Natural attenuation of plumes from waste sites using aqueous and mineral data

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Abstract

Thousands of municipal solid waste landfills operate in the United States. Some, particularly older unlined ones, have released leachate to soil/ground water. Landfill leachate is typically high in labile organic constituents. Escaped leachate is a source of soil, ground water, and occasionally surface water pollution that may persist for decades. A redox series may occur, if a large quantity of a labile organic contaminant is spilled in the subsurface, where one type of electron acceptor is preferentially consumed before another. The common convention is that the order of electron acceptor utilization is $O_2 > NO_3^- > Mn > Fe^{3+} > SO_4^{2-}$ followed by methanogenesis. Significantly more $Fe^{3+}$ and $SO_4^{2-}$, compared to $O_2$ and $NO_3^-$ is often available in the subsurface.

An approach to evaluating the natural attenuation of subsurface contaminants, Aqueous and Mineral Intrinsic Biodegradation Assessment (AMIBA) is described in this paper. The microbial reduction of $Fe^{3+}$ and $SO_4^{2-}$, forms reduced $Fe$ and $S$ mineral precipitates in amounts stoichiometrically equivalent to the contaminant mass oxidized by microbial processes. AMIBA involves measuring $Fe^{3+}$ and reduced $Fe$ and $S$ minerals in affected sediments to assessment intrinsic bioremediation, both expressed and assimilative.

The results from a number of studies are summarized here, including microcosm studies with simulated landfill leachate, fieldwork at an older unlined landfill, and studies conducted at fuel and chlorinated solvent contaminated sites. Results indicate that AMIBA can be used to assess natural attenuation at landfill sites.
1 Introduction

There are thousands of active municipal solid waste landfills in use in the United States. Many have or will release leachate to soil/ground water. In addition to inorganic salts and dissolved metal contaminants, landfill leachate is typically high in organic constituents, with measured COD values in thousands of mg/L. Escaped leachate is a source of soil, ground water, and occasionally surface water pollution that can persist for decades [1].

Leachate can cause a series of redox reactions to occur in the subsurface. The common convention is that the order of electron acceptor utilization is \( \text{O}_2 > \text{NO}_3^- > \text{Mn} > \text{Fe}^{3+} > \text{SO}_4^{2-} \) followed by methanogenesis, as dictated by thermodynamics. Though microbial \( \text{O}_2 \) and \( \text{NO}_3^- \) respiration are thermodynamically favorable, concentrations of \( \text{O}_2 \) and \( \text{NO}_3^- \) are usually small in ground water. In contrast, comparatively large amounts of solid \( \text{Fe}^{3+} \) (\( >1,000 \) mg/kg) and dissolved \( \text{SO}_4^{2-} \) (50 to \( \sim2,000 \) mg/L) can occur naturally, suggesting a dominant role in intrinsic bioremediation.

This paper describes a method for Aqueous and Mineral Intrinsic Biodegradation Assessment (AMIBA). Intrinsic bioremediation is the degradation of contaminants by indigenous microbes under prevailing conditions. Its assessment can be used to demonstrate that a site can be left to naturally attenuate with acceptable risk to human health or the environment. AMIBA can be used to assess a number of aspects of intrinsic bioremediation:

- **Redox processes** - the active microbiological redox processes;
- **Plume fingerprint** – a comparison of the distribution of organic contaminant and respiratory end-products used to determine if the plume is growing or shrinking;
- **Expressed capacity** – the mass of hydrocarbon that has been destroyed via a specific redox process;
- **Assimilative capacity** - the future ability of the aquifer system to degrade hydrocarbon through specific redox processes; and
- **Decay rates** – both of contaminant source and plume, providing necessary parameters for predictive modeling.

In this paper, the results from a number of Landfill/AMIBA related studies are summarized, including microcosm studies with simulated landfill leachate, fieldwork at a closed unlined landfill, and studies conducted at fuel and chlorinated solvent contaminated sites. Results indicate that AMIBA can be used to assess natural attenuation at landfill sites.

2 Natural attenuation and landfill leachate

In addition to intrusive remediation methods, such as excavation and pump-and-treat, natural attenuation has been proposed as a means of effectively addressing the problem of groundwater contamination. Natural attenuation includes
precipitation, sorption, dispersion, advection, volatilization, hydrolysis and intrinsic biodegradation. Because it is passive, non-intrusive and relatively inexpensive, some critics have labeled it a "do nothing" approach. However, natural attenuation, responsibly and effectively applied, requires both extensive site characterization and long term monitoring.

Natural attenuation must be quantifiable in order to be established as a leachate management option. If natural attenuation can eliminate the need for extensive containment or active remediation, landfill costs would be significantly reduced. More than a back up system for landfills with containment systems, natural attenuation may be the only long term means to deal with landfill leachate [2], considering that all containment systems leak.

Requirements for the intrinsic biodegradation of organic compounds include the presence of an organic substrate, microbial consortium, electron acceptors, and the absence of factors that inhibit microbial growth [3]. Natural attenuation processes and rates, while generally understood regarding the treatment of chlorinated solvents and fuels, are not as well understood for leachate. Fewer studies concerning landfill leachate exist, and have primarily dealt with sandy, aerobic aquifers [4]. Complicating factors are involved in the assessment of leachate biodegradation, including the complex mixture of landfill leachate contaminants, the possible presence of several different plumes, and the inability to use chloride production as an indicator [4]. A combination of geochemical and microbiological assessments are needed to establish the processes acting in a given aquifer [5,6]. Research indicates that simple patterns to describe such processes are inadequate, and that it is nearly impossible to develop guidelines to be implemented across the board concerning the ability of the unsaturated zone to effectively remove contaminant [7].

Redox zones are not easily identified based on aqueous parameters, though there are exceptions (e.g., Vejen Landfill, Denmark), but the role of electron acceptors in contaminant reduction is clearly evident in landfills in the US, Canada, and Europe [8]. Redox zones, very much dependent on local conditions, develop after the entry of leachate, and form in such a way that methanogenic conditions are noted near the source, with oxidized conditions along the perimeter [8].

The interaction of landfill leachate with sediment and the development of redox zones have been observed in field studies [9,10]. Laboratory column studies examining leachate or lactate and native sediments have also been conducted [11,12,13]. Microcosm studies have been completed showing leachate degradation from Fe³⁺ and SO₄²⁻ reduction [14,15,16]. Lab results generally tend to underscore those observed in the field [16], but there remains a pressing need for more research in more diverse landfill plumes [17]. A critical review conducted by Christenson et al. [8] indicated that leachate plumes rarely extend beyond the width of the landfill or more than 1000 m downgradient. This indicates that natural attenuation processes work on leachate plumes. The organic components of landfill plumes rarely reach 1000 m, indication that intrinsic biodegradation is occurring.
3 AMIBA background and theory

A more detailed review of AMIBA can be found elsewhere [18,19,20]. A brief introduction to important points is given here.

Very little aqueous Fe$^{3+}$ is typically present in the subsurface, though comparatively large amounts may be present as amorphous to poorly crystalline particles, often as coatings on or in silicates. Only a portion of the total iron present in a subsurface system, the bioavailable Fe$^{3+}$ fraction, is susceptible to direct enzymatic reduction. Biologically available iron may depend on a number of factors, such as surface proximity, surface area, the mineral iron form, exposure time, and the presence of chelating compounds. A 0.5 N HCl extraction is used in the work described here [18]. Reduced iron produced by biodegradation processes is referred to here as biogenic Fe$^{2+}$. It is also extracted using 0.5 N HCl.

Because of solubility constraints, Fe$^{2+}$ produced from Fe$^{3+}$ reduction is typically found in mineral form [14]. The direct enzymatic reduction of Fe$^{3+}$ minerals may produce a certain amount of dissolved Fe$^{2+}$ as:

\[
\text{CH}_2\text{O} + 4\text{Fe}^{3+} + \text{H}_2\text{O} \rightarrow 4\text{Fe}^{2+} + \text{CO}_2 + 4\text{H}^+ \quad (1)
\]

However, Fe$^{2+}$ often precipitates in several mineral forms, including iron monosulfides (\(\sim\text{FeS}\)), siderite (FeCO$_3$), magnetite (Fe$_3$O$_4$), vivianite (Fe$_3$(PO$_4$)$_2$$\cdot$8H$_2$O)).

In aquifers, SO$_4^{2-}$ is typically considered a dissolved ion; however, two mineral forms of sulfate are found in some geographic areas; anhydrite (CaSO$_4$) and gypsum (CaSO$_4$$\cdot$2H$_2$O). A general equation for sulfate reduction is:

\[
\text{CH}_2\text{O} + \frac{1}{2} \text{SO}_4^{2-} \rightarrow \text{HCO}_3^- + \frac{1}{2}\text{HS}^- + \frac{1}{2}\text{H}^+ \quad (2)
\]

Biologically available Fe$^{3+}$ may be consumed before SO$_4^{2-}$; however, SO$_4^{2-}$ reduction often occurs in the presence of substantially large amounts of mineral Fe$^{2+}$ [21]. As summarized by Appello and Postma [22], produced HS$^-$ reacts with mineral iron generating authigenic mineral iron sulfides, keeping aqueous HS$^-$ concentrations low, e.g.:

\[
2\text{FeOOH} \rightarrow + 3\text{HS}^- \rightarrow 2\text{FeS} + \text{S}^0 + \text{H}_2\text{O} + 3\text{OH}^- \quad (3)
\]

As a secondary step, iron monosulfides may combine with elemental sulfur to form pyrite (FeS$_2$).

4 Methods

All sediment samples were obtained under anaerobic conditions and stored under nitrogen at 4°C. AVS, or acid volatile sulfides, are extracted and volatilized.
using 6 N HCl; they correspond to sulfide as FeS. CrES₃ or chromium extractable sulfides, are extracted and volatilized using 1 N Cr₂⁺ and 12 N HCl; they correspond to sulfide as FeS₂ and S⁰ [18]. In each case, the sulfide is captured in a zinc acetate trap and measured by spectrophotometry. The 6 N HCl extraction is also used to measure bulk iron, where bulk iron consists of all, or nearly all, iron coating the sediment. Bioavailable Fe³⁺ and biogenic Fe²⁺ are extracted from sediment using 0.5 N HCl [18] and measured by spectrophotometry. Aqueous Fe is measured by spectrophotometry. Aqueous and sediment volatile organics are also measured, using appropriate methods such as EPA method 8260.

5 Results

5.1 Landfill Microcosms

The work presented in this section is given in greater detail elsewhere [23]. Microcosms were used to study the degradation of simulated leachate under iron and sulfate reducing conditions. Two different native sediments were used as microcosm media; quaternary alluvial sand (Qal) from the South Canadian River and sand from the Permian aged Garber-Wellington (PgW) sandstone formation, both from surface exposures near Norman, Oklahoma. Both Qal and PgW sediments are fine to very fine grained. Microcosms consisted of 85 g of PgW or 100 g Qal sediment in 160 ml serum bottles. Different amounts were used to attain similar pore volume.

A 2,000 mg/L total non purgable organic carbon (NPOC) solution was used to simulate landfill leachate. To each microcosm 22 ml leachate solution was added, sufficient to just cover the top of the sediment.

Different microcosms were constructed by adding mineral gypsum (CaSO₄•2H₂O), mineral ferrihydrite Fe(OH)_₃, or nothing. The amount of Fe and S minerals added was theoretically sufficient to oxidize 95% of the added organic carbon exclusive of any assimilative (anabolic) carbon utilization. Sediment containing bacterial seed was obtained approximately 0.6 m below the surface near the toe of the closed Norman Landfill, Norman, Oklahoma. Five grams of bacterial seed sediment was added to each microcosm. Killed controls were used.

Results indicate that solid gypsum and Fe³⁺ minerals can be used as terminal electron acceptors by bacteria for degrading simulated landfill leachate. Aqueous Fe²⁺ represented only a small fraction of total Fe³⁺ reduced; therefore, evaluating dissolved Fe²⁺ as part of a natural attenuation field study is expected to be a poor indicator of the magnitude of Fe³⁺ reduction. Although relatively large amounts of solid Fe³⁺ minerals were present in native sediments used, only a small portion, between 4 to 15%, was available for enzymatic reduction. For the sediments studied, the 0.5 N HCl extraction gave a reasonable approximation of the biologically available Fe³⁺. Solid Fe³⁺ reduction occurred over a wide redox range, including concurrent with methanogenesis.
The formation of reduced S minerals was found to be rapid compared with typical ground water seepage velocities, indicating that AVS and CrES minerals will precipitate near the point of SO$_4^{2-}$ reduction, provided mineral Fe$^{3+}$ is present. Thus, finding reduced iron and/or sulfide minerals downgradient of a plume is a good indicator that the plume is shrinking.

By chemical balance the amount of organic oxidized via microbial processes could be estimated by quantifying mineral respiratory products. Thus, organic contaminant oxidation by microbial SO$_4^{2-}$ and Fe$^{3+}$ reduction can be conservatively estimated by measuring reduced Fe and S mineral species in aquifer sediments. Sampling for reduced Fe and S mineral species should be considered as part of any natural attenuation analysis protocol.

5.2 Landfill field work

The Norman Landfill is an unlined, closed municipal landfill south of Norman, Oklahoma, first used for disposal in the early 1920’s and closed in 1985 [24,25]. The sediment is river alluvium consisting mostly of fine to coarse sand with thin layers of clay. The water table is approximately 0.6 m below the surface. Six core holes were drilled by the United States Geological Survey, each to a depth of approximately 11 meters. The authors obtained sediment samples and used acid extractions to measure iron and sulfide minerals in two core holes, C-1 and C-2, both in the leachate plume. For more information on this work, see Kennedy et al. [18]. This landfill has been extensively studied. For a list of Norman Landfill related abstracts, see ok.water.usgs.gov/norlan/abstracts.html.

The ratio of Fe$^{2+}$ to total Fe for bioavailable/biogenic iron and bulk iron can aid in identifying zones of significant Fe$^{3+}$ reduction. Exposure to 0.5 N HCl typically extracts only a small portion of the total iron present, e.g., exposed iron surfaces and poorly crystalline iron particles. Alternatively, the 6 N HCl extraction removes much greater amounts of iron including all of the 0.5 N HCl extractable fraction and much of the background bulk iron mass. During microbial reduction, some of the original Fe$^{3+}$ mass is used to form new Fe$^{2+}$ minerals. These biological processes often alter only a small amount of the total iron; thus, there is little change in the bulk Fe$^{2+}$ to total Fe ratio. However, newly formed Fe$^{2+}$ minerals are not evenly distributed in the total iron matrix. Rather, they are deposited almost exclusively as surface coatings or poorly crystalline particulates, which are preferentially dissolved by the weak 0.5 N HCl acid extraction. Therefore, where microbial iron reduction has occurred, the Fe$^{2+}$ to total Fe ratio will tend to be high for the 0.5 N HCl compared to the 6 N HCl extraction. Core hole C-1 shows highly elevated 0.5 N HCl Fe$^{2+}$ ratios across almost the entire thickness of the aquifer (Figure 1). The concentration of reduced Fe can be used to estimate contaminant degradation.

A statistical approach is used to evaluate iron ratios from 6 N and 0.5 N HCl extractions. The 99.9% probability limit is determined for the 6 N HCl extraction data. If percents obtained from the 0.5 N HCl extraction lay primarily outside this range, it is concluded that biodegradation has generated Fe$^{2+}$. In
Figure 1, all of the 0.5 N HCl ratios are outside the 99.9% probability limit, indicating that significant biodegradation via iron reduction has occurred.

Areas of sulfate reduction were also found at the study site (Figure 2). Two fluvial depositional sequences are recognized, denoted by two coarsening-downward sediment grain size sequences. The AVS pattern suggests recent SO$_4^{2-}$ reduction just below the water table and at the base of the aquifer and infers hydrogeologic control of SO$_4^{2-}$ reduction processes. There is a correlation between increased aquifer matrix grain size and increased S mineral deposition.

It is likely that both leachate and SO$_4^{2-}$ mass transport are greater in more porous/permeable aquifer layers, increasing the potential for SO$_4^{2-}$ reduction. High levels of CrES above 4 m may have been caused by preferential leachate and/or SO$_4^{2-}$ migration in porous sand bounded below by a poorly permeable clay layer. Little SO$_4^{2-}$ reduction occurred in the clay layer between 4 to 6 m; however, below that zone CrES levels increased correlative to aquifer grain size. High levels of AVS were again noted at the bottom of the aquifer suggesting recent SO$_4^{2-}$ reduction in permeable gravel. The concentrations of AVS and CrES can be used to estimate contaminant degradation.

5.3 AMIBA field studies

To date, a complete AMIBA assessment has not been attempted at a landfill site. However, studies completed at fuel and chlorinated solvent sites provide results that suggest AMIBA will be effective at landfill sites. At each of the sites studied by the authors, estimates of expressed capacity for oxygen, nitrate, iron, and sulfate were obtained, with oxygen and nitrate estimates made using a sulfate indexing technique [19,20]. Table 1 is used to present results from three sites, a gasoline filling station [19], a military fire-training area [26], and an underground fuel tank (UST) site (work in progress).
Table 1: AMIBA results

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Gasoline Station</th>
<th>Fire Training</th>
<th>UST</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen Expressed Capacity (%)</td>
<td>1.5</td>
<td>4.8</td>
<td>0.5</td>
</tr>
<tr>
<td>Nitrate Expressed Capacity (%)</td>
<td>53.7</td>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Iron Expressed Capacity (%)</td>
<td>36.3</td>
<td>83.2</td>
<td>13.4</td>
</tr>
<tr>
<td>Sulfate Expressed Capacity (%)</td>
<td>56.5</td>
<td>8.0</td>
<td>85.1</td>
</tr>
<tr>
<td>Fuel Degraded (%)</td>
<td>NA</td>
<td>96.0</td>
<td>92.0</td>
</tr>
<tr>
<td>Fuel Degrade (Moles)</td>
<td>NA</td>
<td>52,900</td>
<td>21,373</td>
</tr>
<tr>
<td>Fuel Source Decay Rate (yr⁻¹)</td>
<td>NA</td>
<td>0.24</td>
<td>0.17</td>
</tr>
</tbody>
</table>

NA – Not available

At the gasoline station site, 5 bore-holes were drilled along the plume centerline, to a depth of 7 meters. The sediment is a fine-grained, poorly-cemented, thick bedded sandstone with intermittent lenses of siltstone and shale. At the second and third sites, 18 and 20 bore-holes were drilled, respectively, allowing geostatistical methods to be used to create three dimensional models of sediment concentrations at each site. The sediment at the military fire-training site is fine to coarse sand with traces of gravel and silt deposited as deltaic outwash deposits. The sediment at the UST site consists of three lithologic intervals - alluvium, shale, and siltstone. The alluvium is predominantly clay but also contains channel sands and silts. The shale layer contains intervals that are fractured or crumbly, which appear to be major zones of water transmission. The sediments at all three sites contain iron coatings. Oxygen, nitrate, and sulfate concentrations at the sites are typical, except at the third site, where a layer of solid gypsum results in some extremely high aqueous sulfate concentrations (~2,000 mg/L).

In Table 1, the expressed capacities describe the percent of fuel degraded via each electron acceptor. Fuel degradation is described in terms of both percent of fuel destroyed relative to the amount spilled and moles destroyed. A first order source decay rate is also presented. The results provided in Table 1 indicate that AMIBA can provide valuable information concerning intrinsic biodegradation. It illustrates the importance of iron and sulfate. At each site, over 80% of fuel degradation depended on iron and sulfate; much of this would have been missed if the authors had relied on aqueous concentration analyses alone. The distribution of contaminants remaining at the sites and Fe²⁺ indicated that, at each site, the plume is retreating. This observation is possible because active iron reduction leaves a footprint of either depleted Fe³⁺ or enriched Fe²⁺ minerals. Plume retreat can be inferred when the iron footprint is larger than the observed plume extent. Finally, the source decay constant (k) can be estimated, assuming first order kinetics, given an estimate of average plume age (t), current contaminant mass (Cᵢ), and total expressed capacity for all electron acceptor types (Cₑₓᵖ). This can be used to predict contaminant fate.
6 Conclusions

AMIBA is an approach to natural attenuation that focuses on reduced Fe and S minerals as opposed to measuring aqueous parameters. With a single monitoring event the method can 1) demonstrate plume retreat using the Fe footprint approach, 2) assess bioremediation efficiency and 3) estimate source decay for predictive modeling of contaminant duration. In microcosms, the importance of mineral iron and sulfides in degrading simulated leachate was demonstrated. Fieldwork at a landfill site demonstrated that elevated levels of reduced iron and sulfide minerals are found with in landfill plumes. Furthermore, a statistical method was demonstrated that can be used to identify sediments where biologically mediated iron reduction has occurred. Finally, three fuel contaminated sites were described where AMIBA has been used to successfully assess intrinsic biodegradation which could be viewed as a simplified model for similar landfill analyses.

The heavy reliance on monitoring before evaluating natural attenuation as a treatment alternative can be reduced using AMIBA. AMIBA can maximize the possibility for selecting natural attenuation because important microbial processes are severely under represented when only aqueous analyses are used. Further, if remediation is required AMIBA can aid in treatment system design. For example, at one of the test sites, an assimilative capacity of 21 times the existing fuel mass is present as reactive Fe$^{2+}$ minerals which would provide a strong chemical sink for oxygen or oxidizing agents added for remediation.

References


