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TECHNICAL MEMORANDUM

TO: **Texas Rio Grande Legal Aid**
RE: **Potential Ground Water Remedy for the Former ASARCO Smelter Site in El Paso**
DATE: **October 12, 2012**

In 2012, Skeo Solutions received a work request from the U.S. Environmental Protection Agency (EPA) under the Technical Assistance Services for Communities (TASC) contract to address community concerns regarding potential remedies for the ASARCO-El Paso site. The property comprising the former ASARCO smelter is currently in an environmental custodial trust as a result of ASARCO's bankruptcy action filed in August 2005. The trustee, Project Navigator, manages the property as well as the ongoing cleanup with the oversight of both the Texas Commission on Environmental Quality (TCEQ) and EPA. This memorandum provides an independent technical response to community concerns about the proposed ground water cleanup approach being considered for the ASARCO-El Paso site. Its contents do not necessarily reflect the policies, actions or positions of EPA.

This document includes the following sections:

- Brief Overview of Proposed Ground Water Remedial Approach
- Summary of Community Concerns
- Assessment of Ground Water Remedial Approach
- Final Thoughts and Considerations[1]

I. Brief Overview of Proposed Ground Water Remedial Approach

Historical operations at the ASARCO-El Paso site (the site) have contaminated ground water with chemicals that can harm human health and the environment. Contaminated ground water at the site is a concern because it flows to the Rio Grande, which is one of three drinking water sources for the city of El Paso (El Paso Water Utilities 2012, p. 2).[2] Table 1 lists the chemicals that are above the Texas Risk Reduction Program (TRRP) ground water protective concentration levels (PCLs) (Malcolm Pirnie 2012). Arsenic is the primary chemical of concern in ground water (Texas Custodial Trust 2011a, p. 6-1). In addition to the chemicals presented in Table 1,

[1] Acknowledgements: Preparation of this technical memorandum benefited by three TASC conference calls involving representatives from the site's trustee, Project Navigator, the site's remedial contractor, Malcolm Pirnie, Texas Rio Grande Legal Aid and EPA Region 6. These representatives also reviewed a draft version of this document.
[2] Douglas, Lyke-Ho-Gland and Saenz (2008, p. 12) indicate that the Rio Grande is not a drinking water source for Ciudad Juárez, Mexico.

diesel fuel occasionally appears in ground water in the area of the former Zinc Fuming Plant during periods of low ground water levels (Texas Custodial Trust 2011a, p. 6-2). Diesel is currently addressed by recovery with bailers; a diesel recovery system employing ground water skimmers is being evaluated.

Table 1 – Chemicals in Ground Water at the Site that Exceed Regulatory Standards

Metals

- Antimony*
- Arsenic*
- Cadmium
- Chromium
- Cobalt
- Copper
- Lead
- Manganese
- Mercury
- Molybdenum*
- Selenium*
- Thallium*

Water Quality Parameters

- Fluoride*
- Nitrate

*Present in ground water to be treated by the proposed permeable reactive barriers.

The Trust has proposed a ground water cleanup plan for the northern portion of the site in the 2012 Field Demonstration Report (Texas Custodial Trust 2012, Section 1.1). The Trust has not proposed an overall ground water cleanup plan for the whole site at this time. The northern portion of the site was chosen for the initial ground water remedy because the Trust believes that the northern portion of the site is the source for the majority of arsenic discharged from the site to the Rio Grande by ground water (Texas Custodial Trust 2012, p. 1-2). The proposed ground water cleanup is a combined approach comprised of source control coupled with ground water treatment. The source control is focused on keeping rainwater from infiltrating into the contaminated soil and leaching contaminants into ground water. This would be accomplished by excavating the contaminated soil and covering it with protective soil caps. The protective caps are discussed further in *TASC Technical Memorandum: Potential Mono-fill Remedy for the Former ASARCO Smelter Site in El Paso*.

The Trust proposes to install zerovalent iron (ZVI) permeable reactive barriers (PRBs) at the site to prevent the ground water contamination at the northern portion of the site from discharging to the Rio Grande. A ZVI PRB is a mixture of granular pure iron and clean soil that is placed below ground in a trench across the flow path of the contaminated ground water. The ZVI in the PRB removes arsenic dissolved in ground water by the chemical processes of adsorption and coprecipitation. Adsorption is the binding of molecules to a surface (the arsenic molecules dissolved in ground water will bind to the ZVI particles in the PRB). Coprecipitation occurs when ZVI reacts with ground water to form insoluble iron oxides and arsenic dissolved in ground water adsorbs to the insoluble iron oxides as they form.

ZVI PRBs are proposed as a ground water treatment remedy at the northern portion of the site because ZVI PRBs are a proven technology for removing arsenic from ground water and a "flow focusing" feature, Parker Brothers Arroyo, allows relatively small PRBs to treat ground water from a relatively large area (Texas Custodial Trust 2012, p. 1-2). Additionally, PRBs are a passive treatment technology that require little to no maintenance over their lifetime and the total cost of ground water treatment by PRBs is typically around one quarter of the cost of an active ground water treatment technology (e.g., pump and treat) (ITRC 2005).

Currently, work done to address contaminated ground water at the northern portion of the site consists of soil removal and capping (i.e., source control), laboratory testing that demonstrated ZVI can remove arsenic and selenium from ground water obtained at the site, and initial construction of the field demonstration ZVI PRBs. The intent of the ZVI PRB field demonstration is to: 1) confirm that ZVI PRBs can effectively remove arsenic from ground water at the site; 2) demonstrate that ground water will flow through and not bypass the demonstration PRBs; and 3) evaluate the effective lifetime of the PRBs (Texas Custodial Trust 2012, Section 2.2).

II. Summary of Community Concerns

Texas Rio Grande Legal Aid requested assistance to address the following community concerns and questions about the proposed ground water cleanup approach.

- Will the discharge of the treated ground water into the Rio Grande negatively affect use of the Rio Grande as a drinking water source?
- Will the system address all the chemicals at the site?
- Will the system be adequate to prevent the flow of contaminated ground water to the Rio Grande?
- What are examples of other sites where this approach has been used for the same chemicals present at the ASARCO site?
- Have those approaches been successful and protective in dealing with chemicals that are present at the ASARCO site?
- Will the remedy be protective of human health and the environment?

The assessment section below addresses these community concerns.

III. Assessment of Ground Water Remedial Approach

Will the discharge of the treated ground water into the Rio Grande negatively affect use of the Rio Grande as a drinking water source?

Although unlikely, discharging treated ground water has the potential to negatively impact the Rio Grande because the water chemistry of the treated ground water can mobilize metals including arsenic from soil to ground water. The potential negative effect of treated water discharge to the Rio Grande depends on the discharge rate of treated ground water to the Rio Grande, PRB placement, and the capacity of native soils to return ground water discharging from either the field demonstration or full scale ZVI PRBs to pH and oxidation reduction potential (ORP) values approaching naturally occurring levels.

Ground water with high pH (greater than 8.0) and decreased ORP (less than 0 millivolts (mV)) can mobilize arsenic from soil to ground water (ITRC 2005, Section 6.3.2; Vance 1995, Figure 4). In general, decreased ORP accelerates the mobility of metals from soil to ground water (EPA 1992, p. 10). During the bench scale test, the pH of ground water treated by a 15 percent ZVI PRB increased from approximately 7.5 to 8.8 and the ORP decreased from positive 7.5 mV to negative 539 mV (Texas Custodial Trust 2012, Appendix D Tables 5 and 9). The change of pH and ORP indicates treated ground water discharged from the ZVI PRBs can mobilize arsenic from soil. However, when treated ground water contacts soil that is downgradient of the PRB, that soil has the capacity to reduce the pH and increase the ORP of the treated ground water back to naturally occurring levels, albeit a finite but likely more than sufficient capacity. The return of pH and ORP values to naturally occurring levels should cause any arsenic mobilized to treated ground water to convert to an insoluble form that will be captured in the soil matrix prior to discharge to the Rio Grande. At this time, the Trust expects but does not know whether the soil between the PRB and the Rio Grande can return the pH and ORP of treated ground water to naturally occurring levels. The planned field demonstration monitoring program (Texas Custodial Trust 2012, p. 5-3) should determine the capacity of the soil between the PRB and Rio Grande to return ground water pH and ORP to naturally occurring levels.

Will the system address all the chemicals at the site?

TASC expects that the proposed combination of source control (i.e., soil removal and capping) and ground water treatment with ZVI will address all the chemicals that are in ground water above TRRP ground water PCLs in the northern portion of the site (Table 1). Source control should greatly reduce the mass of chemicals from the northern portion of the site transported by ground water to the Rio Grande by preventing infiltration of rainwater and ponded surface water through contaminated soil. Based on the laboratory ZVI test and the performance of ZVI PRBs at similar sites, the ZVI PRBs should remove arsenic and potentially other metals from ground water. Treating arsenic in ground water is a specific concern because arsenic has been present in the Rio Grande immediately downstream of the site above EPA's maximum concentration level (MCL) for drinking water (Texas Custodial Trust 2012, p. 1-2).

In addition to the chemicals in Table 1, several organic chemicals including solvents, pesticides and PCBs were described as "analytes of interest" for soil in the Trust's 2011 Remedial Action Work Plan (Texas Custodial Trust 2011a, p. 6-2). If these "analytes of interest" are present in soil in the northern portion of the site, they are potentially present in ground water. If present, source control should prevent further contamination of ground water by the "analytes of interest" and will greatly reduce the mass of the "analytes of interest" transported to the Rio Grande by ground water. Additionally, several of the "analytes of interest", specifically the chlorinated organic solvents, can be removed from ground water by ZVI PRBs (EPA 1998, pp. 8, 9; ITRC 2005, p. 15; ITRC 2011, p. 22).

Will the system be adequate to prevent the flow of contaminated ground water to the Rio Grande?

TASC expects that source control by capping contaminated soil in the northern portion of the site will prevent further ground water contamination by preventing rainwater from infiltrating into contaminated soil and leaching contaminants into ground water. Additionally, preventing infiltration also reduces the volume of ground water at the site capable of transporting residual contamination from soil to the Rio Grande. In other words, surface capping alone should greatly reduce the flow of contaminated ground water from the northern portion of the site to the Rio Grande.

In order to prevent contaminated ground water from reaching the Rio Grande, the following conditions must be met:

- The PRBs must be placed across the contaminated ground water flowpath.
- The ground water must not be able to flow around or otherwise bypass the PRBs.
- The PRBs must be able to reduce contaminant levels below the applicable regulatory limits (i.e., EPA MCLs and TRRP ground water PCLs).

It is a concern that PRBs cannot address contaminated ground water from the area between the PRBs and Rio Grande. However, the Trust stated that it would not be feasible to install a PRB next to the Rio Grande because of the increased depth of the alluvium (greater than 70 feet). The Trust also stated, however, that they would address contaminated ground water in this area if ground water sampling during the PRB field demonstration indicates a ground water remedy is warranted. One option if needed, according to the Trust, could include the installation of a third PRB.

To evaluate the potential effectiveness of the proposed PRBs, TASC reviewed the Field Demonstration Report, the October 1998 Remedial Investigation Report prepared by Hydrometrics, and other information made available by EPA, TCEQ and the Texas Water Development Board. Findings are discussed below.

<u>Hydraulic Capture of Contaminated Ground Water</u>

TASC expects that the design of the PRBs as presented in the Field Demonstration Report will be able to hydraulically capture contaminated ground water in Parker Brothers Arroyo. However, the data presented in the Field Demonstration Report does not adequately demonstrate that a portion of the contaminated ground water cannot bypass the PRBs through the underlying sandstone. According to the Field Demonstration Report, the geology of the Parker Brothers Arroyo consists of about 5 to 25 feet of alluvial sediments, which are above a sandstone unit (described as the Upper Mojado Formation) estimated to be 5 to 30 feet in thickness, which is above a shale unit (described as the Lower Mojado Formation) (Texas Custodial Trust 2012, Figure 6 and Figure 7).

The sandstone layer is immediately under the alluvial deposits. The Field Demonstration Report does not state what the hydraulic conductivity of the sandstone layer is and sandstones are typically relatively permeable, with hydraulic conductivity ranging from 8.5×10^{-5} to 1.68 feet/day (Domenico and Schwartz 1998). These values of hydraulic conductivity are less than the estimated values for the alluvium (less than 1 to 116 feet/day) and boring logs for borings advanced in the area of the proposed PRB indicate the sandstone layer is dry (Texas Custodial Trust 2011b). Therefore, there is evidence ground water only flows through the alluvium, but the properties of sandstone indicate a portion of the ground water could bypass the PRB.

If ground water flow is confined to the alluvial sediments of the erosional channel as presented, then it is likely that contaminated ground water upgradient of the proposed PRBs will pass through the PRBs. However, the potential may exist for contaminated ground water to bypass the PRBs and reach the Rio Grande without treatment. The Field Demonstration Report states that one of the primary objectives of the field demonstration will be to confirm the hydraulic performance of the PRBs, which includes determining whether ground water bypasses the PRBs (Texas Custodial Trust 2012, p. 2-2).

PRB Effectiveness

To prevent contaminated ground water from reaching the Rio Grande, the proposed PRBs must first hydraulically intercept contaminated ground water, and then effectively reduce the concentrations of contaminants in ground water below the applicable regulatory limits (i.e., TRRP ground water PCLs and EPA drinking water MCLs). Arsenic is the ground water contaminant of greatest concern, because the Rio Grande's arsenic level is above EPA's MCL immediately downstream of the site (Texas Custodial Trust 2012, p. 1-2). The following ground water contaminants are above TRRP PCLs near the area where ground water from the northern portion of the site discharges to the Rio Grande: antimony, arsenic, molybdenum, selenium, thallium and fluoride (Malcolm Pirnie 2012, Table 1; Texas Custodial Trust 2012, Figure 2).

The Trust conducted a laboratory ZVI treatability test using ground water from the site (Texas Custodial Trust 2012, p. 3-2). The test demonstrates that a properly designed and installed ZVI PRB should remove arsenic and selenium from ground water at the site. However, the test also indicates that fluoride will not be removed from ground water (Texas Custodial Trust 2012, Appendix D Tables 5 and 9). Other research shows that bench-scale ZVI PRBs can remove cationic metals from ground water (ITRC 2011, p. 22). Molybdenum and thallium can be considered "cationic metals" so they should be removed from ground water by a ZVI PRB. The treatability of antimony by a ZVI PRB is unknown; however, analytical data for water samples collected from the Rio Grande at the site demonstrates antimony and fluoride concentrations in the Rio Grande are usually less than EPA drinking water MCLs.

What are examples of other sites where this approach has been used for the same chemicals present at the ASARCO site?

As described previously, the proposed ground water remedy at the site includes controlling the sources of ground water contamination by surface capping and treating ground water with ZVI PRBs. Source control is a common method for addressing ongoing ground water contamination;

therefore, specific examples of other sites with source control are not included. Examples of sites with ZVI PRBs that remove arsenic from ground water are presented below.

ASARCO East Helena Smelter

EPA installed a field demonstration ZVI PRB at the former ASARCO East Helena Smelter in East Helena, Montana, in 2005. The ASARCO East Helena Smelter site is similar to the ASARCO-El Paso site in the following ways: 1) arsenic impacts to ground water were caused by metal smelting; 2) ground water below both sites is contaminated with similar chemicals; 3) source control measures were employed at the ASARCO East Helena Site; and 4) the water chemistry of the two sites is similar. Differences at the sites include: 1) a single PRB was used at ASARCO East Helena site versus the proposed two PRBs for the northern portion of the ASARCO-El Paso site; 2) the influent concentration of arsenic entering the PRB at ASARCO East Helena is approximately 25 milligrams per liter (mg/L) versus approximately 2 mg/L at ASARCO-El Paso; 3) the ASARCO East Helena PRB was constructed entirely from ZVI while the proposed PRBs at ASARCO El-Paso will be constructed from a mixture of ZVI and clean soil;[3] and 4) the PRB at ASARCO East Helena is not installed across a ground water flow channel.

Ground water monitoring data at the ASARCO East Helena site indicates that the ZVI PRB is capable of removing 25 mg/L of arsenic from ground water after three years of operation (EPA 2008). However, the ZVI PRB was not installed as deeply as planned causing the base of the PRB to be approximately three feet above the confining layer. This construction error allows contaminated ground water to pass below the ASARCO East Helena ZVI PRB.

Bodo Canyon Site

Pilot scale PRBs were installed in tanks at the Bodo Canyon Site in Durango, Colorado, to demonstrative the ability of ZVI and other materials to remove arsenic, molybdenum, selenium, uranium, vanadium and zinc from ground water contaminated by mine tailings. The results of the pilot testing demonstrated 99 percent removal of arsenic, molybdenum and selenium after three years of operation (EPA 2002).

Former Mill Site Monticello, Utah

The United States Department of Energy installed a ZVI PRB in 1999 at a former uranium and vanadium ore processing mill to treat ground water contaminated with arsenic, molybdenum, nitrate, selenium and vanadium. The PRB is a “funnel and gate” PRB which uses two underground walls (the funnel) to force ground water to flow through the ZVI PRB (the gate). The PRB reduced arsenic, selenium and vanadium to nondetectable levels downgradient of the PRB (DOE 2005). Molybdenum levels were also reduced by the PRB, but the extent of molybdenum treatment was not reported. However, this PRB has had problems with ground water bypassing one of the walls due to ground water mounding at the PRB. The most likely

[3] According to the Trust, the backfill mix design includes sand/gravel and ZVI to assure flow-through and prevent clogging while assuring treatment of contaminants of concern.

cause of the ground water mounding at the PRB is the loss of permeability caused by precipitation of carbonates within the PRB (DOE 2005).

Have those approaches been successful and protective in dealing with chemicals that are present at the ASARCO site?

Source control is a common means of preventing ground water contamination that has been successful at many sites. The example sites presented above demonstrate that a ZVI PRB can successfully remove arsenic and selenium from ground water. However, contaminated ground water was able to bypass the ZVI PRBs at the ASARCO East Helena site and the Former Mill Site. The causes for the partial failures of those ZVI PRBs are a construction error (ASARCO East Helena) and clogging of the PRB by carbonate precipitation (Former Mill Site).

The Field Demonstration Report states that "excavation will proceed in each cell to approximately two feet below first encountering bedrock, as determined by the field geologist" (Texas Custodial Trust 2012, Appendix H). Following this procedure should prevent the ground water bypass issue experienced at the ASARCO East Helena Site. Ground water bypass caused by carbonate precipitation in the PRBs should also not be a problem at the site, based on the design porosity of the proposed PRBs and the porosity reduction estimates in the Field Demonstration report (Texas Custodial Trust 2012, Appendix B). The design porosity and the porosity reduction estimates indicate that the hydraulic conductivities of the proposed PRBs will be greater than the hydraulic conductivity of the upgradient aquifer over the anticipated lifetimes of the PRBs (20 years). Therefore, ground water should not bypass the proposed PRBs at the site due to carbonate precipitation within the PRB.

Will the remedy be protective of human health and the environment?

The ground water remedy consisting of source control and treatment with ZVI PRBs will probably be protective of human health and the environment eventually but not immediately because:

1. Capping the contaminated soil will prevent ongoing contamination. Clean ground water from upgradient of the site will eventually flush out any residual contamination.
2. The proposed location of the PRBs is such that ground water between the Rio Grande will not be treated by the PRBs and the untreated ground water will continue to discharge to the Rio Grande until displaced by treated ground water. Currently, the time required for treated ground water to displace the untreated ground water is unknown. However, the time required for untreated ground water to discharge to the Rio Grande and the need for treatment of this ground water should be determined during the PRB field demonstration monitoring.
3. No one is exposed to the site's ground water until it enters the Rio Grande. The Rio Grande dilutes the contamination to levels protective of human health during most of the year.
4. ZVI PRBs can successfully remove arsenic from ground water. Arsenic is the only site contaminant that poses a risk to human health and the environment in the Rio Grande.

IV. Final Thoughts and Considerations

The Rio Grande is one of three sources of drinking water for the city of El Paso. Ground water with antimony, arsenic, molybdenum, selenium, thallium and fluoride at levels above TRRP ground water PCLs may be entering the Rio Grande from the northern portion of the site. However, only arsenic is above its EPA drinking water MCL in the Rio Grande.

The proposed ground water remedy for the northern portion of the site consists of source control by capping contaminated soil and treating contaminated ground water with ZVI PRBs. Source control should prevent rainwater from infiltrating through the contaminated soil into ground water. Preventing infiltration should prevent further contamination of ground water by the capped contaminated soil and reduce the volume of ground water that flows through the site, which will reduce the contamination discharged to the Rio Grande. Properly installed ZVI PRBs should remove arsenic, molybdenum, selenium and thallium from ground water based on the Trust's laboratory tests and the performance of ZVI PRBs installed at similar sites. However, the Trust's laboratory tests conducted using ground water from the site demonstrate that ZVI cannot remove fluoride from ground water. It is not known whether ZVI PRBs can remove antimony from ground water. However, fluoride and antimony were not above their drinking water MCLs in the Rio Grande, based on samples collected adjacent to the site in 2011.

Additional concerns related to PRBs as a ground water treatment technology include:

- PRBs cannot treat contaminated ground water that is downgradient of the PRB. Any contamination downgradient of the PRB will be flushed away over time by clean ground water. It is not known how many years it will take until uncontaminated ground water will discharge to the Rio Grande.
- Ground water might bypass the PRB if the site's hydrogeology is not fully understood.
- If the PRBs are not constructed properly, they could develop pathways that allow contaminated ground water to pass through without being fully treated.[4]

The Trust is currently installing two field demonstration ZVI PRBs in Parker Brothers Arroyo at the site. The field demonstration program should provide the Trust with adequate data to demonstrate whether ZVI PRBs can adequately treat contaminated ground water at the site, to demonstrate that the current hydrogeologic characterization of the site is adequate to select PRB locations that prevent ground water bypass, and to demonstrate that the PRB construction techniques will not cause PRB failure.[5]

[4] According to the Trust, a quality assurance/quality control plan is in place and being implemented to document PRB construction and demonstrate that project specifications are being met.
[5] Performance monitoring and evaluation are discussed in the Field Demonstration Report.

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