology, like the surfactant and solvent work, is an attempt to adapt techniques used for enhanced oil recovery to the remediation of hazardous waste sites. Differences in the objectives and conditions under which the work is carried out make this adaptation non-trivial.

It is often possible, indeed desirable, to use pump-and-treat remediation systems in concert with other technologies. For example, to be effective, pump and treat of contaminated ground water must also be combined with efforts to remove contaminants from the vadose zone. Bioremediation of contaminated ground water may be thought of as a pump-and-treat system in which ground water is extracted, supplemented with necessary nutrients to stimulate biodegradation, and reinjected into the aquifer. Efforts to improve pump and treat, particularly with regard to site characterization and subsurface fluid movement, will almost certainly benefit bioremediation as well.

CONCLUSION

It is important to understand the processes that limit the effectiveness of pump-and-treat technology in order to develop more efficient and effective remediation projects. Research has the potential to improve the technology available to characterize the system, to control the movement of fluids in the subsurface, and to influence interactions between the various contaminant phases and the subsurface matrix. It is also important to have realistic expectations about what can, or cannot, be accomplished with pump and treat. With research and additional experience in building and operating pump-and-treat systems, the situation will improve, but it will be many years, nowever, before pump-and-treat technology is at a level where effective and efficient remediation systems can be routinely designed and implement for even moderately complex subsurface problems.

REFERENCES

- Train, R.E., Big question facing the clean up of ground water. <u>EPA Journal</u>, 1987, 13(1), 8 - 11.
- 2. Ward, B., Groundwater Another trend, fad ... or a legitimate Washington issue? Pollution Engineering, 1983,15(10), 14-16.
- 3. Shakespeare, W., Macbeth, Act V, Sc. I, line 30

્ધુ

- 4. Keely, J., Performance evaluation of pump-and-treat remediations. USEPA/540/4-89-005, 1989, 19 pp.
- Weber, W.J., Jr, McGinley, P.M., and Katz, L.E., Sorption processes and their effects on contaminant fate and transport in subsurface systems. <u>Water Research</u>, 1991, 25, 499-528.
- 6. Brusseau, M.L. and Rao, P.S.C., Sorption nonideality during organic contaminant transport in porous media. <u>Critical Reviews in Environmental Control</u>, 1989, 19, 33-99.
- Wilson, J.L., Conrad, S.H., Mason, W.R., Peplinski, W., and Hagan, E., Laboratory investigation of residual liquid organics. USEPA/600/6-90/004, 1990, 267 pp.
- Robert S. Kerr Environmental Research Laboratory, Dense nonaqueous phase liquids -- a workshop summary, Dallas Texas. April 16-18, 1991. (to be published 1992), USEPA/600/, 81 pp.
- 9. Rao, P.S. C., Lee, L.S., and Wood, A.L., Solubility, sorption, and transport of hydrophobic organic chemicals in complex mixtures, EPA/600/M-91/16, 1991.

EN,