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Vadose Zone Remediation Technology Screening Study Tronox LLC Henderson, Nevada

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1.0 INTRODUCTION

This Technical Memorandum presents a remediation technology screening study for contaminated vadose-zone soils at the Tronox Site, located in Henderson, Nevada (the Site). The study was completed on behalf of Tronox LLC (Tronox) by Northgate Environmental Management (NGEM). This screening was conducted to evaluate the potential use of a variety of General Response Actions and specific remediation technologies to address chemicals of concern (COC) in vadose-zone soils that potentially pose a risk to groundwater quality beneath the Site.

Section 2 of this Technical Memorandum describes the purpose of the study. Section 3 presents a description of Site Conditions, including a Conceptual Site Model (CSM) and a summary of chemical distribution in the vadose zone. Section 4 describes the framework for the study and presents the results, and includes recommendations for the next steps needed to more completely evaluate the feasibility of candidate technologies. For reference and additional detail on certain aspects of the study, four appendices have been assembled and are attached. Appendices A through D include detailed information on the potential application of in situ soil flushing, in situ soil bioflushing, in situ direct injection of gaseous electron donors (GEDIT) and ex situ soil biotreatment, respectively. Significant contributions to this study were provided by Patrick Evans of Camp Dresser & McKee Inc. (CDM) specifically related to the GEDIT and ex situ bioremediation technologies and by Jay Diebold of Shaw Environmental (Shaw) for soil bioflushing.

2.0 PURPOSE OF STUDY

The purpose of this technology screening study is to identify potentially suitable remediation technologies as a predecessor to completing a more detailed and focused feasibility study for remediation of contaminated vadose-zone soils at the Site. The primary concern addressed in this study is the protection of groundwater. The Site has a variety of unique challenges and opportunities for remediation of vadose-zone soils, and careful study of the feasibility and potential outcome of applying remediation technologies is essential to maximizing the reduction of risks to groundwater quality, while balancing the technical constraints of the Site and the financial constraints of the responsible parties. This screening study serves to identify the most promising technologies, and presents a framework for focusing further evaluation in terms of engineering and economic evaluations, treatability studies, and/or pilot studies.

3.0 SITE CONDITIONS

3.1 Site Description

The Site is located approximately 13 miles southeast of the city of Las Vegas and is surrounded by the unincorporated area of Clark County, Nevada, that comprises the City of Henderson. It covers approximately 450 acres, and lies in Sections 1, 12, and 13 of Township 22 S, Range 62 E. The Site is located within the Black Mountain Industrial (BMI) complex, which consists of facilities owned and operated by chemical companies, one of which is Tronox, LLC.

3.2 Physical Setting

Elevations across the Site range from 1,677 to 1,873 feet above mean sea level. The land surface across the Site slopes toward the north at a gradient of approximately 0.023 feet per foot (ft/ft). The developed portions of the Site have been modified by grading to accommodate building foundations, surface impoundments, and access roads. Offsite to the north, the topographic surface continues at the same gradient to approximately Sunset Road, at which point it flattens to a gradient of 0.011 ft/ft to the Las Vegas Wash (ENSR, 2005).

3.3 Climate

The climate of the Las Vegas Valley is arid, consisting of mild winters and dry hot summers. Average annual precipitation as measured in Las Vegas from 1971 to 2000 was 4.49 inches. Winds frequently blow from the south- or northwest at a mean velocity around 9 miles per hour (mph), however, velocities in excess of 50 mph are not atypical when weather fronts move through the area. Temperatures can rise to 120°F in the summer, and the average relative humidity is approximately 20%. The mean annual evaporation from lake and reservoir surfaces ranges from 60 to 82 inches per year (see references in Kleinfelder, 1993).

3.4 Regional Geology

The Las Vegas Valley occupies a topographic and structural basin trending northwest-southeast and extending approximately 55 miles from near Indian Springs on the north to Railroad Pass on the south. In the Las Vegas Valley, eroded Tertiary and Quaternary sedimentary and volcanic rocks comprise the unconsolidated basin deposits, which can be up to 13,000 feet thick (ENSR, 2007b). The valley floor consists of fluvial, paludal (swamp), and playa deposits surrounded by more steeply sloping alluvial fan aprons derived from erosion of the surrounding mountains. Generally, the deposits grade finer with increasing distance from their source and with decreasing elevation. The structure within the Quaternary and Tertiary-aged basin fill is characterized by a series of generally north-south trending fault scarps.

3.5 Local Geology

The local geology and hydrology are defined by data collected from the numerous borings and wells that have been installed in the area. The following descriptions are summarized from the CSM report (ENSR, 2005).

3.5.1 Alluvium

The Site is located on Quaternary alluvial (Qal) deposits that slope north toward Las Vegas Wash. The alluvium consists of a reddish-brown heterogeneous mixture of well-graded sand and gravel with lesser amounts of silt, clay, and caliche. Clasts within the alluvium are primarily composed of volcanic material. Boulders and cobbles are common. Due to their mode of deposition, no distinct beds or units are continuous over the area.

A major feature of the alluvial deposits is the stream-deposited sands and gravels that were laid down within paleochannels that were eroded into the surface of the Muddy Creek Formation (MCf) during infrequent flood runoff periods. These deposits are thickest within the paleochannel boundaries, which are narrow and linear. These sand and gravel deposits exhibit higher permeability than the adjacent, well-graded deposits. In general, these paleochannels trend northeastward towards the Las Vegas Wash.

The thickness of the alluvial deposits ranges from less than 1 foot to more than 50 feet beneath the Site. Soil types identified in onsite soil borings include poorly sorted gravel, silty gravel, poorly sorted sand, well sorted sand, and silty sand.

3.5.2 Muddy Creek Formation

A The Pleistocene Muddy Creek Formation (MCf) occurs in Las Vegas Valley as valley-fill deposits that are coarse-grained near mountain fronts and become progressively finer-grained toward the center of the valley. Where encountered beneath the Site, the Muddy Creek Formation is composed of at least two thicker units of fine-grained sediments of clay and silt (the first and second fine-grained facies, respectively) interbedded with at least two thinner units of coarse-grained sediments of sand, silt, and gravel (the first and second coarse-grained facies, respectively). Except for the southernmost 1,000 feet adjacent to Lake Mead Parkway, the first fine-grained facies (MCfg1) separates the first coarse-grained facies (MCcg1) from the overlying Quaternary alluvium at the Site. Within the southern 1,000 feet of the Site, the Muddy Creek Formation's first fine-grained facies (MCfg1) pinches out along a roughly west-northwesterly trending line. South of this line, the coarse-grained facies (MCcg1) directly underlies the Quaternary alluvium. On the Site, the Muddy Creek does not crop out but instead subcrops beneath a veneer of Quaternary alluvium.

3.6 Local Hydrogeology

Depth to groundwater ranges from about 27 to 80 feet below ground surface (bgs) and is generally deepest in the southernmost portion of the Site, becoming shallower as it approaches the Las Vegas Wash to the north. The groundwater flow direction at the Site is generally north to north-northwesterly, whereas north of the facility the direction changes slightly to the north-northeast. This generally uniform flow pattern may be modified locally by subsurface alluvial channels cut into the underlying UMCf, the onsite bentonite-slurry groundwater barrier wall, on-and offsite artificial groundwater highs or "mounds" created around the onsite recharge trenches and City of Henderson Water Reclamation Facility Rapid Infiltration Basins (RIBs), and by depressions created by the groundwater extraction wells at the three groundwater recovery well fields (Northgate, 2010a).

At the Site, the Shallow Zone contains the saturated portions of the Qal and the uppermost portion of the UMCf to depths of approximately 90 feet bgs. Beneath the northern portion of the Site, the first groundwater encountered occurs within the Qal at depths of 30 feet bgs or more, and shallows northward, occurring near the ground surface at Las Vegas Wash. Beneath the central portion of the Site, groundwater is first encountered within the Shallow Zone in the first fine-grained facies of the Muddy Creek Formation (MCfg1), and can be more than 50 feet bgs. South of where MCfg1 pinches out, beneath the southern portion of the Site, the first groundwater encountered occurs within the first coarse-grained facies of the Muddy Creek Formation (MCcg1) and can be more than 70 feet bgs (ENSR, 2006b). Both the horizontal and vertical hydraulic conductivities of the UMCf are substantially less than those of the Qal (ENSR, 2005).

Surface water in the vicinity of the Site flows to the north toward Las Vegas Wash. Surface flow occurs as infrequent storm runoff in shallow washes. Drainage and diversion structures have been constructed around the perimeters of the BMI complex to channel surface water flow. Las Vegas Wash is a tributary to Lake Mead and it is the only channel through which the valley's excess water flows to the lake. Lake Mead is a major reservoir on the Colorado River. There are no water supply wells reported within four miles of the Site that extract water from the Shallow, Middle, or Deep Zones (ENSR, 2005).

3.7 Conceptual Site Model

This section presents a general CSM based on the current understanding of potential on- and off-Site contaminant sources, release mechanisms, and distribution in soil. The CSM for this study is only focused on protection of groundwater from contaminants transported via the soil to groundwater leaching pathway.

3.7.1 Potential Sources of Contamination

Industrial activities have occurred on the BMI complex since 1942, which was originally sited and operated for the U.S. government as a wartime magnesium production plant (Kleinfelder, 1993).

During government operations, extensive volumes of liquid wastes containing dissolved and suspended solids were discharged to four unlined Trade Effluent Ponds. These liquids were generally composed of acid effluent and waste caustic liquor containing high levels of total dissolved solids (TDS), dissolved metals, and to a lesser degree, chlorinated organics. Waste water originating from site processes was also discharged to a storm sewer system that emptied into unlined drainage ditches (e.g., Alpha and Beta Ditches). The unlined drainage ditches routed waste water to a system of unlined ponds currently known as the Upper and Lower BMI ponds. Solid materials were placed in an open area south of the Trade Effluent Settling Ponds and north of the caustic settling ponds. Although originally intended for evaporative disposal, these unlined surface impoundments allowed significant quantities of process effluent to infiltrate into the deep soil and percolate into the groundwater.

Process activities at the Site since 1945 include the production of chlorate and perchlorate compounds, boron and boron-related compounds, and refined manganese oxide. From 1945 until the mid-1970s, process effluents from the chlorate, perchlorate, and boron-related production processes were sent to the unlined Upper and Lower BMI Ponds via the Beta Ditch and manganese-related wastes were disposed in onsite leach beds. In the early 1970s, under the federal National Pollutant Discharge Elimination System (NPDES) program, the industries at the BMI Complex curtailed waste discharges to the Upper and Lower BMI Ponds. Following 1976, process effluents were sent to onsite lined surface impoundments to comply with zero-discharge standards. Several of these lined surface impoundments reported a number of known releases and liner failures and were eventually replaced with more effective double-lined systems.

The Pioneer/Olin Chlor-Alkali/Stauffer/Syngenta/Montrose (POSSM) property to the west of the Site occupies the location of the former BMI Complex chlor-alkali production facility. Post-1945 process activities on the POSSM property include operation of the chlor-alkali facility to produce chlorine gas, hydrochloric acid, and sodium hydroxide. In 1947, additional manufacturing facilities were constructed to produce pesticides and chlorinated organic compounds. Production of agricultural chemicals and organic compounds ceased in 1983, and production facilities were demolished and removed from the POSSM site in 1984. Operations at the chlor-alkali facility are ongoing. Since 1945, extensive volumes of process effluents and solid wastes were disposed of in onsite unlined ponds and buried on the property. These wastes

contained high levels of TDS, chlorinated organic compounds, and extensive amounts of phosphoric acid. Prior to 1976, certain process effluents were routed to the Upper and Lower BMI Ponds. These waste streams included large volumes of sulfuric and hydrochloric acid, as well as sulfonated metabolites of DDT (H+A, 2008).

3.7.2 Distribution of Contaminants in the Vadose Zone

Vadose zone soil remediation (excavation with offsite disposal) is currently underway, and will remove some of the chemicals remaining in soil that could present an ongoing threat to groundwater through leaching. Based on a Site-specific evaluation of potential leaching (Northgate, 2010c) chemicals that will remain in vadose-zone soil after excavation at levels that could potentially present an ongoing threat to groundwater include perchlorate, chlorate, arsenic, manganese, cobalt, magnesium, hexachlorobenzene, chloroform, alpha/beta/gamma-BHC, and dieldrin. Although hexavalent chromium was not identified as a potential leaching threat to groundwater in the previously mentioned study, recent column tests where contaminated soil was flushed with stabilized Lake Mead water have shown that it can be leached from soil. As presented in Phase B Groundwater Investigation, some of these chemicals have impacted groundwater above risk-based groundwater concentrations (RBGCs); however, data available for cobalt, manganese, hexachlorobenzene, beta- and gamma-BHC, and dieldrin indicate only limited impact to groundwater. The evaluation of potential future leaching is ongoing, and will include an assessment of the significance of the potential impact to groundwater. In addition, water flushing and other potential in situ methods to remove remaining vadose zone perchlorate and other leachable chemicals are being evaluated (Northgate, 2010c).

For the purpose of this study, four contaminants were considered for the screening of potential remediation technologies. Perchlorate is representative of the class of highly-soluble salts that can be destroyed through biological reduction. Other similar contaminants in this class include chlorate and nitrate. Hexavalent chromium is representative of the class of redox-sensitive metals that can be treated, stabilized or attenuated through reducing environments such as those brought about by biological reduction. Manganese is representative of the class of redox-sensitive metals that can be stabilized or attenuated in the vadose zone through oxidizing conditions. Other similar contaminants in this class include cobalt and arsenic. Beta-BHC is representative of the class of organochloride pesticides that can be destroyed through biological dechlorination. Other similar contaminants in this class include gamma-BHC (Lindane), the alpha- and delta- isomers of BHC, dieldrin, and hexachlorobenzene. Chloroform is not addressed in this study because its occurrence in groundwater is primarily associated with off-site sources, and the potential contribution to groundwater from on-Site vadose-zone soils via a leaching pathway is not considered to be significant.

3.7.2.1 Perchlorate

Perchlorate compounds were manufactured at the Site from 1945 until approximately 1998. Sodium chlorate and perchlorate were produced in Units 4 and 5 and used primarily as feedstock for the production of ammonium perchlorate in the AP Plant Area. The basements of Units 4 and 5 were used as sumps to collect process liquor, spillage, and wastewater. Deterioration and cracking of their concrete foundations led to the release of significant amounts of chlorate and perchlorate-laden process liquor to underlying soils and groundwater (Kleinfelder, 1993). Operation of the electrolytic cells in Units 4 and 5 was discontinued in the late 1990s (ENSR, 2005).

From 1945 until 1976, process waste streams from the sodium perchlorate and ammonium perchlorate process were discharged to the BMI Ponds via the Beta Ditch. From 1976 until 1983, sodium perchlorate process liquids were sent to Ponds S-1 and P-1. Both of these ponds reported leaks and liner failures. Additional potential source areas for perchlorate contamination include Ponds AP-1, AP-2, and AP-3. A leak from Pond AP-2 was reported in 1979 and the liner was replaced prior to 1980. By late 1983, frequent patching was required to mitigate leaks until the liners were replaced with double-liner systems. Additional potential sources include the area affected by the July 1990 fire, where water used to fight an ammonium perchlorate fire could have infiltrated into the groundwater, the AP Plant Area New D-1 Building Wash-Down, AP Plant Cooling Tower overflows, and reported leaks from AP Plant Transfer Lines to the Sodium Chlorate Process.

A map of perchlorate concentrations in the vadose zone was constructed using chemical analysis data collected during the Phase A and Phase B soil sampling events. Representative concentration values were calculated for 10-foot depth intervals by averaging the values of discrete samples collected within a given interval. Concentration contours were constructed based upon the highest 10-foot depth interval concentration observed at a sampled location. Analysis of perchlorate concentrations in the vadose zone (Figure 1) reveals extensive perchlorate contamination in the region of the Former AP Plant. Localized high levels of perchlorate also exist in the vicinity of Units 4 and 5. Concentrations of perchlorate in discrete soil samples exceed 1,200 mg/kg at depths of 29 feet in the vicinity of the AP Tank Farm, 1,800 mg/kg at depths of 30 feet near Pond AP-1, and over 8,000 mg/kg at a depth of 30 feet adjacent to the AP Plant Area Old Building D-1 Wash-down, and 1,200 mg/kg in soil at depths of 10 feet in the eastern area of the former Unit 4. (Northgate, 2010d-g). Extensive areas of the Site have levels of perchlorate in the vadose zone exceeding the NDEP leaching-based site specific level (LSSL) of 40 µg/kg.

Analysis of perchlorate concentration data in the vadose zone (Table 1) reveals that in excess of 13,000,000 cubic yards of soil are contaminated with perchlorate at levels above the LSSL of 40 μ g/kg. As shown in the table, the majority of the perchlorate mass resides in the 3,600,000 cubic yards of soil that contains greater than 10 mg/kg.

Significant amounts of perchlorate remain in Site vadose-zone soil, and have been identified as presenting an ongoing threat to groundwater through leaching (Northgate, 2010b; *Tronox/NDEP meeting minutes for February 5 and February 12, 2010*). Soil flushing and other remedial options are currently being considered to address this concern (Northgate, 2010c). Provided the potential leaching concern is adequately addressed, perchlorate concentrations should continue to decline in Shallow Zone groundwater due to ongoing groundwater extraction.

Analysis of perchlorate concentration data in the Shallow Water Bearing Zone indicates a plume north of Units 4 and 5 that is contained by the groundwater barrier wall to the north. The highest concentration upgradient of the barrier wall was 2,870,000 μ g/L at well IAR. Between the barrier wall and the Las Vegas Wash, the maximum perchlorate concentration was 892,000 μ g/L (M94) along the northern Site boundary. Concentrations continue to decrease northward with a concentration of 18.4 μ g/L at well MW-K6 at the Las Vegas Wash.

Perchlorate is a large anion with a relatively low diffuse charge. It is non-complexing, forms no insoluble minerals, and sorbs poorly to most solids. Sodium and ammonium perchlorate are highly soluble with solubilities of approximately 200 g/L at 20°C. Partition coefficients describing perchlorate sorption to geologic media are essentially zero. Because perchlorate sorbs so poorly to most geologic materials, in the absence of biodegradation, perchlorate plumes should move at roughly the same velocity as groundwater.

3.7.2.2 Hexavalent Chromium

Hexavalent chromium in the form of sodium dichromate $(Na_2Cr_2O_7)$ was used extensively at the Site from 1945 until approximately 1993 (Kleinfelder, 1993). Sodium dichromate was added to sodium chlorate and sodium perchlorate production solutions to reduce cathode corrosion, increase current efficiencies, and to prevent anodic oxygen generation.

Potential source areas for hexavalent chromium include the basements of Units 4 and 5. These basements were used as sumps to collect process liquor, spillage, and wastewater. Deterioration and cracking of their concrete foundations led to the release of significant amounts of chlorate and perchlorate-laden process liquor to underlying soils and groundwater (Kleinfelder, 1993).

Additional potential source areas include areas where chromium-laden filter cake waste was stored or disposed, including the On-Site Hazardous Waste Landfill, Sodium Chlorate Filter Cake Drying Pad, and the BMI Landfill. Prior to 1976, chromium-laden process solutions and filter cake waste was sluiced to the Upper and Lower BMI Ponds via the Beta Ditch. Following 1976, chromium-laden sodium chlorate waste streams were sent to the Old P-2 Pond, the P-3 Pond, and the new P-2 Pond. The Old P-2 Pond and P-3 Pond reported numerous leaks and liner failures before being closed and replaced with the P-3 Pond (Kleinfelder, 1993). Potential source areas also include Ponds AP-1, AP-2, and AP-3, and Pond AP-4. These Ponds and their associated transfer lines received chromium-laden process liquor.

A map of hexavalent chromium concentrations in the vadose zone (Figure 2) was constructed using chemical analysis data collected during the Phase A and Phase B soil sampling events. Representative concentration values were calculated for 10-foot depth intervals by averaging the values of discrete samples collected within a given interval. Concentration contours were constructed based upon the highest 10-foot depth interval concentration observed at a sampled location. Analysis reveals three distinct areas of contamination. Discrete soil samples from the Phase B soil investigation reveal hexavalent chromium concentrations of 14.9 mg/kg at depths of 37 feet in the northern area of Unit 4, 28.2 mg/kg at depths of 39 feet in the area of the Filter Cake Drying Cake Pad, 8.13 mg/kg at depths of 27 feet in the area of Old P-2 Pond, 8.13 mg/kg at a depth of 27 feet in the area of AP-3 Pond, and 28.2 mg/kg at a depth of 39 feet in the area of AP-4 Pond (Northgate, 2010d-g). Analysis of hexavalent chromium concentrations in the vadose zone (Table 2) reveals that over 17,350 cubic yards of soil are contaminated at levels above 10 mg/kg.

Chromium in the environment exists predominately in two oxidation states: Cr(VI) and Cr(III). Cr(VI) is mobile in groundwater, acutely toxic, and carcinogenic, while Cr(III) is relatively immobile under most groundwater conditions and exhibits low toxicity (Richard and Bourg, 1991). At concentrations present at the Site, Cr(VI) will primarily exist as monomeric chromate (HCrO₄⁻,CrO₄²⁻) anions. However, at higher concentrations, such as those in the sodium chlorate process liquor, Cr(VI) exists as dimeric dichromate (Cr₂O₇²⁻) anions. At the slightly alkaline pH conditions encountered at the Site, Cr(III) is not soluble in water and readily precipitates to an insoluble chromium hydroxide (Cr(OH)₃).

Cr(VI) anions are mobile in groundwater, but have been demonstrated to sorb to surface sites on iron oxyhydroxides (Leckie et al., 1984). The strength of adsorption of Cr(VI) anions is intermediate between those of strongly binding anions, such as phosphate and arsenate, and weakly binding anions like sulfate (Davis et al., 2000). It has been demonstrated that high

concentrations of sulfate will reduce chromate adsorption, but this typically occurs under acidic conditions that are not observed at the Site (Leckie et al., 1984). Other naturally occurring anions such as bicarbonate and dissolved silica can also compete for adsorption sites (van Geen et al., 1994; Zachara et al., 1987). The high sulfate and bicarbonate concentrations on the Site should reduce the natural sorption of Cr(VI) onto mineral surfaces.

Analysis of hexavalent chromium data from the Shallow Water Bearing Zone indicates a large plume north of Units 4 and 5 that is largely contained by the groundwater barrier wall to the north. The highest concentration upgradient of the barrier wall was 33.6 mg/L at well M50. Between the barrier wall and the Las Vegas Wash, the maximum hexavalent chromium concentration was 5.1 mg/L (PC-64). Concentrations continue to decrease northward towards the Wash with a maximum concentration of 0.024 mg/L at well PC-94.

Leaching calculations based upon generic Kd's have indicated Cr(VI) remaining in vadose-zone soil is not expected to significantly impact groundwater (Northgate, 2010c). However, recent column studies have showed that detectable levels of hexavalent chromium are leachable from Site soil samples. Concentrations of Cr(VI) at the Site are expected to decrease over time due to the ongoing groundwater extraction and treatment, by natural attenuation via sorption onto mineral surfaces, and via reduction to insoluble Cr(III) hydroxides through reactions with organic carbon.

3.7.2.3 Manganese

Manganese dioxide has been produced at the Site since 1951, primarily for the manufacture of dry cell batteries. Manganese-bearing ore is roasted to increase the manganese solubility and then leached with sulfuric acid to produce a concentrated manganese sulfate solution at the manganese dioxide leach plant. The solution is then fed to the electrolytic cells in Units 5 & 6. Prior to 1986, chemicals in Unit 6 were known to have leaked into vadose-zone soils and groundwater through cracks in the concrete basement.

A map of manganese concentrations in the vadose zone (Figure 3) was constructed using chemical analysis data collected during the Phase A and Phase B soil sampling events. Representative concentration values were calculated for 10-foot depth intervals by averaging the values of discrete samples collected within a given interval. Concentration contours were constructed based upon the highest 10-foot depth interval concentration observed at a sampled location. Analysis reveals manganese contamination of the vadose zone in the areas where leachate from the manganese tailings pile and wastewater from the dewatering of manganese tailings were released onto on-site Leach Beds and infiltrated into the soil. Analysis of discrete



Site vadose-zone soil samples reveals manganese concentrations of 160,000 mg/kg at depths of 10 feet and at 2,000 mg/kg at depths of 51 feet in the area of the Leach Beds (Northgate, 2010d-g). Additional contamination was found where manganese tailings were disposed in the Historic Manganese Tailings Area. Analysis of discrete soil samples in this area reveals manganese concentrations of 21,600 mg/kg at depths of 34 feet in the area of the Former Eastern Leach Beds (Northgate, 2010d-g). Analysis of manganese concentrations in the vadose zone (Table 3) reveals that over 410,000 cubic yards of soil are contaminated at levels above the LSSL of 2,400 mg/kg.

Analysis of total manganese in the Shallow Water Bearing Zone indicates what appears to be a plume with concentration levels exceeding 200,000 μ g/L to the north of Unit 6 and exceeding 49,000 μ g/L in the area of the Former Eastern Leach Beds. However, dissolved manganese (i.e., filtered samples) data show a maximum concentration of 987 μ g/L in the area of the Former Eastern Leach Beds. These data suggest that the total manganese concentrations likely reflect chemical analysis of suspended manganese-containing precipitates and not dissolved manganese in solution.

Manganese in soils and groundwater typically exists in the Mn(II) and Mn(IV) oxidation states. Mn(IV) is the predominate state in aerobic environments and tends to exist as insoluble oxyhydroxides (Scott et al., 2002). In neutral to slightly acidic groundwater with low oxygen levels, Mn(IV) can be reduced to Mn(II) via oxidation-reduction (redox) reactions that may be abiotic or microbially mediated. Reduction of Mn(IV) to Mn(II) in neutral to slightly alkaline groundwater can lead to the formation of insoluble manganese carbonates.

Although manganese remaining in Site vadose-zone soils has been identified as a potential concern for ongoing leaching to groundwater, dissolved manganese levels in Site groundwater are likely to remain at relatively low levels unless redox and pH conditions are changed from their current state. If reductive in situ bioremediation of perchlorate in the vadose zone is performed in areas with manganese-contaminated soil, the local oxidation reduction potential (ORP) will be lowered, leading to reduction of insoluble Mn(IV) to soluble Mn(II). It is likely that Mn(II) released into groundwater will reoxidize to insoluble Mn(IV) as it leaves the reaction zone and mixes with groundwater under oxidizing conditions, based upon the apparent rapid attenuation of dissolved manganese at the Site.

3.7.2.4 Beta-BHC

Stauffer produced agricultural chemical products from 1946 through 1984, including Lindane (gamma-BHC) from 1946 through 1958. Historic correspondence notes stockpiling of over



200,000 cubic yards of alpha- and beta-BHC on the Stauffer or BMI property between 1946 and 1958 (Stauffer, 1987). These isomers were considered waste stock from the production of gamma-BHC. Waste BHC isomers were also stockpiled in three areas of the former Stauffer facility. These stockpiles were eventually consolidated into "BHC Cake Pile 3" and capped under 1-foot of clay in 1980. From 1945 through 1975, waste effluent from the Stauffer operations and the Montrose facilities, as well as storm water runoff from the two properties, was discharged to the sewer system (H+A, 2008). Stauffer constructed an asphalt cap over the sites of the former Lindane plant and BHC Cake Piles 1 and 2 in 2003-2004. Alpha-, beta-, delta- and gamma-BHC have been detected in the vadose zone and in the Shallow and Middle Zones beneath the POSSM properties (H+A, 2008; H+A, 2010). No on-Site sources of BHC have been identified.

A map of beta-BHC concentrations in the vadose zone (Figure 4) was constructed using chemical analysis data collected during the Phase A and Phase B soil sampling events. Representative concentration values were calculated for 10-foot depth intervals by averaging the values of discrete samples collected within a given interval. Concentration contours were constructed based upon the highest 10-foot depth interval concentration observed at a sampled location. Analysis reveals widespread contamination of beta-BHC in Site vadose-zone soils mostly likely though wind-blown dispersal from the off-Site source. Analysis of Beta-BHC concentrations in the vadose zone as a function of depth (Table 4) reveals that over 7,900,000 cubic yards of soil are contaminated at levels above the LSSL of 0.0017 mg/kg. Based on the concentrations and distribution of alpha-, beta-, and gamma-BHC in groundwater, it is likely that these chemicals are migrating beneath the Site via groundwater movement and chemical diffusion from off-site sources to the southwest.

BHC isomers have relatively low solubilities in water and the pure products are denser than water. Accordingly, they are considered DNAPLs, and when released into groundwater, can migrate downward, leaving residual DNAPL in soil pore spaces (Anderson et al., 2007). Estimated retardation factors for alpha-BHC range from 3.5 to 22.5, with a similar range reported for beta- and gamma-BHC (Anderson et al., 2007). BHC isomers persist in soils in a wide variety of climates (Singh et al., 2000). Based on laboratory soil column leaching studies that used soils of both high and low organic carbon content, alpha- and gamma-BHC have low mobility in soils and adsorption to soil particulates is generally a more important partitioning process than leaching to groundwater, but not to the extent that leaching to groundwater is not possible (see references in ATSDR, 2005a). The presence of BHC in soil may inhibit both oxidation and reduction reactions and may be inhibitory or toxic to certain populations of bacteria. However, there appear to be a number of microorganisms that are capable of

biodegrading BHC isomers via dehalogenation, dehydrohalogenation, isomerization, and oxidation (see references in ATSDR, 2005a and Singh et al., 2000).

3.7.3 Current Groundwater Remediation Program

Tronox operates two groundwater remediation systems at the Site: (1) a hexavalent chromium remediation system in two parts that treats water from a) an on-Site Interceptor well field and b) from the off-Site Athens Road well field. Both parts using ferrous sulfate to reduce hexavalent chromium to trivalent chromium, and (2) a perchlorate remediation system that treats water from the on-Site Interceptor well field, the off-Site Athens Road well field, the off-Site Seep well field, and the off-Site Seep surface-flow capture sump using perchlorate-reducing bacteria in nine fluidized bed reactors. The Interceptor well field consists of a series of 23 groundwater extraction wells that are located immediately upgradient (south) of a low-permeability barrier wall and combined pump approximately 70 gallons per minute (gpm). Tronox is currently working on the infrastructure upgrades necessary to connect seven additional extraction wells to the Interceptor well field recovery system (Northgate, 2010a). The Athens Road well field consists of a series of 14 groundwater extraction wells pumping a total of approximately 530 gpm (Northgate, 2010a).

In accordance with the Consent Order for remediation of chromium-impacted groundwater finalized on September 9, 1986, and the Administrative Order on Consent for remediation of perchlorate-impacted groundwater in the Henderson area, Tronox conducts an annual groundwater sampling event that is coordinated with several neighboring companies. Groundwater samples are collected and analyzed for perchlorate, hexavalent chromium, TDS, chlorate, and nitrate. Groundwater sample and potentiometric data collected by neighboring companies are considered in the evaluation of Site conditions. Groundwater monitoring results and details regarding the remediation systems' operations are provided in annual remediation performance reports (e.g., Northgate, 2010a). In addition, Tronox is currently performing a capture zone evaluation that incorporates the results of additional field investigations at the Site, and developing a three-dimensional hydrogeologic flow model.

Chromium and perchlorate concentrations in monitoring wells immediately downgradient of the onsite groundwater barrier have declined significantly since the early 2000s, reflecting groundwater capture in the Interceptor well field and dilution by Lake Mead water in the recharge trenches. Concentrations of total chromium at the Seep well field continue to be below the laboratory method reporting limit. Perchlorate loading in the Las Vegas Wash has declined

by nearly 94% over the last 10 years of groundwater capture system operation (Northgate, 2010a).

Chemical analysis of the perchlorate remediation system influent and effluent streams indicates that the fluidized bed reactor (FBR) is capable of treating several of the leachable contaminants of concern. The FBR was able to lower hexavalent chromium concentrations from approximately $50 \ \mu g/L$ to non-detect ($<0.1 \ \mu g/L$) levels. The hexavalent chromium was likely transformed to trivalent chromium in the reducing environment in the FBR either abiotically or by hexavalent chromium reducing bacteria. The treatment process was also able to lower arsenic concentrations from approximately 70 ug/L to $<20 \ ug/L$. The mechanism for arsenic removal is likely related to the use of ferric chloride to coagulant biosolids following the FBR and prior to sand filtration. Levels of alpha-, beta-, and delta-BHC in the FBR are reduced from approximately $0.5 \ \mu g/L$ to non-detect ($<0.1 \ ug/L$) levels. Analysis of the biomass indicates that the BHC isomers are likely bioaccumulated by the perchlorate-reducing bacteria rather than reduced.

4.0 STUDY FRAMEWORK

The framework used to develop this technology screening study involved several steps, each of which is described below in sections 4.1 through 4.5.

The first step consisted of focusing the remedial action objectives for impacted vadose-zone soils at the site with respect to the primary chemicals of concern (COCs) and their potential to leach from the vadose zone to the groundwater. The primary representative COCs are considered to be: perchlorate; hexavalent chromium; manganese; and, organochloride pesticides, primarily the alpha-, beta- and gamma-BHCs, with beta-BHC being the most widely distributed. Independent screening evaluations were thus conducted for perchlorate, hexavalent chromium, manganese, and beta-BHC.

The second step consisted of developing a list of candidate General Response Actions that could be implemented to protect groundwater quality. Under each General Response Action, one or more technologies were identified that were potentially applicable to the site and the primary representative COCs.

For the third step, screening criteria were established based in part on typical federal National Contingency Plan (NCP) Feasibility Alternative criteria, and on other factors that are of particular importance at the Site. Each technology was evaluated according to its ability to meet the criteria, and assigned either a (+) for favorable, (0) for uncertain or neutral, and (-) for unfavorable performance.

The fourth step was to identify if the technology should be retained for further feasibility evaluation. Because the Site is large and complex, technologies that potentially could have an overall favorable outcome with respect to protection of groundwater under a variety of specific conditions within the Site were recommended for further evaluation.

The final step of the study was to develop recommendations for follow-on actions that would be necessary to fully evaluate the feasibility, effectiveness, and cost of the retained technologies.

4.1 Potential Remedial Action Objectives

Potential remedial action objectives were identified to provide a basis for comparing the relative performance of each technology. Currently, there are no approved remedial action objectives for vadose-zone soil at the Site that address protection of groundwater. Recently, Northgate prepared a Technical Memorandum regarding the Calculation of Leaching-Based, Site-Specific Levels (LSSLs) for the Soil-to-Groundwater Pathway Using NDEP Guidance (Northgate,

2010c). In that Technical Memorandum, chemicals of potential concern (COPC) were identified as having the potential to leach from unsaturated soil into shallow groundwater at the Site, and LSSLs were calculated for each chemical. For the purposes of this technology screening study, the LSSLs for the inorganic compounds perchlorate and manganese, and the organic pesticide beta-BHC, were identified as the potential remedial action objectives on which to compare the performance of the candidate technologies. For hexavalent chromium, a concentration of 10 mg/kg was used as an indicator that vadose-zone soil has been impacted and therefore potentially a candidate for treatment. As described in Section 3, the Site is particularly challenging from a soil remediation perspective in terms of the soil volumes and areas that potentially require treatment. Though LSSLs were used as a means for comparing relative performance of the technologies and constraints, and that are achievable within the limits of available technologies and resources to remediate such large quantities of contaminants that are widely distributed.

4.2 General Response Actions and Applicable Technologies

For the overall goal of effectively protecting groundwater quality, the General Response Actions were identified as follows:

- No Action;
- Administrative Controls;
- Preventing Surface Water Infiltration;
- In situ Treatment or Removal of Contaminants; and
- Removal, Ex situ Treatment, Replacement and /or Offsite Disposal of Contaminated Soil.

Under each Response Action, other than No Action, one or more candidate technologies were selected for evaluation. Table 5 provides a brief description of each candidate technology. Table 6 provides additional detail for each technology with regard to its development status (e.g., is the technology commonly used, has it been tested at the pilot and field application scales), in general what are its positive and negative attributes, and are there particular site-specific considerations for the potential use of the technology. For four of the technologies that are considered innovative and are not yet commonly used for this type of application, more detailed descriptions of the technology, implementability, potential performance, and cost, have been prepared and are included as Appendices A through D. The four technologies are in situ soil flushing, in situ soil bioflushing, in situ gaseous electron donor injection technology, and ex situ bioremediation.

4.3 Performance Criteria

The performance criteria used for the technology screening are described below. The performance criteria have been tailored to site-specific conditions, and where a particular condition has an impact on evaluating a specific criterion's performance, the criterion has been further subdivided. For example, a particular technology may be effective for destroying perchlorate, but not for destroying co-located organic compounds. Similarly, a technology may be applicable to areas of the Site where soil is accessible, but not to areas where soil is not accessible. Table 7 summarizes the results of the technology screening evaluation, measured against the performance criteria.

4.3.1 Effectiveness – Protection of Groundwater

For the purposes of this study, effectiveness is measured according to the technology's ability to protect groundwater from contaminants leached from vadose-zone soils. Because the Site already operates a groundwater remediation system, the focus of this criterion is to minimize further impacts to groundwater and to reduce reliance on the groundwater remediation system. The technology's performance is measured by its ability to reduce the chemical mass, concentration, or mobility to the degree necessary to minimize leaching of chemicals via infiltrating surface water, or to reduce the amount of surface water infiltration through the vadose zone. Because this criterion can be sensitive to the particular COC, effectiveness has been evaluated separately for perchlorate, metals treated or stabilized through reduction (hexavalent chromium), metals treated or stabilized through oxidation (manganese), and organic pesticides (beta-BHC).

4.3.2 Implementability

This criterion addresses the ability to technically construct the technology and verify its effectiveness. It accounts for site-specific constraints, including treatment of localized volumes that contain high chemical concentrations, versus widespread volumes that contain relatively lower chemical concentrations. Implementability is also judged on the technology's ability to be used in accessible versus inaccessible areas (e.g., under structures, utilities, or remediated areas that have been backfilled).

4.3.3 Permanence

This criterion gives preference to destructive technologies over other technologies that transfer contaminants from one location to another or from one media to another.

4.3.4 Technology Readiness Level

This criterion addresses the maturity of evolving technologies and their suitability for immediate application as a remediation technology. It takes into account whether or not the technology has been shown to be successful in laboratory studies, and whether it has been demonstrated and successful at pilot-scale tests or full-scale applications.

4.3.5 Minimization of Needs for Studies

This criterion addresses the need for additional site investigation, treatability studies, pilot studies, or engineering evaluations prior to final assessment of technology applicability to the site.

4.3.6 Cost Effectiveness

This criterion addresses relative cost effectiveness of implementing and operating/maintaining the technology. Because the COCs are present at the site in both localized, concentrated distributions, as well as widespread but lower concentration distributions, cost-effectiveness was subdivided to reflect cost-sensitivity to remediating the COCs under these two broad conditions.

4.3.7 Addresses Co-Contaminants

This criterion addresses whether the technology can be used to treat all of the potentially leachable contaminants in the vadose zone. It also addresses the potential undesirable mobilization of non-target contaminants. An example of the latter is the use of anaerobic degradation to destroy perchlorate but in the process generates reducing conditions that may mobilize manganese. It is desirable if a technology can successfully treat multiple COCs without causing undesirable consequences.

4.3.8 Impact on Current Groundwater Remediation System

Vadose-zone treatment technologies that rely on the use of water may result in water percolation to the groundwater table that potentially contains untreated COCs and other constituents. Based on capture evaluation studies (Northgate, 2010h), the water will eventually be recovered by the current groundwater extraction and treatment system (GWETS). This criterion is used to assess if the technology could negatively impact the operation of the GWETS in terms of hydraulic capacity, mass loading or treatment effectiveness, or if the GWETS could be a positive asset to the technology's effectiveness and implementability.

4.3.9 Potential for Reuse of GWETS Treated Effluent

This criterion addresses whether the technology could utilize the treated effluent from the GWETS. Reuse of effluent potentially minimizes the use of scarce external resources and could allow the Site to transition to a zero-discharge status with respect to water loads to the Las Vegas Wash.

4.3.10 Sustainability

Sustainable remediation is broadly defined as a remedy or combination of remedies whose net benefit on human health and the environment is maximized through the judicious use of limited resources. To accomplish this, sustainable approaches to remediation provide a net benefit to the environment and to the extent possible: (1) minimize or eliminate energy consumption or the consumption of other natural resources; (2) reduce or eliminate releases to the environment, especially to the air; (3) harness or mimic a natural process; (4) result in the reuse or recycling of land or otherwise undesirable materials; and/or (5) encourage the use of remedial technologies that permanently destroy contaminants.

4.4 Technologies Retained for Further Consideration

Based on the results of the technology screening, technologies were selected for further consideration. A qualitative evaluation of the Site conditions under which the technology could be successful as a function of contaminant concentration and accessibility was completed. Table 8 identifies the technologies recommended for further consideration. The following technologies warrant further consideration based on this screening evaluation.

- **Institutional Controls** Institutional controls consist of enforceable land use restrictions and local ordinances that limit the use and development of a property. Examples include restrictions on future placement of water distribution lines or prevention of irrigation in areas with leachable contaminants. Institutional controls are potentially applicable to all Site conditions.
- **Capping** Capping involves placing a low-permeability surface barrier above source areas to limit infiltration of precipitation and storm water. A combination of capping and moving water distribution lines aboveground is potentially applicable to all Site conditions.
- **Natural Attenuation** Natural attenuation involves reliance on natural processes to biodegrade, disperse, retard, or transform chemical contaminants. Natural attenuation is applicable for soils contaminated by metals stabilized by oxidation (e.g., manganese, arsenic) or to soils impacted with low levels of organic pesticides or perchlorate. Natural attenuation is not applicable to localized areas with higher COC concentrations but may be applicable to these areas following source treatment or removal.



- **In-Situ Chemical Stabilization** This technology could be applied at the Site to treat localized high-concentration hexavalent-chromium contamination in the soil. Application would involve applying a ferrous sulfate solution that would leach through the soil column and react with hexavalent chromium, thereby converting it to immobile and less toxic trivalent chromium. This technology is not applicable to widespread areas with lower COC concentrations and soils contaminated by metals stabilized by oxidation.
- In Situ Soil Flushing and GWETS This technology involves using water to flush leachable contaminants to groundwater followed by extraction and treatment at the existing groundwater treatment facility. In situ soil flushing and GWETS is applicable to soils contaminated with high concentrations of perchlorate or leachable metals (e.g., hexavalent chromium). This technology is not applicable to widespread areas with lower COC concentrations.
- In Situ Enhanced Bioremediation Using Liquid Electron Donor (i.e. Bioflushing) This technology involves injecting or infiltrating water containing liquid electron donor compounds (e.g., glycerin) into contaminated soils to stimulate biodegradation of contaminants. Bioflushing is applicable to most Site conditions with the exception of widespread areas with lower COC concentrations, and soils contaminated by metals stabilized by oxidation.
- In Situ Enhanced Bioremediation using Gaseous Electron Donor This technology involves injecting gaseous electron donor (e.g., hydrogen in a nitrogen carrier gas) into contaminated soils to stimulate biodegradation of contaminants. This technology is applicable to most Site conditions with the exception of widespread areas with lower COC concentrations.
- Ex-Situ Chemical Stabilization This technology involves the excavation of contaminated soils followed by mixing with amendments that chemically stabilize leachable contaminants of concern. This technology could be applied at the Site to treat localized high-concentration hexavalent-chromium contamination in the soil. Application would involve mixing contaminated soils with a ferrous sulfate solution that would react with hexavalent chromium, thereby converting it to immobile and less toxic trivalent chromium. Ex-situ chemical stabilization is applicable only to localized areas with high concentrations of hexavalent chromium.
- **Ex Situ Anaerobic Biotreatment** This technology involves the excavation of contaminated soils followed by the addition of electron donor amendments (e.g., glycerin), water, and nutrients (e.g., diammonium phosphate). Soils are then placed in above-ground enclosures where anaerobic degradation of contaminants occurs. Ex situ anaerobic biotreatment is applicable only to localized areas with higher COC concentrations where soil is accessible, and is not suitable for soils contaminated by metals stabilized by oxidation.

• **Excavation and Off-Site Disposal** – This technology consists of excavating contaminated soils and disposing of them in an appropriate off-Site landfill. This technology is only applicable to localized areas with higher COC concentrations where soil is accessible.

4.5 Recommendations for Further Evaluation

The feasibility of a particular technology to successfully reduce risks to groundwater quality depends on a variety of factors. Firstly, a clear definition of the remedial action objectives that will be necessary to accomplish a desired level of risk reduction is needed. The remedial action objectives will provide the basis upon which technology effectiveness and feasibility can be measured. Secondly, further evaluation of the promising technologies is needed. It is clear that no single technology will serve as a Site-wide solution, and a remedial approach that utilizes several technologies most likely will result in the best overall solution. Our recommendations here focus on the steps necessary to further evaluate the retained technologies from a technical feasibility perspective, and this information will inform the process by which remedial action objectives are developed and compared against.

The retained technologies vary in their requirements for additional study to quantitatively assess their feasibility in terms of effectiveness, implementability, and cost. The retained in situ and ex situ technologies have not been widely used at sites with conditions similar to this Site, therefore site-specific data will be required to fully evaluate their feasibility. Table 8 summarizes the specific next steps that are recommended to further evaluate the feasibility of using a particular technology, including engineering and economic evaluation, selective soil sampling and analysis, analysis of the impact the technology may have on the operation of the GWETS, bench-scale treatability testing, and pilot testing. We recommend these following steps be conducted sequentially:

- Selective sampling and analysis is recommended to support development of Site-specific RAOs and to obtain data necessary for detailed feasibility analysis of specific technologies. For example, leaching analysis using stabilized Lake Mead water to obtain Site-specific soil-water partition coefficients (Kd's) will be important in developing Site-specific RAOs. Site-specific data on subsurface conditions that may impact the effectiveness of natural attenuation and in situ technologies will provide the basis for designing treatability testing, pilot testing, and evaluating potential remediation success.
- Conduct an engineering and economic analysis of retained technologies to assess the viability of full-scale application and ability to meet potential vadose zone soil RAOs. This step will include developing potential remediation scenarios and detailed cost information to compare cost/benefit ratios of each technology in terms of potential mass removal, concentration reduction, and technology implementability and limitations.



- An assessment of the potential impact of selected technologies on the existing GWETS and in particular the functioning of the fluidized bed reactor is recommended. The potential impact, in terms of hydraulic capacity and mass loading, will need to be accounted for in the overall assessment of technology implementability.
- If results of the above-mentioned steps are positive for specific in situ or ex situ technologies, then bench-scale treatability testing for effectiveness under site-specific conditions is recommended to determine the ability of these technologies to meet RAOs. Because there already is site-specific treatability testing data for several of the technologies, including in situ soil flushing and bioflushing, the remaining technologies that potentially would be candidates for treatability testing include in situ enhanced bioremediation with gaseous electron donor and ex situ anaerobic biotreatment methods.
- If the results of treatability testing and other analyses are promising, field-scale pilot testing may be recommended for selected technologies. Potential technologies where pilot-scale testing would be recommended prior to full-scale application are in situ soil flushing, in situ bioflushing, and in situ enhanced bioremediation with gaseous electron donor. Pilot testing of ex situ soil bioremediation is not considered to be necessary for this technology.

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