Groundwater Ecosystems and the Service of Water Purification

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I. Introduction

The ability of groundwater microorganisms to decompose matter provides a number of significant ecosystem services. These include rendering harmless potential human pathogens, breaking down organic wastes and, the net result, purifying groundwater. The importance of uncontaminated groundwater to functioning ecosystems is undisputed. Over 90% of the world's unfrozen freshwater is stored underground, compared to only 3.6% found in lakes and reservoirs.[1] It has long been thought that most subterra-

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1. *See* Ralph C. Heath, *Basic Ground-Water Hydrology*, 2220 U.S. Geological Survey Water-Supply Paper 1 (1982).

nean waters are lifeless—large underground rivers and reservoirs containing pure water "mechanically filtered" by the soil. Recent research, however, has disproved this popular assumption and uncovered the critical role of living organisms in groundwater.[2] In fact, there is now an entire research field known as "groundwater ecology" that studies the structural and functional relationships between biotic and abiotic components of subsurface aquatic systems.[3]

Given the importance of the groundwater purification service, one might expect strong legal protections. And, indeed, there are some. The primary authority for maintaining and restoring this ecosystem service is the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), which is also known as Superfund.[4] Contamination at Superfund sites often leaches into the groundwater, injuring the microorganism community and its ability to biodegrade wastes. CERCLA provides that Natural Resource Damages (NRD) may be assessed as compensation for injuries on property owned by the federal, state, or local governments (and in some cases Indian tribes). Potentially responsible parties are liable for injury to natural resources as well as ecosystem services, including the costs for rehabilitation and restoration to baseline conditions.[5] Because injury to services is compensable under the regulations, officials are authorized to require collection of

2. *See generally* FRANCIS H. CHAPELLE, GROUND-WATER MICROBIOLOGY AND GEOCHEMISTRY (1993) (comprising the classic exposition on the occurrence and nature of microorganisms in groundwater).

3. *See generally* JANINE GIBERT ET AL., GROUNDWATER ECOLOGY (1994) (comprising the first attempt to bring the field together in a published text).

4. 42 U.S.C. §§ 9601-9675 (1994).

5. Potentially responsible parties are liable for "injury to, destruction of, or loss of natural resources, including the reasonable costs of assessing such injury, destruction, or loss resulting from such a release." *Id.* § 9607(a)(4)(C). The implementing regulations also provide recovery for replacement, rehabilitation, restoration, and acquisition of equivalent resources. *See* 43 C.F.R. § 11.15(3)(ii) (2000). They explicitly authorize compensation for damages to "services," broadly defined to include "the physical and biological functions performed by the resource including the human uses of those functions. These services are the result of the physical, chemical, or biological quality of the resource." *Id.* § 11.14 (nn). Costs for restoration and rehabilitation include "actions undertaken to return an injured resource to its baseline condition, as measured in terms of the injured resource's physical, chemical, or biological properties or the services it previously provided, when such actions are in addition to response actions completed or anticipated . . . ." *Id.* § 11.14 (ll). Costs for replacement or acquisition of equivalent resources include "the substitution for an injured resource with a resource that provides the same or substantially similar services [as before], when such substitutions are in addition to any substitutions made or anticipated as part of response actions . . . ." *Id.* § 11.14 (a).

data on services throughout the assessment process.[6] But in practice, is the ecosystem service of groundwater purification protected (or even recognized) in Superfund cleanups? And, if not, how could this be done?

It is an oversimplification, though not a gross one, to describe most Superfund site remediation efforts as exercises in completing a "checklist" of contaminants. Since Congress has never specified the level of cleanup required for compliance with CERCLA, "how clean is clean" varies depending upon the relevant remediation standards.[7] Thus the stringency and cost of each remediation depend entirely on the maximum contaminant standards set for each site by the agency official, and these can be drawn from any number of regulatory sources. Once the applicable clean-up requirements have been established, the site is remediated, usually through pump-and-treat technology, until the contaminants in the water samples are below the maximum allowable concentrations. At that point in time, to be sure, the groundwater should be sufficiently clean for the agency official to "check off" each contaminant as meeting the remediation standards. It is not known, however, whether the site's *ecosystem services* have been restored by the remediation efforts and, we would suggest, under current practice no one seems to know or care.

In this paper, we explore a strategy that differs from the checklist approach, one we believe is required under the law but has not been implemented. In particular, we examine the possibility of using protection of groundwater ecosystem services as a guiding principle for restoration efforts. Part II considers why we should care about restoration of services in CERCLA remediation, identifying the major ecosystem services occurring in groundwater and focusing on the service of water purification. Part III considers when action is appropriate, assessing when the contaminants found at Superfund sites will degrade the service of water purification. Parts

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6. Data may be collected by the official or by potentially responsible parties (under the direction of the official). So long as the EPA has jurisdiction over the site—and it will if the site is a Superfund site—EPA officials are authorized to play a role in NRD assessments, through cooperation and coordination with other agencies having concurrent jurisdictions. *See id.* § 11.32.

7. CERCLA does not establish uniform clean-up standards. Instead, Section 121(d) of CERCLA requires that each remediation comply with federal or more stringent state environmental standards that are "applicable or relevant and appropriate." *See* 42 U.S.C. §9621(d) (1994). Known as "ARARs," these maximum contaminant levels might be drawn from the Safe Drinking Water Act, Clean Water Act, or other laws and can differ from site to site.

IV and V address what we should do, describing the challenges in establishing indicators for groundwater purification services, assessing the impact of standard pump-and-treat remediation on services, and considering whether services can adequately restore themselves without intervention. Parts VI and VII describe alternatives to pump-and-treat remediation, arguing for greater use of remediation technologies that restore, rather than destroy, ecosystem services.

II. Provision of Groundwater Ecosystem Services

It is estimated that there are 521,000 km^3 (125,000 mi^3) of subsurface openings in the soils and bedrock underlying the United States, most of which contain water.[8] The ubiquitous and hidden nature of this ecosystem should not, however, obscure its many benefits to us. The National Research Council, in its study entitled *Valuing Ground Water: Economic Concepts and Approaches,* identified thirteen types of goods and services provided by groundwater stored in an aquifer.[9]

Goods

- Potable water
- Irrigation for landscape and turf
- Irrigation for agricultural crop
- Livestock watering
- Food product processing
- Other manufacturing processes
- Heated water for geothermal power plants
- Cooling water for other power plants

Services

- Prevention of land subsidence
- Erosion and flood control through absorption of runoff
- Medium for wastes and other byproducts of human economic activity
- Improved water quality through mechanical and biochemical water purification

This article focuses on the last of these services, water purification, both because it is often the most valuable service provided by groundwater ecosystems and because many of the clean-up standards at Superfund sites are based on human health standards for

8. *See* Heath, *supra* note 1, at 1.

9. National Research Council, Valuing Ground Water: Economic Concepts and Approaches 22 (1997) [hereinafter NRC 1997a].

drinking water.[10] In this part, we describe the provision of groundwater purification and identify some of the factors that make water purification a valuable ecosystem service.

Groundwater accounts for 40% of the water used in the United States, exclusive of hydroelectric power generation and power plant cooling.[11] Groundwater withdrawals average eighty-one billion gallons per day, and more than half of the population of the United States draws its drinking water from the ground. These users require clean water,[12] but a variety of human activities have had a negative impact on the quality of the subsurface environment and the water resources held there, and we are paying to remedy the damage.[13]

The passage of CERCLA has driven most of the groundwater remediation efforts,[14] establishing both the price to be paid and the methods to be used. Since the passage of CERCLA in 1980, hundreds of billions of dollars in public and private funds have been spent on cleanup at Superfund sites and analogous sites under the control of the Departments of Defense and Energy.[15] In 1996 alone, the federal government spent nine billion dollars on cleanup of Superfund sites.[16] Between 300,000 and 400,000 contaminated soil and groundwater sites remain in need of cleanup and, at many of these sites, CERCLA requires restoration of contaminated water to drinking water quality.[17] The estimated cleanup cost for all these contaminated sites in 1997 was between 500 billion and one trillion dollars.[18]

The standard method for treating groundwater contamination at Superfund sites has been pump-and-treat technology, which is

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10. CERCLA § 121(b) mandates remedial actions that are "protective of human health and the environment." ARARs can be drawn from any relevant and appropriate federal or state laws. See *supra* note 7. The Safe Drinking Water Act has often been used for this purpose. *See* Amy L. Du Vall, *Cleanup Processes and Standards of CERCLA and RCRA: Shortcomings and Recommendations*, 4 BUFF. ENVTL. L.J. 225, 243-245 (1997).

11. *See* NRC 1997A, *supra* note 9, at 15.

12. *See* OFFICE OF WATER, UNITED STATES ENVIRONMENTAL PROTECTION AGENCY, PUB. NO. 815-K-97-002, WATER ON TAP: A CONSUMER'S GUIDE TO THE NATION'S DRINKING WATER (1997), *available at* http://www.epa.gov/safewater/wot/wheredoes.html.

13. *See* NATIONAL RESEARCH COUNCIL, INNOVATIONS IN GROUND WATER AND SOIL CLEANUP: FROM CONCEPT TO COMMERCIALIZATION 22 (1997) [hereinafter NRC 1997B].

14. *See* Heath, *supra* note 1, at 1.

15. *See* NRC 1997B, *supra* note 13, at 18.

16. *See id.* at 19.

17. *See* discussion of ARARs, *supra* note 7.

18. *See* NRC 1997B, *supra* note 13, at 18.

used in over 90% of groundwater cleanup efforts.[19] Pump-and-treat remediation methods rely on dilution. In simple terms, water is pumped into the site and, at a separate well, pumped out and treated to remove the contaminants. This method may be inadequate for several reasons. First, it may be ineffective at removing contaminants. Many contaminants may not dissolve in water, may diffuse into micropores and other sites that cannot be pumped, or may be partitioned to subsurface materials such as clay; thus, they will not be pumped and cannot be treated.[20] Moreover, many sites may never be restored. In a 1994 National Research Council study of seventy-seven sites, only eight had been cleaned up and thirty-four can probably never be restored to suitable quality using standard technology.[21] Most importantly, even if a site is treated and the contaminants are removed, simply restoring groundwater to a desired quality endpoint may not satisfy the statutory mandates of CERCLA or achieve full restoration of ecosystem function.

Although the passage of CERCLA implicitly acknowledged the value of groundwater, it failed to acknowledge the value of groundwater services. Groundwater is usually not considered in the context of ecosystems or ecosystem services. Indeed the whole idea of pristine groundwater and the near mystical belief in its quality (as witnessed by the prices consumers are willing to pay for bottled water from springs) argues against the possibility of finding life in groundwater except at contaminated sites. In fact, however, nearly every groundwater sample, even those collected from depths almost one kilometer, has bacteria suspended in it.[22] While not the focus of this paper, this bacterial community provides a large sink for carbon.[23]

These groundwater ecosystems play an important role in determining groundwater quality. Organic compounds enter aquifers naturally by infiltration through soils and streambeds and through human activity by a plethora of waste-disposal practices employed

19. *See id.* at 19.
20. *See id.* at 32.
21. *See id.* at 18.
22. *See* CHAPELLE, *supra* note 2, at 206.
23. The presence of bacteria in groundwater has resulted in over half of the world's cellular carbon located in subsurface habitats. However, the prokaryotic subsurface community is much less metabolically active than surface communities of bacteria. For example, the turnover time of soil bacteria is about 2.5 years, while that of subsurface bacteria is 1,000 to 2,000 years. Thus, the subsurface ecosystem is less important in the global carbon cycle than the reservoir size would suggest. *See* William B. Whitman et al., *Prokaryotes: The Unseen Majority*, 95 PROC. NAT'L ACAD. SCI. U.S.A. 6578, 6578 (1998).

in modern society.[24] Microbial bacteria provide the major purification service. Bacteria degrade organic compounds by using carbon as an energy source; this oxidation of contaminant carbon is accompanied by the reduction of an electron-accepting compound. A consortium of bacteria can act to maximize both the range of compounds that can be degraded, as well as the rate at which they are degraded. They thereby minimize the dissolved organic content of the groundwater.

The chemical diversity of microbial degradation of organic compounds is remarkable. Various bacterial strains are capable of transforming widely used and environmentally ubiquitous chemicals such as petroleum hydrocarbons and synthetic halogenated organic compounds into one or several products of more benign environmental behavior and effects.[25] These reactions may occur aerobically or, in the absence of dissolved oxygen, anaerobically, using other chemical species as electron acceptors in the overall biodegradation process. A variety of factors may limit a chemical reaction in the environment, including which electron acceptors are available, what other essential nutrients for microbial life are available, and how the contaminant chemically changed through aging in the environment. The final expression of the biodegradation potential in natural aquifers, which provide water purification services, is dependent on a large number of variables including strains of microorganisms present, nature of contaminant compound, and availability of electron accepting chemical compounds and nutrients for microbial growth. The exact rate and extent of biodegradation reactions that can be expected in a natural aquifer are not well established.

III. THE PROVISION OF WATER PURIFICATION

Site contamination can obviously degrade the quality of a site's groundwater. Whether it also degrades the ability of the groundwater ecosystem to *purify* water, though, is a separate issue. Once most of the contaminants have been removed there are two further issues that must be considered: what we would look for to measure

24. The protozoa in groundwater may also provide purification services by eating pathogenic viruses and other microbes, but this service is less significant in most cases than degradation of organic compounds especially since protozoa are generally rare. *See* J.L. Sinclair & William C. Ghiorse, *Distribution of Protozoa in Subsurface Sediments of a Pristine Groundwater Study Site in Oklahoma*, 53 APPLIED & ENVTL. MICROBIOLOGY 1157, 1157 (1987).

25. *See* RENE P. SCHWARZENBACH ET AL., ENVIRONMENTAL ORGANIC CHEMISTRY 485 (1993).

restoration of the site's ecological functions and how we would ascertain that we had succeeded. In this part, we explore the conditions necessary for bacteria to degrade pollutants and explain how these conditions are affected by the presence of contaminants in the soil. Part IV then turns to development of indicators.

Natural aquifers come in many varieties, demonstrating a wide range of environmental conditions. There are three generally recognized groundwater habitats (also known as biomes). *Shallow, porous aquifers* comprise sand and gravel of old lakes and streams, and are sometimes called interstitial habitats. They are not usually major sources of water, but do play an important role in groundwater-surface water interactions. Their biological community is diverse, both sharing species in common with streams, lakes, and springs, and having unique subsurface species. *Karst aquifers* include aquifers usually at shallow to intermediate depth that are characterized by large cavities formed as the result of the dissolution of the bedrock (usually carbonate). *Deeper groundwater* (also known as the phreos) is often found in porous rock or sediments, and is a major source of water in many regions. All three types of groundwater habitat have a rich microbial community.

Shallow, porous aquifers are the focus of our discussion because they are important sources of water and they are relatively well studied. These aquifers show major variation in their "natural" condition. Uncontaminated aquifers may be entirely aerobic, with bacteria using oxygen as the major electron acceptor for organic degradation. However, shallow, porous aquifers are likely to contain regions or "zones" of different redox (reduction/oxidation) potential, with different bacteria using different electron acceptors to oxidize and transform organic compounds.[26] The use of the various electron acceptors occurs in an orderly sequence according to how much energy the bacteria derive from the reaction: O_2 (gas), NO_3^+, Mn^{2+}, Fe^{3+}, SO_4^{2-}, and CO_2 (gas) (methanogenesis).[27] As organic matter degradation proceeds, zones of different redox

26. A single strain of bacteria cannot "do it all." There are some bacteria that have some flexibility, but most often their biochemical function is strain-specific. So, we need different strains to accomplish all these reactions. A range of function exists, however, within any consortium of bacteria.

27. In other words, a reaction that yields more energy will be completed before other less-energy-yielding reactions occur. For example, the function of sulfate reduction does not occur if oxygen is available. Once the most efficient electron acceptors are depleted from the aquifer, other functions take over. *See* W. STUMM & J.J. MORGAN, AQUATIC CHEMISTRY—CHEMICAL EQUILIBRIA AND RATES IN NATURAL WATERS 474 (3rd ed. 1996). Methanogenesis is the process of the production of methane in which the carbon in either CO_2

conditions develop in the aquifer as each electron acceptor is depleted. The resulting chemical environments follow the same sequence: aerobic, nitrate-reducing, manganese-reducing, and so on.

Reductions in habitat quality may lessen the benefits that microbial communities provide, and may even destroy the microbes themselves. Organic pollutants are frequently added to groundwater in dissolved and suspended form, entering the groundwater through percolating and other water that is recharging the aquifer. Most Superfund sites are contaminated by organics, especially through leaking underground storage tanks.[28] Such contamination compromises the groundwater ecosystem service of purification in two ways. First, the groundwater ecosystem service of degradation works most effectively on organic compounds but changes in availability of electron receptors may affect the ability of the bacterial community to degrade particular compounds. Second, site contamination by non-organics (heavy metals) can poison most or all of the microbial community and thus permanently impair its ability to break down organic pollutants in the groundwater.[29]

To maximize the service of degradation, a range of redox environments should be available.[30] Aerobic respiration is not always the most effective reaction mechanism for biodegradation of all compounds. Some degradation works best under aerobic conditions, while some is best under anaerobic conditions. For example, anaerobic respiration under iron-reducing conditions was found to be more effective than aerobic respiration in degrading chlorinated organic compounds in a freshwater tidal wetland.[31] Naphthalene degradation, on the other hand, may occur more rapidly under sulfate-reducing conditions.[32] Having a variety of electron acceptors available assures that a variety of processes can be used to

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or acetate serves as the electron acceptor. For example, $4H_2 + CO_2 \Leftrightarrow CH_4 + 2H_2O$. CHAPELLE, *supra* note 2, at 86.

28. *See* NRC 1997B, *supra* note 13, at 31.

29. The reason that bacteria are more effective than heavy metals on organics is that organics are a source of energy and heavy metals are not. Chapelle, *supra* note 2, discusses bacterial metabolism of organics on pages 71-102 and the acclimation to heavy metals on pages 317-20.

30. You also need a range of bacteria, since a range of bacteria most effectively uses a range of electron acceptors. However, there is always a range of bacteria in nature.

31. *See* Michelle M. Lorah & Lisa D. Olsen, *Natural Attenuation of Chlorinated Volatile Organic Compounds in a Freshwater Tidal Wetland: Field Evidence of Anaerobic Biodegradation*, 35 WATER RESOURCES RESEARCH 3811, 3822 (1999).

32. *See* James F. Barker & John T. Wilson, *Natural Biological Attenuation of Aromatic Hydrocarbons Under Anaerobic Conditions*, *in* SUBSURFACE RESTORATION 289, 289-90 (C. Herb Ward et al. eds., 1997).

degrade a variety of compounds. Ironically, the potential of the groundwater community to provide purification services may be destroyed as the site is "cleaned" by pump-and-treat methods that introduce oxygenated water into the aquifer and mix groundwater that had become segregated into various redox zones.

IV. Indicators of Groundwater Purification Services

This section explores the challenge involved in selecting indicators for the ecosystem service of water purification at Superfund sites, and explains why it is so difficult to obtain necessary measurements in the field. Assume the EPA official supervising a CERCLA clean-up determines that contamination has injured the ability of the site to purify groundwater and requires the potentially responsible party to restore this ecosystem service. The party performing the clean-up needs to know when to stop. "How clean is clean" can be easily determined by a chemical assay of groundwater. But it is more difficult to determine when the ecosystem service has been sufficiently restored. To do so, we need accurate indicators of service function. Indeed, accurate indicators are a precondition for effective legal requirements of service restoration.

This section explains the chemistry and chemical methods underpinning the selection of water purification service indicators. The conclusion (for readers without any background in chemistry) is straightforward. Because very little research has been done on indicators of groundwater purification, we cannot yet specify the precise identity and concentrations of chemical indicators for particular Superfund sites. We can, however, clearly show that this could be done, both by demonstrating the occurrence of microbially mediated biodegradation reactions and by making robust measurements of the reactions for aquifers with variable conditions. We review several methods of assessing the occurrence of degradation reactions and their shortcomings.

Scientists have used different approaches to assess the nature and extent of the various electron-accepting reactions occurring in the subsurface. Derek Lovley et al. suggest that dissolved hydrogen (H_2) can be used to determine the distribution of redox reactions occurring in groundwater because the concentration of H_2 can be linked directly to specific metabolic processes.[33] But this is easier

33. *See* Derek R. Lovley et al., *Use of Dissolved H2 Concentrations to Determine Distribution of Microbially Catalyzed Redox Reactions in Anoxic Groundwater*, 28 Envtl. Sci. Tech. 1205, 1205-10 (1994).

said than done. Whereas the measurement of ionic concentrations of electron acceptors and biodegradation products is relatively straightforward, dissolved hydrogen measurement requires an expensive and fragile mobile gas chromatograph, rather sophisticated analytical methods, and measurement within two hours of collection of the sample. In addition, the accuracy of H_2 measurements decreases with H_2 concentration, so it is difficult to distinguish metabolic processes that are characterized by very low H_2 concentrations.

A very different approach uses microbial microcosms that are either constructed from aquifer solids and groundwater[34] or created for deployment into the aquifer as *in situ* microcosms.[35] Although these microcosms were meant to reveal the metabolic processes taking place *in situ*, it is uncertain whether the results of studies using microcosms reflect the extent and rate of biodegradation reactions in real aquifers. Problems with simulation of aquifer conditions and non-invasive monitoring of microcosms have plagued the application of this technique. Therefore, most studies of the redox environments of the subsurface are based on measurements of electron acceptors and reaction products in the actual groundwater system.[36]

The most widely employed measure of the presence of different redox environments is the presence of the various electron acceptors and the products of the redox reactions in different regions of the aquifer.[37] This measure remains the standard for measuring biodegradative capabilities. For aerobic reactions, the presence of an electron acceptor indicates the potential for reaction: the higher the redox measurement, the greater the potential for reaction. The loss of an electron acceptor over time—or, equivalently, along an isolated groundwater flowpath—indicates how much degradation actually occurred. For several of the important redox "couples" or reactions, it is straightforward to analyze for both the electron acceptor and the reduced product. The presence

34. *See* L. Ludvigsen et al., *Anaerobic Microbial Redox Processes in a Landfill Leachate Contaminated Aquifer*, 33 J. CONTAMINANT HYDROLOGY 273, 273-91 (1998).

35. *See* E. Michael Godly et al., *Determining BTEX Biodegradation Rates Using In Situ Microcosms at the Bemidji site, Minnesota: Trials and Tribulations*, *in* U.S. GEOLOGICAL SURVEY WATER, PUB. NO. 99-4018C, 3 SUBSURFACE CONTAMINATION FROM POINT SOURCES 159, 159-67 (1999).

36. *See, e.g.*, Ludvigsen et al., *supra* note 34, at 273.

37. *See supra* note 27 and accompanying text.

of reduced product indicates that an electron-accepting reaction has occurred.

To give an example of this standard method, sulfate (SO_4) is a common solute in marine-influenced systems, such as coastal groundwater. It is reduced to hydrogen sulfide (H_2S). Dissolved H_2S is, therefore, present only in subsurface waters in which microbially-mediated sulfate reduction has occurred. The loss of sulfate coupled with the increase of sulfide, either over time or along a groundwater flowpath, demonstrates biodegradation by sulfate reduction. Sampling, preservation, and analysis of dissolved sulfate and sulfide are standard techniques, so this process is easily measured. In contrast, complete determination of the iron redox couple—that is, determination of both the initial (Fe^{3+}) and the reduced (Fe^{2+}) forms—is both impractical and unnecessary. Ferric iron (Fe^{3+}), a viable electron acceptor in microbially mediated biodegradation reactions, occurs in the mineral solids of the aquifer but has only minimal natural solubility. Ferrous iron (Fe^{2+}), however, dissolves and can be measured. The presence of significant levels of the reduced form is a clear indication of that the metabolic process occurred.

Even if one uses redox levels as indicators of service potential, it is difficult to set exact standards for essential chemical species and their abundances for successful biodegradation because not all aquifers contain all possible electron acceptors. In contrast to the marine example above, many freshwater aquifers contain only limited sulfate. Other electron acceptors may be more abundant and more efficient. For example, dissolved nitrate is a very efficient electron acceptor for reactions such as benzene biodegradation, and is much more common in shallow groundwater, or groundwater contaminated with agricultural chemicals or fecal wastes, than in deep or pristine groundwater. The absence of nitrate, though, does not mean that benzene will not biodegrade. The reaction can proceed by other electron-accepting reactions. For example, it might proceed by iron reduction, since iron is a common constituent of most sediments and soils.

In short, to assure the presence of a suite of microbially-mediated biodegradation reactions capable of acting on a variety of compounds—that is, conditions that would be able to provide water purification services for a wide variety of pollutants—a groundwater ecosystem should have a variety of electron receptors.

V. THE EFFECTS OF REMEDIATION ON PURIFICATION SERVICES

As discussed in the last section, there is a natural dynamic in groundwater ecosystems resulting from the process of degradation. As degradation proceeds and a variety of redox environments develop, a greater variety of microbial functions is in effect across the aquifer as a whole. Site remediation efforts may reverse the benefits of this redox zonation and the variety of biodegradation reactions possible in the aquifer. Introducing oxygenated groundwater and mixing groundwater within the aquifer homogenize the system, thereby reducing the variety of biodegradation reactions. Thus, site remediation efforts may reduce or destroy the potential for bacteria to provide water purification services.

The standard treatment of groundwater contamination at Superfund sites is pump-and-treat[38] and 93% of contaminated sites are treated *only* in this way.[39] While the pump-and-treat technology varies among sites in its effectiveness in removing the contaminant, it always has the effect of homogenizing the groundwater and eliminating or greatly reducing differences in redox potential. Moreover, if the treated water, still containing some contaminant, is injected outside the immediate area, then the contaminant plume spreads, potentially degrading larger volumes of groundwater. Thus, pump-and-treat technology does little, if anything, to improve the efficiency of biodegradation and, by spreading the plume, may make it worse. Pump-and-treat provides a short-term benefit—it eliminates a fraction of the contaminant, but it reduces or destroys the ability of the system to provide water purification services in the future.[40]

There is strong evidence that site remediation activities can disrupt desirable ecosystem function. As an example, consider the petroleum spill in Bemidji, Minnesota,[41] which has been under study for over nineteen years since the initial contamination occurred. Studies have focused on the long-term impacts of contaminant hydrocarbons on the chemical composition of Bemidji's groundwater and aquifer sediments, and on the evolution of redox zonation.[42]

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38. *See supra* Part II for an explanation of the method.

39. *See* NRC 1997B, *supra* note 13, at 37.

40. *See id.* at 18.

41. *See* William N. Herkelrath, *Impacts of Remediation at the Bemidji Oil-spill Site*, *in* U.S. GEOLOGICAL SURVEY WATER, PUB. NO. 99-4018C, 3 SUBSURFACE CONTAMINATION FROM POINT SOURCES 195, 195-200 (1999).

42. Redox zonation results from the electron acceptors being used up (reduced) in the sequence described in the previous section. Thus there are different zones where dif-

From upgradient oxygenated water, the chemical composition of the groundwater evolves to an iron-reducing composition first, and then further downgradient methanogenesis occurs. In Bemidji, natural microbially-mediated biodegradation of contaminant hydrocarbons in the groundwater led to reduced concentrations of benzene, toluene, and xylene, as might be expected. The most abundant electron acceptor in this system was ferric iron (Fe^{3+}), and the presence of dissolved reduced iron (Fe^{2+}) was readily determined, indicating that ferric iron was used in biodegradation reactions.[43] There was little dissolved nitrate or sulfate, however, so reactions that used these electron receptors were not possible. Biodegradation is now occurring via methanogenesis, the least effective biodegradation reaction, in portions of the aquifer.

The Bemidji site may soon provide evidence that remediation activities can disrupt desirable ecosystem function. State regulatory agencies have recently insisted that remediation be undertaken at the Bemidji site, and several pumping wells have been installed for pump-and-treat remediation efforts. The goal is to remove the separate-phase oil, which will require pumping large amounts of groundwater. The groundwater pumping is likely to produce local reversals in groundwater flow direction which, combined with pumping, will act to mix the currently stratified redox zones in the aquifer. As a result, the remediation effort will "change the ground-water flow regime and alter the subsurface conditions that have resulted in natural biological degradation of dissolved contaminants."[44] The pump-and-treat effort is expected to remove about 17% of the oil in the aquifer, but it will probably destroy the aquifer's remaining ability to degrade contaminants.

VI. Alternative Methods of Restoring Purification Services

As described in the preceding section, the removal of contaminants with pump-and-treat technology imposes an ecosystem service cost. This short term fix has long term and potentially counterproductive consequences because it disturbs biogeochemical conditions (i.e., it homogenizes the redox environments). In

ferent electron acceptors (*e.g.*, oxygen, SO4, Fe3+) predominate in redox reactions. *See* William H. Schlesinger, Biogeochemistry: An Analysis of Global Change 231-42 (1997) for a readable account of redox reactions in natural environments.

43. *See* discussion *infra* Part IV.

44. *See* Herkelrath, *supra* note 41.

this part, we consider the criteria for methods that avoid such effects, and propose alternatives to pump-and-treat remediation.

To minimize organic pollutants and maximize biodegradative capacity, two requirements must be satisfied. First, the appropriate microbes capable of carrying out the biodegradation must be present. Second, the appropriate electron acceptors must be present. But in some cases, bacteria capable of using preferred degradative reactions may not be available. The chemical environment sometimes indicates that sulfate reduction, which is energetically favorable, should be occurring, but microcosm tests indicate that methanogenesis is occurring.[45] These results may be unreliable, though.[46] There are only a few well-documented situations where the appropriate microbes are not present, probably because the metabolic capabilities of subsurface organisms are quite diverse.[47] Thus, while there is not universal agreement on this point, it appears that the rate-limiting step for biodegradation is usually the availability of electron acceptors.

There are several innovative technologies that augment the natural processes of degradation, termed "natural attenuation" in the remediation literature. To compensate for the loss of electron acceptors due to degradation, electron acceptors, such as nitrate or suspended iron oxide minerals, can be added to the aquifer. Other factors that influence biological activity also can be enhanced. Some have attempted to add nutrients like nitrate and an alternative energy source, such as acetate, at a number of sites.[48] Bacterial strains selected for their particular ability to carry out a specific biodegradation reaction can also be added to the native microbial community, although in an unengineered situation this approach

45. *See* Lorah & Olsen, *supra* note 31, at 3824.

46. The nature of the reaction cannot be known with certainty because of the extraordinary difficulty in obtaining a measure of ongoing metabolic activity in the aquifer, and attempts to culture bacteria almost certainly lead to biases because of the differential abilities of various bacterial strains to be cultured.

47. *See, e.g.*, Edward J. Bouwer, *Microbial Remediation: Strategies, Potentials, and Limitations*, *in* INTEGRATED SOIL AND SEDIMENT RESEARCH: A BASIS FOR PROPER PROTECTION 533, 533-544 (H.J.P. Eijsackers & T. Hamers eds., 1993).

48. For synthesis of new biomass, all living organisms require the matter with which to build biomass, like carbon (C), nitrogen (N), sulphur (S), etc., and an energy source (i.e., a source of electrons) in addition to electron acceptors. Lack of any of these constituents can limit degradation. If nitrogen for protein synthesis is lacking, for instance, the addition of nitrate supplies that need. If the microorganism cannot use the contaminant compound as an energy source, then an alternative energy source, like acetate, is a critical amendment.

has not been shown to be effective.[49]

Understanding the character of a successfully functioning microbial ecosystem has been the goal of research at a number of contaminated sites. The interaction of chemical and physical characteristics of aquifers with the microbial community shows that most of the conditions required for appropriate populations of microorganisms are likely to be found at most sites.[50] As discussed above, the effectiveness of the microorganisms depends upon the development of redox zonation, and the availability of electron acceptors could be considered in devising novel methods of restoration that maximize groundwater-ecosystem function. We are not, however, aware of any reports that speak to attempts to restore groundwater-ecosystem function, or that evaluate attempts to establish a functioning microbial ecosystem as part of site remediation efforts. Future research involving the manipulation and monitoring of functioning microbial ecosystems could provide key insights.

Perhaps the most vexing issue in groundwater remediation is the question of time. Because groundwater, with the exception of some karst aquifers, moves at a rate of a few centimeters a day or less, biodegradation occurs slowly. For example, at a site near Aberdeen, Maryland, organic solvents that contaminated the groundwater took ten years to move a few hundred meters to a creek.[51] At the Bemidji petroleum spill, populations of iron- and manganese-reducing bacteria, a major component of the biodegradative process, did not reach maximum size for twelve years following the spill, and methanogens still have not reached a maximum population level after twenty years of monitoring.[52] Even when bench-top microcosms were used to demonstrate reasonably rapid biodegradation rates for polycyclic aromatic hydrocarbons, contami-

49. *See* NATIONAL RESEARCH COUNCIL, IN SITU BIOREMEDIATION: WHEN DOES IT WORK? 2-3 (1993).

50. *See* Barbara A. Bekins et al., *Chemical and Physical Controls on Microbial Populations in the Bemidji Toxics Site Crude-oil Plume, in* U.S. GEOLOGICAL SURVEY, PUB. NO. 99-4018C, 3 SUBSURFACE CONTAMINATION FROM POINT SOURCES 133, 133-42 (D.W. Morganwalp & H.T. Buxton eds., 1999).

51. *See* Michelle M. Lorah et al., *Natural Attenuation of Chlorinated Volatile Organic Compounds in a Freshwater Tidal-Wetland, Aberdeen Proving Ground, Maryland, in* U.S. GEOLOGICAL SURVEY, PUB. NO. 97-4171, WATER RESOURCES INVESTIGATION REPORT (1997); Telephone Interview with Michelle M. Lorah, Research Hydrologist, U.S. Geological Survey (Oct., 2000).

52. *See* Barbara A. Bekins et al., *Progression of Natural Attenuation Processes at a Crude Oil Spill Site: Controls on Spatial Distribution of Microbial Populations* (2000) (unpublished manuscript, on file with authors).

nant persistence *in situ* was far longer.[53] A decades-long view is essential to look at restoration of ecosystem function.

Even when a long-term view of groundwater cleanup is taken, pump-and-treat technology sacrifices long-term gain for short-term gain. The long-term sacrifice occurs because of the disruption of redox zonation. There are technologies available that would seem to accelerate the natural process of biodegradation (natural attenuation), often by increasing the availability of electron acceptors. Air sparging which results in increased availability of oxygen as an electron acceptor as well as removing volatile organic compounds is but one example.[54] The goal of these technologies is to maximize the long-term rate of biodegradation.

VII. Conclusion

In this study, we have argued that pump-and-treat remediation, the dominant remediation approach, may sometimes succeed in removing many of a site's contaminants but, in doing so, significantly reduces the ability of the site to break down remaining and future contaminants. Ironically, in attempting to clean up the site we simultaneously may degrade the very service we most value—water purification. Innovative technologies such as air sparging and bioremediation will typically be far more effective in maintaining and restoring groundwater ecosystem functions than pump-and-treat methods. While more common in the cleanup of leaking underground storage tanks than in the past, the use of these technologies at CERCLA sites is still rare.[55] CERCLA clearly provides authority to restore and protect contaminated sites' ecosystem services. The next step is to undertake the focused scientific research necessary to develop accurate and practical indicators of service provision. To do so, however, first requires recognizing the value of these services that makes them worth protecting.

53. *See* Edward J. Bouwer et al., *Biodegradation of Coal Tar Constituents in Aquifer Sediments*, *in* Soil and Aquifer Pollution 173, 173-90 (Hillel Rubin et al. eds., 1998).

54. *See* NRC 1997b, *supra* note 13, at 92.

55. *See* NRC 1997b, *supra* note 13, at 19 (concluding that "[t]he reasons for the limited use of new ground water cleanup technologies are complex. They include regulatory programs that inhibit market development, lack of consistent data on technology cost and performance, and the uniqueness of each contaminated site.").