# RCRA FACILITY INVESTIGATION-REMEDIAL INVESTIGATION/ CORRECTIVE MEASURES STUDY-FEASIBILITY STUDY REPORT

## CONTAMINANT FATE AND TRANSPORT

## SECTION 8.0: ATTACHMENT 1

## CD ROM, Physical, Chemical, and Biological Processes That Influence Contaminant Transport and Persistence in the Environment

June 2006

# TABLE OF CONTENTS

# LIST OF FIGURES

# 1.0 PHYSICAL TRANSPORT PROCESSES

## 1.1 Erosion - Water

Soil erosion occurs when precipitation exceeds the infiltration capacity and surface storage capacity of the surface soil, creating overland flow that entrains soil particles and carries them down slope (Dreicer et al. 1984; Kidwell et al. 1997). Snowmelt runoff usually occurs more slowly than rainfall. However, if the soil is frozen and temperatures become high, then large amounts of runoff may occur rapidly. Both rain and runoff from snowmelt have the potential to transport soil across the Rocky Flats Environmental Technology Site (RFETS or site) landscape. Storm events with hail can potentially accelerate erosion processes. Movement of soil particles, along with associated contaminants bound to the soil, such as plutonium-239/240, americium-241, or chromium, can cause migration of the contamination.

There are two basic forms of overland flow that cause erosion of surface soil: rill flow and interrill (sheet) flow. A rill is an area on the soil surface that supports concentrated flow. A rill can be thought of as a microchannel. Concentrated rill flow is the flow of runoff in these microchannels. Both soil and plant growth characteristics contribute to the morphology of rills. Most of the erosion that occurs in rills is due to the energy of the flowing water (Lane et al. 1987). Erosion between rills, interrill flow, is less obvious than that due to rill flow, with water running over the soil surface in a diffuse sheet. Much of the energy for detachment of soil particles for transport by interrill flow comes from raindrop impact, although the proportions of detachment due to rainfall impact and surface flow depend on other factors, including slope, cover, and soil type (Ellison 1947; Kinnell 1985; Quansah 1985).

Many physical and biological factors affect soil erosion and sediment yield on rangeland watersheds. The susceptibility of a soil to erosion is controlled by soil characteristics, soil cover, and hillslope steepness. Soil characteristics affecting erodibility include hydraulic conductivity (rate of infiltration), surface roughness, soil texture, bulk density, soil organic matter content, and the degree and stability of soil aggregation (Gutierrez and Hernandez 1996; Simaton et al. 1991; Dadkah and Gifford 1980; Blackburn 1975). Factors affecting erosion of the soil cover include the amount of plant cover, rock cover, and biomass. At RFETS, dense vegetation, which creates a large amount of soil cover in the Walnut and Woman Creek watersheds, provides protection against erosion. Areas with less cover and unpaved roads are interspersed throughout the watersheds; these areas account for much of the soil erosion occurring at the site.

In addition to overland flow, channel flow also can cause erosion and its associated transport of particulate, colloidal, and dissolved constituents.[1] Precipitation runoff and

---

[1] A general operational definition for particles, colloids, and dissolved phase constituents, based on size, is: a) particles are larger than 0.1 micron in diameter, b) colloids are approximately 0.1 micron to 0.001 micron in diameter, and c) dissolved is less than 0.001 micron in diameter.

releases from the detention ponds cause turbulent flows in channels that are capable of resuspending and transporting streambed sediments.

Factors that affect particulate mobility in surface water streamflow include:

- Stream bed composition;
- In-stream vegetation, such as cattails, that can physically filter out the particulates; and
- Diversion dams or other physical barriers that slow surface flow and enhance particle settling.

Particulate transport occurs through combinations of the above processes and not any single mechanism. The results of the watershed erosion and sediment transport modeling conducted for the Actinide Migration Evaluation (AME) indicated that specific soil erosion and runoff controls will be needed to protect surface water quality. In addition, removal of buildings and pavement has decreased runoff volumes and peak discharge rates, which will reduce soil erosion, with its associated plutonium and americium transport and impact on surface water and sediment. Improvement is based on the assumption that vegetation is established, soil is stabilized, and widespread soil disturbance does not occur in areas with residual plutonium and americium in the soil.

## 1.2 Erosion - Wind

Wind acting on the soil surface and vegetation entrains and resuspends contaminated particles. Airborne particles are transported some distance downwind before being deposited on the ground or in water by a variety of mechanisms that remove particles from the air, such as rainout or dry deposition. Over time, repeated cycles of resuspension and redeposition have spread the initial contamination in a downwind direction; this process will continue to affect and redistribute remnant surface soil contamination.

Ongoing contaminant resuspension at RFETS is episodic in nature and influenced primarily by meteorological variables (wind speed and rainfall), soil properties (moisture level, and particle size and density), and surface characteristics (density and type of vegetative growth and presence or absence of snow cover). In a vegetated area, a primary source of contaminated soil resuspension is likely to be the dust-laden vegetation and litter, with less potential for direct resuspension from soil surfaces except during high-wind events.

As wind speed increases, soil particulate resuspension increases in a nonlinear fashion. Some types of surfaces have been shown to have a definite threshold for initiation of wind erosion; wind erosion does not occur until winds exceed this threshold velocity. Wind tunnel studies at RFETS, however, have not demonstrated a definite threshold for wind erosion, although erosion has been shown to increase rapidly when winds at 10-meter (m) height increase above approximately 40 miles per hour (mph) (MRI 2001). Below those speeds, resuspension of soil occurs but at a very low rate. This lack of a definite threshold for initiation of wind erosion occurs because there are multiple contributors to wind-generated particulate matter emissions: (1) bulk soil, (2) settled surface dust trapped by vegetation, and (3) the vegetation itself. The particle releases from these sources are all driven by different mechanisms, each with a different wind speed dependance.

Wind erosion also varies seasonally because of differences in soil moisture levels, changes in vegetation cover, and variations in wind speed. Moist soil and snow cover are effective in limiting resuspension. Growing vegetation may have a more complicated effect by decreasing erosion from the soil surface, while providing an enhanced source of erodible particles on the leaf surfaces. Wind erosion of undisturbed, vegetated areas occurs at a low rate. However, any activity that disturbs the soil or removes the covering vegetation would increase emissions for a period of time. Such activities might include vehicle traffic or fires; the magnitude of the increase would depend on the frequency of disturbance and whether the disturbance is followed by high winds before the soil crusts or the vegetation is restored.

As stated earlier, in a vegetated area, a primary source of contaminated soil resuspension is likely to be the dust-laden vegetation and litter, with less potential for direct resuspension from soil surfaces except during high-wind events. Higher winds are more effective in causing resuspension of particles; however, it is important to note that total airborne soil and radionuclide emissions are ultimately limited by the available reservoir of erodible particles on the soil or leaves. A high-wind event will rapidly deplete the erodible particles. The first few minutes of high winds may result in significant airborne emissions but the emission rate will decrease with time as fewer and fewer erodible particles remain. Sustained windy periods will not result in further emissions until the erosion potential is replenished by deposition or by other factors that generate erodible particles (such as freeze/thaw cycles, rainsplash, animal activity, and so forth).

Once released into the air, particles of soil with attached radionuclides are transported away from source areas by the wind (dispersion). Concentrations of airborne radionuclides will generally be higher closer to the source areas; the contaminant concentrations become diluted as they are transported downwind. During transport, particles are brought down to the surface through the combined processes of turbulent diffusion and gravitational settling. Once near the surface, they may be removed from the atmosphere and deposited on soil or water surfaces (deposition).

The distance a particle travels before being deposited depends on the particle’s size and density. Larger, denser particles are deposited closer to the source, while very small particles may remain suspended and be carried much farther downwind.

The concentration and deposition of radionuclides in the RFETS environment depends on the local patterns of wind flow. Figure 8.9 (in Section 8.0) shows a joint frequency distribution of wind speed and direction (wind rose) for a representative year. The figure shows that prevailing winds occur from the northwest quadrant, but that winds from other directions also occur, with reduced frequency.

More importantly, the figure shows that higher-speed winds occur almost exclusively from the northwest quadrant. This is significant because wind erosion emissions are a function of wind speed; larger amounts of soil are resuspended by high winds than by lower-speed winds. The higher-speed winds are also more effective at transporting particles away from source areas (farther downwind), where many of these particles will be redeposited as wind speeds decrease. Finally, wind speed influences the range of particle sizes emitted and transported. Higher-speed winds are capable of resuspending and transporting larger particles than lighter winds.

## 1.3 Sediment Transport

Sediment transport is an important mechanism for migration of constituents associated with solids. Contaminants with high partition coefficients will preferentially sorb on to suspended solids in the water column, which are then transported along with the solids in the bulk advective flow. In addition to advective transport of contaminants in the water column, contaminants sorbed to particles in the sediments can be resuspended by channel scour mechanisms.

In locations where the surface water velocity is reduced because of either natural or constructed features, such as in broad, natural channels or in constructed detention ponds, the features act to settle out particulate matter suspended in the water column. Water quality data for pond effluent compared with data for stormwater inflows supports this conclusion by indicating a significant reduction in total suspended solids (TSS) downgradient from the ponds.

In general, sediment transport in the RFETS closure configuration will be reduced compared with the historic developed condition, because the elimination of buildings and pavement will result in diminished runoff and reduced peak flow rates during storm events, when the majority of sediment transport occurs. In addition, vegetative cover over previously exposed soil areas will also promote reduced deposition and migration of sediments.

## 1.4 Advection

Advection is the most important transport process driving contaminant migration in the subsurface (K-H 2002b). Solute transport by advection (acting alone) would carry an aqueous (dissolved) groundwater contaminant downgradient at a velocity that is directly proportional to the hydraulic gradient and the hydraulic conductivity of the porous medium. Ignoring other processes, advective transport from a continuous source would produce a plume with a sharp concentration front. Upgradient of the solute front the analyte of interest (AOI) concentration would be the same as that at the source area. Downgradient of the front, the AOI concentration is zero. In nature, an advancing plume front is actually spread out by the additional processes of dispersion and diffusion.

Furthermore, transport of an AOI is retarded by biodegradation and abiotic chemical reactions, as well as by sorption to the porous medium.

### 1.5 Dispersion

Hydrodynamic dispersion is the process that spreads out a contaminant plume in three dimensions: parallel to the direction of migration (longitudinal), laterally (transverse), and vertically. The underlying processes are mechanical dispersion and molecular diffusion. Mechanical dispersion is the most important at ordinary groundwater velocities, and its magnitude is directly proportional to groundwater velocity and dispersivity.

Dispersion is a mixing process caused by local variations in groundwater velocity and direction due to heterogeneities in the porous medium at microscopic to megascopic scales. The result of dispersion is spreading and mixing at the plume edges. This causes the plume front to grade from zero concentration at its downgradient leading edge with successively increasing concentrations upgradient of the edge.

### 1.6 Colloidal Transport

It is generally accepted that a fraction of soil particles are mobile as colloidal particles (diameter less than 0.1 micron), and soil colloids may transport contaminants in both the vadose zone and in groundwater (de Jonge et al. 2004; Ranville et al. 2005). The size distribution, particle shapes, mineralogy, and surface chemistry are known to influence colloid transport and deposition (Ranville et al. 2005). Colloidal transport of contaminants through soil and groundwater is an active area of research.

### 1.7 Recharge and Dilution

Dilution reduces contaminant concentrations as groundwater recharge (infiltration) adds uncontaminated water to the contaminated groundwater system. The most common causes of dilution are infiltration of precipitation and leakage of surface water to a shallow water table aquifer. However, mixing of groundwater from different sources or lithologies may also lead to dilution.

### 1.8 Discharge

Discharge occurs where the water table intersects the ground surface at a seep, spring, or stream. Groundwater discharge is a pathway to surface water in streams, ponds, springs, and seeps and may directly transport contaminants from groundwater to surface water.

### 1.9 NAPL Migration

Dense solvents (such as tetrachloroethene, trichloroethene, and carbon tetrachloride) may pool on impermeable sediments or bedrock to form a separate phase called dense non-aqueous phase liquids (NAPLs) (DNAPLs). DNAPLs sometimes move (migrate) under the action of gravity at different velocities and sometimes in different directions relative to associated groundwater (Figure A1.1). Capillary forces may retain residual pockets of DNAPL at various depths in the porous medium (subsoil). DNAPLs have been identified and remediated down to the upper hydrostratigraphic unit (UHSU) water table by soil excavation at RFETS Individual Hazardous Substance Site (IHSS) 118.1, at historical Oil Burn Pits Nos. 1 and 2, and in some of the historical East Trenches (T-3 and T-4).

Fuels with a density less than that of water and low solubility in water may float as a thin layer on top of the groundwater table. Such chemicals are called light nonaqueous phase liquids (LNAPLs). LNAPLs may also migrate at different rates than the underlying groundwater. No LNAPLs of substantial extent have been identified at RFETS. Bunker oil found in subsurface soils at the Steam Plant might have formed an LNAPL if groundwater had been present. Thus NAPL migration is not believed to be a significant contaminant pathway at RFETS, although residual DNAPL may provide a long-term contaminant source supplying volatile organic compound (VOC) plumes in site groundwater.

### 1.10 Volatilization

Some chemicals readily volatilize from shallow or discharging groundwater to air. Volatilization is a nondestructive attenuation mechanism that removes contaminant mass from groundwater. The degree of volatilization of a chemical from water depends on its vapor pressure and its water solubility (Howard 1989). Henry's Law describes the partitioning of a contaminant between the aqueous phase and the gaseous phase. The law is defined as $H = C_a/C_w$, where parameter H is the Henry's Law constant, $C_a$ is the concentration in air, and $C_w$ is the concentration in water. Chemicals with H values less than $10^{-7}$ volumetric atmospheres per mole (atm-$m^3$/mole) are less volatile than water and their groundwater concentrations should increase as water evaporates. Chlorinated Aliphatic Hydrocarbons (CAHs) are much more volatile with H values ranging from a low of 0.001 atm $m^3$/mole for 1,2-dichloroethane to approximately 1.22 atm $m^3$/mole for vinyl chloride. However, the overall volatilization rate from groundwater is influenced by water table depth, soil moisture content, the presence of sorbents such as organic matter, and other environmental factors (Howard 1989). Except for vinyl chloride, and portions of plumes that are shallower than 1 m, attenuation due to volatilization (that is, reduction in concentrations) from groundwater can generally be neglected (EPA 1998).

## 2.0 CHEMICAL PROCESSES

### 2.1 Sorption, Desorption, and Ion Exchange

Sorption is a generic term for several complex processes by which chemicals are removed from water and bound onto a solid. Sorption and desorption are opposing processes, and they are frequently of unequal magnitude. Sorption of some contaminants on specific substrates may be irreversible, allowing negligible desorption to occur. Sorption is a process where dissolved contaminants chemically bind to minerals or organic matter in the aquifer matrix thus decreasing their dissolved concentrations in groundwater. Desorption is the reverse process by which contaminants are released from the soil matrix increasing their concentrations in groundwater.

As mentioned, sorption is a generic term for several chemical attenuation mechanisms that will not be discussed here: adsorption, coprecipitation, and precipitation. Ion exchange is commonly discussed as the exchange of metal cations on clay surfaces. However, Langmuir (1997) observed that ion adsorption is always part of an ion exchange reaction.

Sorbents with net negative surface charges have cation exchange capacity, while sorbents with net positive surface charge have anion exchange capacity (Langmuir 1997). The clay kaolinite and metal hydroxides have a pH-dependent surface charge that is net positive in acid solution and net negative at higher pHs (Langmuir 1997). It is important to note that many common minerals of particular interest as sorbents of contaminants have a net negative surface charge at the near-neutral to slightly alkaline pH values (6 to 9) of most groundwater. Under these pH conditions cationic contaminants in groundwater are usually sorbed (for example, ammonium ion), while anionic contaminants (for example, chromate ion) are in general highly mobile. EPA (2004) notes that cation sorption is greatest at high pH because it is coupled with the release of $H^+$. Minerals expected to have net negative surface charge in neutral to alkaline groundwaters include Na- and K-feldspars, quartz, Mn oxides, hematite, goethite, kaolinite, and smectite clays such as montmorillonite (Langmuir 1997).

The most simplistic and widely used model of sorption and desorption assumes that they are reversible processes that can be modeled by a parameter called the “distribution coefficient,” $K_d$. Sorption acts to slow the transport velocity contaminants ($V_c$) relative to the velocity of the groundwater ($V_w$) which is defined as $V_c = V_w/R$, where R is the coefficient of retardation. At chemical equilibrium in a mixture of water and soil, $K_d$ equals the mass of contaminant bound to the soil ($C_s$) divided by the contaminant concentration remaining in groundwater ($C_g$), or $K_d = C_s/C_g$. The larger the $K_d$ value, the greater the fraction of contaminant that will be bound to the aquifer soil, resulting in a larger retardation factor.

$K_d$ values are specific to the contaminant of interest, the mineralogy of the porous medium, and the chemical composition of the groundwater. Literature values of $K_d$ often vary over several orders of magnitude; $K_d$ values for many analytes (particularly metals) are strongly pH-dependent. The degree of sorption of a contaminant is also dependent on its aqueous speciation, and on the concentrations of other ions competing for sorption sites. There are numerous pitfalls and technical issues associated with measuring, selecting, and applying $K_d$ values in a meaningful way (EPA 1999, 2004). It is noted that $K_d$ is not an appropriate representation for migration of contaminants in an insoluble, particulate form, such as plutonium and americium (K-H 2002a).

Many classes of organic molecules tend to bind strongly to the natural organic carbon found (in low percentages) in many sedimentary aquifer host rocks and sediments. Therefore, the sorption behavior of manmade organic compounds, such as CAHs and polychlorinated biphenyls (PCBs), is commonly quantified by the “organic carbon distribution coefficient,” $K_{oc}$. $K_{oc}$ is defined as the mass of contaminant sorbed per gram of organic carbon, divided by the contaminant mass per milliliter of water (that is, its aqueous concentration). Values of $K_{oc}$ can vary by more than seven orders of magnitude for different organic chemicals (Langmuir 1997). $K_d = K_{oc}$ times the fraction of organic carbon in the soil or sediment.

The properties of each specific contaminant interact with the geochemical and hydrological properties of the groundwater environment to determine its mobility in groundwater. Substances whose properties produce little retardation relative to the groundwater velocity are said to be highly “mobile” in the environment. Chemicals with high solubility in water and weak sorption properties tend to be very mobile. Chemicals with large $K_{oc}$ values usually have very low solubility in water. For manmade organic compounds (VOCs, semivolatile organic compounds [SVOCs], and PCBs), $K_{oc}$ is a good indicator of both mobility and aqueous solubility. Low $K_{oc}$ values up to 50 milliliters per gram (mL/g) indicate “very high” mobility and high solubility in water. $K_{oc}$ >50 to 150 means “high” mobility, >150 to 500 is “moderate” mobility, >500 to 2,000 is “low” mobility, >2,000 to 20,000 is “slight” mobility, and >20,000 is considered “immobile” (Fetter 1988).

As a first approximation, the above mobility ranges of Fetter (1988) can be described in terms of $K_d$ ranges by assuming an average organic carbon content of 1 percent in soil. Then, $K_d = K_{oc}/100$, and, for example, “slight” mobility would be defined by $K_d$ values in the range >20 to 200, while $K_d$ >200 mL/g is “immobile.” This rule of thumb is in good agreement with Drever (1988, p.96) who considers $K_d$s for metals >100 mL/g as “essentially immobile.”

## 2.2 Hydrolysis

Hydrolysis refers to the direct reaction of a CAH molecule with water. An important example is the hydrolysis of 1,1,1-trichloroethane to form acetic acid ($C_2H_3OOH$). This process is relatively rapid, with a hydrolysis half-life of 0.5 to 1.7 years (Vogel et al. 1987). A chloride ion is released to groundwater and the generated acetate ions are consumed by bacteria or are oxidized to carbonic acid dissociation species, such as bicarbonate ion.

A second example is the hydrolysis of chloroethane to form ethanol ($CH_3CH_2OH$). Hydrolysis is very rapid with a chloroethane half-life of 0.12 years (Vogel et al. 1987). Similarly, methanol is produced from the hydrolysis of chloromethane, a compound formed in the carbon tetrachloride decay series.

In general, monochloroalkanes hydrolyze with half-lives of approximately 1 month, while polychlorinated molecules hydrolyze at a slower rate (that is, have longer half-lives). Carbon tetrachloride slowly hydrolyzes with a half-life of 41 years, while its daughter chloroform has a half-life of 3,500 years (Wiedemeier et al. 1999).

## 2.3 Oxidation-Reduction

Oxidation-reduction (redox) reactions may change the chemical form, mobility, and toxicity of contaminants that contain elements, which may exist in different valence states. Specific redox environments are recognized in groundwater by the types and abundances of redox chemicals present (for example, dissolved $O_2$ [DO], $NO_3^-$ versus ammonia, and sulfate versus dissolved sulfide). When groundwater contacts a supply of reducing agents (reductants such as organic carbon), the oxidants in the water are reduced (consumed) in the order of strongest to weakest oxidant. The exact order is pH-dependent, but the common order of reduction is first DO, then nitrate, Mn(IV), Fe(III), sulfate, and $CO_2$.

Redox reactions can affect contaminant fate and transport in a number of ways. For example, Fe(III) precipitates as ferric hydroxide, a highly adsorptive solid that sorbs trace metals, while in comparison Fe(II) phases are relatively soluble under moderately oxidizing conditions. In a reducing groundwater the reduction of ferric hydroxide releases ferrous iron and formerly sorbed trace metals (McLean and Bledsoe 1992).

Chromium is an example of the effect of redox on mobility. Cr(VI) is an industrial pollutant that may be highly mobile in “oxidizing” groundwater in which it moves as the chromate anion. However, in a reducing environment chromium is relatively immobile in the Cr(III) valence as it forms a Cr(III) hydroxide solid phase of low solubility.

An example of the effect of redox on chemical fate is that groundwater containing more than approximately 1 milligram per liter (mg/L) DO is considered too “oxidizing” for biodegradation of CAHs by reductive dechlorination.

## 2.4 Solubility, Precipitation, and Dissolution

The solubility of contaminant-bearing phases in waste, contaminated soil, or NAPL is an important process allowing contaminants to reach pore water and groundwater. The relative solubility of a mineral in water is specified by its “solubility product constant,” Ksp. If the “ion activity product” of the relevant ions in aqueous solution exceeds the Ksp, then the solid may precipitate. If the ion activity product is smaller than the Ksp, and if the solid phase was pre-existing, then the solid may undergo “dissolution” (that is, dissolve).

Solubility is commonly affected by the pH of the groundwater or surface water, as well as other factors such as the availability of complexing ligands. Good examples of this are the amphoteric metals Al and Fe. The solubility of the Al-hydroxide gibbsite has a solubility minimium at pH 6.3, while the Fe-oxyhydroxide goethite has a minimum at pH 8.0 (Langmuir 1997).

## 2.5 Complexation and Speciation

When a contaminant dissolves in water it often exists in more than one dissolved chemical form, or "aqueous species." Some species are more abundant that others depending on the water chemistry and the chemistry of the element. Speciation of an aqueous element or contaminant refers to the prediction of the set of chemical entities that probably exist when the element dissolves in natural water. A "complex ion" or "complex" is an aqueous chemical species that forms from the chemical association of a cation (usually a metal) with one or more anions or neutral molecules. Complexation is important to contaminant transport and fate for several reasons (Langmuir 1997, 1978).

Most trace metals are transported in groundwater and surface water as complex ions rather than free ions. Common examples in aerobic groundwater are uranium, arsenic, and sulfur, which form the oxyanions, $UO_2^{2+}$, $AsO_4^{2-}$, and $SO_4^{2-}$ respectively.

Assume a contaminant is a constituent of a mineral whose solubility product may be limiting the concentration of that contaminant in water. If the contaminant forms complexes in water the solubility of the mineral is usually increased over its solubility in the absence of complexing. This leads to increased contaminant concentrations in water.

The aqueous concentrations of many trace metals are limited by sorption. The sorption of charged complex ions may be either favored or inhibited relative to that of the free ion. For example, hydroxy complexes of uranyl ion ($UO_2^{2+}$) are strongly sorbed on hydroxide and oxide minerals, while in contrast, uranyl carbonate complexes such as the tricarbonate (UTC or $UO_2[CO_3]_3^{4-}$) are poorly sorbed and highly mobile in aerobic groundwater (Langmuir 1997, 1978).

The bioavailability to plants, and the toxicity of metals to aquatic life, depends on their complexation. Examples of bioavailability varying with speciation include Cu, Fe, Mn, and Zn (Langmuir 1997). Examples of metal toxicity to fish are cupric ion ($Cu^{2+}$) and monomethyl mercury ($HgCH_3^{+}$), in contrast to less toxic complexes such as $CuCO_3^{0}$ (Langmuir 1997).

## 2.6 Radioactive Decay

Radioactive isotopes have unstable nuclei that spontaneously form new elements through the nuclear processes of alpha decay, beta decay, or spontaneous fission. The "half-life" is the time required for 50 percent of the current amount of a radioactive nuclide to decay, and is an intrinsic property of each nuclide. Alpha decay is the nuclear process by which a parent nuclide (for example, uranium-238) emits an alpha particle (helium-4 nucleus) decreasing the parent's atomic number by two and its atomic weight by four atomic mass units to form a daughter nuclide (for example, thorium-234). The following radionuclides decay by alpha decay: uranium-233, uranium-234, uranium-235, uranium-236, uranium-238, plutonium-238, plutonium-239, plutonium-240, and americium-241.

Many of the radionuclides present as contaminants at RFETS have relatively long half-lives. For example, the half-lives of americium-241, plutonium-239, and uranium-238 are approximately 432 years, 24,110 years, and 4.5 billion years, respectively. Because it requires several half-lives to diminish the radionuclide activity to an insignificant level, radioactive decay is not a relevant factor for the fate and transport of several of the radionuclides addressed as AOIs.

The source of americium-241 is the beta decay of plutonium-241, an “impurity” from production of plutonium-239/240. Plutonium-241, with a half-life of 14 years, has decayed substantially since the production of plutonium-239/240. The americium-241 activity (with a half life of 432 years) will continue to decrease.

## 3.0 BIOLOGICAL PROCESSES

### 3.1 Biodegradation

Numerous investigations have shown that microorganisms indigenous to groundwater environments can degrade a variety of manmade organic chemicals including chlorinated ethanes, chlorinated ethenes, chlorobenzenes, and components of gasoline, kerosene, and diesel fuel (EPA 1998). This biologically mediated degradation is termed biodegradation and at many sites it is the most important process by which CAHs in the environment are destroyed. Therefore, an overview of biodegradation is provided below.

Biodegradation of CAHs occurs most rapidly in anoxic, reducing groundwater environments, and causes or is associated with measurable changes in groundwater geochemistry such as the following:

- Parent CAH concentrations decrease.
- Daughter CAH concentrations may increase downgradient prior to decreasing with distance and time.
- Oxidants such as DO, nitrate ion, nitrite ion, Mn(IV, III) minerals, Fe(III) minerals, and sulfate ion may be absent or much lower in concentration in the biodegradation area.
- Concentrations of chloride ion, Fe(II), Mn(II), hydrogen sulfide, alkalinity, and methane may increase in the zone of biodegradation.

Alkalinity increases because $CO_2$ is produced by the biodegradation of organic carbon compounds. Dissolving $CO_2$ in water forms carbonic acid dissociation species. Two of these, bicarbonate ion and carbonate ion, may be measured when a water is analyzed for total alkalinity. Alkalinity is increased during aerobic respiration and in all of the anoxic environments during biodegradation of CAHs and fuel hydrocarbons. Areas contaminated by petroleum hydrocarbons often have a higher total alkalinity than background areas (Wiedemeier et al. 1999).

Several common chlorinated solvents (including tetrachloroethene, trichloroethene, and carbon tetrachloride) biodegrade from the parent compound through a series of progressively less chlorinated daughter compounds. This progression is a type of decay series analogous to radionuclide decay chains. As an example, carbon tetrachloride degrades to daughter chloroform, which degrades to methylene chloride, which degrades to chloroform, and finally to methanol or methane.

Biodegradation of CAHs in groundwater takes place by three general mechanisms, of which “reductive dechlorination” is most important:

- Reductive dechlorination – Anaerobic microbial use of the organic compound as an oxidant;
- Aerobic biodegradation – Microbial use of the organic compound as a reductant and primary substrate for growth; and
- Cometabolism – Fortuitous degradation by microbes.

Under aerobic biodegradation, the primary bacterial growth substrate is also used as a reductant. Examples include fuel hydrocarbons and the less oxidized chlorinated ethenes and ethanes, vinyl chloride, chloromethane, and chloroethane. Under aerobic conditions (aerobic respiration), DO is coupled with these reductants. Under anoxic conditions, reductive dechlorination uses the more oxidized CAHs as oxidants, including carbon tetrachloride, tetrachloroethene, trichloroethene, dichloroethene, trichloroethane, and dichloroethane. During cometabolism, the organism gains no apparent benefit from the compound being degraded. Cometabolic degradation is a fortuitous side-reaction with microbial enzymes produced for other purposes. Further details of these three mechanisms are presented in the Biodegradation Report (K-H 2004a).

Biodegradation of fuel hydrocarbons (for example, benzene in gasoline) is known to be relatively rapid under aerobic conditions; the degradation rate is limited by the availability of DO in groundwater (EPA 1998). Microbes also perform aerobic biodegradation of the less chlorinated ethenes and ethanes, particularly vinyl chloride, dichloroethene, and 1,2-dichloroethane. These CAH compounds act as reductants and provide organic carbon and energy to the bacteria as they are oxidized by DO. Vinyl chloride is the chlorinated ethene most susceptible to aerobic biodegradation. Vinyl chloride is oxidized to carbonic acid species. This aerobic biodegradation of vinyl chloride is more rapid than other mechanisms of vinyl chloride degradation, such as reductive dechlorination.

Bacteria can anaerobically biodegrade fuel hydrocarbons in most groundwater redox environments including denitrification, Mn(IV) reduction, Fe(III) reduction, sulfate reduction, and methanogenesis (Wiedemeier et al. 1995).

Thirty-five biodegradation rate constants were determined by the method of Buscheck and Alcantar (1995) for CAH compounds in contaminant plumes at RFETS (K-H 2004a). These rates may be expressed as chemical half-lives. The mean biodegradation half-lives for CAHs in UHSU groundwater are 1,1-dichloroethane for 30.3 years, trichloroethene for 22.4 years, 1,1,1-trichloroethane for 15.9 years, tetrachloroethene for 10.8 years, cis-1,2-dichloroethene for 10.4 years, methylene chloride for 8.1 years, 1,1-dichloroethene for 3.0 years, and chloroform for 0.8 years (K-H 2004a) (considered to be at the low end of the range for half-life estimates). Based on data and modeling at RFETS, it is likely that inferred VOC sources and associated downgradient groundwater concentrations will persist for decades to hundreds of years, if not longer, even with source removal (considered to be the upper range for half-life estimates) (see persistence discussion below for details). Comparison of CAH biodegradation rates for RFETS with other solvent-contaminated sites indicates that the RFETS rates are very low and are near the low end of published biodegradation rate constants (K-H 2004a).

Although evidence of biodegradation is found in UHSU groundwater, it seems to occur most rapidly in local areas of favorable groundwater chemistry where anoxic conditions support reductive dechlorination. Reductive dechlorination is widely considered to be the main mechanism by which CAHs biodegrade. Most shallow UHSU groundwater appears to be oxygenated with a mean DO content of 5.7 mg/L (K-H 2004a). Reductive dechlorination may not occur under such oxidizing conditions, although vinyl chloride may be rapidly oxidized.

One-time enhancement of remedial actions using enhanced *in-situ* biodegradation accelerates the naturally occurring degradation of VOCs through the addition of microorganisms, food substrates, electron acceptors, or other necessary microbial nutrients into a contaminated media. *In-situ* biodegradation is a viable technology for groundwater remediation at the site and has successfully been demonstrated at the Property Utilization and Disposal (PU&D) Yard Plume Treatability Study to reduce contaminant load in the soil. In addition to the historical PU&D Yard, this one-time enhancement has been used at the Carbon Tetrachloride Plume, the historical Oil Burn Pit No. 2, and the historical 903 Pad/Ryan’s Pit area. Further details are provided in the Groundwater Interim Measure/Interim Remedial Action (IM/IRA) Report (DOE 2005).

### 3.2 Denitrification and Ammonification

Denitrification may be thought of as a specialized type of biodegradation. It is the process by which certain bacteria can reduce nitrate ion ($NO_3^-$) to nitrogen gas ($N_2$). The oxygen in nitrate is used to oxidize organic carbon to $CO_2$, while the nitrate-nitrogen becomes biologically inert nitrogen gas (Langmuir 1997).

Nitrite ion ($NO_2^-$) contains trivalent nitrogen, less oxidized than the pentavalent nitrogen of nitrate. Nitrite ion is less abundant than nitrate in most natural waters. Because nitrite is a weaker oxidant than nitrate, nitrite should be reduced to ammonia in a reducing environment containing organic matter after all of the nitrate has been reduced. Decaying plants and animal waste products such as urea naturally undergo “ammonification,” the process in which organic nitrogen compounds are converted to ammonia.

### 3.3 Assimilation and Bioconcentration

Assimilation refers to incorporation of a chemical into protoplasm via ingestion by an organism. The degree of accumulation of the chemical may be quantified by the "bioconcentration factor," which equals the concentration in an organism (for example, trout) divided by the concentration in water. High $K_{oc}$ usually indicates a high bioconcentration factor (BCF), while low $K_{oc}$ indicates little propensity for bioconcentration (Langmuir 1997). PCBs tend to have high BCF and $K_{oc}$ values, while chlorinated solvents such as tetrachloroethene and carbon tetrachloride have low BCF values and low to moderate $K_{oc}$ (Langmuir 1997).

Contaminants in groundwater may be taken up by plant roots as in the remedial process of phytoremediation. For example, some legumes are known to bioaccumulate the metal molybdenum. Some microorganisms can utilize the carbon from chlorinated solvent compounds in groundwater to make protoplasm. Other contaminants may be used as an energy source by subsurface bacteria (for example, sulfate reducers).

### 3.4 Evapotranspiration

Evapotranspiration (ET) is the loss of groundwater from soil by interception from the vegetation, evaporation from free-water surfaces, soil evaporation, and transpiration from plants (K-H 2002b). The near-stream hydrology at RFETS is dominated by losses to ET, as demonstrated by site surface water flow monitoring and confirmed by an integrated hydrologic model of RFETS. The loss to ET is significant because it helps attenuate VOCs before groundwater discharges as baseflow to streams, seeps, ponds, or overland flow. The relatively small portion of infiltrating precipitation that does become shallow groundwater, and is thereby available to transport any contamination present, ultimately discharges to surface water before reaching the eastern site boundary. Therefore, UHSU groundwater that has been impacted by site activities, both in the former Industrial Area (IA) and Buffer Zone (BZ), discharges to surface water prior to leaving RFETS.

## 4.0 PERSISTENCE IN THE ENVIRONMENT OF ANALYTES OF INTEREST

### 4.1 Persistence of Radionuclides

The half-lives of radionuclides identified as AOIs are:

- Americium-241 – 432 years;
- Plutonium-239 – 24,110 years;
- Plutonium-240 – 6,564 years;
- Uranium-233 – 159,200 years;
- Uranium-234 – 245,500 years;
- Uranium-235 – 704,000,000 years; and
- Uranium-238 – 4,468,000,000 years.

Because it requires several half-lives to reduce the radioactivity to an insignificant level for most of the radionuclide AOIs, it will require an extended time period for them to dissipate via radioactive decay.

## 4.2 Persistence of VOCs

Estimating long-term persistence of VOCs in groundwater at RFETS requires a good understanding of the behavior and characteristics of both the source and dissolved-phase plume. For the VOC transport modeling effort, detailed information on the location and characteristics of source areas was uncertain. As a result, Historical Release Report (HRR) information was used, in combination with fate and transport modeling, to determine approximate locations and concentrations of sources that explained the distributions of observed downgradient dissolved-phase VOC concentrations in groundwater.

An important assumption made in this modeling effort was that source concentrations were constant in time. This assumption was reasonable because inferred sources were most likely caused by release of DNAPLs, and because VOC groundwater concentrations appear relatively steady in time (K-H 2004b). Modeling showed that constant source area concentrations influence how long downgradient VOC concentrations will persist in groundwater, while attenuation processes such as biodegradation and ET control the downgradient concentration distributions. Current literature on the long-term fate of DNAPL sources (http://www.epa.gov/superfund/resources/gwdocs/non_aqu.htm) indicates that these will persist from decades to hundreds of years, if not longer. Therefore, downgradient concentrations in groundwater can be expected to last at least as long as VOC sources exist.

Estimating the persistence of DNAPLs is very difficult, depends on many factors, and continues to represent a major topic of current research (EPA 2003). Kram et al. (2001) indicates that the current lack of appropriate methods for detecting and delineating DNAPL has been identified as one the most significant challenges limiting effective cleanup. Figure A1.1 shows several ways that a DNAPL source can occur in the subsurface (EPA 1991). These configurations can affect groundwater concentrations and persistence in different ways. Current DNAPL fate and transport research (EPA 1991, 2003) indicates the following:

- DNAPL distribution and extent depend on a number of factors (that is, release volume, rate, duration, and areal extent, heterogeneity, DNAPL properties, soil properties, and groundwater depth), and they cannot be effectively determined at most field sites.
- Estimating the long-term impacts of DNAPL sources on downgradient groundwater quality is uncertain. This is even more so without detailed source and aquifer characterization.
- Current estimates of the persistence of DNAPL sources appear to range from decades to hundreds, if not thousands, of years (EPA 2003).

- Currently, no field studies exist that demonstrate plume cleanup below maximum contaminant levels (MCLs) for DNAPL source remediation (EPA 2003). It is difficult to predict whether source removal technologies will be successful at a particular site in reducing groundwater impacts, without more detailed site characterization.
- Even where source locations are known, current sampling methodologies often are unable to detect or confirm the presence of DNAPL (Abriola 2005).

At RFETS, like many sites throughout the United States, details of VOC source areas are uncertain and not well characterized, because of the difficulty locating and characterizing the large number of localized, small-volume historical releases, whose locations remain uncertain (that is, within even hundreds of feet). Using the groundwater quality data, it is also difficult to make detailed conclusions about DNAPL entrapment architecture (mode and spatial distribution) for any of the inferred source areas. The relatively constant groundwater VOC concentrations suggest that inferred VOC sources at RFETS are, in most cases, likely from either residual DNAPL in the vadose zone, or as relatively stable pools above low-permeability strata within the saturated zone. Depending on the soil texture heterogeneity at RFETS, it is also possible that the mass of dissolved VOCs in the plume may be a result of the dissolved DNAPL constituents that are returned to the groundwater as a result of back diffusion from low-permeability zones.

Characteristics of dissolved-phase groundwater VOC plumes and their long-term fate and transport at RFETS were assessed in detail in modeling (K-H 2004b). Biodegradation rate constants were also determined by the method of Buscheck and Alcantar (1995) for VOC compounds in contaminant plumes at RFETS (K-H 2004a). Comparison of these biodegradation rates for RFETS with other solvent-contaminated sites indicates that the RFETS rates are very low and are near the low end of published biodegradation rate constants (K-H 2004a). Results of the VOC fate and transport modeling also support this conclusion (K-H 2004b). Additional influence on the rate of biodegradation is the addition of the enhanced *in-situ* biodegradation which accelerates naturally occurring degradation. As discussed above in Section 3.1, the one-time enhancement was applied at historical PU&D Yard, the Carbon Tetrachloride Plume, the historical Oil Burn Pit No. 2, and the historical 903 Pad/Ryan’s Pit area. Further details are provided in the Groundwater IM/IRA Report (DOE 2005).

In summary, given published information and available data at RFETS, it is likely that inferred VOC sources and associated downgradient groundwater concentrations will persist for decades to hundreds of years, if not longer, even with source removal. Although it is possible to reduce the long-term persistence of the source term with appropriate technology (EPA 2003), it would be technically impracticable to attempt to locate and characterize each source, given the large number, and very localized impacted areas due to relatively small release volumes (many < 100 gallons). Long-term fate and transport modeling showed that, assuming sources remain the way they are now, impacts to surface water would be minimal due to the following:

- Many sources will not impact groundwater above surface water standards at discharge points.
- Where concentrations are above surface water standards, the total flux into streams is limited due to the ephemeral nature of baseflow and seep flow to streams.
- Groundwater plume treatment systems and source area enhancements have been implemented in these areas (K-H 2005).

### 4.3 Persistence of SVOCs

Microbial metabolism is the major process for degradation of polynuclear aromatic hydrocarbons (PAHs) in soil environments. Photolysis, hydrolysis, and oxidation generally are not considered important processes for the degradation of PAHs in soils (Sims and Overcash 1983). Although there are differences in the biodegradation half-life values estimated by different investigators, their results suggest that the biodegradation half-lives of PAHs with more than three rings will be considerably longer (>20 days to hundreds of days) than PAHs with three or fewer rings.

For the specific PAHs identified as AOIs in RFETS soils, all with more than three rings (benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, dibenz[a,h]anthracene, and indeno[1,2,3-cd] pyrene), longer biodegradation half-lives (greater than 20 days to hundreds of days) are expected (ATSDR 1995).

### 4.4 Persistence of Metals

Metals are stable and do not degrade in the environment. Thus metals will persist indefinitely.

## 5.0 REFERENCES

Abriola, L., 2005, “Contaminant Source Zones: Remediation or Perpetual Stewardship?” Guest Editorial, *Environmental Health Perspectives*, Vol. 113, Number 7, July.

ATSDR, 1995, Toxicological Profile for Polycyclic Aromatic Hydrocarbons, U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, August.

Blackburn, W.H., 1975, “Factors Influencing Infiltration and Sediment Production of a Semiarid Rangeland in Nevada,” *Water Resources Res*. 11:729-737.

Buscheck, T.E. and C.M. Alcantar, 1995, Regression techniques and analytical solutions to demonstrate intrinsic bioremediation, in Hinchee R.E., J.T. Wilson, and D.C. Downey (eds.), p. 109-116. Battelle Press, Columbus.

Dadkah, M. and G.F. Gifford, 1980, "Influence of Vegetation, Rock Cover, and Trampling on Infiltration Rates and Sediment Production," *Water Resources Res.* Vol. 16, pp. 979-986.

de Jonge, L.W., C. Kjaergaard, and P. Moldrup, 2004, "Colloids and Colloid-Facilitated Transport of Contaminants in Soils," *Vadose Zone J.*, V.3, p. 321-325.

DOE, 2005, Final Interim Measure/Interim Remedial Action for Groundwater at the Rocky Flats Environmental Technology Site, Golden, Colorado, June 21.

Dreicer, M., T.E. Hakonson, C. White, and F.W. Whicker, 1984, "Rainsplash as a Mechanism for Contamination of Plant Surfaces," *Health Physics* Vol. 46:1, pp. 177-188.

Drever, J.I., 1988, *The Geochemistry of Natural Waters*, 2nd edition, Prentice-Hall, Upper Saddle River, New Jersey.

Ellison, W.D., 1947, "Soil Erosion Studies I and II," *Agr. Eng.* 28:145-146 and 197-201.

EPA, 1991, Dense Nonaqueous Phase Liquids – A Workshop Summary, Dallas, Texas, April 17-18, EPA/600-R-92/030, Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma, http://www.epa.gov/swerust1/cat/gwwkshop.pdf.

EPA, 1998, Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater, EPA/600/R-98/128.

EPA, 1999, Understanding Variation in Partition Coefficient, Kd, Values, EPA402-R-99-004B, Volume II.

EPA, 2003, The DNAPL Remediation Challenge: Is There a Case for Source Depletion? Expert Panel on DNAPL Remediation, Co-Chairs, M. Kavanaugh and S. Rao, EPA/600/R-03/143.

EPA, 2004, Understanding Variation in Partition Coefficient, Kd, Values, EPA402-R-04-002C, Volume III.

Fetter, C.W., 1988, *Applied Hydrogeology*, 2nd edition, Merrill Pub. Co., Columbus, Ohio, 592 pp.

Gutierrez, J and I.I Henandez, 1996, "Runoff and Interrill Erosion as Affected by Grass Cover in a Semi-Arid Rangeland of North Mexico," *Journal of Arid Env.* 34:287-295.

Howard, P.H., 1989, *Handbook of Environmental Fate and Exposure Data for Organic Chemicals*, Vol. I and II, Lewis Publishers, Chelsea, Michigan.

K-H, 2002a, Actinide Migration Pathway Analysis Report, Summary Report and Technical Appendix, Rocky Flats Environmental Technology Site, Golden, Coloraodo, April.

K-H, 2002b, Site-Wide Water Balance Model Report for the Rocky Flats Environmental Technology Site, Golden, Colorado, May.

K-H, 2004a, Evaluation of Natural Attenuation and Biodegradation Potential of Chlorinated Aliphatic Hydrocarbon Compounds in Groundwater at Rocky Flats, Rocky Flats Environmental Technology Site, Golden, Colorado, March.

K-H, 2004b, Final Fate and Transport Modeling of Volatile Organic Compounds at the Rocky Flats Environmental Technology Site, Golden, Colorado, April.

K-H, 2005, Summary of Recent Hydrologic and VOC Transport Modeling at the Rocky Flats Environmental Technology Site, Golden, Colorado, September.

Kidwell, M.D., M.A. Weltz, and D.P. Guertin, 1997, “Estimation of Green Ampt Effective Hydraulic Conductivity for Rangelands,” *Journal of Range Management*, Vol. 50:3, pp. 290-299.

Kinnel, P.I.A., 1985, Runoff Effects on the Efficiency of Raindrop Kinetic Energy in Sheet Erosion in Soil Erosion and Conservation, El-Swaify, S.A., W.C. Moldenhauer, and A. Lo (eds.), Proceedings of Malama Aina ’83, International Conference on Soil Erosion and Conservation, Honolulu, Hawaii, Soil Cons. Soc. of Am., Ankeny, Iowa.

Kram, M.L., A.A. Keller, J. Rossabi, and L. Everett, 2001, DNAPL Characterization Methods and Approaches, Part 1: Performance Comparisons, Ground Water Monitoring and Remediation (in press), pp. 109-123.

Lane, L.J., T.E.Hakonson, and G.R. Foster, 1987, Watershed Erosion and Sediment Yield Affecting Contaminant Transport, Environmental Research on Actinide Elements, Conf-841142 (DE860087-13), pp. 193-223.

Langmuir, D., 1978, “Uranium Solution-Mineral Equilibria at Low Temperatures With Applications to Sedimentary Ore Deposits,” *Geochimica et Cosmochimica Acta,* V.42, pp. 547-569.

Langmuir, D., 1997, *Aqueous Environmental Geochemistry*, Prentice-Hall, Upper Saddle River, New Jersey, 600 pp.

McLean, J.E. and B.E. Bledsoe, 1992, Behavior of Metals in Soils, EPA/540/S-92/018.

MRI, 2001, Effect of Controlled Burning on Soil Erodibility by Wind, Final Test Report, MRI Project No. 110056, Kansas City, Missouri, May 16.

Quansah, C., 1985, Rate of Soil Detachment by Overland Flow, with and without Rain, and its Relationship with Discharge, Slope Steepness and Soil Type, Soil Erosion Conservation, El-Swaify, S.A., W.C. Moldenhauer, and A. Lo (eds.), Proceedings of

Malama Aina ’83, International Conference on Soil Erosion and Conservation, Honolulu, Hawaii, Soil Cons. Soc. of Am., Ankeny, Iowa.

Ranville, J.F., D.J. Chittleborough, and R. Beckett, 2005, “Particle-Size and Element Distributions of Soil Colloids,” *Soil Sci. Soc. Am. J.*, V. 69, p. 1173-1184.

Simaton, J.R., M.A. Weltz, and H.D. Larsen, 1991, “Rangeland Experiments to Parameterize the Water Erosion Prediction Project Model: Vegetation Canopy Effects,” *Journal of Range Management*, 44:276-282.

Sims, R.C. and M.R. Overcash, 1983, “Fate of Polynuclear Aromatic Compounds (PNAs) in Soil-Plant Systems,” *Res Rev* 88:1-68.

Vogel, T.M., C.S. Criddle, and P.L. McCarty, 1987, “Transformations of Halogenated Aliphatic Compounds,” *Environ. Sci. Technol.*, V. 21, No. 8, p. 722-736.

Wiedemeier, T.H., J.T. Wilson, D.H. Kampbell, R.N. Miller, and J.E. Hansen, 1995, Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater, U.S. Air Force Center for Environmental Excellence.

Wiedemeier, T.H., H.S. Rifai, C.J. Newell, and J.T. Wilson, 1999, *Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface*, John Wiley & Sons, New York, New York.

# Figure A1.1
# Types of DNAPL Source Configurations