APPENDIX O – MONITORED NATURAL ATTENUATION EVALUATION

FINAL REMEDIAL INVESTIGATION REPORT
CASMALIA RESOURCES SUPERFUND SITE
CASMALIA, CALIFORNIA

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LIST OF ACRONYMS

µg/L	micrograms per liter
BTEX	benzene, toluene, ethylbenzene, and xylenes
$CaCO_3$	calcium carbonate
COC	chemical of concern
CSC	Casmalia Steering Committee
CVOCs	chlorinated volatile organic compounds
DCE	dichloroethylene/dichloroethene
DQO	data quality objective
Fe(II)	ferrous iron
Fe(III)	ferric iron
FS	Feasibility Study
HSU	Hydrostratigraphic Unit
IPR	Interim Progress Report
LNAPL	light non-aqueous phase liquid
MCL	maximum contaminant level
mg/L	milligrams per liter
Mn(II)	manganese (II)
Mn(IV)	manganese (IV)
MNA	monitored natural attenuation
NAPL	non-aqueous phase liquid
ND	Not Detected
NT	Not Tested
ORP	oxidation-reduction potential (redox)
PCE	tetrachloroethylene/tetrachloroethene
PSCT	Perimeter Source Control Trench
RGMEW	Routine Groundwater Monitoring Element of Work
RI	Remedial Investigation
RI/FS	Remedial Investigation/Feasibility Study
TCE	trichloroethylene/trichloroethene
TDS	total dissolved solids
TMB	trimethylbenzene
VC	vinyl chloride
VOC	volatile organic compound

1.0 INTRODUCTION

In the Interim Progress Report (IPR) of February 2005 and November 2005 IPR Addenda, the Casmalia Steering Committee (CSC) published a preliminary evaluation of evidence for natural attenuation at the Casmalia site. This Appendix to the Final Remedial Investigation (RI) Report presents a further evaluation of organic and inorganic parameters indicative of natural attenuation of chemicals of concern (COCs) present in groundwater at the site in accordance with the Superfund policy and technical protocol guidelines set forth in OSWER directive 9200.4-17P (OSWER, 1999). Additionally, an evaluation of the appropriateness of monitored natural attenuation (MNA) as a part of site remedial strategies, pursuant to the requirements set forth in the Remedial Investigation/Feasibility Study (RI/FS) Work Plan is presented.

As a part of these evaluations, the CSC analyzed historical and recent inorganic and organic chemistry data from groundwater monitoring wells across the site, collected information on the distribution of various dissolved gases via bubble-strip sampling, assessed the occurrence of biodegradation of solvent-class COCs and fuel-derived hydrocarbons, and identified potential data gaps for additional MNA analyses. Many options exist to remediate the upper and lower Hydrostratigraphic Unit (HSU) with respect to the mixture of chlorinated volatile organic compound (VOCs), their associated degradation products and petroleum hydrocarbons, with one option being MNA. Natural attenuation is defined as "*…naturally occurring processes in soil and groundwater environments that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in those media. These in-situ processes include biodegradation, dispersion, dilution, adsorption, volatilization, and chemical or biological stabilization or destruction of contaminants*" (*OSWER, 1996*). Natural attenuation in groundwater systems results from the integration of several subsurface attenuation mechanisms that are classified as either destructive or nondestructive. Biodegradation is the most important destructive attenuation mechanism, and is the primary process discussed in this report.

Fuel hydrocarbons are biodegraded via biological oxidation when electron donors and electron acceptors are combined to produce energy for microbial growth (and metabolic byproducts). Petroleum hydrocarbons serve as electron donors in microbial metabolism. Electron acceptors include oxygen, nitrate, manganese (IV) (Mn[IV]), ferric iron (Fe[III]), sulfate, and carbon dioxide. Carbon dioxide, water, nitrogen gas, manganese (II) Mn(II), ferrous iron (Fe[II]), and hydrogen sulfide, and methane are some of the metabolic byproducts typically produced from the biodegradation of petroleum hydrocarbons. The biodegradation of petroleum hydrocarbons, especially benzene, toluene, ethylbenzene, and xylenes (collectively known as BTEX), is mainly limited by electron acceptor availability, and generally will proceed until all of the organic contaminants that are biochemically accessible to the microbes are oxidized. It is generally observed that an adequate supply of electron acceptors is present in most, if not all, hydrogeologic environments.

Halogenated organic compounds (e.g. chlorinated solvents) biodegrade via the process of reductive dechlorination; in these biologically mediated reactions the electron acceptors is the chlorinated aliphatic hydrocarbons and electron donors include compounds such as non-chlorinated fuel hydrocarbons, landfill leachate, or natural organic carbon. If electron donors are depleted from the contamination site before the chlorinated compound is degraded, then dechlorination may cease and allow the continued downgradient migration of the contaminant. Reductive dechlorination may occur as a sequential process where the chlorinated compound loses chlorides, degrading sequentially to less chlorinated compounds under reducing

conditions. For example, tetrachloroethene (PCE) may sequentially degrade to trichloroethene (TCE), then to cis-1,2-dichloroethene (cis-1,2-DCE) and trans-1,2-dichloroethene (trans-1,2-DCE), then to vinyl chloride (VC), then to ethene, and ultimately to ethane and carbon dioxide. DCE and VC also can directly oxidize to carbon dioxide under oxic conditions. The degradation of chlorinated solvents is dependent on the geochemical conditions and specific microorganisms present in the subsurface. The dechlorination pathway, reaction kinetics, and nature of the intermediate and ultimate daughter products may vary depending on these conditions.

Inorganic compounds (e.g., metals and oxy-anions) are capable of undoing biologically mediated and abiotic transformation. Typically for metals, the transformation for a toxic compound to an inert compound involves a chemical reaction where the metal ion undergoes a change of state, e.g., reduction of mobile Chromium VI to immobile Chromium III. During the change of state, the metal ion transforms from a soluble species to a solid species (i.e., precipitates out of solution to form an immobile solid). Most metal ions are in a soluble state under acidic aqueous conditions and will precipitate under alkaline aqueous conditions.

In addition to destructive biodegradation from microbial processes, nondestructive physical processes that also account for the natural attenuation of chemical compounds, include:

- Dilution – is the physical reduction in chemical concentration due to the addition of water, processes at the site that aid dilution includes rainfall recharge and groundwater underflow.
- Dispersion – involves chemical and physical processes. Chemical diffusion is where the concentration of a chemical will continue to spread and dilute from areas of higher concentration to areas of low concentration. The rate of chemical dispersion is driven by the concentration gradient between the two areas. Physical dispersion is the process where the movement of the chemical within the porous matrix acts to “volumetrically expand” the plume by virtue of the tortuous path of the chemical migration. Notably, historic groundwater monitoring data would suggest that COC plumes are relatively stable at their edges indicating that dilution (groundwater advection) and dispersion processes are not actively spreading the plumes or that other MNA processes are active that counterbalance the spreading of the plume by groundwater advection and dispersion.
- Volatilization – is the process where the chemical undoes a phase change from the liquid phase to the gas phase. Volatilization is governed by temperature and pressure and is likely a dominant process for the reduction of high concentration VOCs. Volatilization is likely a significant MNA process within the P/S landfill. With the addition of black landfill caps, the additional heat supplied to the landfill cell has likely increased the rate of volatilization of VOCs within the landfill. The P/S Landfill black HDPE layer is capped with a 2-foot vegetative cover that will reduce the additional heat supplied to the landfill cell. Adsorption and absorption - are processes where the chemical is bound to the matrix material. Adsorption is the adhesion of a substance to a surface. Absorption is the incorporation of a substance in one state into another of a different state (e.g. liquids being absorbed by a solid or gases being absorbed by a liquid). Organic compounds are capable of being absorbed by free organic carbon within the soil matrix. Metals may be absorbed into the soil matrix via cation or anion exchange reactions with soil (clay mineral) grains. The adsorption of inorganic compounds to mineral surfaces is strongly dependent on the macrochemistry

- Abiotic processes – are non-biological chemical reactions that result in a transformation of the molecules involved. Abiotic processes may occur when groundwater of different origins mixes or when chemicals in groundwater react with the soil matrix during transport. For example, an abiotic reaction may occur when reduced sulfide–rich groundwater mixes with oxidized metal-rich groundwater, resulting in the formation of an insoluble metal sulfide precipitate.

- The transformation of inorganic compounds by either adsorption to mineral surfaces or chemical reaction to form a precipitate is strongly dependent on the redox conditions and general macrochemistry of the groundwater. As illustrated below in the form of Eh-pH diagrams, groundwater conditions favorable for the immobilization of arsenic are not identical to those favorable for the immobilization of selenium (EPA, 2007)

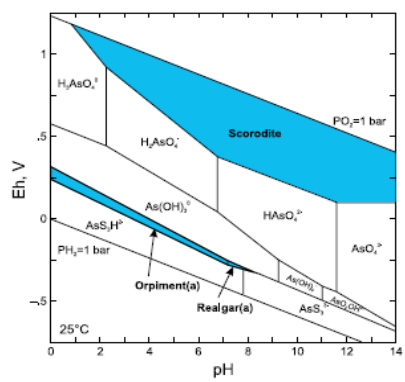

Figure 6.2 *Eh-pH diagram for arsenic at 25 °C. System As-H_2O-Fe-S, with ΣAs=10^{-5} (750 µg L^{-1}), ΣFe=10^{-4} (5.6 mg L^{-1}), and ΣS=10^{-3} (32 mg L^{-1}). Solid stability fields are shaded blue. Orpiment(a) and Realgar(a) are poorly crystalline forms of As_2S_3 and AsS, respectively. Arsenopyrite and crystalline forms of As_2S_3 and AsS are suppressed.*

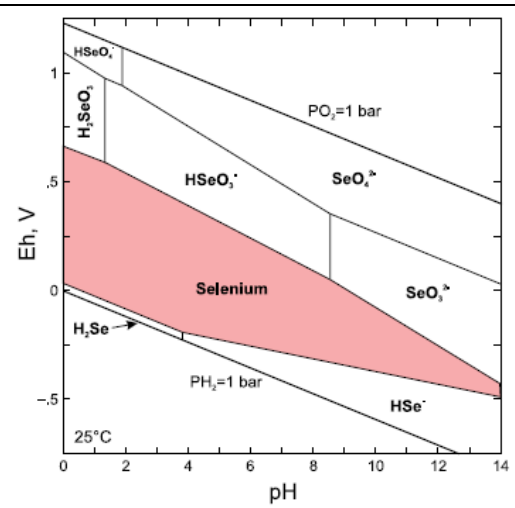

Figure 7.1 *Eh-pH diagram for selenium at 25 °C using thermodynamic data from Séby et al. (2001). ΣSe=10^{-5} (790 µg L^{-1}). Solid stability field for elemental selenium is shaded pink.*

Reference (EPA, 2007)

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Chemical mass removal from groundwater also occurs via onsite groundwater extraction.

1.1 Purpose of Investigation

The MNA investigation was conducted to determine the actual or potential occurrence of natural attenuation of both fuel hydrocarbons and chlorinated solvents, including PCE, TCE, DCE, and VC, concentrating in the Site area downgradient of the Perimeter Source Control Trench (PSCT) where MNA might be an appropriate ancillary remedial option to the extraction and treatment system in the PSCT itself, and to assess any data gaps associated with the analytical parameters necessary to adequately monitor for natural attenuation. The evaluation of MNA for inorganic compounds was not a primary focus of this study, because the preliminary FS work suggests that pond closure and other site capping remedies are anticipated to both reduce the seasonal variation in inorganic compound concentrations in the area south of the PSCT and to significantly reduce the extraction rates of the PSCT and PCT features. At this time, the CSC expects that the site groundwater remedy will continue to include extraction from the PCT. In the

event that is not the case, data collected for the MNA evaluation of organic compounds can be used to assess the potential for natural processes to transform mobile inorganic compounds to less mobile states in the future. If performed in the future, this assessment will be performed considering the following recent USEPA guidance documents:

- *Monitored Natural Attenuation of Inorganic Contaminants in Groundwater. Volume 1 – Technical Basis for Assessment.* EPA/600/R-07/139.
- *Monitored Natural Attenuation of Inorganic Contaminants in Groundwater. Volume 2 – Assessment for non-Radionuclides Including Arsenic, Cadmium, Chromium, Copper, Lead, Nickel, Nitrate, Perchlorate, and Selenium.* EPA/600/R-07/140.

1.2 Scope of the Investigation

In order to evaluate the appropriateness of natural attenuation as a remedial option, evidence is collected to assess primary and secondary lines of evidence.

For a dissolved plume, primary evidence is generally based on measured analyte concentrations and distribution in space and time which may demonstrate expanding, shrinking, or stable plume dynamics. A shrinking or stable plume can be evidence of natural attenuation where the rate of natural attenuation either exceeds or equals the mass loading rate of COCs to groundwater. In cases where other active remedy methods complicate the calculation of such rates, primary lines of evidence can be more easily obtained by examining the ratio of parent to daughter products.

Secondary lines of evidence are provided by direct qualitative correlation between observed spatial distribution of COCs and reduced levels of electron acceptors or increased levels of their reaction products.

For this MNA evaluation, historic and current groundwater concentrations of COCs and other natural attenuation parameters were reviewed. The data review focused on areas adjacent to, and downgradient of the PSCT in the Upper HSU. Maps of contaminants, their degradation products, electron acceptors, and metabolic end products were compared for specific wells downgradient of PSCT as potential indicators of natural attenuation. The following sections describe and discuss the observed data supporting the apparent natural attenuation.

2.0 METHODOLOGY

2.1 Review of Wells Chosen for MNA Study

Figure O-1 shows the Site wells evaluated for MNA indicator parameters, along with their locations relative to likely groundwater flowpaths through the Zone 1 area. Data trends along the flowpaths in the Upper HSU were evaluated for evidence of MNA potential and occurrence.

The groundwater flowpath (A) is located between the western side of the North Ridge and the PCT-A Trench, and includes the following Upper HSU wells from north (upgradient) to south (downgradient): RG-11B, SW-44, PSCT-4, PSCT-3, PSCT-2, PSCT-1, RG-7B, and RAP-3A (Figure O-1). Groundwater flowpath (B) was identified between the eastern side of the North Ridge south to PSCT-1 and to the PCT-A Trench, and includes Wells WP-7S, WP-8S, SW-31, RG-1B, RG-7B, and MW-18C. These flowpaths were used to chart concentrations of COCs for Fall 2004 and Spring 2005 sampling events. (See Figures O-2 through O-5.)

2.2 Monitored Parameters

Historical groundwater chemistry data between January 1998 and October 2008 were reviewed to assess trends both in organic and inorganic parameters indicative of natural attenuation and COC and daughter compound concentration trends. Charts and tables with this data are presented in Appendix G as follows:

- Attachment G-1 – VOC concentrations over time
- Attachment G-2 – General Mineral concentrations over time

Maps and graphs of indicator parameters and COCs over time were prepared and evaluated for evidence of biodegradation. The individual time-series charts for VOCs are posted on the Total VOC concentration contour maps in Figures 5-18, 5-19, and 5-20 for the Upper HSU and Lower HSU wells in the main report.

2.2.1 Contaminants and Daughter Products

Volatile organic compounds, including the chlorinated solvent COCs measured semi-annually since January 1998 and used in this MNA investigation, include PCE and TCE and their degradation products (cis-1,2-DCE, trans-1,2-DCE, VC, and ethene). Benzene is also evaluated as representative of the total BTEX concentration trends, as the concentrations of toluene, ethylbenzene, and xylenes follow similar patterns. These data are collectively summarized in Attachment G-1 (time-concentration graphs) and in Table O-1. The benzene, PCE, TCE, cis-1,2-DCE, and VC data for the upper HSU are summarized on Figures G-22 through G-26 and on Figures G-29 through G-33 for the lower HSU (COC plume maps). Note for all MNA analytes evaluated, non-detect values were assigned a proxy value of one-half the detection limit for graphical representation. These concentration trends, measured over time in Upper HSU monitoring wells, were evaluated as indicators of reductive dechlorination and biological oxidation.

2.2.2 Bubble Strip Dissolved Gases

In November 2005, samples from six wells were tested for hydrogen, methane, ethane, and ethene via Microseep's Bubble Strip Method. The Bubble Strip Method is a chemical testing method developed specifically for the purpose of determining the concentrations in well water of dissolved hydrogen and other gases having very low molecular weight. The measured concentrations of hydrogen are indicative of the predominant biodegradation pathways as shown in Figure O-6 and the organic gases are degradation endproducts indicative of biodegradation as summarized in Tables O-2 and O-3 and mapped on Figures O-7 through O-9.

2.2.3 Electron Donors and Acceptors

Compounds that have been measured since January 1998 and used in the MNA investigation include dissolved oxygen, nitrate, dissolved manganese, sulfate, and sulfide. These data are mapped on Figures O-10 through O-13 and summarized in Table O-2.

2.2.4 Metabolic Endproducts

Additional inorganic compounds and field parameters that have been measured since January 1998 and used in the MNA investigation include alkalinity as calcium carbonate ($CaCO_3$), oxidation reduction potential (redox), dissolved methane, dissolved ethane, and chloride. These data are mapped on Figures O-7, O-9, O-14 through O-15, and summarized in Table O-3.

3.0 DISCUSSION OF RESULTS

3.1 Evidence of Natural Attenuation for Chlorinated Volatile Organic Compounds (CVOCs) and Fuel Hydrocarbon Derivatives

3.1.1 Contaminant and Daughter Products

3.1.1.1 PCE, TCE, and DCE

PCE and TCE and the degradation products analyzed during the semiannual sampling events since January 1998 were used to evaluate MNA. Concentrations of PCE and TCE and the degradation products give an indication of the presence or absence of reductive and oxidative processes at the site (*Parsons, 1998*). The presence of VC and cis-1,2-DCE are typically reliable indicators that reductive dechlorination is occurring. Also, if cis-1,2-DCE comprises more than 80 percent of the total DCE, then the DCE is likely from reductive dechlorination (*Wiedemeier et al., 1996b*). DCE that has been historically detected at the site appears to be from reductive dechlorination because cis-1,2-DCE, where detected, comprises approximately 80 to 100 percent of the total DCE. Table O-4 provides the ratio of cis-1,2-DCE to trans-1,2-DCE for the wells that were evaluated in this MNA evaluation.

Time–concentration plots for VOCs in selected wells are presented in Attachment G-1 and 5-18, 5-19, and 5-20. As illustrated on the time-concentration charts, the changes in VOCs over time have remained relatively consistent, indicating the overall stability of the plume.

To assist in gauging potential MNA across the Site, Figures O-2 through O-5 provide snapshots of VOC concentrations along the Upper HSU “flowpaths”. Figures O-2 (Fall 2004) and O-3 (Spring 2005), represent Flowpath “A”, which includes wells: RG-11B, SW-44, PSCT-4, PSCT-3, PSCT-2, PSCT-1, RG-7B, and RAP-3A and corresponds to a transect from the western North Ridge south to PSCT-4, southeast along the PSCT to PSCT-1 and south to PCT-A. Figures O-4 (Fall 2004) and O-5 (Spring 2005) represent Flowpath “B”, which includes wells: WP-7S, WP-8S, SW-31, RG-1B, RG-7B, MW-18C, and corresponds to a flowpath from the eastern North Ridge through the Metals Landfill area southwest to the PSCT, and south to PCT-A. The flowpaths were aligned based on the groundwater flow analyses documented in Appendix F and considered both measured and model-simulated groundwater elevations and inferred flow directions.

The VOC distributions along the Upper HSU flowpaths are characterized by high concentrations near the source areas north of the PSCT, with downgradient portions of the plume exhibiting much lower or non-detect concentrations. Increases in degradation product concentrations relative to PCE and TCE concentrations are also observed. Further examination of Figures O-2 through O-5 shows that the ratio of PCE to TCE generally appears consistent along both flowpaths A and B. Maximum values occur near the source areas north of the PSCT and minimum values occur at the peripheral parts of the plume represented by Wells RG-11B, RAP-3A, WP-7S and MW-18C, respectively. Comparison of the TCE and PCE isopleths maps (Figures G-23 and G-24) and cis-1,2-DCE and VC (the metabolic byproducts) isopleth maps (Figures G-25 and G-26) shows that there is a strong correlation between areas with elevated contamination levels and elevated metabolic byproducts, suggestive of the reductive

dechlorination. The concentration of VC relative to PCE, TCE and DCE north of the PSCT, in the BTA, and CDA areas would indicate that reductive dechlorination is well established.

Figure O-16 depicts VOC speciation ratios for Upper HSU wells. DCE detected in wells south of the PSCT appears to have occurred from reductive dechlorination. The cis to trans DCE ratio for the wells with evaluated VOCs averaged 96.4 percent (Table O-4), which is indicative of reductive dechlorination. While TCE is as reductive product of PCE, TCE is also a source contaminant at the site, as such; TCE concentrations likely represent a combination of primary and daughter compound concentrations.

An additional line of natural attenuation evidence is observed in the change of relative concentrations from higher parent chemical concentrations in the source area to higher daughter product concentrations downgradient of the source area. In Figures O-2 and O-3, TCE concentrations exceed cis-1,2-DCE concentrations in the source areas whereas cis-1,2-DCE concentrations exceed TCE concentrations in the downgradient area. This indicates that TCE has been dechlorinated to cis-1,2-DCE.

3.1.1.2 VC

The presence of VC, as the terminal chlorinated product of the reductive dechlorination degradation pathway, is strong evidence of the biodegradation of chlorinated solvents. The distribution of VC correlates well with the core areas of the PCE and TCE plumes, areas of the site where reduced groundwater conditions predominate.

3.1.1.3 Ethene

The presence of ethene, even at low concentrations, is indicative of reductive dechlorination (*Wiedemeier et al, 1996a*). As discussed previously, reductive dechlorination of chlorinated ethenes occurs by sequential dechlorination from PCE to TCE to DCE to VC to ethene. A review of the analytical data as presented in Table O-3 and Figure O-8 revealed the presence of ethene in all wells tested, with areas of higher concentration corresponding to areas of higher chlorinated contaminant concentration (Figures G-23 through G-26), and notably mirrors the VC distribution. These data are evidence of the accumulation of daughter products associated with reductive dehalogenation of chlorinated solvents.

3.1.1.4 Benzene

A twofold evaluation of the concentration trends of benzene was performed to assess evidence of MNA. As a COC with daughter products of its own, benzene's concentration trends give an indication of the presence of biological oxidation. As the primary substrate for the microbial degradation of CVOCs, benzene's concentration trends are indicative of the presence of reductive dechlorination. An examination of the data as collectively summarized on Figures G-22, O-2 through O-5, and in Table O-1 reveals that benzene concentrations were relatively low in the MNA study wells, with only a few wells exceeding the maximum contaminant level (MCL). This is indicative of the presence of biodegradation.

3.1.2 Dissolved Hydrogen

Dissolved hydrogen can be used as an indicator of the predominant pathway of biodegradation. In an aquifer where biodegradation of organic compounds are occurring, fermentative

microorganisms produce hydrogen as they metabolize the organic matter (*Wiedemeier et al, 1996b*). Simultaneously, hydrogen is consumed by resperative microorganisms, which use a terminal electron acceptor as an electron sink. The concurrent processes of hydrogen production and hydrogen consumption can produce a steady-state concentration of dissolved hydrogen, the magnitude of which depends on the predominant terminal electron acceptor in the process. Therefore, hydrogen concentration in a given aquifer (when considered in conjunction with other information such as depletion of terminal electron acceptors and accumulation of reduced products) is a reliable indicator of which process dominates.

Of the six wells tested for hydrogen (Figure O-6), the three wells (RIMW-3, RGPZ-5B and RG-38) located with the footprint of the VOC plume and had the highest concentrations of dissolved hydrogen. The upgradient background well, RP-1D and two downgradient indicator wells, RP-103B and RP-65B, have hydrogen levels below the required concentration for active reductive dechlorination. The presence of dissolved hydrogen at concentrations conducive for reductive dechlorination correlates with areas of elevated VC and ethane; however; only in well RIMW-3 can this positive correlation be confirmed. The lack of dissolved hydrogen in upgradient and downgradient areas of the Site, likely represents the absence of suitable organic material. (e.g., petroleum hydrocarbons) available for fermentative bacteria, and also these are areas of higher dissolved oxygen and more energetic metabolic reactions are favored for the breakdown of organic matter.

3.1.3 Supply of Electron Donors and Acceptors

A variety of biodegradation mechanisms use nitrate, manganese, iron, sulfate, and, sulfide, and carbon dioxide as electron donors and acceptors to metabolize organic compounds such as CVOCs and fuel hydrocarbons. The assessment of concentrations of potential electron donors and acceptors provides supporting evidence of microbial activity by identifying redox zones. The progression from aerobic to anaerobic conditions is as follows, with each process continuing until it is limited by substrate availability: oxygen to nitrate reduction, nitrate to manganese reduction, manganese to iron reduction, iron to sulfate reduction, and sulfate to methanogenesis. Only the concentrations of dissolved oxygen, nitrate, manganese, sulfate, and sulfide will be discussed in this report.

3.1.3.1 Dissolved Oxygen

Dissolved oxygen in groundwater is generally lower in source, plume, and downgradient areas compared to background because oxygen is preferentially utilized by the microbes. Dissolved oxygen historically has been found to be as high as 11.1 milligrams per liter (mg/L) in background Well MW-7BU, and was found to be generally less than 1 mg/L in the plume wells with values increasing away from the areas of heaviest contamination (Table O-2 and Figure O-13). Dissolved oxygen is readily consumed in aquifer systems by aerobic bacteria and free metal ions, and both elevated petroleum hydrocarbon and metal concentrations correlate with areas of low dissolved oxygen. The consumption of dissolved oxygen will lead to anaerobic conditions which will foster the degradation of halogenated hydrocarbon via the reductive dechlorination process.

3.1.3.2 Nitrate

A decrease of nitrate would be expected from the background well relative to wells located in the plume, as microbes utilize nitrogen in the metabolic degradation processes. An examination

of the isopleth maps reveals a general correlation between areas of high concentrations of contaminants and low concentrations of nitrate (Table O-2, Figures G-23 through G-26 and Figure O-10), with plume wells such as RIMW-3 and RG-1B measuring non-detect less than 4.4 mg/L during the RI sampling events and a cross- and upgradient wells such as WP-8S and SW-44 measuring as high as 72 and 140 mg/L, respectively. These spatial trends in nitrate concentrations indicate reducing conditions and are indicative of natural attenuation. Those wells within the plume exhibiting elevated nitrate concentrations, for example Well RP-4B, can most likely be explained by nitrate contributions from the landfill itself.

3.1.3.3 Manganese

Once the dissolved nitrate has been depleted, microorganisms in the aquifer matrix will preferentially reduce the solid manganese on soil particles. The resulting dissolution of manganese into groundwater would be expected to raise the concentrations of dissolved manganese in the presence of anaerobic degradation. An examination of the data from the RI sampling events reveals concentrations of dissolved manganese to be higher in the plume relative to upgradient and downgradient wells (Table O-2 and Figure O-11). For example, in the Spring 2005 sampling event, the dissolved manganese concentration at Well RIMW-3 was measured to be 11,000 micrograms per liter (μg/L), while the upgradient Well WP-7S was measured to be non-detect less than 50 μg/L and the downgradient Well MW-18C was found to contain 80 μg/L dissolved manganese.

3.1.3.4 Sulfate and Sulfide

Sulfate depletion or the presence of sulfide in an area of contamination is indicative of aerobic biodegradation of organic carbon. Examination of the sulfate and sulfide trends from the RI sampling events reveals a lower concentration of sulfate in the plume relative to upgradient and downgradient wells. The presence of detectable sulfide in Wells SW-17 and RIMW-3 is indicative of reduced groundwater conditions (Table O-2 and Figure O-12).

3.1.4 Metabolic End Products

3.1.4.1 Dissolved Methane

The production of methane is generally observed at a site where reductive dechlorination of alkenes is ongoing. Methane concentrations above background levels in areas with BTEX contamination are indicative of methanogenesis, another anaerobic process. Review of the data from the RI sampling events presented in Table O-3 and Figures O-9 and G-23 through G-26 reveals a strong correlation between areas with elevated contaminant levels and elevated methane concentrations. In November 2005, concentrations of dissolved methane were found to vary from lows of 0.86 and 1.0 mg/L and in the down- and upgradient Wells MW-18C and RG-11B-2, respectively, to a high of 250 mg/L in plume Well RIMW-3. This is indicative of the presence of reductive dechlorination of alkenes.

3.1.4.2 Dissolved Ethane

Ethane is the final degradation product of the reductive dechlorination pathway. The presence of ethane indicates that VC is being degraded, even under anaerobic conditions. This is important because the accumulation of VC under anaerobic conditions is a negative indicator for the application of MNA because VC is more toxic than the original contaminants. A review of

the data from the RI sampling events presented in Tables O-1 and O-3 and spatially in Figures O-7 and G-23 through G-26 reveals a strong correlation between areas of greater concentrations of chlorinated contaminants and greater concentrations of ethane. For example, during the Fall 2005 sampling event, concentrations of dissolved ethane were found to vary from lows of 0.051 and 0.02 mg/L and in the down- and upgradient Wells MW-18C and RG-11B-2, respectively, to a high of 18 mg/L in plume Well RIMW-3. This is indicative of the presence of reductive dechlorination of alkenes. This is a positive indicator for the application of MNA.

3.1.4.3 Redox Potential (ORP)

The redox or ORP of groundwater is a measure of electron activity that indicates the relative ability of solution to accept or transfer electrons. As electron acceptors and nutrients are depleted by microbial activity during biodegradation of contaminants, the redox potential of contaminated aquifers decreases. Although the redox measurements from the RI events seem to follow no discernable pattern, either spatially or over time (Table O-3), all measured values are well within the range of 750 to -250 millivolts within which reductive dechlorination is possible (*Wiedemeier et al, 1996a*).

3.1.4.4 Alkalinity as $CaCO_3$

Benzene biodegradation will result in the formation of alkalinity in the groundwater due to the formation of organic acids, and elevated levels of alkalinity can be used as an indicator of benzene biodegradation both aerobically and anaerobically (except with methanogenesis). Alkalinity is also expected to be higher in the plume area because carbon dioxide from microbial degradation can dissolve minerals in the soil, resulting in higher alkalinity values. In addition, respiration of dissolved oxygen, nitrate, iron (III), and sulfate tends to increase the total alkalinity of groundwater. An examination of the alkalinity results during the Fall 2004 and Spring 2005 RI sampling events reveals elevated alkalinity values in the plume relative to upgradient and downgradient wells, in keeping with historical trends (Table O-3 and Figure O-14).

3.1.4.5 Chloride

An increase in the concentration of chloride ions is indicative of reductive dechlorination of chlorinated solvent compounds. However, the presence of chloride in solution also occurs naturally as a result of the high total dissolved solids (TDS) groundwater environment at the site, and likely masks any trend analyses for chloride as an indicator of natural attenuation. As seen in Table O-3 and illustrated graphically in Figure O-15, chloride concentrations are higher at PSCT-1 and in wells downgradient of the PSCT as compared with upgradient wells. Increases in chloride concentrations suggest chloride accumulation in groundwater from north to south across the site. The distribution of elevated chloride concentrations occurs in areas of the Site where water evaporation occurs. Should pond levels decline such that pond levels dry and wet with seasonal rains, metal precipitation in the form of salt deposits may occur.

3.2 Trimethylbenzene Isomers and Calculation of Biodegradation Rates

In order to accurately calculate biodegradation rates, measured contaminant concentrations must be normalized for the effects of dispersion, dilution, sorption, and pumping in the PSCT treatment system. A convenient way to do this is to use compounds or elements, called tracer

compounds, associated with the contaminant plume that are relatively unaffected or predictably affected by biologic processes occurring within the aquifer.

At sites where commingled fuel hydrocarbon and chlorinated solvent plumes are present, the biologically recalcitrant trimethylbenzene isomers (TMB) can be useful when estimating the biodegradation rates for BTEX and CVOCs. An analysis of the TMB concentration at this site shows that in the great majority of the wells selected for the MNA study, TMB is non-detect and is thus not useful as a tracer.

Another compound commonly used as a tracer for sites with ongoing reductive dechlorination is chloride. At this site the high native levels of chloride resulting from elevated TDS values combined with the elevated chloride levels in the areas of the various ponds that result from continuing evaporation make chloride a poor choice for a tracer compound.

Lack of a suitable tracer compound combined with the complex chemistry and hydrogeology of the site prevent a quantitative evaluation of biodegradation rates as described in *Wiedemeier et al, 1996a*.

A qualitative measure of the rate can be seen in the stability of the plume as seen in plots of VOC concentrations over time (Attachment G-1).

3.3 MNA Summary

MNA encompasses multiple processes that act to either destroy or dilute the concentrations of COCs. The MNA data provides strong evidence that biological mediated degradation of petroleum and halogenated hydrocarbons is occurring, through aerobic, anaerobic and fermentative metabolic pathways. The rates of biologically mediated degradation (as evidenced by the concentrations of daughter products) are variable across the Site, with the most active areas of biodegradation occurring in the BTA and CDA north of the PSCT. Due to the nature of landfill deposits, conditions at the landfill cells appear favorable for continued biological activity, with the supply of readily available supply organic matter (petroleum hydrocarbons) and bionutrients compounds (e.g. nitrate).

Indicator parameters collected historically and during the RI sampling events of Fall 2004 and Spring 2005 indicate biological degradation of organic chemicals in the source and plume areas is occurring, and supports evidence that a reductive dechlorination zone exists to the south of the PSCT trench. In summary:

- Supply of electron donors and acceptors: The relative concentrations of nitrate, sulfate, and dissolved manganese are consistent with biological degradation. Concentrations of nitrate decrease relative to background concentrations in groundwater downgradient of the PSCT; dissolved manganese concentrations increase in the source and plume wells, and sulfate concentrations decrease in the plume relative to upgradient and downgradient wells. The noted microbial utilization of nitrate and sulfate and formation of dissolved manganese in the groundwater between the PSCT and downgradient wells indicates the presence of a zone of reductive dechlorination;
- Presence of end products: The presence of end products dissolved methane and dissolved ethane in the source and plume areas indicates biological degradation of chlorinated hydrocarbons (naturally elevated chloride concentrations make chloride not a useful indicator); and

- General parameters: A decrease in redox potentials and an increase in alkalinity from the background to the source and plume areas indicate biodegradation.

Indicator parameters indicate that bioactivity conducive to reductive dechlorination is continuing. Strong evidence of current or recent biodegradation is also indicated by the following:

- Stable VOC concentration trends;
- The ratio of cis-1,2-DCE to trans-1,2-DCE exceeding 80 percent;
- Spatial and temporal changes in electron acceptor concentrations (reduced oxygen, nitrate and sulfate concentrations, and increased dissolved manganese concentrations); and
- The accumulation of degradation daughter and end byproducts.

Results from monitoring data indicate that natural attenuation is occurring in the area to the north of the PSCT (BTA, P/S Landfill, and CDA) and south of the PSCT and that MNA is a viable part of site remedial strategies for organic compounds. With the addition of black landfill caps, the additional heat may have increased volatilization of VOCs within the P/S landfill. The presence of a vegetative layer on top of the black HDPE layer will reduce this heating effect. Significant dilution and dispersion of dissolved organic COCs does not appear to be a significant MNA process as evidenced by plume stability over the years. While MNA is not considered a primary remedy for inorganic compounds, as water levels continue to drop in the ponds, MNA for elevated inorganic compounds may results in precipitation of metal ions (salt formation).

4.0 EVALUATION OF ADDITIONAL DATA NEEDS

The MNA evaluation indicates that reductive dechlorination process is occurring at the site. As a part of the RI/FS, additional evaluations of natural attenuation were conducted using historical data and new groundwater chemistry data obtained during the RI/FS groundwater sampling investigations (see Appendix G) conducted in Fall 2004 and Spring 2005 and semi-annual groundwater monitoring events through Fall 2008. During the future semi-annual groundwater monitoring events, selected wells will be sampled for COCs and the MNA indicator parameters presented in this report with the exception of dissolved hydrogen, methane, ethane, and ethene.

The historical data summarized in this Appendix were evaluated with respect to the groundwater Data Quality Objectives (DQOs) identified in the RI/FS Work Plan. RI/FS Work Plan Sections 4.3 through 4.6 identify specific decisions and decision rules for issues related to this task, including those related to contaminant fate extent and transport, and Feasibility Study (FS) evaluations. The RI/FS Workplan identifies all of the RI/FS DQO decisions and provides an evaluation of additional data needs associated with each, and the decisions specific to well and piezometer drilling are listed below. Note some of these groundwater decisions are also addressed in Appendix G (Groundwater Chemistry).

4.1 DQO Decisions Related to Groundwater Contaminant Fate and Transport

The specific decisions and decision rules for MNA issues related to groundwater contaminant fate extent and transport that were included in the DQOs of the RI/FS Work Plan are as follows:

- How have concentrations of different water quality parameters changed over time?
- Based on the observed water quality trends, what are the anticipated future concentration trends?

The CSC believes that the groundwater chemistry and MNA data collected as a part of these RI investigations are adequate for evaluating the occurrence of natural attenuation processes and contaminant fate extent and transport DQO decisions noted above. The extent of and trends in groundwater impacts have been characterized, and the RGMEW groundwater sampling program has provided and will continue to provide extensive information on the distribution of indicator parameters and COCs, and temporal variability and the existing data are sufficient to evaluate future water quality trends.

The additional groundwater sampling conducted as a part of the RI has provided characterization of the presence and distribution of additional potential COCs and monitored for additional natural attenuation indicator parameters.

4.2 DQO Decisions Related to FS Evaluations for Groundwater

The specific decisions and decision rules for issues related to the FS evaluations for groundwater that were included in the DQOs of the RI/FS Work Plan are as follows:

- What is the chemical nature and physical extent of the contaminated area requiring remediation?

Groundwater data collected as a part of these RI investigations are adequate for conducting FS evaluations for groundwater. As described above the inorganic and organic groundwater chemistry data collected to date which are necessary to assess FS alternatives are sufficient for these analyses.

5.0 REFERENCES

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