Title: Using Green Remediation Technology to Remediate Impacted Soil and Groundwater

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Abstract: Traditional remediation technologies such as air sparging with or without vacuum or dual phase extraction or pump and treat require electricity or fossil fuel to power the equipment used to remove the contamination in the soil and groundwater. Once the contaminants are extracted from impacted soil or groundwater, the extracted fluids are sent to a wastewater treatment system for additional treatment, to the atmosphere when contaminants are below specific concentrations or landfills when filters are used. Green remediation technologies such as chemical oxidation or bioaugmentation do not require a continued supply of electrical power or transfer the contamination from underground to the atmosphere, water ways, or lands. Both remediation techniques create in-situ reactions that destroy organic contaminants in place, often in less time than the traditional technologies. Recent chemical oxidation pilot tests in Florida have achieved reduction in contaminate concentrations in a fraction of the time that it normally takes traditional electric-powered technologies 1 to 2 years to reach resulting in reduced energy costs to remediate organic contamination in the groundwater. This article will discuss the results of three pilot tests conducted in Florida at sites with hydrocarbon contamination and how using chemical oxidation can reduce energy costs and solid waste.

Keywords: Remediation, Chemical Oxidation, Petroleum, Badger Injection Systems, Green Technology

[1]. Florida Department of Environmental Protection, Oculus Public Database File for FACID# 60/8521917, Utility Related (2006)

Introduction

Traditional remediation technologies such as air sparging with or without vacuum extraction (AS/SVE) or pump and treat require electricity or fossil fuel to power the equipment used to remove the contamination in the soil and groundwater at a 2006 cost of $9/nameplate horsepower[1]. Once the contaminants are extracted from impacted soil or groundwater, the liquid stream is sent to a carbon filter prior to discharge into for additional treatment and the extracted vapors are sent to an air stripper/carbon filter train until the petroleum compounds are below a specific concentration before being discharged to the environment. Used carbon beds are either recycled or disposed of at an approved landfill.

Green remediation technologies such as chemical oxidation or bioaugmentation do not require a continued supply of electrical power or transfer the contamination from subsurfaces to the atmosphere, water ways, or lands. Both remediation techniques create in-situ reactions that destroy organic contaminants in place, often in less time than the traditional technologies. Recent chemical oxidation pilot tests in Florida have achieved a reduction in contaminate concentrations in a fraction of the time that it normally takes traditional electric-powered technologies 1 to 2 years to reach resulting in reduced energy costs to remediate organic contamination in the groundwater. This article will discuss the results of three pilot tests conducted in Florida at sites with hydrocarbon contamination and how using chemical oxidation can reduce energy costs and solid waste.

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Current Treatment Protocols in Florida

In Florida, remediation of most petroleum contaminated sites is funded and managed by the Florida Department of Environmental Protection (FDEP) or selected county environmental protection departments (EPD). The FDEP/EPD program requires responsible parties or their designated contractor to submit a proposal and cost estimate on templates to the FDEP or EPD for approval before work can begin. The templates define the activities and associated costs that will be reimbursed from the various trust funds established to pay for the cleanup. Under this program, determining the horizontal and vertical extent of the soil and groundwater plumes should take 3 to 4 years and remediation plan preparation and installation of a remediation system using AS/SVE based technology should take 1 year. Remediation is expected to take 3 to 5 years to reach the appropriate cleanup target levels (CTLs) followed by one to two years of post remediation monitoring to verify the site can maintain the CTLs. The remediation program has been in operation for about 14 years and is not working as envisioned when first implemented in the mid 1990’s.

Remediation Issues to Address

In 2004, the FDEP issued new remediation guidelines (RAI) to reduce the time spent reaching and maintaining the CTLs using AS/SVE or other mass transfer systems and thereby reducing the operating cost to remediate a site. New design and maintenance criteria for operating the treatment systems were issued and reimbursement of expenses would be based on systems operating rates, reaching intermediate CTLs and following preventative maintenance schedules. Even with these changes, many sites that have had active remediation systems operating for more than 10 years could not reach or maintain monitoring points at or below the CTLs increasing the cost to remediate a site and reducing the amount of money that could be spent on new sites.

Detailed evaluation of the operating, maintenance, utility and monitoring data detected several problems inherent to using mass transfer to meet CTLs. Many contractors did not conduct a pilot test of the planned AS/SVE configuration at the site in question but used the design from similar systems installed at other sites with some customization for site specific chemicals of concern (COC) and plume size. Any differences in site lithology or groundwater quality parameters were not considered. This lack of site specific operating data collected during a pilot test created a treatment system that could not reached the CTLs within the set timeframe or was not appropriate for the site or were so inefficient that the systems would take up to 47 years to remediate the site[2]. The lack of water quality data did not allow the contractor to plan for excess solids buildup in the groundwater extraction and treatment trains nor for the impact anaerobic bacteria has on filters and carbon steel fittings. These issues caused the treatment systems at the third site covered in this paper to run only 35% of the time and generated a monthly utility bill of about $1,000 [1] for electric power until the systems was shut down in 2007 for failure to reach milestones.

Test Sites for Chemical Oxidation

Even with the RAI requirement to conduct a pilot test to obtain site specific operating data, many petroleum impact sites are not candidates for the AS/SVE technology. Site with heterogeneous lithology such at the three sites discussed in this

[4]. Gimpelson, L.: O&M Annual Report, Year 3, CSXT Wildwood, Area C, Clermont, Florida (2007)

paper were not good candidates due to difficulty in installing monitoring wells to complete the site assessment. The subsurface (Figure 1) is composed of various thickness of sands (yellow) clayey sands (orange and brown), sandy clays (reds), clays mixed with sandy clay (grape) and silty clays (brick red). Standard drilling equipment such as direct push or hollow stem augers were damaged when used to install shallow (15 to 20 feet depth) monitoring wells. Only the sonic drilling rigs could install monitoring wells on-site without being damaged. Since AS/SVE would require the installation of multiple sparge and vacuum extraction wells, the FDEP/EPD were not inclined to approve the cost to install these wells unless AS/SVE was the only treatment option.

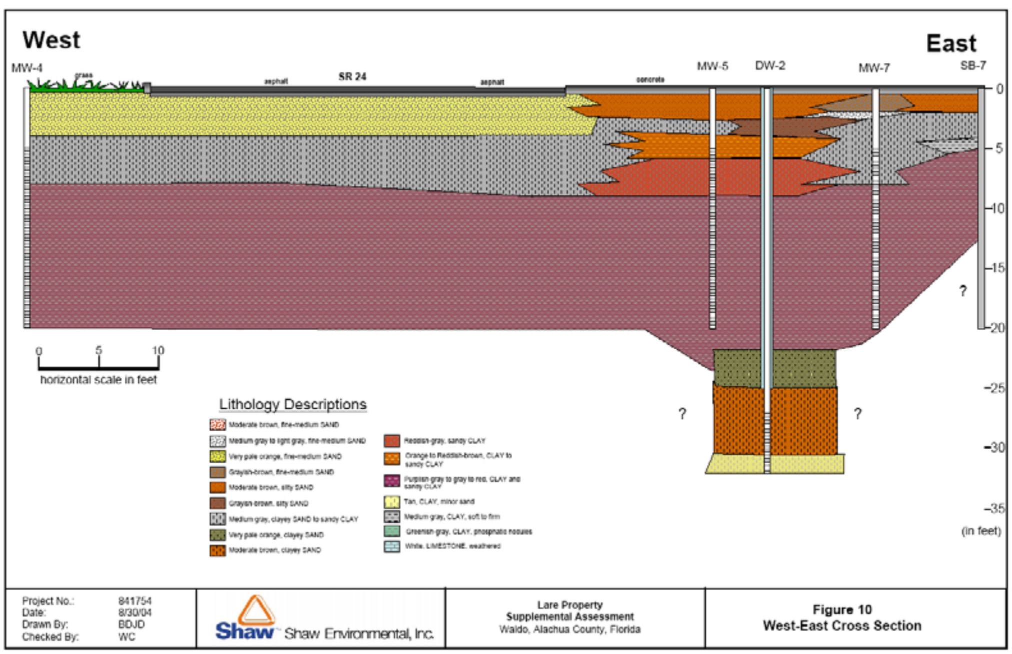

Figure 1: Typical Lithology at Pilot Test Sites in Florida[3]

Beside the difficulty in installing the air distribution and extraction wells and piping trenches, an AS/SVE system needs a 15 foot by 20 foot area to locate the extracted air

[4]. Howard, K.: Template site Assessment Report – Lare Property – Waldo Market (2006)

and water treatment trains, the blowers to generate the vacuum and air supply, control systems, air coolers and storage area for spare parts, manuals and sampling equipment. It helps if the power and water supply and sewer lines are located along one side of the site to reduce connectivity costs. On two sites, the space to install the treatment equipment was limited as shown in Figure 2.

Figure 2: Typical site with utilities - Waldo, Florida.[5]

On the third site (Figure 3), that had its three AS/SVE systems shut down due to operating problems, finding an open space not covered by native plants near the utility distribution lines was a problem. Alternative power supplies were not an option due to the need to generate and maintain a continuous power supply to meet a daily power demand of 624 kilowatt-hours.

[5.] Photographer: K. Howard, Shaw environmental and Infrastructure, Inc., (2005)

Figure 3: Third Site without utilities or open space – Wildwood, Florida. [5]

The third criteria that encouraged the FDEP and EPD to consider chemical oxidation were the variation in groundwater elevations that occurs in the course of one year. In Florida, groundwater elevation can fluctuate up to 6 ft after a hurricane or tropical storm passes through the area. After the 2004 and 2008 Hurricane Seasons, depth to water at the monitoring wells located on these three sites averaged 3 ft higher than before the hurricane season. This large a variation in groundwater can cause the SVE system to extract more groundwater than the water treatment train can process and cause the treatment system to shut down until groundwater elevations return to normal limiting the operations of the system to less than 80% run time. Several AS/SVE systems I have worked on had floats installed that shut down an extraction well or trench when groundwater elevation reaches a pre-set level. While the use of the floats minimized damage to the extraction compressor and associate motor, run time averaged less than 50% well below the FDEP design standards of 80%.

[5.] Photographer: K. Howard, Shaw environmental and Infrastructure, Inc., (2005) The final criteria that has the FDEP and EPD considering chemical oxidation is Governor Crist's executive orders instructing state agency to reduce energy use by using renewable energy sources, conserving energy and implementing green technologies and procedures when ever possible. Chemical oxidation does not require a reliable power supply 24/7 nor does it transfer greenhouse organics from the subsurface to the environment.

Pilot Test Plans for Chemical Oxidation

The first site to receive approval to conduct a chemical oxidation pilot test[6] using both the injection well and powered injection points system was the site in Waldo, Florida and shown in Figure 2. The site is small and the mural on the right needed to remain visible at all times. Also a residential neighborhood is located across the street to the left so noise control would be an issue when operating a treatment system at night and on weekends.

The former gas station has its underground storage tanks (USTs) removed in 1997. Site assessment activities detected levels of benzene, toluene, ethylbenzene, and xylenes (collectively known as BTEX) and methyl tert-butyl ether (MTBE), polynuclear aromatic hydrocarbons (PAHs) and total recoverable petroleum hydrocarbons (TRPH) above the respective CTLs in nine of the 26 monitoring wells associated with the site prior to the start of the pilot test. Concentrations of benzene and naphthalene were detected above the active remediation levels (NADC) in three wells prior to the start of the pilot test.

The approved pilot test plan established the test parameters used in this pilot test and the pilot test conducted at two other sites. Two two-day injection events would

[6.] Gimpelson, L.: Pilot Test Plan, Lare Properties (2007) occur 60 days apart. The oxidizing chemical selected for the pilot test was a weak hydrogen peroxide solution with ferric sulfate solution as the catalyst to minimize reactions with nearby underground utility line and subsurface clays and limestone.

One injection well was installed upgradient of the plume to a depth of 25 ft to obtain operating parameters for use in developing the remediation action plan (RAP). Six injection points would be installed during each injection event using the patented Badger powered injection system (Badger) developed by Renegade Environmental Services (Renegade). The Badger system allows the site supervisor to inject the chemical oxidation liquids anywhere on-site, adjust injection point locations in response to real time events and inject more material into the aquifer during each injection event that using injections wells and gravity feeders.

Groundwater samples from key and parameter wells were collected and analyzed before and after the injection events for BTEX, MTBE, PAHs, TRPH, total iron, total sulfates, bacterial plate count and other water quality compounds.

The pilot test plan[7] for a site in Ocala, Florida followed the same basic procedures as noted in the Waldo pilot test plan with a few modifications. The level of petroleum impact at this site was similar to the level of impacted noted at the Waldo site but the tank had been removed in 1992. The levels of BEX, TRPH and PAHs were above the CTLs in 13 out of the 32 monitoring wells associated with the site. Concentrations of two compounds were above the NADCs in nine monitoring wells.

Due to financial constraints, the injection well was not installed. To compensate for not installing the injection well, four additional injection points using the Badger system were installed. Depths of each injection point were determined by how deep the

[7] Gimpelson, L.: Pilot Test Plan, TriCity Aluminum (2007)
[8.] Gimpelson, L.: Pilot Test Plan, CSXT Wildwood Area C (2008)

Renegade DPT rigs could install the specialized, retractable Badger "VVDN" injection nozzles before hitting refusal and installed depths ranged from 17 to 32 feet below land surface (bls). Also a secondary goal for the pilot test was to establish a barrier to minimize plume movement under US 301.

The third site selected is located in Wildwood, Florida in a remote section of an active rail yard as shown in Figure 3. This site had been using three AS/SVE systems that were designed to extract petroleum laded groundwater as well as air to reduce the groundwater plume to below the CTLs. In November 2006, the FDEP ordered the three treatment systems turned off due to the inability of the systems to cleanup the impacts within 5 years. Also the operating systems were using 7,1000 kilowatts of power per month at the site wide 45% run time without reducing the measured TRPH concentrations.

The third pilot test plan[8] was modified due to financial constraints imposed by the FDEP. An injection well was not installed at site and only one injection event could be conducted. Since the site is located in heavy brush and off the utility grid, portable power and water supplies had to be brought to the site. Further complicating the pilot test was the presence of free product in one monitoring well located in the southeast section of the test area. Injection points and fluid concentrations had to be closely monitored to prevent excessive off gases bleeding out the area monitoring wells and injection points and to prevent a run away reaction with the free product. The FDEP approved a single three-day injection event around two monitoring wells to determine if chemical oxidation could remediate the site faster than the three AS/SVE systems had over the last ten years.

[7] Gimpelson, L.: Pilot Test Plan, TriCity Aluminum (2007)
[8.] Gimpelson, L.: Pilot Test Plan, CSXT Wildwood Area C (2008)

RESULTS

The chemical oxidation pilot test conducted at the Waldo Site using the Badger system in the shallow aquifer and gravity feed system in the deep aquifer, reduced the organic concentrations to below the GCTLs (groundwater cleanup target levels) at DW-2, MW-1, MW-5, MW-6, and MW-20. Concentrations were reduced to below the GCTLs at MW-3 (ethylbenzene, 1-methylnaphthalene, and 2-methylnaphthalene), MW-8 (TRPH and 2-methylnaphthalene), and DW-1 (toluene). Reductions of at least 50% in the chemical concentrations that remained above the GCTLs were noted in MW-3 (benzene and naphthalene), MW-8 (benzene) and DW-1 (benzene and naphthalene). No petroleum concentration increased in MW-3 or DW-5. Overall the two chemical injection events reduced the size of the plume by 50% and the average concentrations by 45%. Each monitoring well that showed a reduction in organic concentrations was located within 15 ft of one or more injection points. When compared to the baseline data collected in August 2007, the organic plate count has increased up to 400% indicating an increase in biological activity, especially in the monitoring wells that experienced the greatest reduction in petroleum concentrations. The only power consumed during the pilot test was about 400 gallons of diesel to power the Badger system and gravity feed injection system. Table 1 presents some of the results from the pilot test sampling events[9.] Figure 4 depicts the change in benzene plume horizontal dimensions.

[7.] Gimpelson, L.: Pilot Test Report, Lare Property (2007)

Table 1- Summary of analytical results – Waldo, Florida

Key Wells	Date	Benzene ug/l	Naphthalene ug/l	Dissolved Oxygen mg/l	Plate count CFU/ml
DMW-1	Baseline	120	62.4	00.06	180
	Post Injection	36.1	17.4	18.66	330
MW-3	Baseline	82.4	294	00.01	NA
	Post Injection	45.6	170	1.46	710
MW-5	Baseline	230	16.6	1.01	240
	Post Injection	1.00 U	1.00 U	19.19	235

µg/L = micrograms per liter
mg/L = milligrams per liter
NA = Not Analyzed
U = Below Detection limits
CFU/ml = colony frequency units per milliliter

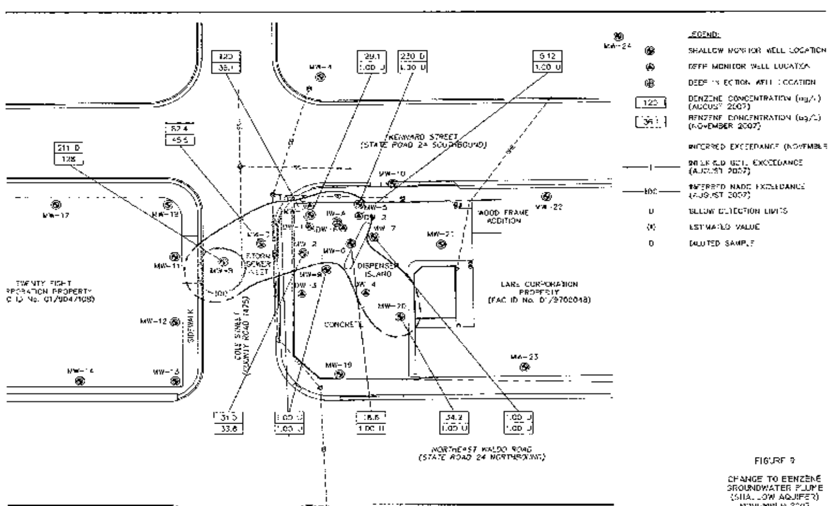

Figure 4: Change in benzene plume, Waldo Florida

The chemical oxidation pilot test conducted at the Ocala Site[10] using the Badger system reduced the organic concentrations by up to 90% in the shallow monitoring wells except for a sight increase in PAHs at DW-1, MW-22, and MW-27 and ethylbenzene at MW-7 and MW-9. The greatest reduction in concentrations occurred at DW-1, MW-11, and MW-13 where ethylbenzene dropped from above the NADC to below the GCTL and

[10.] Gimpelson, L.: Pilot Test Report, Tri-city Aluminum (2008)
[11] Gimpelson, L.: Pilot Test Report, CSXT Wildwood Area C (2008)

total xylenes dropped from above the NADC to below the GCTL at DW-1 and MW-11. Other monitoring wells that experienced a decrease of at least 70% include ethylbenzene and total xylenes at MW-4 and DW-1, ethylbenzene at MW-10, and total xylenes and 2-methylnaphthalene at MW-13. The remaining wells experienced a reduction of 10% to 50% in the analyzed components. The greatest decrease was experienced in the monitoring wells that were within 15 ft of one or more injection points. Although DW-1 and MW-27 were not within 15 ft of an injection point, concentrations of one or more components were decreased to below the GCTL especially at DW-1. Reductions at DW-1 occurred even though the screen interval for DW-1 (45 to 50 ft bls) was about 15 to 20 ft below the depth of the closest injection point. The only power consumed during the pilot test was about 200 gallons of diesel to power the Badger system. Table 2 presents some of the results from the pilot test sampling events.[7] Figure 5 depicts the change in 1-methyl naphthalene concentrations.

[10.] Gimpelson, L.: Pilot Test Report, Tri-city Aluminum (2008)
[11] Gimpelson, L.: Pilot Test Report, CSXT Wildwood Area C (2008)

Table 2- Summary of analytical results – Ocala, Florida

Key Wells	Date	Ethyl Benzene ug/l	1-methyl Naphthalene ug/l	Dissolved Oxygen mg/l	Plate count CFU/ml
DMW-1	Baseline	399	51.4	0.07	12
	Post Injection	12.8	31.9	0.71	192
MW-10	Baseline	62.4	69.9	0.01	NA
	Post Injection	50.6	33.2	5.31	NA
MW-11	Baseline	250	56.3	0.09	29
	Post Injection	1.00 U	23.7	1.11	9,360

µg/L = micrograms per liter
mg/L = milligrams per liter
NA = Not Analyzed
U = Below Detection limits
CFU/ml = colony frequency units per milliliter

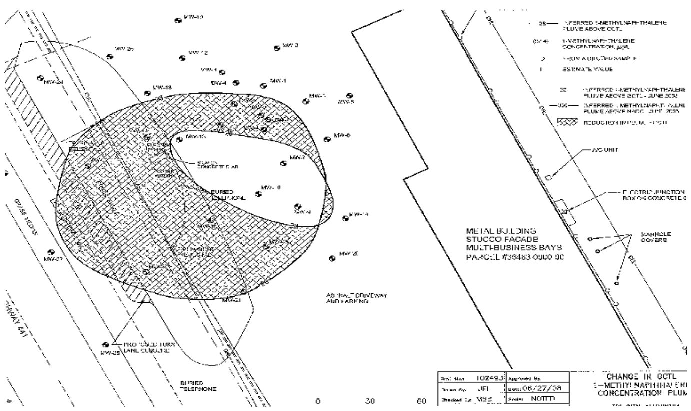

Figure 5: Change in 1-methyl naphthalene concentrations – Ocala, Florida

The chemical oxidation pilot test conducted at the Wildwood Site[11] using the Badger system reduced the organic concentrations by approximately 27% in the deep aquifer and 22% in the shallow aquifer. While a slight increase in TRPH concentrations were detected in two monitoring wells, the pilot test area experienced an overall decease in TRPH concentrations of 20%. The dissolved oxygen (DO) content was detected above the maximum instrument reading when measured during the pilot test and was still above the maximum instrument reading 45 days later when measured during the groundwater sampling event, except at DMW-37 which was 900% higher than before the pilot test. The aquifer parameters were at concentrations expected when conducting a groundwater sampling event 4 to 6 weeks after a chemical injection pilot test. High DO and a drop in TOC concentrations indicated that aerobic bacteria were present and active in destroying the dissolved petroleum plume. The only power consumed during the pilot test was about 200 gallons of diesel to power the Badger system and water supply truck. Table 3 presents some of the results from the pilot test sampling events.

Table 3- Summary of analytical results – Wildwood, Florida

Key Wells	Date	TRPH ug/l	Dissolved Oxygen mg/l
DMW-34	Baseline	32,200	0. 74
	Post Injection	24,200	Exceed Meter Scale
SMW-6	Baseline	43,100	0.45
	Post Injection	6,710	Exceed Meter Scale
SMW-30	Baseline	15,700	0.09
	Post Injection	3,110	Exceed Meter Scale

µg/L = micrograms per liter
mg/L = milligrams per liter

CONCLUSION

Chemical oxidation remediation technologies were tested at three petroleum impacted sites in Central Florida with one or more petroleum compounds above the NADCs in several monitoring wells. Also the Wildwood pilot test was conducted to compare results with the historical operating data and costs using AS/SVE treatment systems. Each pilot test injected varying amounts of retail strength hydrogen peroxide and ferric sulfate solutions into the impacted aquifer using the Badger system. One site also used gravity feed through one injection well to insert the oxidizing solutions into the aquifer when the Badger system was not operating.

Each system achieved a reduction in measured concentrations equal to one to two years of operating an AS/SVE system without the monthly electric, telephone and sewer bills while only using 200 to 400 gallons of diesel fuel to provide temporary power needed during the injection event or about 36 kilowatt-hours per injection event. For the Wildwood site, the 20% reduction in detected concentrations equaled the amount the three AS/SVE systems had removed during their six years of actual operating time without the need for 624 kilowatt-hours each day the systems were running.

Beside the reduction in the amount of fossil fuels consumed to destroy the contamination, chemical oxidation reduces the amount of waste generated or transferred to the environmental. Other than air emissions that were generated only when the Badger system was injecting the chemicals into the aquifer or about 10 minutes per hour, air emissions were not released. Solid waste was limited to the empty drums holding the oxidizers that were returned to the chemical supplier. No used filter bags or other media containing petroleum products were generated.

After reviewing the results, the FDEP/EPD approved a RAP to remediate the Waldo and Ocala sites using chemical oxidation process. Both the Badger system and injections wells will be used to insert the oxidizing solutions into the aquifer. The FDEP has accepted the use of chemical oxidation at the Wildwood site as a viable alternative to AS/SVE but the presence of free product must be addressed before active remediation can be implemented. Due to budget constraints, only the Waldo site RAP has been funded. The other two sites will be funded when budgets are more robust and higher priority sites have been address.