Comparing Effectiveness of Activated vs. Un-activated Sodium Persulfate During In Situ Remediation of Petroleum Hydrocarbons

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Introduction/Background

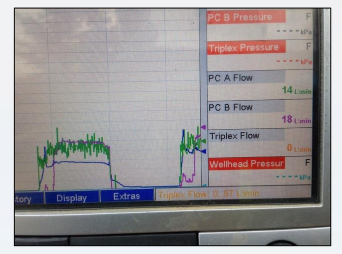
- A retail petroleum site in SE Alberta, Canada (in operation since prior to 1929) had a history of petroleum hydrocarbon (PHC) contamination in both soil and groundwater;
- The site is characterized by fine-grained soils (e.g.: clay till and silt);
- PHC impacts exist off-site beneath a main road through the village and beneath residential properties adjacent to the site. PHC parameter concentrations were elevated such that remedial strategies (e.g.: soil vapour extraction, air sparge, peroxide injection) were implemented on site to mitigate potential risk;
- Remedial strategies were successful at decreasing the plume area. However, benzene concentrations remained high and were considered to be recalcitrant;
- Persulfate is widely used to facilitate contaminant degradation through chemical oxidation;
- Activated persulfate will produce sulfate radicals that will stimulate the rapid, short-lived degradation of benzene. Un-activated persulfate will provide oxidative degradation, as well as stimulate anaerobic degradation of PHCs by producing sulfuric acid which will liberate soil-bound phosphate;
- Prior research by Federated Co-operatives Limited has indicated that orthophosphate is an important nutrient in stimulating bacterial communities;
- Delivery of persulfate through hydraulic fracture propagation was selected for the site due to the fine-grained nature of the lithology; and
- Limited research on persulfate chemox in fine-grained (e.g.: clay till and silt) lithology.

Conclusions

- The recalcitrant benzene concentrations were greatly reduced in multiple wells within the treatment areas;
- Based on the results of the investigation, there was no difference in efficacy of benzene degradation using either NaOH activated versus un-activated persulfate;
- Groundwater temperature may be a major influencing factor on the degradation of persulfate;
- Natural activation (e.g.: dissolved/total iron in soil/groundwater) of persulfate may have occurred, which possibly contributed to the lack of difference between activated and un-activated persulfate treatment areas;
- The large increase in bacterial population indicates that orthophosphate is becoming available, and is being consumed immediately after release from the lithology; and
- Hydraulic fracturing was a valuable mechanism for persulfate delivery into fine-grained soils. Preferential pathways may exist using this technology.

Methods

- Hydraulic fracturing adjacent to monitoring well MW-1



- Display of fracture pressures during hydraulic fracturing

- Injection rod and transfer hosing installed within investigation area

- Monitoring of hydraulic fracturing pressures

Site Plan

- Low-flow sampling of groundwater monitoring wells within investigation area

- Investigation area within village

- Mixing of NaOH activator with persulfate

- Daylighting of persulfate within adjacent monitoring well

Results

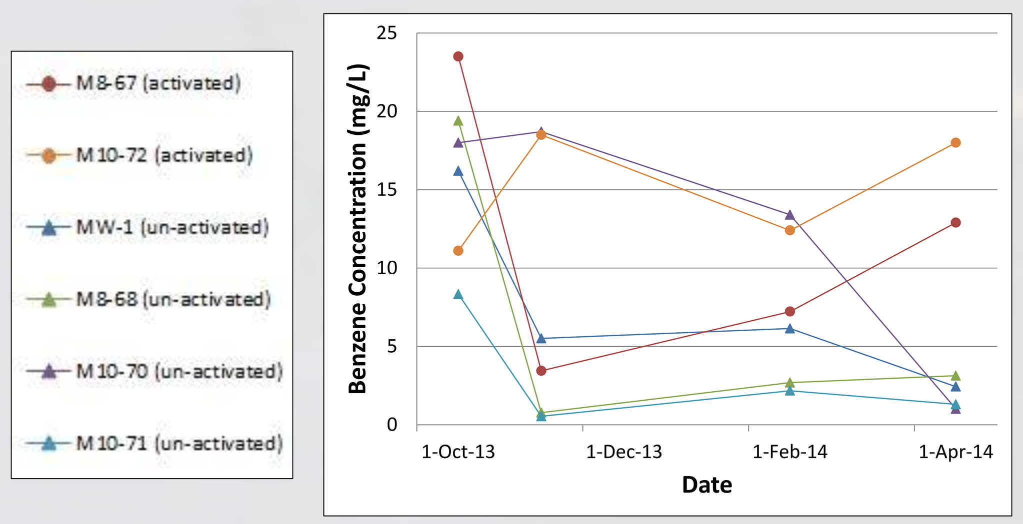


Figure 1. Benzene concentrations in groundwater pre- and post-injection in select wells inside the PHC plume.

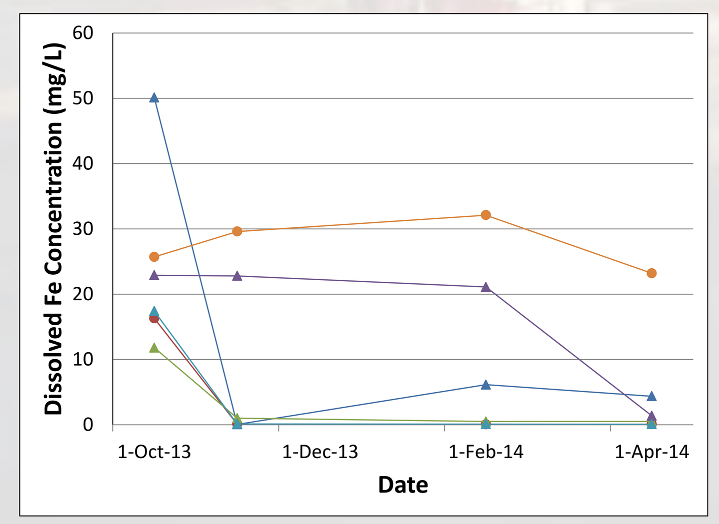


Figure 2. Dissolved Fe concentrations in groundwater pre- and post-injection in select wells inside the PHC plume. Similar trends were observed with dissolved Mn concentrations in groundwater.

Sample ID	Sample Date	Bacteria (CFU/ml)			
		Sulphate Reducing	Iron Reducing	Heterotrophic Aerobic	Pseudomonad and related
M2-28	8-Oct-13	100,000	35,000	680	500
	21-Nov-13	5,000	35,000	38	12,000
	26-Feb-14	ND	9,000	16	350,000
	21-Apr-14	ND	9,000	310	350,000
M3-65	8-Oct-13	18,000	35,000	138	10
	21-Nov-13	5,000	35,000	195	12,000
	26-Feb-14	500	9,000	6	2,500
	21-Apr-14	ND	140,000	3	350,000
M8-67	8-Oct-13	18,000	35,000	330	12,000
	21-Nov-13	1,200	ND	49	100
	26-Feb-14	ND	25	13	500
	21-Apr-14	ND	35,000	81	500
M10-70	8-Oct-13	5,000	35,000	480	500
	21-Nov-13	5,000	9,000	11,100	66,000
	26-Feb-14	1,200	9,000	260	2,500
	21-Apr-14	ND	540,000	250	350,000
M10-72	8-Oct-13	5,000	35,000	1,350	2,500
	21-Nov-13	18,000	35,000	740	66,000
	26-Feb-14	18,000	35,000	110	12,000
	21-Apr-14	ND	540,000	780	1,800,000

Table 1. Bacteria concentrations from select wells from both inside and outside of the PHC plume

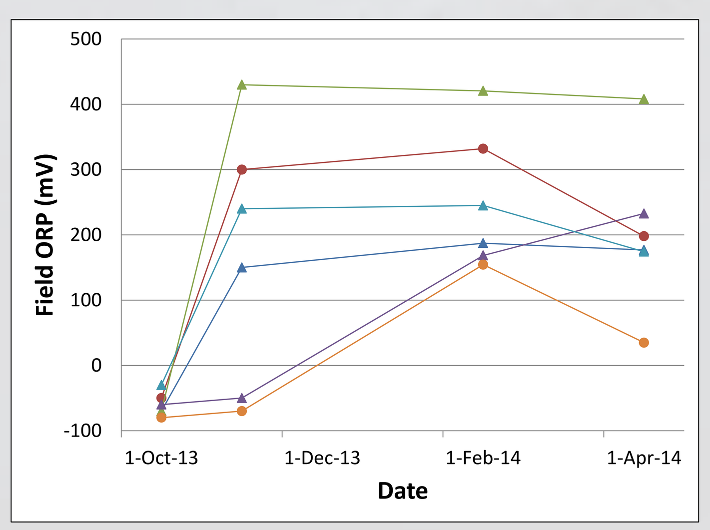


Figure 3. Field groundwater ORP values pre- and post-injection from select wells inside the PHC plume.

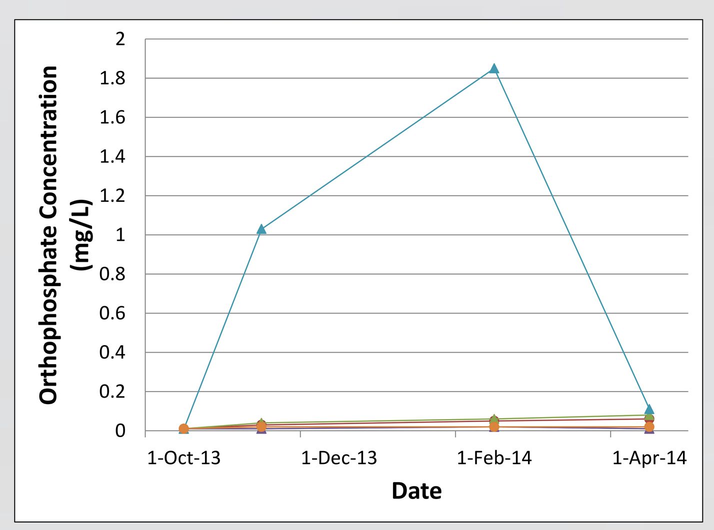


Figure 4. Orthophosphate concentration pre- and post-injection in groundwater from select wells inside the PHC plume.

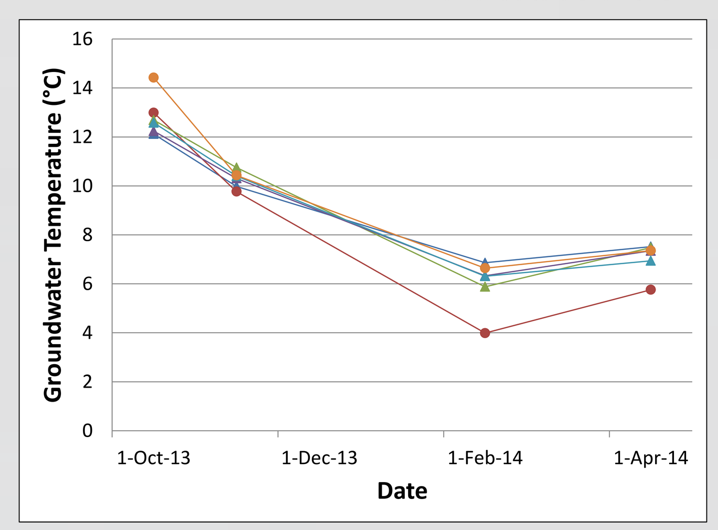


Figure 5. Field groundwater temperature pre- and post-injection in select wells inside the PHC plume.

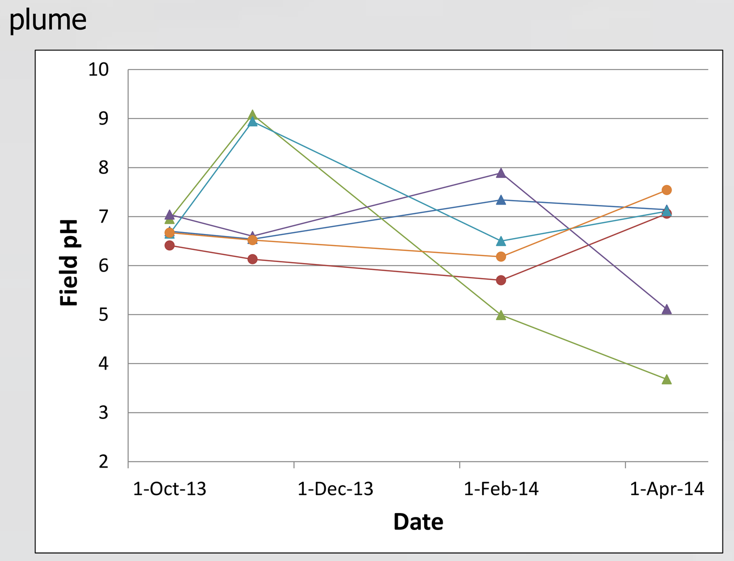


Figure 6. Field pH pre- and post-injection groundwater from select wells inside the PHC plume.

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Discussions

- Benzene concentrations in groundwater decreased sharply in most wells in the first post-injection monitoring event. Based on this investigation, there were no differences in degradation efficacy between activated and un-activated persulfate (Figure 1);
- Dissolved iron and manganese concentrations throughout the treatment areas decreased as a result of catalytic conversion of persulfate (Figure 2);
- Field-measured ORP demonstrated a rise from negative to positive values following persulfate treatment (Figure 3);
- Orthophosphate was measured in multiple monitoring wells within the investigation area. However orthophosphate concentrations were not significantly higher, possibly as a result of immediate bacterial consumption (Figure 4);
- Low groundwater temperatures (Figure 5) appear to have influenced persulfate degradation in both the activated and un-activated treatment areas as evidenced by delays in maximum values of ORP;
- Field measured pH values indicate that select monitoring wells in both treatment areas became acidic (Figure 6). pH of the investigation area remained relatively neutral, possibly as a result of the buffering capacity of fine-grained soils (clays, silts);
- Sulfate-reducing bacteria concentrations were reduced to below detection limits in the monitoring wells tested as a result of continued elevated ORP. Pseudomonad and related bacteria populations showed a sharp increase during the same period (Table 1);
- Pseudomonad bacteria are well documented as hydrocarbon degraders, and as such, reduction in benzene concentrations is anticipated to continue;
- Iron-reducing bacteria concentrations have rebounded after an initial decrease, indicating that ORP may continue to decrease (Table 1);
- Degradation of the benzene concentration in monitoring well M10-70 (un-activated treatment area) was initially static but showed a sudden decrease in post-injection event #3 (Figure 1). This decline suggests a delay in persulfate activation as evidenced by lower dissolved iron and manganese concentrations (Figure 2); and
- Hydraulic fracturing may have introduced preferential pathways for persulfate delivery, which may explain variance in results throughout the treatment areas.