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8 October 1996

U.S. Environmental Protection Agency
Region III
841 Chestnut Building
Philadelphia Pennsylvania 19107

Attn: Mr. Frank Klanchar (3HW22)
Remedial Project Manager

Re: Elizabethtown Landfill Superfund Site
Docket No. III-90-44-DC
Information Regarding Natural Attenuation & Monitoring

Mr. Klanchar:

I enclose for your information the following articles/information which relate to natural attenuation and monitoring which I thought might be of interest to you regarding the Elizabethtown Site.

- Article entitled "In Situ Bioremediation: Defining the Limits", by Stephen Hart, taken from Environmental Science & Technology, September 1996 (Vol.30 No. 9);
- Article entitled "Environmental Isotope Characteristics of Landfill Leachates and Gases", by Hackley, Liu, & Coleman, taken from Ground Water, September-October 1996 (Vol. 34, No.5);
- Copies of handouts from a recent presentation by Peter Feldman, OSWER, USEPA taken from "Seminar Series on Bioremediation of Hazardous Waste Sites: Practical Approaches to Implementation"; and
- Copy of discussion paper entitled "Introductory Talk: Where Are We Now With Public And Regulatory Acceptance? RCRA and CERCLA", by Lovelace and Feldman, OERR, USEPA.

It seems that quite a bit of attention is being given to this subject, both from the EPA and the environmental scientific community. I must receive at least a paper a week regarding the prospect of this technique as a viable alternative, considering other factors are met. These other factors usually relate to alternative water supplies and source control. Since these are the very issues contemplated in the Alternative Remedial Plan (ARP) for the Elizabethtown Site, I thought the articles may be pertinent to the upcoming remedy decision-making process.

I will contact you soon to schedule the meeting to review the ARP and potential monitoring program components for the Elizabethtown Site. Until then, please feel free to contact me with any questions.

Sincerely,

Treva J. Houser
Remedial Projects Manager

AR308110

In Situ Bioremediation: Defining the Limits

New approaches to engineered and intrinsic bioremediation are being developed and field tested.

STEPHEN HART

Promoted as less expensive and faster than other cleanup methods but questioned for its effectiveness and applicability, in situ bioremediation has yet to fulfill its potential. A 1993 National Research Council (NRC) report sought to "eliminate the mystery that shrouds this highly multidisciplinary technology" (1). Since then, researchers have tried to clear up the uncertainty and expand the applications of this technology. A renaissance in the field of microbial ecology, fueled in part by the advent of molecular genetics, has led to new efforts to selectively engineer the growth of on-site organisms and quantify their effectiveness in biodegrading contaminants in soil and water.

"There's a tremendous excitement in what one would call questions of microbial ecology," said Bruce E. Rittmann, professor of environmental engineering at Northwestern University and chair of the NRC report committee. "This is not so much about genetics or the details of biochemistry but the things that control what organisms are selected, what organisms are dominant in a given environment. Because what you're really doing in in situ bioremediation is creating environments that are conducive to the right organisms doing our work." Microbial populations at contaminated sites have been able to degrade hydrocarbons, chlorinated solvents, phenols, polychlorinated biphenyls (PCBs), and certain pesticides (1).

In situ bioremediation is no panacea, researchers emphasize. Bacteria may not degrade all contaminants, or they may degrade them too slowly to be practical. And some degradable contaminants may not be available to organisms because, for example, they are too tightly bound to soil particles. For these and similar reasons, bioremediation researchers now consider containment rather than cure (2).

"Bioremediation is not the 'silver bullet' that will cure all waste sites," said Edward J. Bouwer of Johns Hopkins University. "As long as we have 'health-

based' cleanup standards, it is extremely difficult for any current technology to meet the low standards." But despite its limitations, Bouwer sees promise for the process. "The Europeans have been using bioremediation with success for many years now, both above ground and in situ. So in the context of remedial options, bioremediation is certainly among the viable technologies."

Engineered bioremediation applications

"Bioremediation has been quite successful for controlling hydrocarbon contamination," noted Bouwer. A leaking gasoline storage tank, a common contamination problem, can create a pool of gasoline in the soil near the groundwater table. Without remediation, Rittmann said, "It will serve as a source of pollution into the water, forever, almost." Some soil bacteria can degrade hydrocarbons such as gasoline by using the pollutant as an energy and carbon source. But these reactions require oxygen, generally in short supply deep underground.

"There are all kinds of organisms everywhere," Rittmann said. "If you provide the right environment, and you give them plenty of oxygen—they've got the hydrocarbon from the gasoline in ample quantity—the right organisms will grow and they will essentially surround the contamination."

Two methods of supplying oxygen to organisms, bioventing and sparging, have become widely used methods of engineering in situ bioremediation at moderately contaminated sites. In bioventing, several wells are sunk into relatively porous soils, and air is drawn down through the soil. The wells can also deliver water and nutrients deep underground. The contaminated area gradually shrinks as bacteria degrade the gasoline.

If the gasoline has reached the water table, bioventing works less well, and sparging can be used to supply oxygen. Engineers pump compressed air into the water table; the air then diffuses upward. "You can view it as bubbling up into the water and sup-

plying oxygen from below," Rittmann said.

Whereas these bioremediation technologies rely on stimulating the growth of any oxygen-loving bacteria at a contamination site, other engineered bioremediation strategies being developed attempt to foster particular microbes. Three decades of research about the molecular biology and genetics of biodegradation have produced a long list of particular microbes that can degrade particular compounds. The list includes such compounds as benzenes, dioxins, DDT, PCBs, styrene, and xylenes, as well as explosives, tires, and plastic-based aircraft paint.

Targeting specific microbes

"Probably most exciting is the bioremediation of chlorinated solvents, things like trichloroethylene (TCE) and trichloroethane," said Rittmann. "There's a tremendous amount of research going on right now, and it's beginning to get into field studies."

One field test of TCE degradation, at the Department of Energy's Savannah River site, relies on fundamental research into biodegradation, engineered bioremediation, and clever monitoring. Gary S. Saylor of the Center for Environmental Biotechnology at the University of Tennessee in Knoxville detailed his laboratory's work at this site at the annual meeting of the American Society for Microbiology in May. "Historically, we take organisms from the environment, we find out who they are, how they degrade the compound, what's the biochemistry, what genes are involved," Saylor said.

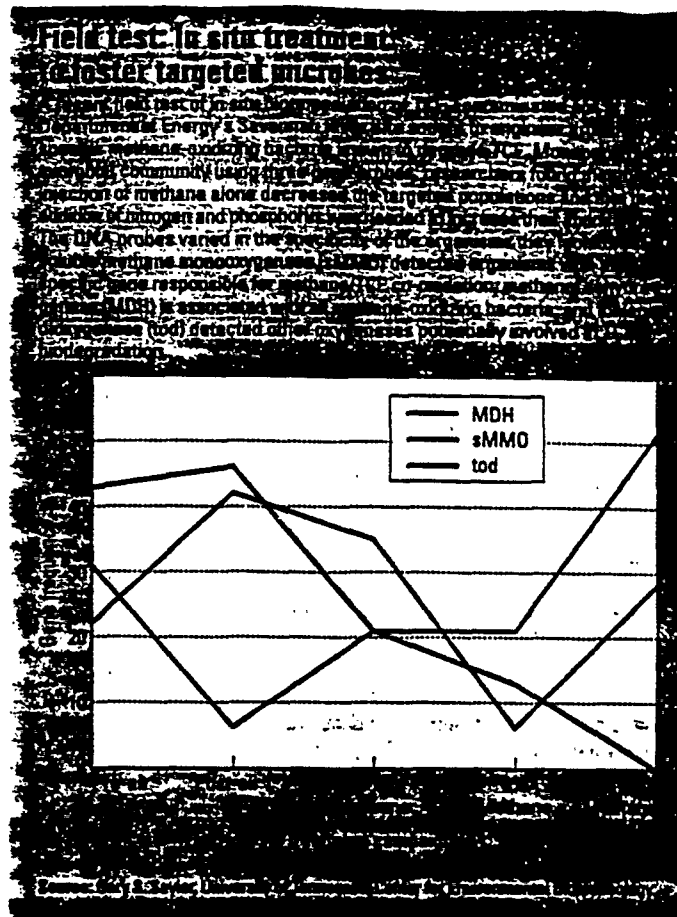
Out of basic research on biodegradation has come the knowledge that certain bacteria can degrade TCE to an oxide that subsequently breaks down hydrolytically. The enzyme responsible is part of a group that allows bacteria called methanotrophs to use methane as an energy source. The first enzyme in this pathway, called soluble methane monooxygenase, can also degrade TCE (3). The resultant intermediates eventually kill the bacteria, so only a healthy, growing population of methanotrophs could effectively clean up a TCE-contaminated site.

The two-year Savannah River field test, completed in 1994, consisted of pumping gases into the site through horizontal wells. Researchers began with air, added 1% methane, and finally increased the methane content to 4%. Saylor's monitoring of specific microbial populations in soil samples revealed a surprising result: The methane and air alone did not appear to boost the TCE-degrading microbes. The methanotrophs did not respond to the addition of methane until "fertilizer" in the form of gaseous nitrogen and phosphorus was also added (see figure).

"Not until they added essentially balanced nutrients did those samples respond and the organisms really proliferate in the sediment matrix itself," Saylor said. On the basis of more than 200 samples, he estimates that adding methane plus the two fertilizer gasses caused TCE remediation to increase 20-30% above the baseline over the two years.

Effectiveness of intrinsic bioremediation

Because engineered bioremediation systems can be costly, a newer, cheaper approach has attracted a great deal of interest in the past few years. If bacteria capable of biodegradation already exist in soils,



might they grow even without the engineered addition of oxygen and other nutrients? This question led to the concept of intrinsic bioremediation, or natural attenuation. Intrinsic remediation may sound at first like a pipe dream of potentially responsible parties hoping to avoid costly cleanups, but Rittmann said the approach works in certain cases. "It requires a very careful assessment of the site," he said. The site must have a relatively high natural supply of oxygen and nutrients, often resulting from a good groundwater flow rate, and the source of contamination must be relatively small.

Monitoring results, important in engineered bioremediation, becomes even more so in intrinsic bioremediation. "It requires a very well-designed monitoring system to ensure that the intrinsic activity is sufficient. The trick, of course, is that you have to remember the monitoring part," Rittmann insisted.

Saylor described an inadvertent demonstration of intrinsic bioremediation at a muddy Air Force site in Mississippi in 1993. "It was uncontaminated," he said, "until the Air Force did a deliberate injection of tritium and carbon-14-labeled xylene into this site for the purposes of tracking and looking at the mobility of these test contaminants under a realistic hydrodynamic regime."

With 300 monitoring wells spread across the site, the scientists could effectively track the marker substances. As expected, the tritium traveled with the groundwater, moving down gradient, and the xylene stayed near the point of injection, sticking to the

Intrinsic bioremediation: Effective option or gross negligence?

While there are a number of bioremediation, or natural attenuation, options available, the topic of a heated debate that is spreading across the globe (<http://www.ozsa.com>) in January 1996 from the United States, which began with a message from Mental Air, is now represented below.

It is not a panacea, nor is it a new technology. So-called "natural attenuation" is not treatment but gross negligence, the environmental equivalent of our Bosnian policy. *—Suzanne Lesage, Environment Canada, NWRI, Burlington, Ontario*

Natural attenuation is neither a treatment panacea nor is it a "wait and see" approach. Successful implementation involves significant up-front, as well as follow-up, work to ensure contaminants of concern are being destroyed at reasonable rates. This is clearly a reasonable approach at sites where the source has since been removed and there is a low risk for potential receptors. *—Richard Schaffner, Jr., P.E., GZSooEnvironmental, Inc., Manchester, N.H.*

There are many cases where leaving [benzene-toluene-ethylbenzene-xylene] BTEX in the ground makes sense, especially sites that have characteristics allowing reduced risk of exposure. When risk assessment is paired with cost-benefit analysis, gross negligence would be excavating 40 feet of BTEX-laden clay that poses little or no risk to human health and the environment. *—Maureen Leavitt, Science Applications International Corporation, Oak Ridge, Tenn.*

Natural attenuation is neither a panacea, a conspiracy, nor a new technology. What is new is more widespread understanding of the fundamental processes which cause the occurrence of natural attenuation. *—Richard A. Helmert, P.E., CH2M HILL, Santa Ana, Calif.*

There is a place for allowing biological remediation at some sites, but one important factor in thinking intrinsic bioremediation is to come up with treatments that are biocompatible. Some physical-chemical techniques leave the soil essentially sterile. We should move away from that, toward a more integrated approach. *—Suzanne Lesage, Environment Canada, NWRI, Burlington, Ontario*

"Intrinsic is an option, but to show it is occurring and viable as a remediation strategy is not trivial. We have been monitoring a BTEX plume for five years and have measured intrinsic biodegradation rates in situ. But one of our conclusions is that individual boreholes are not able to show that a plume is stable or shrinking. Better/cheaper monitoring options are needed. *—Greg Davis, Centre for Groundwater Studies, Western Australia*

soil particles. "However, if they looked at the carbon-14 associated with xylene, it was smeared all the way down gradient just like the tritium was," Saylor reported. The carbon-14 label, originally marking xylene, traveled with groundwater and showed up in samples taken all along the gradient, far from the site of injection.

Saylor explained that after about 200 days of study, when the carbon-14 measurements were taken, intrinsic bacteria had degraded most of the carbon-14-labeled xylene into inorganic carbon, which is as free to move as tritium. After about 400 days, virtually all of the pollutants had disappeared.

Role of microbes in wetlands

Most people think of soil and groundwater as candidates for intrinsic bioremediation, but the process also takes place in wetlands. Alex Horne, professor of civil and environmental engineering at the University of California—Berkeley, has studied a 2000-acre wetland on the Santa Anna River in southern California. Horne decided to "see what nature will give us if we give it a tweak," he said.

The Santa Anna River suffers from severe nitrate-nitrogen (nitrate-N) and chlorinated hydrocarbon pollution. During some parts of the year, most of the river's water comes from upstream water treatment plants. The river also flows through the highest concentration of dairies in the United States. Downstream, Orange County pumps the water into wells to recharge aquifers.

Degrading nitrate-N is not a difficult trick for bacteria, given the right conditions. Horne found that areas experimentally planted with cattails reduced nitrate-N nearly four times as much as areas planted with bulrushes, from about 8 milligrams/liter to less than 1 (4). When flow drops during the summer, nitrate-N levels could reach 10 milligrams/liter, which can cause the so-called blue baby syndrome in humans. Bacteria degrade nitrate-N under low-oxygen conditions created in the layer of loose, leafy detritus just above the bottom. By supplying bacteria with plenty of organic carbon in the form of detritus and, perhaps more important, organic carbon secreted by algae, and with the proper oxygenation conditions, particular wetland plants can foster a wide variety of biodegradative bacteria (5).

New monitoring tools needed

In engineered and intrinsic bioremediation, the difficult question is how to determine if the remediation process is working below the surface. In the gasoline leak scenario, for example, groundwater samples could be taken and decreases in hydrocarbons measured, but only some of the gasoline dissolves in water, so these measurements will not give a complete picture of biodegradation activity.

Consequently, indirect or surrogate measurements are being developed to supply these answers. Rittmann and his colleagues are developing protocols for in situ bioremediation monitoring. "Normally, you can't rely on just one measurement. So what we're doing is trying to put together a rational suite of different kinds of measures," he said.

The biodegradation of hydrocarbons uses oxygen and releases carbon dioxide. Researchers would therefore expect to see a decrease in oxygen and an increase in CO₂, indicating aerobic biodegradation is taking place. But Rittmann advocates a more systematic approach. For example, his monitoring protocol takes measures of oxygen and CO₂ one step further by making a comparison between the number of molecules of oxygen lost and the number of molecules of CO₂ gained. He has also added another twist to measurements of inorganic carbon produced by bioremediation.

Carbon dioxide in the subsurface can be produced from the breakdown of hydrocarbons by organisms and from the dissolving of calcium carbonate rocks, which makes it difficult to correlate CO₂ lev-

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els with biodegradation. Rittmann's team addresses this problem by measuring the ratio of two stable isotopes of carbon: carbon-12 and carbon-13. The ratio of carbon-13 to carbon-12 differs in CO₂ derived from different sources. Petroleum hydrocarbons contain less carbon-13 than do calcareous rocks. The difference is large and detectable with a mass spectrometer. A given water sample could have a carbon-13 to carbon-12 ratio resembling that of hydrocarbons, rock, or something in between, indicating a mixture of sources.

The most recent technology added to Rittmann's integrated suite of monitors moves from measuring the effects of biodegrading bacteria to measuring the bacteria. Borrowing a tool from the field of molecular microbial ecology, Rittmann's team uses nucleic acid probe technology to detect the ribonucleic acid (RNA) of bacterial ribosomes, cellular structures involved in protein synthesis.

The technique overcomes the problems of standard enumeration methods, which require growth of a culture, by directly detecting the organism in situ. The probe uses small pieces of nucleic acid custom-made to make complementary bonds to known sequences of ribosomal RNA. By using probes specific for the bacterial species suspected of carrying on the bioremediation, researchers can add one more confirmation to the integrated mix of measurements (6).

At the Savannah River experiment in engineered bioremediation, Sayler's group extracted nucleic ac-

ids from soil samples—by using probe technology similar to that used by Rittmann—to detect the presence of the soluble methane monooxygenase gene. But the gene probe detected only the presence of organisms possessing the soluble methane monooxygenase gene, not whether that gene became active to produce messenger RNA (mRNA) and eventually the enzyme itself. A member of Sayler's lab responded by developing a method to directly measure soluble methane monooxygenase mRNA in bulk soil samples.

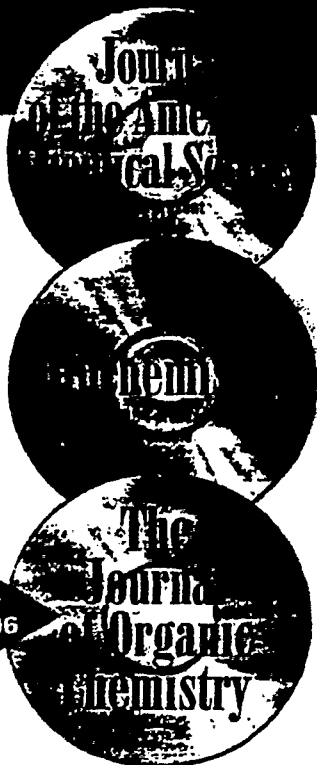
"In various depths from various wells, we could indeed show that the soluble methane monooxygenase RNA molecules could be quantified," Sayler said. "It gives us hope that we can look at not only the abundance of degradative genes responsible for metabolism, but also the kinetics relative to gene expression under field conditions."

References

- (1) Rittmann, B. E. et al. *In Situ Bioremediation*; 2nd ed.; Noyes Publishers: Park Ridge, NJ, 1994.
- (2) National Research Council. *In Situ Bioremediation: When Does It Work?* National Academy Press: Washington, DC, 1993.
- (3) Trombly, J. *Environ. Sci. Technol.* 1995, 29, 560A.
- (4) Horne, A. J. *Water Sci. Technol.* 1995, 31, 341-51.
- (5) Widrig, D. L.; Gray, K. A.; McAuliffe, K. S. *Water Res.*, in press.
- (6) Raskin, L. et al. *Appl. Environ. Microb.* 1994, 60, 1232-40.

Stephen Hart, author of *The Language of Animals* (Henry Holt, 1996), is a science writer and editor based in Port Angeles, Wash.

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Environmental Isotope Characteristics of Landfill Leachates and Gases

by K. C. Hackley^a, C. L. Liu^a, and D. D. Coleman^b

704
October 1996

Abstract

The isotopic characteristics of municipal landfill leachate and gases (carbon dioxide and methane) are unique relative to the aqueous and gaseous media in most other natural geologic environments. The $\delta^{13}\text{C}$ of the CO_2 in landfills is significantly enriched in ^{13}C , with values as high as $+20\text{‰}$ reported. The $\delta^{13}\text{C}$ and δD values of the methane fall within a range of values representative of microbial methane produced primarily by the acetate-fermentation process. The δD of landfill leachate is strongly enriched in deuterium, by approximately 30‰ to nearly 60‰ relative to local average precipitation values. This deuterium enrichment is undoubtedly due to the extensive production of microbial methane within the limited reservoir of a landfill. The concentration of the radiogenic isotopes, ^{14}C and ^3H , are significantly elevated in both landfill leachate and methane. The ^{14}C values range between approximately 120 and 170 pMC and can be explained by the input of organic material that was affected by the increased ^{14}C content of atmospheric CO_2 caused by atmospheric testing of nuclear devices. The tritium measured in leachate, however, is often too high to be explained by previous atmospheric levels and must come from material buried within the landfill. The unique isotopic characteristics observed in landfill leachates and gases provide a very useful technique for confirming whether contamination is from a municipal landfill or some other local source.

Introduction

The prevention of ground-water pollution is the primary objective of environmental protection codes for municipal waste landfills. The early detection of ground-water pollution and the determination of the source of contaminants is important when considering cleanup or containment programs as well as legal issues that are frequently associated with polluted ground water. Municipal landfills are often located in areas where other sources of contaminants exist, such as hazardous waste disposal facilities, chemical industries, sewage treatment facilities, buried pipelines carrying petroleum or natural gas, and highways where road deicing salts are applied. In some areas, especially the midwestern U.S., the subsurface sediments contain significant amounts of buried organic material where natural microbial processes produce notable amounts of methane (Meents, 1960; Simpkins and Parkin, 1993). When multiple sources of contaminants usually used to identify landfill leachate, such as heavy metals, chlorides, and hydrocarbons, are present near a landfill, the interpretation of chemical data from monitoring wells around the landfill may be complicated. This type of situation

could result in delaying early identification of landfill gas or leachate contamination.

This paper advocates the use of environmental isotope analysis of the major constituents of landfill gas (CO_2 and CH_4) and leachate (water and dissolved inorganic carbon) as a technique for definitively identifying landfill contamination. The stable and radiogenic isotope characteristics of carbon dioxide, methane, and associated leachates generated within municipal landfills are quite unique relative to the gaseous and aqueous media found in most surrounding environments (Coleman et al., 1993; Liu et al., 1992; Rank et al., 1992). Although there have been many studies involving environmental isotopes in hydrologic and geochemical investigations of the natural environment, there have been only a few applications of environmental isotope analysis to landfill studies.

The following discussion briefly reviews some relevant aspects of environmental isotopes and then examines the unique isotopic characteristics of carbon, hydrogen, and oxygen in leachates and gases obtained from published and unpublished data from several different landfills. We do not go into much detail about case studies but instead wish to emphasize the typical isotopic compositions that can be expected in gases and leachates of municipal landfills and how such data can be used. We also address some of the reasons why the leachate and gases from landfills have such characteristic isotopic values. The unique isotopic characteristics observed in landfill leachates and gases provide a very useful technique for confirming whether contamination in the subsurface environment is from a municipal landfill or some other local source.

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Environmental Isotopes (General Background)

Environmental isotopes generally refer to the naturally occurring isotopes of hydrogen (^1H , ^2H , and ^3H), carbon (^{12}C , ^{13}C , and ^{14}C), oxygen (^{16}O and ^{18}O), sulfur (^{32}S and ^{34}S), and nitrogen (^{14}N and ^{15}N). In this paper the characteristics of ^{13}C , ^2H (deuterium, D), ^{18}O , ^{14}C , and ^3H (tritium) are presented for both landfill leachates and gases. Sulfur and nitrogen isotopes were not examined since sulfate and nitrate concentrations were usually very low in most of the leachates we collected. However, Fritz et al. (1994) have shown that, in cases where sulfate concentrations are sufficient, sulfur isotopes could be quite useful in landfill studies.

Notation

The stable isotope data are expressed in the conventional "delta" (δ) notation, which is the per mil (‰ , parts per thousand) difference in the ratio of the less abundant isotope to the most abundant isotope in a sample relative to the same ratio in a known standard. This is illustrated in the following equation,

$$\delta X_{(\text{sample})} = [(R_{\text{sample}} - R_{\text{standard}}) / R_{\text{standard}}] \cdot 1000$$

where δX represents the isotope of interest ($\delta^{13}\text{C}$, δD , or $\delta^{18}\text{O}$); and R represents the ratio of $^{13}\text{C}/^{12}\text{C}$, $^2\text{H}/^1\text{H}$, or $^{18}\text{O}/^{16}\text{O}$. The reference standard used for reporting the carbon results is the internationally accepted standard PDB (Peedee Belemnite) as defined by Craig (1953). The reference standard for the hydrogen and oxygen results is V-SMOW [Vienna-Standard Mean Ocean Water, Hoefs (1980)] originally defined by Craig (1961a).

The results of the tritium (^3H , $T_{1/2} = 12.4$ yrs) and carbon-14 (^{14}C , $T_{1/2} = 5730$ yrs) data are reported in "tritium units" (TU) and percent modern carbon (pMC), respectively. One TU is defined as one ^3H atom in 10^{18} H atoms. For ^{14}C , the reference standard material is, by convention, defined as 100% modern and represents the "normal" ^{14}C content of the atmosphere, prior to anthropogenic effects.

$\delta^{18}\text{O}$ and δD in Water

Oxygen and hydrogen isotopes in precipitation around the world generally follow a consistent relationship characteristic of latitude and climatic conditions (Craig, 1961b). This relationship results in a straight line, referred to as the "Global Meteoric Water Line" (MWL) and is represented by the following equation:

$$\delta\text{D} = 8 \cdot \delta^{18}\text{O} + 10$$

The oxygen and hydrogen isotopes are generally nonreactive in shallow ground-water systems, and the $\delta^{18}\text{O}$ and δD values are normally preserved after the precipitation enters the ground-water flow system. The conservative nature of $\delta^{18}\text{O}$ and δD allows these isotopes to be used as tracers in leakage or mixing studies between two reservoirs of water that are isotopically distinct (Hendry, 1988; and Fritz et al., 1976).

There are some physical and chemical processes which do affect the isotopic composition of the water subsequent to precipitation and can cause deviations from the meteoric line. Figure 1 shows the MWL and how the isotopes of the water are affected by certain physicochemical processes such as: evaporation, high- and low-temperature exchange reactions with rock minerals, hydration of silicates, CO_2 -exchange reactions, H_2S -exchange reactions, and, we have added, methanogenesis. The most important process, when considering isotopic alteration of

water in landfill environments, is methanogenesis, which is discussed in a later section.

$\delta^{13}\text{C}$ and δD of CH_4 , CO_2 , and DIC (Dissolved Inorganic Carbon)

The isotopic composition of methane ($\delta^{13}\text{C}$ and δD) is useful for distinguishing different sources of methane gas produced in the natural environment (Fuex, 1977; Stahl, 1977; Coleman et al., 1977; Schoell, 1980; Barker and Fritz, 1981; Rice and Claypool, 1981; Coleman et al., 1981; Whiticar et al., 1986; Coleman et al., 1988; Grossman et al., 1989; Simpkins and Parkin, 1993; and others). The majority of methane (CH_4) in nature is formed by two principal processes, thermal decomposition of organic matter and microbial decomposition of organic matter. These two processes fractionate both the carbon and hydrogen isotopes to different degrees resulting in fairly distinct isotopic compositions for the different sources of CH_4 . The $\delta^{13}\text{C}$ of thermogenic CH_4 generally ranges between -25‰ and -60‰ , while the $\delta^{13}\text{C}$ of microbial methane generally ranges between -50‰ and -90‰ (Fuex, 1977; Schoell, 1980; Whiticar et al., 1986).

During microbial generation of CH_4 , referred to as methanogenesis, the CH_4 is enriched in the lighter carbon isotope (^{12}C) and the CO_2 associated with microbial methane production is enriched in the heavier isotope (^{13}C). The two primary metabolic pathways by which microbial methane is produced are CO_2 -reduction and fermentation of acetate and other simple organic substrates (Whiticar et al., 1986). The methane produced by each of these metabolic pathways has different isotopic characteristics. The typical ranges for $\delta^{13}\text{C}$ and δD are approximately -60 to -95‰ and -160 to -250‰ , respectively, for the CO_2 -reduction pathway, and approximately -47 to -63‰ and -275 to -375‰ , respectively, for methane generated by the acetate-fermentation pathway (Whiticar et al., 1986).

Tritium

Prior to the 1950s, the ^3H content in the atmosphere is estimated to have been 5 to 10 TU (Payne, 1972). After the atmospheric testing of thermonuclear devices in the early 1950s through the 1960s, the ^3H content in the atmosphere was

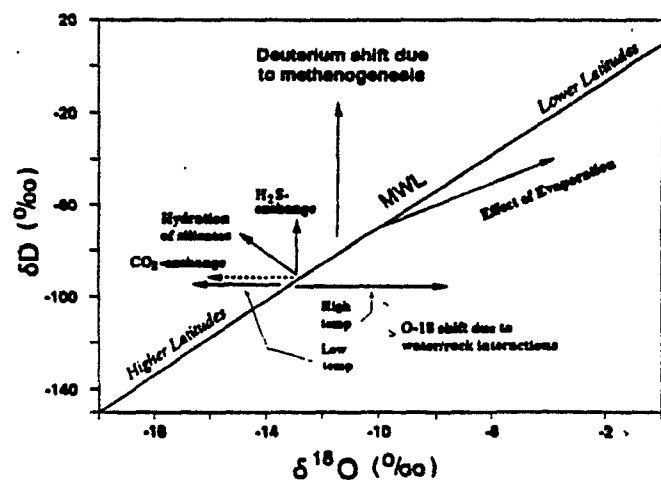


Fig. 1. Plot of Meteoric Water Line showing the effects of certain physicochemical processes on the isotopic composition of the water (modified from IAEA T.R.S. No. 228, 1983).

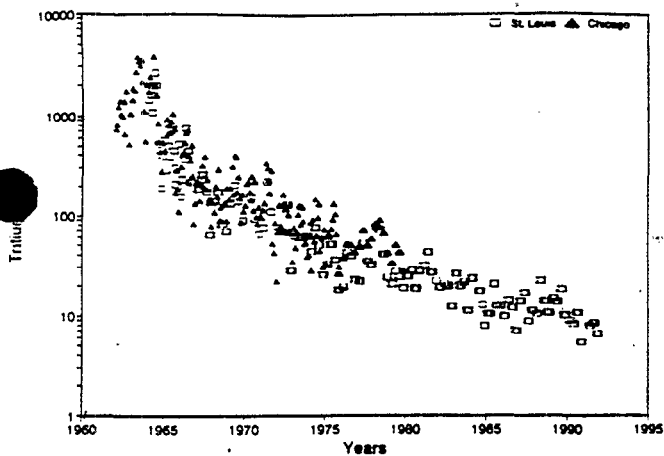


Fig. 2. Concentration of tritium in precipitation versus time in years for St. Louis, MO, and Chicago, IL (IAEA, 1969-1994).

increased to many hundreds and sometimes thousands of TU depending on geographic location (Gat, 1980). The largest concentration of tritium in precipitation was recorded in 1963 for the northern hemisphere. After atmospheric testing of thermonuclear devices stopped in the late 1960s a continuous decrease in the ^3H concentration of the atmosphere has been recorded. Figure 2 shows the tritium content of precipitation for the midwestern U.S., collected at St. Louis, Missouri, and Chicago, Illinois, from 1962 to 1991. The recent, mean tritium concentration, based on annual amounts of precipitation from 1986 to 1991 in St. Louis, averaged about $11.5 \text{ TU} \pm 3 \text{ TU}$ (IAEA, 1990 and 1994).

Landfills constructed in the 1950s to 1970s would have received precipitation enriched in ^3H , which could make this isotope useful as a tracer for identifying ground water contaminated by leachate migration. Using tritium as a tracer for landfill leachate based on historical concentration levels of ^3H in precipitation assumes that a significant portion of the initial water in the landfill from precipitation is trapped and has a relatively long residence time due to the construction of artificial or natural clay liners. As the landfill is filled with refuse and capped there should, theoretically, be less dilution of ^3H in the leachate than in the ground water and surface water in the area surrounding the landfill. The leachate would thus be expected to have a relatively higher concentration of ^3H than surrounding ground water. Tritium results from ground water surrounding landfills have been used in the past to calculate travel times of leachate contaminated ground water assuming tritium concentration in leachates are directly connected to the historical tritium record associated with past precipitation (Egboka et al., 1983 and Fritz et al., 1994). However, in view of the amount of tritium measured in leachates from several different landfills (reported in a later section) the practice of interpreting tritium concentrations at municipal landfill sites based on historical precipitation levels may be misleading.

Carbon-14

The ^{14}C content of the atmosphere also increased due to atmospheric testing of thermonuclear devices (Figure 3). This increased atmospheric ^{14}C concentration is important for recent landfills because a significant amount of the organic material

being put into landfills probably originated from plants that grew in the last 40 years which would therefore have elevated ^{14}C concentrations. Thus, gases produced from recently buried refuse will reflect the enriched ^{14}C content and have significantly higher ^{14}C activity relative to most other major sources of CO_2 and CH_4 (Coleman et al., 1993).

The principal source of commercial deposits of methane is of thermogenic origin, associated with the generation of petroleum. The organic material from which thermogenic gas is produced is the remains of plants and animals that lived millions of years ago, and, therefore, thermogenic CH_4 has no remaining ^{14}C activity. It is this type of methane which predominates in storage reservoirs and the many natural gas pipelines throughout the country. Another significant source of subsurface methane is microbial decomposition of buried organic material. In the midwestern United States this type of methane is relatively common in glacial tills and is often referred to as "drift gas" (Meents, 1960). The organic substrate from which the drift gas originates is normally many thousands of years old, and therefore drift gas generally has ^{14}C concentrations less than 30 pMC (Coleman et al., 1988).

Isotopic Characteristics of Landfill Gases and Leachates $\delta^{13}\text{C}$ of Carbon Species

The major components of landfill gas (CH_4 and CO_2) have rather distinctive isotopic compositions relative to the methane and carbon dioxide in soils and subsurface sediments. Coleman et al. (1993) reported on the isotopic composition of landfill methane, which has a $\delta^{13}\text{C}$ ranging from approximately -42 to -61 ‰ and a δD ranging from approximately -255 to -340 ‰. Similar isotopic values have been reported by Games and Hayes (1976 and 1977) and Liu et al. (1992) for landfill methane. These isotopic values are characteristic for methane produced in shallow fresh-water environments (Whiticar et al., 1986) but are isotopically distinct from other sources such as thermogenic methane and drift gas (Coleman et al., 1993).

The $\delta^{13}\text{C}$ of the carbon dioxide associated with the production of landfill methane also has rather distinct isotopic characteristics relative to CO_2 in most soils and ground water around landfills. Once methanogenesis is established, the $\delta^{13}\text{C}$ composi-

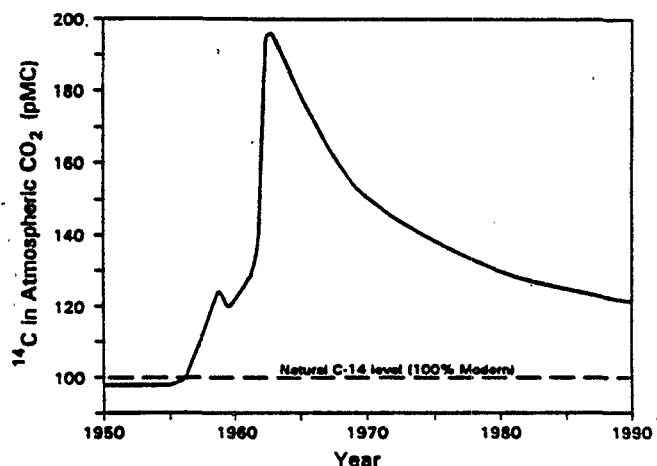


Fig. 3. ^{14}C activity of atmospheric CO_2 , adopted from Levin et al. (1980) and Coleman et al. (1990).

Table 1. $\delta^{13}\text{C}$ of CO_2 and CH_4 Sampled from Several Different Landfills

Landfill location	$\delta^{13}\text{C}$ CO_2	$\delta^{13}\text{C}$ CH_4
Indiana ¹	+20	-50
Indiana ²	+16.6	-52.1
Indiana ²	+16.1	-48.5
Delaware ³	+10.3 to +18.4	—
Illinois I ⁴	+ 8.2	-54.1
Illinois I ⁴	+ 9.4	-53.5
Illinois II ⁴	+14.0	-57.0
Illinois IV ⁴	+ 9.3	-54.6
West U.S. b ⁴	+ 9.5	-60.0
West U.S. b ⁴	+ 9.6	-58.8
East U.S. g ⁴	+10.0	-55.5
East U.S. g ⁴	- 6.9	-49.5
East U.S. m ⁴	+ 2.0	-53.6
East U.S. j ⁴	+ 6.9	-54.6
East U.S. j ⁴	+12.4	-55.2
East U.S. n ⁴	- 4.7	-50.6
East U.S. n ⁴	- 7.4	-50.6
East U.S. n ⁴	- 1.4	-51.0
East U.S. n ⁴	+ 1.2	-51.7
East U.S. n ⁴	+ 7.3	-51.0
East U.S. n ⁴	+ 6.9	-51.5
East U.S. n ⁴	+ 7.7	-51.5
East U.S. n ⁴	+ 8.3	-52.7

¹Games and Hayes, 1974; ²Games and Hayes, 1976; ³Baedecker and Back, 1979b; ⁴this paper.

tion of CO_2 in a landfill becomes, isotopically, very heavy. Table 1 shows $\delta^{13}\text{C}$ data for CO_2 and CH_4 collected directly from vent or extraction wells in landfills from Illinois, several landfills in the eastern U.S., and one in the western U.S. along with data from previous investigations of landfills in Indiana (Games and Hayes, 1974 and 1976) and Delaware (Baedecker and Back, 1979a). These data show relatively positive $\delta^{13}\text{C}$ values for CO_2 in landfills, with most samples ranging from approximately +1 to +20 ‰. However, a few of the CO_2 samples from landfills have negative values, as low as -7 (Table 1). Coleman et al. (1993) have reported $\delta^{13}\text{C}$ values as low as -25 ‰ for CO_2 associated with some landfills. Many of the isotopically light values for CO_2 observed by Coleman et al. (1993) have been explained by microbial oxidation of isotopically light CH_4 . During microbial oxidation of CH_4 , the methanotrophic bacteria preferentially oxidize the $^{12}\text{CH}_4$ resulting in isotopically light CO_2 and residual CH_4 that is enriched in ^{13}C (Barker and Fritz, 1981; Coleman et al., 1981; Whiticar and Faber, 1985).

Besides microbial oxidation, some of the variation in the isotopic composition of the CO_2 within landfills is also probably related to the maturity of the landfill. Younger parts of a landfill, where biodegradation has just begun, tend to show less enrichment of the heavier isotope relative to older, more mature parts of a landfill. This effect has been observed by Baedecker and Back (1979b) in a Delaware landfill as well as by the authors at a landfill in northern Illinois. The newest part of the northern Illinois landfill (containing refuse buried less than one year) gave the isotopically lightest $\delta^{13}\text{C}$ values for DIC (-5.1 ‰), intermediate portions of the landfill (2-7 yrs) had $\delta^{13}\text{C}$ values of +15 ‰ while the older parts of the landfill (7-12 yrs) had greater amounts of DIC and $\delta^{13}\text{C}$ values ranging from +16 to +22 ‰ (Figure 4). These observations can be explained by the different phases of biodegradation that a landfill goes through.

During the initial phase of organic degradation within a landfill, free oxygen is consumed by aerobic oxidation of organic compounds. This phase is followed by anaerobic oxidation, hydrolysis, and acidification reactions which result in a buildup of CO_2 and organic acids (such as acetic, propionic, and butyric) and a drop in pH (Pohland and Harper, 1986 and Lechner et al., 1993). The input of CO_2 during these initial aerobic and anaerobic oxidation phases of biodegradation would be isotopically light and have a $\delta^{13}\text{C}$ value between -10 and -35 ‰, which covers the range of most terrestrial plants (Deines, 1980). As anaerobic degradation continues, methanogenesis becomes more prevalent in landfills, and a phase of steady methane production is established. A decrease in acetic and other organic acids is associated with an increase in pH and an increase in methane generation as the methanogenesis phase is developed (McCarty, 1971; Rees, 1980; and Lechner et al., 1993). Several microbial studies indicate that landfill CH_4 is generated by both acetate-fermentation and H_2/CO_2 -utilizing methanogens (Sleat et al., 1987; Barlaz, 1988; Fielding et al., 1988; and Barlaz et al., 1989). The initial input of isotopically light CO_2 associated with the earlier biodegradation phases would soon be overcome during the methanogenesis phase by the constant input of isotopically heavy CO_2 associated with acetate-fermentation and microbial CO_2 -reduction. During CO_2 -reduction, microbes preferentially utilize the isotopically light carbon from the available CO_2 to produce ^{12}C enriched CH_4 , which causes the residual CO_2 to become isotopically enriched in ^{13}C . Thus, in a semi-closed environment such as a landfill, the $\delta^{13}\text{C}$ of the CO_2 is strongly affected by the methanogenesis reactions.

Using crossplots of the carbon and hydrogen isotopes of CH_4 and the carbon isotope composition of CO_2 and CH_4 from several different sources, Whiticar et al. (1986) were able to distinguish the sources of CH_4 as well as the predominant methanogenic pathways involved with the generation of microbial methane. When the $\delta^{13}\text{C}$ and δD values of landfill CH_4 are plotted on a $\delta\text{D}_{\text{CH}_4}$ versus $\delta^{13}\text{C}_{\text{CH}_4}$ diagram, the data consistently fall into the range typical of methane from fresh-water environments produced predominantly by acetate-fermentation (Figure 5).

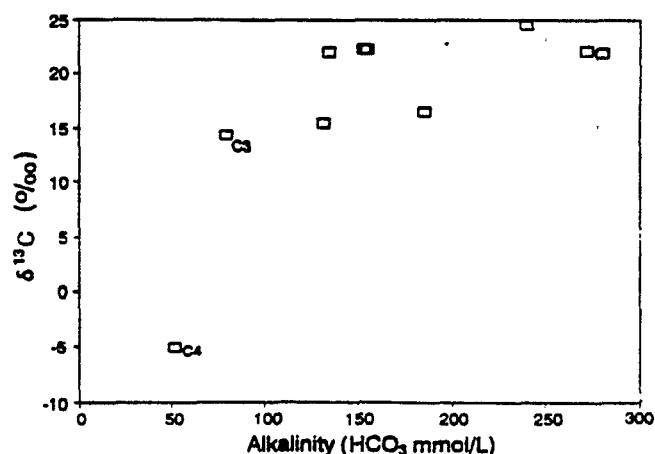


Fig. 4. $\delta^{13}\text{C}$ of DIC vs alkalinity for leachate samples from a landfill in northeastern Illinois (landfill II). Sample C4 is from an area with refuse buried less than one year. Sample C3 is from an area with refuse buried approximately 2 to 7 years. The rest of the samples are from areas with refuse buried for 7 to 12 years.

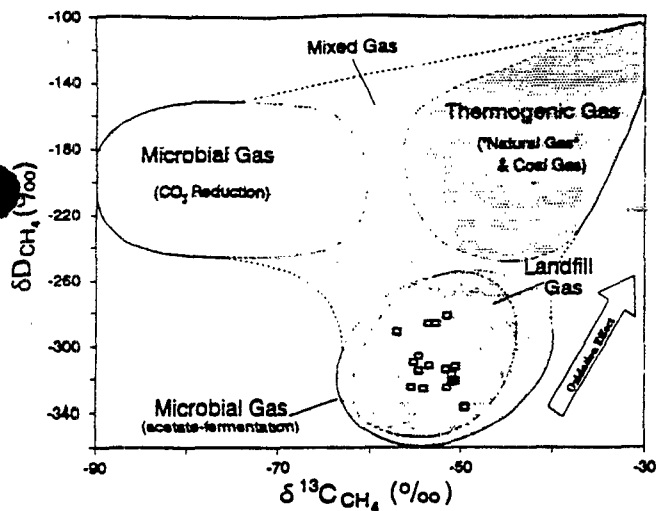


Fig. 5. Crossplot of $\delta^{13}\text{C}$ and δD of methane showing the areas where methane of different sources typically plot (Coleman et al., 1993; and Whiticar et al., 1986). All of the landfill samples shown in Table 1 fall within the acetate-fermentation domain.

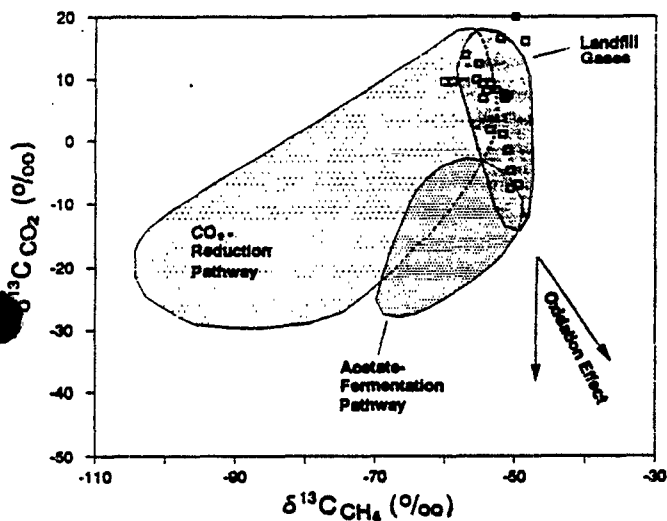


Fig. 6. Crossplot of $\delta^{13}\text{C}$ of CO_2 and CH_4 showing the areas where gases of different sources, including landfill gases, typically plot (Coleman et al., 1990; and Whiticar et al., 1986).

Figure 6 shows landfill gas data on a plot of $\delta^{13}\text{C}_{\text{CO}_2}$ versus $\delta^{13}\text{C}_{\text{CH}_4}$ graph. The landfill data plot in a domain which is primarily above the acetate-fermentation gases and on the edge of the CO_2 -reduction type gases. As suggested by Coleman et al. (1993), perhaps the range of isotopic values identified on a $\delta^{13}\text{C}_{\text{CO}_2}$ vs $\delta^{13}\text{C}_{\text{CH}_4}$ crossplot as typical of methane produced primarily by the acetate-fermentation process should be expanded to include the more positive $\delta^{13}\text{C}_{\text{CO}_2}$ values observed in landfill gases.

It appears from the $\delta^{13}\text{C}$ data of CO_2 and DIC from landfills that there is an upper limit of approximately $+18\text{‰} \pm 2\text{‰}$ for CO_2 (or mid +20's for DIC). This upper limit suggests that a steady-state condition is reached between CO_2 input and CH_4 production by the processes involved in microbial decomposition of landfill refuse. Many studies of methanogenesis in

surficial fresh-water environments have shown that the contribution of methane by acetate-fermentation is normally around $65\% \pm 10\%$ of the total methane measured (Ward and Winfrey, 1985). The remainder of the methane produced is primarily due to the microbial CO_2 -reduction process. The explanation for the unusually heavy isotopic composition of CO_2 is probably related to the sheer volume of isotopically positive CO_2 created by the acetate-fermentation and the CO_2 -reduction process within a finite system where the input of light CO_2 is minimal. It is also possible that other microbial processes are occurring in landfills which are not being considered but which could be affecting the isotopic composition of the CH_4 and CO_2 gases. Further discussion of the specific mechanisms responsible for the isotopic effects observed in these gases is beyond the scope of this paper and is an area that could benefit from further investigation when considering landfill environments.

δD in Leachates

The large amount of methane produced during the anaerobic degradation of organic material within a landfill not only affects the $\delta^{13}\text{C}$ of the carbon species but also the δD of the leachate water. Significant enrichment in deuterium of leachate water has been observed by Baedeker and Back (1979) and Rank et al. (1992). Fritz et al. (1976) observed enriched D and ^{18}O in ground water contaminated by leachate from a nearby landfill. Table 2 gives δD and $\delta^{18}\text{O}$ data we have obtained in leachates from three active landfills in Illinois (included is the average isotopic composition of local precipitation). Most of the leachates have unusually heavy deuterium values. The δD of leachate sampled in the mature portions of the landfills was approximately 30 to nearly 60‰ enriched in deuterium relative to the average δD of local precipitation. A few samples had fairly negative δD values and represent leachate taken from either the newer parts of the landfills or areas of the landfills where surrounding ground water had apparently infiltrated and mixed with the leachate. This is discussed in more detail later.

The enrichment of deuterium observed in municipal landfills is undoubtedly a result of the very active formation of

Table 2. $\delta^{18}\text{O}$ and δD of Leachates from Landfills in Illinois, Including Average Composition of Local Precipitation

Landfill	δD (‰)	$\delta^{18}\text{O}$ (‰)
Site-I-10	+14.0	-7.6
Site-I-06	-60.0	-9.8
Site-II-c3	-22.0	-6.7
Site-II-L3	+10.8	-6.2
Site-II-L2a	-11.0	-8.8
Site-II-L4	+7.7	-6.7
Site-II-c1	-7.6	-7.3
Site-II-c6	-5.4	-8.0
Site-II-c5	-13.3	-8.1
Site-II-L2	+14.5	-8.0
Site-II-L5	-0.9	-9.0
Site-II-L1	-6.9	-7.7
Site-II-c4	-35.6	-5.6
Site-II-c2	-74.7	-11.5
Site-III-1	-17.0	-8.1
<i>Local precipitation</i>		
Chicago Ave.*	-43.3	-6.0

* 6-yr weighted average values (IAEA, 1969, 1971, 1975, and 1983).

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microbial methane within a closed system over time. Rank et al. (1992) sampled an experimental landfill on a monthly basis and showed δD increasing in leachate from three different refuse cells over a period of approximately six months to two years. They observed a similar degree of deuterium enrichment in the leachate from the experimental landfill as we observed in Illinois landfills. The deuterium data collected from leachates indicate that there is probably a steady-state situation that develops between the input of isotopically light hydrogen from water infiltrating into a landfill and the rate of consumption of the light hydrogen isotope during the methanogenesis process.

According to Whiticar et al. (1986 and others referenced in that paper), during methanogenesis, a significant amount of the hydrogen incorporated in the CH_4 (25 to 100%, depending on the metabolic pathway) comes from the surrounding water or, in the case of municipal landfills, the surrounding leachate. The microbes preferentially utilize the isotopically light hydrogen when producing CH_4 ; therefore, the remaining hydrogen in the aqueous medium is enriched in deuterium. In normal geological environments, where the reservoir of water is much greater than the amount of CH_4 generated, this effect is usually not observed. However, in the relatively closed environment of landfills where the generation of microbial methane is comparatively large, with respect to the limited reservoir of water present, it is possible to observe this deuterium enrichment. A plot of the δD of leachates versus the alkalinity, reported as bicarbonate concentration (mg/l), is shown in Figure 7. It is assumed that the alkalinity generally increases during the processes of anaerobic waste decomposition and maturation of a landfill environment. Thus, as a landfill matures and more methane is generated there is a significant increase of deuterium in the leachate.

Besides the effect of methanogenesis, it is possible that some of the deuterium enrichment observed in landfill leachates is due to isotopic exchange with H_2S , which would be generated during SO_4 reduction in landfills. However, this effect is probably miniscule relative to the effect of methanogenesis. According to IAEA (1983), for every gram of SO_4 reduced per liter of water, there is about a 0.1 ‰ enrichment of deuterium in the water. Sulfate concentrations in landfill leachates generally range from 10 to 1000 mg/l (Lee and Jones, 1993); therefore, the overall effect due to H_2S -exchange reactions would only be on the order of tenths of a per mil.

¹⁴C and ³H in Landfill Gases and Leachates

Recent investigations have indicated that concentrations of the radiogenic isotopes, carbon-14 (¹⁴C) and tritium (³H), in landfill leachates and gases are also unique relative to the surrounding ground water (Liu et al., 1992). The ¹⁴C in landfill methane is significantly enriched relative to most other sources of CH_4 and ranges from approximately 120 to 150 pMC (Coleman et al., 1990; Liu et al., 1992; and Coleman et al., 1993). The majority of ¹⁴C concentrations in DIC from leachates we have analyzed have values similar to those observed for landfill methane (Liu et al., 1992). The elevated ¹⁴C activities for gases and leachates observed thus far can be explained by the influence of atmospheric testing of nuclear devices that caused the increased radiocarbon content in the atmosphere and thus in the organic materials decomposing in modern landfills. The relatively high levels of tritium observed, however, cannot be explained so easily.

There have been relatively few tritium analyses of landfill

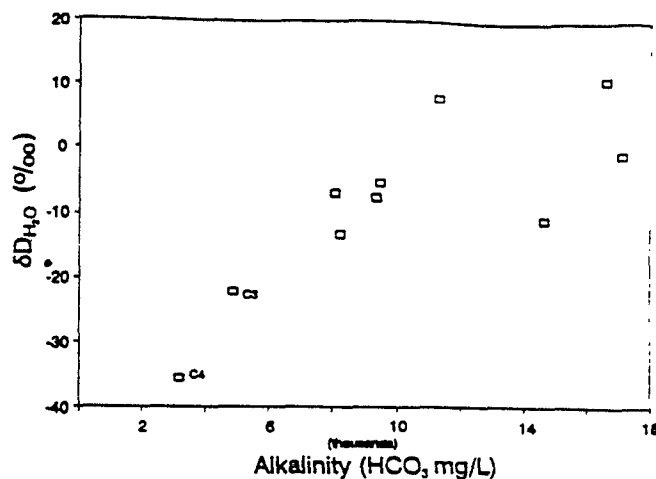


Fig. 7. δD versus alkalinity of leachate samples from a single landfill in northeastern Illinois.

leachates or gases. We recently reported that for three different landfills the hydrogen of landfill CH_4 was enriched in ³H, ranging from 160 to approximately 2800 TU (Coleman et al., 1993). Rank et al. (1992) measured the tritium content of leachate in samples from the Breitenau Experimental Landfill in Austria and observed tritium contents up to about 2000 TU with a few leachate samples showing 3000 TU. The tritium content of leachates from three different municipal landfills in Illinois range from 227 to 8000 TU (Table 3). These large variations in tritium content, even within one landfill, stress the importance of measuring the level of tritium within a landfill before tritium is used to identify leachate contamination or to calculate travel times for leachate plumes.

Most of the tritium values we have observed in municipal landfills, as well as those observed by Rank et al. (1992) and a few anomalous values observed by Egboka et al. (1983), are too high to be explained by input from the local contemporaneous precipitation. For example, the three landfills for which tritium data are given in Table 3 were opened in the late 1970s or early 1980s when tritium in precipitation in the Midwest was generally less than 50 TU (Figure 2). Thus, some other source or sources of tritium within the refuse of municipal landfills are giving rise to the relatively high tritium values observed. The most probable

Table 3. ¹⁴C and ³H of Leachates from Landfills in Illinois

Landfill	¹⁴ C (pMC)	³ H (TU)
Site-I-10	126.1	227
Site-I-06	140.5	338
Site-II-c3	123.9	8001
Site-II-L3	135.5	6726
Site-II-L2a	133.1	4647
Site-II-L4	169.9	2894
Site-II-c1	130.5	2436
Site-II-c6	134.6	2318
Site-II-c5	136.0	2247
Site-II-L2	134.9	1343
Site-II-L5	130.6	1140
Site-II-L1	143.0	831
Site-II-c4	118.6	275
Site-II-c2	146.3	225
Site-III-1	132.0	323

source is luminescent paints (Ostland, pers. commun., 1992; Coleman et al., 1993) used in watch dials and clocks as well as other luminescent instrument dials (UNSCEAR, 1977), that could easily be disposed of in municipal landfills. These luminescent paints contain tritiated hydrocarbons that could biodegrade in a landfill and add to the overall tritium concentration. According to the UNSCEAR (1977) report, luminescent timepieces contain approximately 1 to 25 mCi (milli-Curie). To put this into perspective, 1 TU is equal to approximately 3.19 pCi/kg (Taylor and Roether, 1982), or 1 mCi is equal to approximately 3.125×10^3 TU.

Potential Utilization

Radiocarbon and stable isotope analysis of carbon and hydrogen have already been shown to be very useful for distinguishing landfill gas from thermogenic gas and microbial drift gas (Coleman et al., 1990; Hackley et al., 1992). The very positive $\delta^{13}\text{C}$ values for CO_2 and the characteristic $\delta^{13}\text{C}$ values for landfill CH_4 are useful for distinguishing these gases, that may have migrated out of a landfill, from background gases sometimes found in surrounding soils and ground water. Soil CO_2 , for example, is primarily produced from decay of organic matter and plant root respiration, and therefore the $\delta^{13}\text{C}$ of soil CO_2 is related to the type of vegetation in the area. The $\delta^{13}\text{C}$ values of soil CO_2 range between approximately -12 to -27 ‰, including both arid and humid climates (Parada et al., 1983). As seen from Table 1, landfill CO_2 will usually be significantly more enriched in ^{13}C .

In most situations the combination of a $\delta\text{D}_{\text{CH}_4}$ vs $\delta^{13}\text{C}_{\text{CH}_4}$ plot (i.e., Figure 4) and a $\delta^{13}\text{C}_{\text{CO}_2}$ vs $\delta^{13}\text{C}_{\text{CH}_4}$ plot (i.e., Figure 5) will be quite effective for distinguishing landfill gas from other sources of methane, such as thermogenic and microbial methane produced primarily by the CO_2 -reduction process. However, there are a few situations that could complicate the interpretation of the stable isotope data on gases. For example, microbial oxidation of landfill gases migrating away from the fill area could result in significantly altering the isotopic composition of the migrating CH_4 and CO_2 . The δD and $\delta^{13}\text{C}$ of the residual methane would increase while the $\delta^{13}\text{C}$ of the resulting CO_2 would decrease due to microbial oxidation. Such oxidation effects could result in methane with $\delta^{13}\text{C}$ and δD values similar to that of thermogenic methane. Another possible complication is the presence of microbial methane produced primarily by acetate-fermentation in near-surface or recent fresh-water environments, such as in lake sediments, marshes, or swamps close to a landfill site. Methane produced by the acetate-fermentation pathway in natural fresh-water environments would have $\delta^{13}\text{C}$ values similar to that observed in landfills. In these types of situations, ^{14}C analysis of the CH_4 can be used to help verify the source of gas. Thermogenic methane, for example, will be devoid of ^{14}C and easily distinguished from landfill gas by ^{14}C analysis. The ^{14}C activity of microbial methane produced in natural environments or found dissolved in ground water will usually be significantly less than landfill CH_4 (Coleman et al., 1993).

Recent data indicate that the additional analysis of tritium in the hydrogen of methane samples provides an even more sensitive diagnostic tool for identification of landfill gas (Coleman et al., 1993). Although the carbon-14 analysis will usually be conclusive for distinguishing landfill gas from most other sources, if CH_4 derived from a landfill migrates into the surrounding geological deposits and mixes with naturally occur-

ring microbial methane that has a relatively low ^{14}C concentration, such as drift gas, the resultant ^{14}C value may resemble a marsh or wetland gas. The expected ^{14}C activity for methane originating from marshes or wetlands ranges from approximately 40 to 120 pMC (Coleman et al., 1993). Gases generated from sewers and compost areas may also be difficult to distinguish from landfill CH_4 using ^{14}C analyses. In cases such as these, tritium analyses of the methane hydrogen should be particularly helpful for identifying the presence of landfill CH_4 .

The elevated levels of deuterium in leachate offer a potentially effective means of tracing leachate migration from a landfill. For example, Figure 8 graphically shows how the δD values of leachates from a landfill in northern Illinois (Site-II, Table 2) stand out relative to average local precipitation and uncontaminated ground water sampled at a few different depths below the surface near Site-II. The major aquifer of concern at this site was a confined dolomite, located approximately 90 ft below the surface, with a very negative δD value of approximately -119 ‰. Thus, a large natural difference was established between the isotopic composition of the landfill leachate and the major aquifer for the area. This large inherent isotopic difference made δD an effective tracer of leachate migration for this landfill (Liu et al., 1992). As mentioned previously, a few leachate samples we analyzed have rather negative δD values and, as shown in Figure 8, fall close to the MWL. The two samples shown in Figure 8 indicate the importance of knowing where the samples were taken in a landfill and the general operations of the landfill. Leachate sample C4, for example, was taken from a new area of the landfill where refuse had just been buried earlier that year. Thus, decomposition was probably still in its early stages and little, if any, methanogenesis had occurred in that section of the landfill resulting in a δD value similar to that of local precipitation. Leachate sample C2, however, was taken from an older section of the landfill and represents an area where isotopically light ground water was apparently infiltrating and mixing with the leachate, diluting the δD value of the leachate. This is supported by lower tritium levels for this same sample as indicated in Table 3.

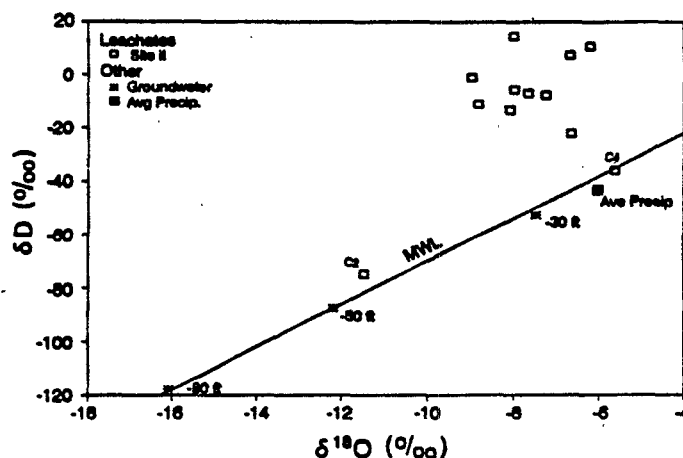


Fig. 8. δD and $\delta^{18}\text{O}$ data of leachates from a municipal landfill in Illinois (Site-II, Table 2). Included in this plot are: the average isotopic composition of precipitation for the area, the isotopic composition of uncontaminated ground water sampled at different depths nearby the landfill, and a background well screened 90 ft below the surface at Site-II.

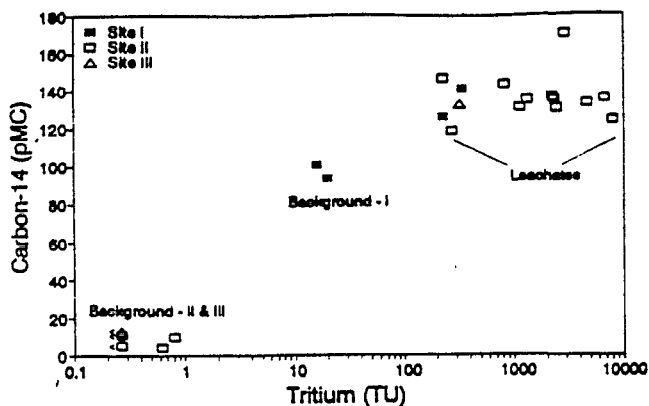


Fig. 9. ^{14}C and ^3H values measured in leachates sampled from three different landfills in Illinois (Table 3) compared with background samples taken at each site. (Tritium values plotted as < 0.25 were reported to have $0 \text{ TU} \pm 0.09$ from the tritium laboratory.)

The radiogenic isotopes of ^3H and ^{14}C have the potential to be even more sensitive than deuterium as tracers of leachate based on the differences observed between uncontaminated ground-water samples and leachates shown in Figure 9. As Figure 9 indicates the contrast between the ^{14}C and ^3H values of leachate and background water at landfills differ from one site to another depending on whether the background water being monitored is close to the surface and open to atmospheric exchange or is a confined ground-water unit. The background values for Site-I, for example, represent water sampled from a surface reservoir and the top few feet of the unconfined ground water on site. The background samples from the other two landfills were taken from confined aquifers located approximately 90 feet below the surface. The confined aquifers had significantly less tritium and ^{14}C activity, increasing the sensitivity of the isotope tracers at these two sites.

An advantage of using environmental isotopes, such as δD , $\delta^{18}\text{O}$, and ^3H , as tracers for leachate is that the alteration of the isotopic composition of the leachate water during migration is less severe than most inorganic or organic compounds dissolved in the leachate. For example, deuterium, oxygen-18, and tritium are isotopes of one of the main constituent atoms of water and are generally considered conservative environmental tracers of ground water. Deuterium and tritium are not influenced by most of the chemical and biological processes that influence dissolved components (Fritz et al., 1976; Fontes, 1980; and Hendry, 1988).

Another positive aspect of using environmental isotopes is that the sampling techniques are relatively simple. Collecting samples for the stable isotopes and tritium analysis basically involves putting the samples in well sealed containers and shipping them off to an isotope laboratory for analysis. Sampling for ^{14}C analysis is somewhat more involved, requiring a relatively large sample when using conventional analysis techniques. For example, gas samples may require approximately 4 to 65 liters, and water samples may require approximately 8 to 50 liters, depending on the amount of carbon present in the samples. Usually 2 grams of carbon is sufficient for conventional ^{14}C analysis. Methods of collecting and analyzing samples for their isotopic composition are generally reviewed in IAEA Technical Report Series No. 228 (1983).

Summary

The confining structure of municipal landfills creates a unique environment where anaerobic microbial degradation of organic debris can result in the production of large quantities of CH_4 and CO_2 (Stecker and Rodgers, 1985; Bogner and Spokas, 1993). It is this prolific microbial activity that alters the ^{13}C and D abundance in different compounds and results in the unique stable isotope signatures that can be used to characterize and trace the gases (CO_2 and CH_4) and leachates from municipal landfills. The fractionation associated with methanogenesis in landfills results in $\delta^{13}\text{C}$ values of CH_4 ranging between approximately -48 to -60 ‰, which is typical of microbial methane produced primarily by the acetate-fermentation process. The $\delta^{13}\text{C}$ for the CO_2 associated with methane production in landfills ranges from approximately -7 to $+18$ ‰. Since the methanogenesis process utilizes the isotopically light hydrogen from the water the δD of the leachate becomes isotopically enriched in deuterium by approximately 30 to 60‰. This deuterium enrichment renders deuterium a useful tracer for delineating leachate migration.

The radiogenic isotopes of ^{14}C and ^3H appear to be the most sensitive tracers for identifying landfill pollutants. Both the leachate and methane from municipal landfills are significantly enriched in ^{14}C and ^3H relative to concentrations normally found in ground water and other sources of methane. The typical range of ^{14}C values for CH_4 and DIC in landfill leachate is from 120 pMC to 150 pMC. This elevated range of ^{14}C can easily be explained by the decomposition of organic material that contain elevated levels of ^{14}C due to atmospheric testing of nuclear devices in the 1950s and 60s. Tritium concentrations in landfill leachates generally range from a few hundred TU to several thousand TU and cannot be explained so easily. The predominant source of the tritium is probably luminescent paints used in watch dials and clocks as well as other luminescent instrument dials that could easily be disposed of in municipal landfills. In light of the variable tritium levels measured in leachates from several different landfills it is important to acquire tritium measurements from within a landfill prior to using tritium data downgradient from a landfill for delineating a leachate plume or calculating travel times.

The application of isotope geochemistry to contamination problems that occur near municipal landfills can help confirm, independently, whether the contamination observed is from a municipal landfill or some other potential source in the area. Isotopic analyses are well suited to help define both gas migration and/or leachate migration problems. The conservative nature of environmental isotopes, such as D, ^{18}O , and ^3H , helps preserve the original isotopic signatures associated with landfill leachate and therefore makes the isotopes reliable tracers for leachate migration. The combination of isotope analyses with chemical and hydrologic data will result in a better assessment of subsurface contamination problems that occur near municipal landfill sites.

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EPA's Policy Perspective on Natural Attenuation

Presented by
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Why Use the Term "Natural Attenuation?"

- Various names and definitions exist
 - Intrinsic remediation
 - In situ biodegradation
 - Passive remediation
 - Natural attenuation
 - Other vernacular names
- "Natural Attenuation" recognized by RCRA, Superfund, UST Programs
- Consistency and clarity a plus

What Is "Natural Attenuation?"

- EPA program offices' existing definitions include most relevant processes:
 - Dilution
 - Dispersion
 - Adsorption
 - Biodegradation
- Volatilization, other chemical processes lacking

Regulatory Framework

- Natural Attenuation is:
 - A recognized remedy for ground-water cleanup
 - Used to *attain* required cleanup standards
 - Used under specific circumstances

as a recognized remedy alternative . . .

- Natural Attenuation
 - Should be evaluated along with, and in similar manner to other (remedial) measures
 - Is not a default option
 - Differs fundamentally from active remediation
 - Its usage encouraged where appropriate

Circumstances Appropriate for Natural Attenuation

- Site characterization data adequately demonstrate natural attenuation's effectiveness
- Where natural attenuation will
 - Result in attainment of cleanup levels
 - In reasonable timeframe
- ★ Time "comparable" to that of active remediation

When Should Natural Attenuation Be Used?

- Where longer remediation timeframes acceptable:
 - No demand for GW resource while remedy in progress
 - Alternate supplies available if needed



When Should Natural Attenuation Be Used? (Continued)

- In combination with active remedial measure, e.g.:
 - Sources: treatment/containment/removal
 - Plume: treatment of higher concentration areas
 - Plume: containment, or other measures as appropriate
- To "finish up" active remediation

SOURCE CONTROL

When Should Natural Attenuation Be Used? (Continued)

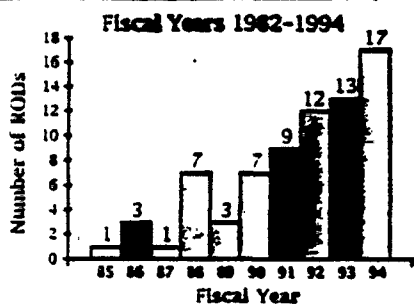
- Will not result in unacceptable contaminant migration
- Capability exists to adequately monitor to ensure protectiveness
- With contingencies for active measures if remedy expectations not met
- Accepted by lead/supporting agencies and local community



How Has Natural Attenuation Been Used?

- Superfund Program Example
 - 73 ground-water RODs have selected natural attenuation between 1982 and 1994
 - Represents approximately seven percent of GW RODs
 - Trend of increasing use since 1985 (chart)

Ground Water RODs Using Natural Attenuation



How Has Natural Attenuation Been Used? (Continued)

- Variety of sites, including MLFs, industrial LFs, refineries, recyclers, etc.
- At all but six sites, natural attenuation used in combination with active remedy components
- Often have low exceedences of cleanup levels
- Contingencies for active measures

Use of Natural Attenuation in Superfund Remedies

Remedy Includes	Number of Sites
Capping	26
Source treatment	19
Source removal/Disposal	25
GW pump and treat	10
GW interceptor trench/Runoff controls	4
NAPLs recovery	2
Natural attenuation only	6

*Sites may have more than one active remedy component.

Promoting Greater Acceptance of Natural Attenuation

- ★ Communicate that natural attenuation is a **responsible, managed remediation approach (not a walk-away)**
- ★ Present site-specific data and analyses that demonstrate occurrence
- Develop defensible conceptual model supporting natural attenuation
- Build defensible predictive models, where appropriate

Promoting Greater Acceptance of Natural Attenuation (Continued)

- ★ → Control/treat/remove sources
- ★ → Thoroughly monitor plume and downgradient areas
- ★ → Include contingencies for other measures if natural attenuation fails to meet desired goals
- ★ → Involve regulatory agencies *early in process*

**Introductory Talk: Where Are We Now With Public and Regulatory Acceptance?
(Resource Conservation and Recovery Act [RCRA] and Comprehensive
Environmental Response, Compensation, and Liability Act [CERCLA])**

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10.7.96

Introduction

The U.S. Environmental Protection Agency (EPA) remains committed to the goal of restoring contaminated ground waters to their beneficial uses. The Agency also recognizes that, in certain circumstances, remedies using natural attenuation can be more cost-effective than "active" remediation approaches in achieving cleanup objectives equally protective of human health and the environment. The Agency also recognizes that many technical questions remain to be answered regarding the efficacy of this approach, which underscores the importance of continued scientific research as well as the need to employ remedies using natural attenuation in a consistent and responsible manner.

What is Natural Attenuation?

Natural attenuation is discussed in the preamble of the National Oil and Hazardous Substances Pollution Contingency Plan (NCP), which is the regulatory framework for the Superfund program (1). In the NCP, natural attenuation is described as a process that "will effectively reduce contaminants in the ground water" to concentrations "protective of human health and sensitive ecological environments in a reasonable timeframe." The NCP goes on to recognize that natural attenuation may include any or all of the following processes:

- Biodegradation
- Dilution
- Dispersion
- Adsorption

Thus, the NCP definition includes biodegradation, which alters or destroys the contamination as well as physical

processes that lower contamination concentrations and availability without necessarily altering the chemistry. Other processes not mentioned in the NCP are not necessarily excluded from the definition (e.g., volatilization). Other EPA remediation programs also recognize this definition, including the Corrective Action program under the Resource Conservation and Recovery Act (RCRA) and Underground Storage Tank (UST) programs.

Some terms, such as "intrinsic remediation" or "passive remediation," are essentially equivalent to the NCP's definition of natural attenuation. Other terms used in recent literature, including "intrinsic bioremediation" or "in situ bioremediation," appear to be more restrictive in scope than "natural attenuation." In addition, natural attenuation is the term used in existing EPA guidance (e.g., U.S. EPA [2]).

Regulatory Framework

Natural attenuation is recognized as a legitimate remedial approach for ground-water cleanup under the Superfund, RCRA Corrective Action, and UST remediation programs. A directive clarifying EPA's policy regarding the use of natural attenuation for remediation of sites regulated under these programs is currently under development (3). Remedies selected for contaminated ground water (and for other media) under these programs must protect human health and the environment, regardless of the particular remediation technology or approach selected. Remedies may achieve protection through a mix of treatment, which reduces or destroys contaminants; containment and other engineering controls, which limit exposure; and other means identified as part of the remedy selection process. Each EPA program has guidance suggesting when specific meth-

EPA recognizes that natural attenuation may be an appropriate remediation method for contaminated ground water under the right circumstances. Natural attenuation should continue to be carefully evaluated along with other viable remedial approaches or technologies within the existing remedy selection framework. *Natural attenuation is not to be considered a default or presumptive remedy for a given site under any of these EPA programs.*

Cleanup policies for Superfund have addressed the use of natural attenuation in some detail; most of the relevant discussion can be found in the NCP preamble. The following NCP language specifies the definition and cleanup expectation for remedies using natural attenuation:

"[S]election of natural attenuation by EPA does not mean that the ground water has been written off and not cleaned up but rather that biodegradation, dispersion, dilution, and adsorption will effectively reduce contaminants in the ground water to concentrations protective of human health in a timeframe comparable to that which could be achieved through active restoration . . ." (1).

Thus, the NCP expects that a remedy employing natural attenuation will be fully protective and attain the required cleanup levels for the aquifer in a timeframe that is not unreasonably long. Since the other EPA remediation programs have similar expectations, use of natural attenuation as a remedy does not reduce EPA's responsibility to protect human health and the environment, and to satisfy the cleanup levels and other remediation objectives selected for a given site. *In short, use of natural attenuation does not imply that EPA has agreed to a "no action" remedy or that EPA or responsible parties may "walk away" from their remedial obligations at a site.*

When Is Natural Attenuation Appropriate?

Because of the longer timeframes needed for remedies using natural attenuation, such an approach is best suited for sites where there is no demand for the ground water in the near future. For example, where adequate alternate water sources are available, future demand for the contaminated ground water is likely to be low. Also, the timeframe required for natural attenuation should be reasonable compared with more active alternatives. Other site conditions that favor the use of natural attenuation as a remediation approach are discussed below.

Large, Dilute Contaminant Plumes

The types of contaminants, their concentrations, and hydrogeologic conditions should indicate that natural attenuation is a viable remediation approach for a given site. Natural attenuation is more likely to be an appropriate remediation approach at sites with large plumes

and relatively low contaminant concentrations. For these types of sites, natural attenuation may be able to attain the required cleanup levels in a reasonable timeframe and at a much lower cost than other alternatives.

Sources Controlled or Controllable

Natural attenuation will not be effectively used to reach desired cleanup levels if the rate of contamination entering ground water exceeds the rate of the natural attenuation processes. Therefore, contaminant sources should have been controlled by previous actions or site characterization data should indicate that contaminant sources are no longer present. Otherwise, remedies using natural attenuation should include measures for controlling sources, such as removal, treatment, or containment of source materials. Sources of contaminants to ground water could include surface facilities, landfill wastes, contaminated soils, or nonaqueous-phase liquids (NAPLs) in the subsurface.

*
CONTROL
SOURCE
THEN
MONITOR
CONDITIONS!

Protected Drinking Water or Environmental Resources

Cross contamination of other aquifers or discharge of contamination to surface waters or sensitive ecological environments is more likely if contamination is left in the subsurface for long periods. Site conditions should indicate a low potential for migration of contaminants into uncontaminated media, or measures for controlling plume migration should be included in remedies using natural attenuation. In addition, the issue of whether daughter products of natural attenuation will pose a significant risk must be addressed.

Combining Natural Attenuation With Other Methods

For sites where natural attenuation alone is not capable of achieving desired cleanup levels in a reasonable timeframe, natural attenuation combined with more active remediation methods may prove to be effective. Some areas of the plume may require a much longer time to attenuate naturally than others, such as areas with relatively high contaminant levels ("hot spots"). In this situation, natural attenuation of dilute plume areas combined with extraction and treatment to control source areas and remediate plume hot spots may be an effective remediation approach, especially for sites where dilute portions of the plume cover a relatively large area.

In some cases, it may be appropriate for natural attenuation to be used as a followup to active remediation. In this approach, active measures are used to reduce contaminant concentrations, followed by natural attenuation

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Promoting Regulatory and Public Acceptance

In general, promoting acceptance of natural attenuation will require detailed site characterization and analysis to demonstrate that this approach will achieve remediation goals, careful monitoring of remediation progress, and identification of contingency measures. These provisions are necessary to convince regulatory agencies and the public that natural attenuation is a valid remediation approach rather than a "walkaway" and will be sufficiently protective.

Building confidence in the approach can also be promoted by involving the responsible regulatory agencies as early in the process as possible. For example, up-front agreement on the type of characterization data needed to demonstrate the efficacy of natural attenuation can save considerable effort later in the remedy selection process.

Detailed Site Characterization

Convincing regulatory officials and local citizens that natural attenuation will be effective starts with a detailed site characterization and a clear conceptual model of site conditions. A conceptual model of how natural attenuation will perform at a given site is essential to show that natural attenuation will be effective and that potential adverse impacts to human health and the environment can be prevented over the long period required for cleanup. The burden of proof of the viability of natural attenuation is on the proponent, not the regulator.

Site-specific data should be used to demonstrate that the required cleanup levels can be attained in a reasonable timeframe compared with other remedial alternatives. Such a demonstration can be supported by the following types of site data:

- Contaminant concentrations have decreased over time.
- Geochemical or microbiological parameters are characterized to the extent needed to support predictive models.
- Predictive models show required cleanup levels will be attained in a timeframe that is reasonable for the site.

Exposure Prevention Measures

Prevention of exposure to contaminated ground water over the long period required for cleanup is critical to ensure protectiveness. Remedies using natural attenuation should include effective measures for ensuring that

contaminated ground water does not reach public or private wells, or for providing effective treatment prior to use.

* ALTERNATIVE
WATER
Supply!

Performance Monitoring

A thorough monitoring network and plan are necessary to evaluate the progress of natural attenuation. Remedies using natural attenuation should include a monitoring plan to ensure that remedy performance matches predictions, there are no adverse impacts, and unanticipated events can be detected in time to develop an appropriate response.

Contingency Measures

Contingencies for initiating active remediation measures should be incorporated into remedies using natural attenuation. Such contingencies provide assurance that remedy protectiveness will be maintained should natural attenuation not progress as expected. The trigger(s) for implementing such contingencies should be clearly spelled out in site decision documents.

Summary

EPA believes that natural attenuation should continue to play an important role in the cleanup of sites with contaminated ground water. Furthering the technical understanding of the underlying treatment processes and promoting the responsible use of this remediation method should serve to enhance the role that natural attenuation plays in restoring the nation's ground water. Greater regulatory and public acceptance of natural attenuation will require demonstrating that such remedies will be effective in meeting remediation goals and in protecting human health and the environment over the long period required for cleanup. Demonstrating the effectiveness of remedies using natural attenuation will involve thorough site characterization, careful monitoring of remedy progress, and contingency measures to ensure long-term reliability and protectiveness.

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