#### Application of Mulch Biowall for Anaerobic Treatment of Perchlorate in Shallow Groundwater

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**ABSTRACT:** The anaerobic reduction of perchlorate is becoming a widely accepted method for the bioremediation of perchlorate impacted groundwater. A full scale in situ passive permeable reactive biobarrier (PRB) was installed to mitigate the migration of perchlorate contaminated groundwater from entering a nearby tributary to a large river. The full-scale PRB consists of the installation of a series of mulch wall biobarriers immediately upgradient from the tributary and downgradient of the identified perchlorate groundwater plume. The PRB was designed and installed to facilitate the development of anaerobic reducing conditions that would encourage the growth of specific microorganisms capable of reducing the identified perchlorate concentrations as groundwater migrates through the trench towards the tributary. After two years of operation the field measured geochemical parameters indicate that reducing conditions have been developed at least 15 feet (4.6 meters) downgradient of the biobarrier. Perchlorate concentrations ranging from 0.048 mg/L to 0.008 mg/L have been observed in the upgradient monitoring locations whereas the corresponding downgradient monitoring locations continue to demonstrate nondetectable results indicating the effectiveness of the biobarrier.

#### BACKGROUND

Groundwater data collected during a RCRA Facility Investigation (RFI) at an industrial Facility in 2005 indicated elevated perchlorate concentration in the shallow groundwater aquifer less then five hundred feet from a tributary to a large river. Historical investigations at the site and recently verified by groundwater modeling, indicated that the perchlorate contaminated groundwater would eventually migrate to the tributary. Perchlorate concentrations identified in the RFI ranged from 8–13 mg/L upgradient of the trench in the source area. Groundwater in this area of the site is typically observed to range from an elevation of 5-15 feet (1.5-4.6 m) below ground surface with seasonal groundwater fluctuations of 10 feet. In December 2006 an Interim Measure was installed to mitigate the migration of perchlorate in groundwater from potentially discharging into the tributary. The interim measure design included the installation of a passive permeable reactive mulch biobarrier to create anaerobic treatment barrier to prevent the migration of perchlorate into the tributary. The barrier trench was positioned downgradient of the identified perchlorate contamination and between the tributary to prevent the potential discharge of contaminated groundwater into the tributary. A total of 1,600 linear feet of a mulch biobarrier were installed using one pass trenching technology.

The area geology consists of Quaternary Terrace Deposits of clay, silt, sand and gravel from the ground surface down to the base of the gravel deposits. The Quaternary Terrace deposits may be generalized as yellow, orange, light brown, and light gray in color. Except for perched groundwater that occurs seasonally in shallow silts and sands, the unit comprises a single water table aquifer. Wells screened in differing depth intervals

at the same location exhibit similar potentiometric heads throughout the vertical sequence, indicating hydraulic communication. The Quaternary Terrace deposits consist typically of the following sequence, starting at the surface:

- 1. **Shallow Silt or Sand.** Silt or very fine-grained sand is generally present at the ground surface, down to approximately 5 feet (1.5 meters) below ground surface (bgs). Perched groundwater has been seasonally observed in this unit.
- 2. **Shallow Clay**. Variable silty clay and clayey silt grading in some cases down to fine sand predominate in the interval from approximately 5 feet (1.5 meters) bgs down to as deep as 15 to 20 feet (4.6– .4 meters).
- 3. **Gravel-Bearing Sediments.** The gravels are typically found within the depth range of greater than 10 feet (3.0 meters) and less than 30 feet (9.1 meters) bgs. The gravel consists of rounded fine pebbles to cobbles and contains varying combinations of sand, silt, and clay in the matrix.
- 4. **Poorly Graded Fine Sand.** Fine, well-sorted, loose sand is sometimes present beneath the gravel units. Where present, the top of the unit is typically identified at a depth of 30 feet (9.1 meters) bgs or greater.

#### MATERIALS AND METHODS

**Trench Installation.** The mulch biobarrier was installed in 4 - 400 foot (121.9 meters) segments to a depth of 25 feet (7.6 meters) below ground surface to contact the more permeable, perchlorate-impacted gravel zone. A cross section of the trench with an overly of the typical geology conditions in which the trenches were installed is presented in Figure 1.

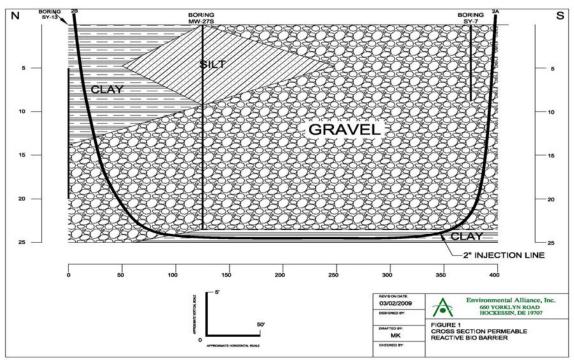


FIGURE 1. Cross section permeable reactive biobarrier.

Each trench segment was installed using a one-pass trenching system to a total depth of 25 feet (7.6 meters) below ground surface. The biobarrier was backfilled with a 50 / 50mixture of pea gravel and hardwood mulch from 25 to 10 feet (7.6-3.0 meters) below ground surface. A 2-inch injection line was installed at the bottom of the trench to accommodate the addition of liquid substrate, if necessary to augment the hardwood mulch. The hardwood mulch was installed as a long-term electron donor substrate to facilitate the development of anaerobic reducing conditions required for perchlorate degradation. Pea gravel was mixed with the hardwood mulch to limit the potential for compaction of the hardwood mulch which could in turn limit flow rates through the trench, thus limiting the effectiveness of the trench. The 2-inch injection pipe was installed to allow for the addition of supplemental carbon donor substrates should the hardwood mulch not be sufficient in maintain suitable conditions for the microbial activity required for perchlorate reduction. The ability to add substrate extends the operational life-time of the bio barrier by being able to compensate for reduced efficiency of the hardwood mulch as it becomes less effective overtime. Upon backfilling the trench with the mulch as previously described the remaining portion of the trench was backfilled with native soil and lightly compacted at the surface to minimize subsidence.

A monitoring well network was installed to monitor the effectiveness of the PRB. The monitoring well network consisted of upgradient and downgradient monitoring wells to evaluate groundwater geochemical parameters and to evaluate perchlorate reduction within in the trench as contaminated groundwater migrates through the trench. Refer to Figure 2 for the overall layout of the trench and monitoring well network.

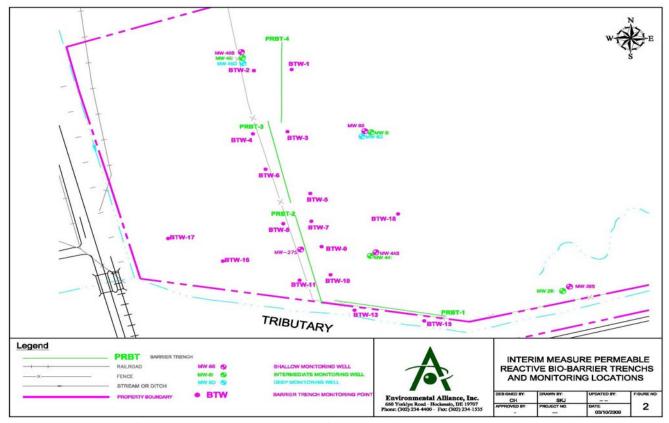


FIGURE 2. As-built diagram of the interim measure.

#### **RESULTS AND DISCUSSIONS**

The PRB interim measure was installed in December 2006 and has been operating continuously until the present day. The closest upgradient monitoring well has been observed to have perchlorate concentrations ranging from 0.048 mg/L to 0.008 mg/L over the past two years of monitoring. The corresponding downgradient monitoring location has consistently been reported as <0.004 mg/L indicating that the PRB has successful created conditions that facilitate perchlorate reduction. Since the interim measure has been installed, reproducible perchlorate concentrations have not been observed downgradient of the PRB. These results indicate that the PRB has created conditions that are suitable for the microbial degradation of perchlorate and preventing the migration of perchlorate into the tributary.

Groundwater geochemical parameters (dissolved oxygen, oxygen reduction potential, and ferrous iron) that are key indicators of the success of creating anaerobic reducing conditions for in situ bioremediation have been monitored to determine the effectiveness of the PRB.

- Dissolved oxygen readings prior to installation of the interim measure were generally greater the 1.5 mg/L. Since the interim was installed dissolved oxygen readings collected downgradient from the PRB are observed to generally be below 0.5 mg/L while measurements collected from the upgradient wells are generally greater then 1.0 mg/L indicating that dissolved oxygen in the groundwater is being depleted as groundwater migrates through the trench which indicates anaerobic conditions are being created within the trench.
- ORP measurements downgradient of the PRB have been observed to be decreasing and generally range between 50 and -230 mV while conditions upgradient of the trench are typically observed to be positive and greater then 50 mV. The negative ORP measurements indicate that conditions that are favorable for anaerobic reduction are being created as groundwater migrated through the trench.
- Ferrous iron measurements collected from downgradient of the trench indicate concentrations ranging from 5–10 mg/L while concentration upgradient display limited if any ferrous iron. Elevated concentrations of ferrous iron indicate that reduction is occurring within the groundwater environment and that groundwater is an anaerobic environment.

Table 1 provides a summary of perchlorate and key geochemical parameters from an upgradient well and a respective downgradient well. The information provided in Table 1 demonstrates the effectiveness of the PRB at generating the appropriate conditions for perchlorate reduction and the reduction of perchlorate as groundwater migrates through the PRB.

	Upgradient Well				Downgradient Well			
Sample	Perchlorate	DO	Fe <sup>2+</sup>	ORP	Perchlorate	DO	Fe <sup>2+</sup>	ORP
Date	mg/L	mg/L	mg/L	mV	mg/L	mg/L	mg/L	mV
01/25/07	0.048	5.10		74.2	< 0.004	2.85		95.1
03/28/07	0.017	3.86		522.6	< 0.004	0.51		446.2
04/16/07	0.030	3.25		408.2	< 0.004	2.98		429.1
05/15/07	0.034	3.57	0.0	519.6	< 0.004	3.23	0.0	360.2
06/20/07	0.032	4.00	0.0	309.2	0.005	1.23	0.6	204.1
07/24/07	0.023	3.48	0.0	174.2	< 0.004	2.99	5.6	76.2
08/22/07	0.023	4.51	0.0	293.2	< 0.004	4.00	10.0	191.1
09/18/07	0.010	3.50	0.0	168.8	< 0.004	0.22		-174.2
10/16/07	0.031	1.23	0.0	276.2	< 0.004	2.62	0.0	108.2
11/01/07	0.030	2.00	0.0	373.2	< 0.004	0.94	3.4	244.2
12/10/07	0.034	2.20	0.0	166.2	< 0.004	0.99	0.8	167.1
01/21/08	0.008	2.74	0.0	160.6	< 0.004	1.52	3.2	87.1
02/27/08	0.018	2.15	0.0	159.8	< 0.004	1.61	2.4	158.40
03/24/08	0.010	1.94	0.2	-40.8	< 0.004	0.99	2.0	-61.90
04/22/08	0.030	2.62	0.0	56.2	< 0.004	0.98	5.2	-34.20
05/19/08	0.030	2.52	0.0	75.6	< 0.004	1.97	7	-42.2
06/25/08	0.035	2.19	0.4	-64.9	< 0.004	0.97	1.2	-37.1
09/24/08	0.032	3.73	0.0	231.3	< 0.004	3.12	1.0	231.1
12/11/08	0.030	0.48	0.0	100.1	< 0.004	0.21	1.0	172.0

 TABLE 1. Perchlorate and geochemical parameter summary table.

As presented in Table 1 dissolved oxygen measurements have been observed to decrease as groundwater migrates through the trench. The reduction of dissolved oxygen as groundwater migrates through the trench is evaluated to determine the effectiveness of the hardwood mulch installed within the trench. Figure 3 presented below presents dissolved oxygen measurements over time for an upgradient and respective downgradient monitoring well.

Figure 3 indicates that the hardwood mulch is effectively reducing dissolved oxygen measurements within the groundwater to create a suitable conditions for perchlorate reduction. Dissolved oxygen concentrations are used in part to evaluate the effectiveness of the hardwood mulch installed within the trench and determine when supplemental electron donor substrates must be added to maintain the established reduction environment. The mulch will be considered to be ineffective when dissolved oxygen readings begin to increase downgradient of the trench and the trend line presented in Figure 3 becomes positive. It will be at this point that supplemental electron donor substrates will be required to maintain the treatment zone.

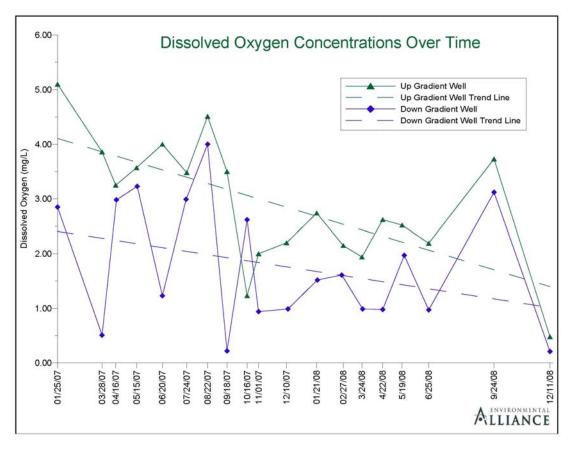


FIGURE 3. Dissolved oxygen concentrations over time.

Additionally, Figure 3 demonstrates that upgradient diffusion of anaerobic conditions is occurring within the interim measure. Since the interim measure was installed; conditions upgradient of the trench have been observed to become more anaerobic (specifically a reduction is dissolved oxygen), indicating the potential for the upgradient diffusion of anaerobic groundwater. This observation is supported by the results of the recently completed groundwater model, which indicated very slow groundwater gradient across the facility, generally <50 feet per year. The upgradient diffusion that is occurring will help to facilitate perchlorate reduction and extend the overall treatment zone that is created by the trench.

#### CONCLUSION

The geochemical parameters in conjunction with the observed reduction of perchlorate indicate that the trench is successful in generating conditions that are suitable for in situ anaerobic degradation of perchlorate. The data also indicates that the hardwood mulch installed during construction is sufficient in maintaining and creating conditions favorable for perchlorate reduction after two years of operation. Continued monitoring of the PRB will be performed to ensure the mulch is capable of maintaining the proper groundwater conditions for perchlorate reduction. At which time the geochemical data indicates that the mulch is no longer an effective in generating the appropriate groundwater conditions a carbon donor substrate will be utilized to prolong the operational life of the interim measure at a minimal cost.

The results to date indicate that remedial strategy implemented in this given instance is a cost effective means to prevent the migration of perchlorate into a surface water body. While initial costs to install the trench may be higher then other remedial option, the ongoing operation and maintenance costs have been observed to be limited to periodic monitoring and sampling providing a substantial cost savings over other remedial options. Application of Mulch Biowall for Anaerobic Treatment of Perchlorate in Shallow Groundwater

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# Site Background

- Active industrial facility operating since the early 1980's.
- DOD subcontractor, primarily manufacturing rocket motors and solid rocket propellant.
- Perchlorate is the main ingredient for solid rocket propellant as an energetic.
- Main facility is approximately 2 square miles in area.
- Facility is located in a low-lying region bisected by a local tributary that acts as storm water drainage pathway for the southern and northern portion of the facility. Groundwater flow is generally towards the tributary.



# Geology/Hydrogeology

- Shallow Silt or Sand- Silt or very fine-grained sand present to approximately 5 feet (1.5 meters) below ground surface (bgs).
- Shallow Clay- Variable silty clay and clayey silt grading to fine sand from approximately 5 feet (1.5 meters) bgs down 15 to 20 feet (4.6 – 6.4 meters).
- Gravel-Bearing Sediments- Typically found from 10 feet (3.0 meters) to less than 30 feet (9.1 meters) bgs consisting of rounded fine pebbles to cobbles. Contains varying combinations of sand, silt, and clay in the matrix.
- Poorly Graded Fine Sand Fine, well-sorted, loose sand beneath the gravel unit. The top of sand unit is typically identified at a depth of 30 feet (9.1 meters) bgs or greater.



# Site History

- A RCRA Facility Investigation has recently been completed for the facility.
- During the RFI it was determined that perchlorate had impacted soil and groundwater at the site.
- Several interim measures were designed and installed based on the data collected during the RFI.
- These interim measures were designed and installed to address surface water, groundwater and soil concerns at the site.



### Interim Measure Technologies

- Remedial strategies implemented at the site
  - Surface Water Impoundments
  - Ex Situ Anaerobic Biocells
  - Semi-Passive Injection Barriers
  - Active Permeable Reactive Biobarriers
  - Passive Permeable Reactive Biobarrier (PRB)



# Soil and Groundwater Assessment for Passive Permeable Reactive Biobarrier

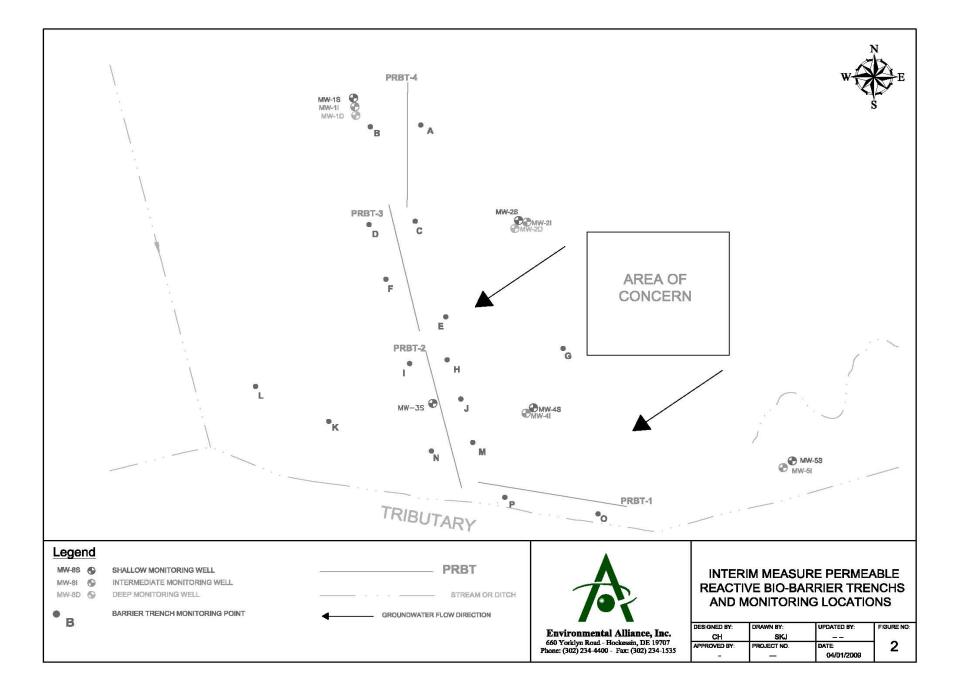
- Up-gradient of the interim measure several areas of concern were identified during the RFI.
- Perchlorate concentrations up-gradient of the interim measure were identified to range from 8-13 mg/L in shallow groundwater.
- Perchlorate concentrations in soil ranged from 13.1 to <0.004 mg/L.</li>
- Groundwater elevation measurements collected from the site monitoring well network indicated that groundwater in the area of concern was migrating towards the tributary.
- Groundwater modeling for the facility indicated that shallow groundwater would likely discharge to the tributary.



# Protection of the Tributary

- To be protective of the tributary an interim measure was designed and installed to mitigate the migration of perchlorate contaminated groundwater prior to discharge to the tributary.
- A passive permeable reactive biobarrier trench (PRBT) was selected as the interim measure remediation strategy.
- Interim measure consisted of a series of trenches positioned between the area of concerns and the tributary.
- Each trench was designed and installed to promote the development of anaerobic perchlorate reducing conditions capable of degrading perchlorate in groundwater as it migrates through the trench.





# Permeable Reactive Biobarrier Trench Design

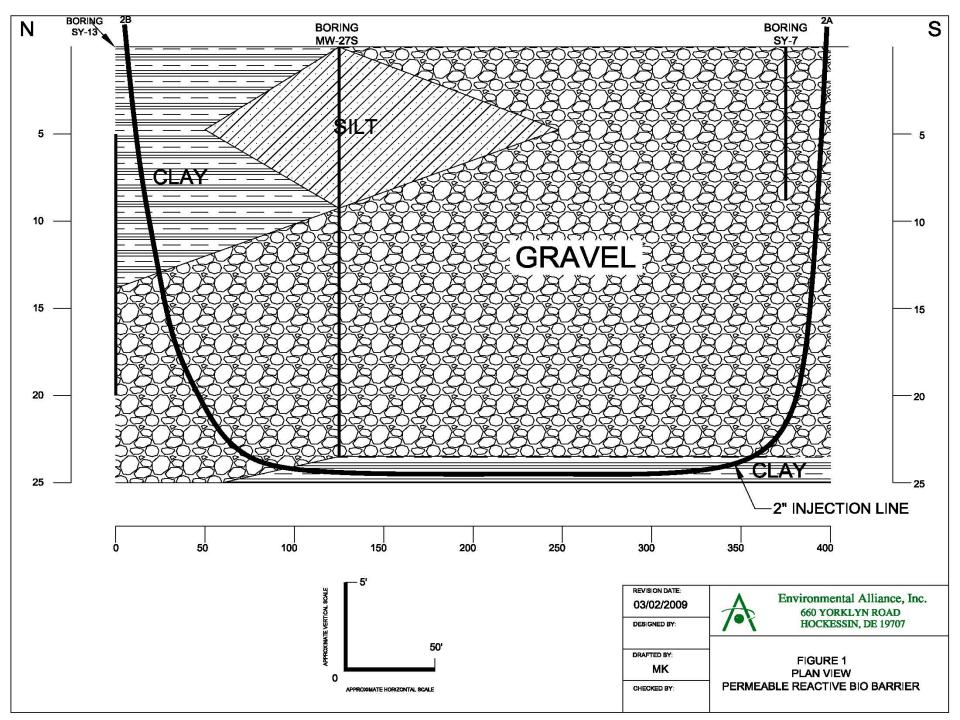
- The PRBT was installed using one-pass trenching to a total depth of 25 feet below ground surface. This depth was selected to target the more permeable gravel zone.
- The Trench was installed in a series of 4-400 foot (121.9 meters) trenches to create an effective barrier between the tributary and the area of concern.
- The one pass trenching was selected to allow for greater trench depth and minimize the potential of the trench collapsing during installation due to site specific geology.
- The presence of the gravel zone would have made conventional trenching with a track-hoe difficult and expensive as shoring of the trench would be required.



# Trench Design (cont.)

- The trench was backfilled from 25 feet below ground surface to 10 feet below ground surface with a 50/50 mixture of hardwood mulch and pea gravel.
- Hardwood mulch was installed to provide a long lasting electron / carbon donor source to facilitate the development of an anaerobic environment to encourage indigenous microorganism to degrade the identified perchlorate contamination.
- The pea gravel was installed to increase the permeability of the mulch and minimize the potential that the hardwood mulch will compact and inhibit groundwater flow.
- An injection pipe was installed at the base of the trench to provide a means for supplemental electron donor additions should the mulch become an inadequate electron source.









#### **Trench Effectiveness**

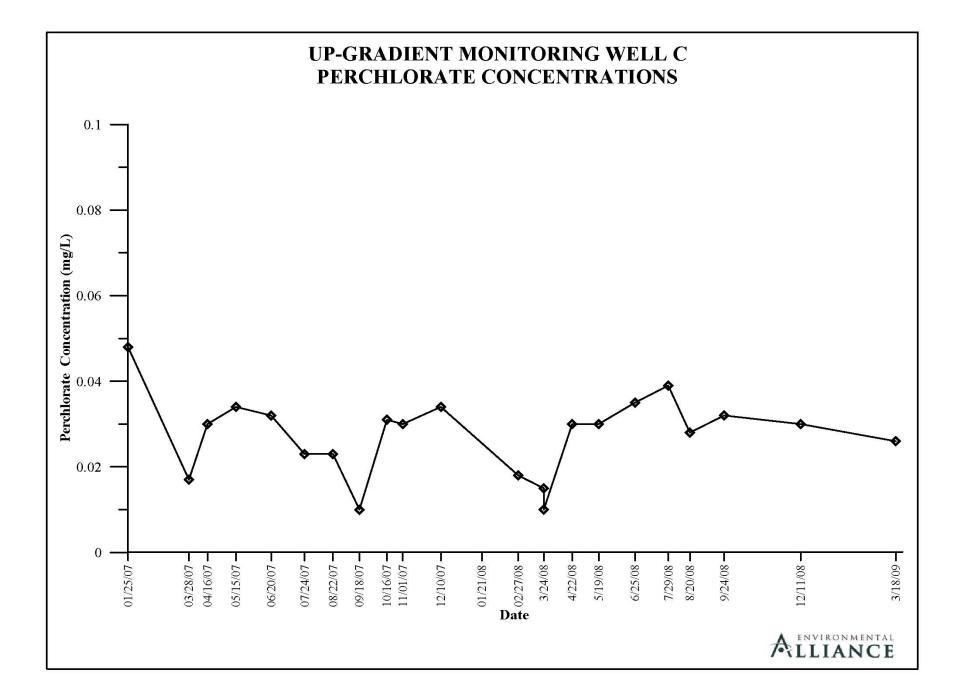
- The PRBTs have been operational for approximately 2.5 years.
- Geochemical readings indicate that suitable conditions for perchlorate reduction have been created at least 15 feet down-gradient of the PRBT.
- Geochemical conditions up-gradient of the trench have also been observed to become increasing anaerobic as a result of the PRBT. This has been attributed to the relatively shallow groundwater gradient and flow velocity (approximately 25-51 feet per year) which allowed groundwater conditions to defuse up-gradient of the trench.

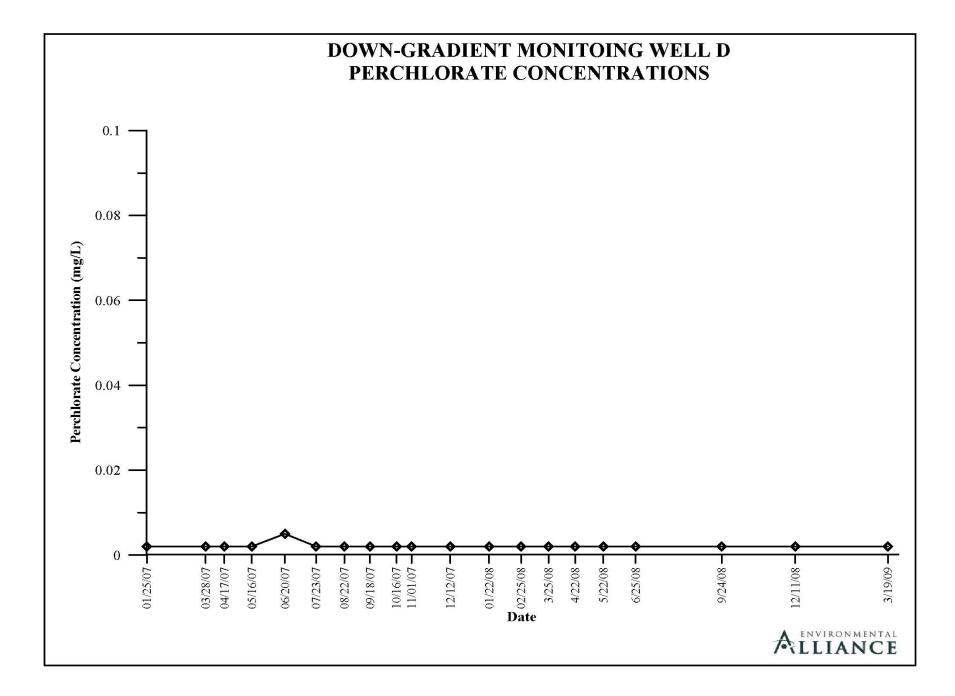


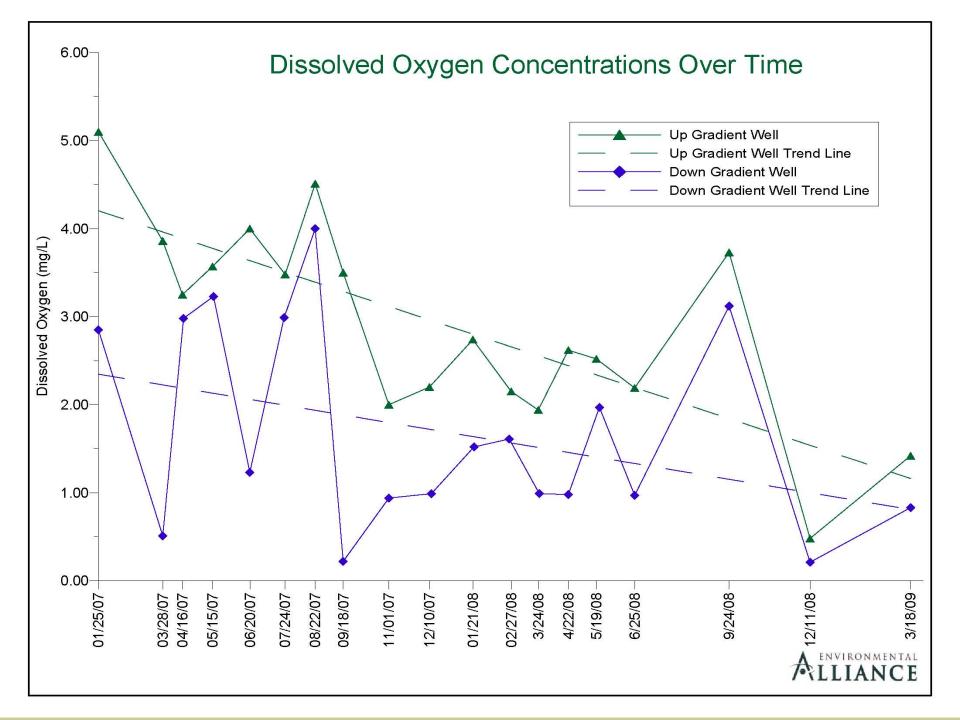
# Geochemical Data

- Dissolved Oxygen measurements down-gradient of the trench have been reduced from ambient concentrations of 3-4 mg/L to <1.0 mg/L.</li>
- Ferrous Iron measurements have been increasing since the installation of the PRBT indicating that reducing conditions have been developed.
- ORP measurements down-gradient of the PRBT have been observed to be as low as -295 mV while up-gradient of the trench are generally positive.









# Summary

- Perchlorate concentrations immediately up-gradient of the PRBT have been observed to range from 0.048 mg/L to 0.008 mg/L.
- Perchlorate concentrations immediately downgradient of the PRBT continue to demonstrate nondetectable results.
- These results indicate that the PRBT is effectively facilitating the reduction of perchlorate within the groundwater at the site.



### Conclusions

- After 2.5 years of operation the hard wood mulch is sufficient in creating reducing conditions within the site groundwater and maintaining an anaerobic environment to support the microbial degradation process.
- The PRBTs are acting as an effective barrier to be protective of the tributary and prevent perchlorate migration into the tributary.
- Based on the data gathered to date it is estimated that the hard wood mulch will be an effective substrate for at least the next 3-4 years. Continued monitoring will be performed to ensure that an effective barrier is maintained.



# Conclusion (cont.)

- Installation costs to install the interim measure via the one passing trenching were approximately \$185 per liner foot.
- Cost estimates to perform the installation of the interim measure using traditional methodologies were estimated at over \$215 per linear foot.
- Operation and Maintenance cost have been limited to periodic sampling to monitor effectiveness of PRBT.
- The interim measure has been a cost effective and reliable long term remediation strategy with minimal O/M costs.



### Acknowledgements

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## Questions?

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- Environmental Alliance, Inc.

