Bioremediation of Hydrocarbons – Has Your Design Considered Potential Residual Contaminants Relating to Your Amendments?



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Outline

Introduction

2 Study Site Remediation

3 Nitrate Source Identification

4 Conclusions



- Landfarming is a common method used to reduce concentrations of petroleum hydrocarbons (PHC) in excavated soils through the use of biodegradation
 - Heaping contaminated soils into stockpiles
 - Stimulating aerobic biodegradation through aeration and addition of nutrients and moisture
- Landfarming design elements
 - Land requirements
 - Aeration equipment
 - Water management
 - pH adjustment (if necessary)
 - Supply of nutrients and moisture
 - Site security
 - Air emission controls



- Microorganisms require inorganic nutrients such as nitrogen and phosphorus to support cell growth and sustain biodegradation processes
- Symbolic equation for nutrient uptake
- $aHPO_4^{2-} + bHCO_3^{-} + cNO_3^{-} + dH_2O + eH^+ = C_bN_cP_aH_qO_r$
- Redfield et al. (1958) have defined an organism stoichiometry of $C_{106}N_{16}P_1H_{263}O_{110}$
 - Redfield (1958) C:N:P ratio: 106:16:1
 - EPA (2004) ratio: 100:10:1
 - Cleveland and Liptzin (2007) modified the Redfield ratio to 60:7:1

Cleveland, C. C. and Liptzin, D. C:N:P stoichiometry in soil: is there a ''Redfield ratio'' for the microbial biomass? Biogeochemistry, 85, 235-252. EPA. 2004. How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites Redfield, A. 1958. The Biological Control of Chemical Factors in the Environment. American Science, 46, 205-221.



- However, lots of landfarming practices didn't calculate appropriate doses of nutrients, but relied on the application of excessive amounts of nutrients.
- Excessive nutrient application has been observed to cause cross contamination. This is especially true for excess nitrogen nutrient conditions.



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- Excessive nutrient application has been observed to cause cross contamination. This is especially true for excess nitrogen nutrient conditions.
- The following slides will introduce one study site where landfarming successfully removed PHCs from subsurface but amendment contamination occurred.







2 Study Site Remediation

- Approximately 750 m³ of PHC impacted soil were excavated in 2007
- Material removed from the sump area excavation was spread on the land treatment area (LTA)
 - Mixed with approximately 0.9 tonnes of fertilizer consisting of 11-48-0 and 46-0-0 (N-P-K) blend in 2008
 - Additional treatment activities were conducted in 2009



2 Study Site Remediation

- Soil samples were collected from the stockpile soil and the LTA base
 - One hydrocarbon exceedance was reported from the LTA base, resulting in additional excavation
 - Additional confirmatory soil samples were reported at levels below the applicable guidelines
 - A composite soil sample from the treated soil reported nitrate + nitrite concentration of 13.5 mg/kg
- Concentrations of dissolved-phase PHCs in groundwater were lower than the applicable guidelines
 - Nitrate concentration in groundwater collected from 09-MW06 and MW15-01 exceeded the applicable guideline
- Site closure cannot be achieved due to the nitrate exceedance



Site Plan in 2016

Legend: Lease Boundary **Buried Discontinued Pipelines** Buried Active Gas Pipelines Topographical Property / Legal Lines Access Road / Trails Fence Lines Bushes / Trees Gates Water Injection Well - Abandoned B Horizon Soil Stockpile A Horizon Soil Stockpile (Topsoil) Mulch Treated Soil Stockpiles Monitoring Wells Active Borehole Soil Sample Location



2 Study Site Remediation

Sample Location	Parameter	pH (units)	p - Alkalinity (asCaCO ₃)	T - Alkalinity (as CaCO ₃)	Bicarbonat e	Carbonate	Hydroxide	Electrical Conductivity (µS/cm)	Chloride	Nitrate	Nitrate-N	Nitrite-N	Nitrate + Nitrite-N	Sulfate
Guideline ¹	Sample Date	6.5-8.5	n/v	n/v	n/v	n/v	n/v	1,000	100	n/v	10	1.0	100	500
05-MW02	16-Oct-09	7.6	< 5	395	482	< 6	< 5	758	3	-	0.27	< 0.005	0.27	38.2
	21-Jun-10	7.8	<5	410	501	<5	<5	772	2		0.226	<0.015	0.226	44
	28-Sep-10	8.3	<5	437	534	<5	<5	753			0.271	<0.015	0.271	41
	19-May-11	8.2	<5	402	491	<5	<5	702	3	1.2	0.271	<0.015	0.271	41
	12-Oct-11	8.2	<5	409	499	<5	<5	745	3	0.7	0.158	< 0.015	0.158	10
	23-May-12	7.9	<5	398	485	<5	<5	/06	3		0.248	<0.015	0.248	40
	2-Oct-12	8.2	<5	396	483	<5	<5	/46	3	0.9	0.203	< 0.015	0.203	40
	1/-May-13	8.1/	<5	389	4/5	<5	<5	/	2	0.9	0.203	< 0.015	0.203	36
	30-Sep-13	8.15	<5	391	4//	<5	<5	/44	2	1.3	0.294	<0.015	0.294	39
	18-NOV-14	8.20	<5	395	482	<5	<5	/4/	2	0.9	0.20	<0.01	0.20	0.20
	5-JUN-15	-	-	-	-	-	- - E	-	5.2	2.1	0.4//	-	0.4//	-
09-MW06	21 Jun 10	7.00 7.0	< 5	004 202	007	<0 ~5	<5	1,270	13.0		0.10	< 0.005	0.10	74.I 00
	21-JUII-10 28-Sep-10	7.0 Q	\5	070 718	040 874	<5	<5	1,450	00 45		12.3	<0.015	0.427	00
	19-May-11	R R	<5	676	825	<5	~5	1,470	 ∕1	49.8	15.9	<0.015	15.8	99
	12-Oct-11	8	<5	670	773	<5	<5	1,240	49	245	55.3	<0.015	55 3	102
	23-May-12	79	<.5	663	809	<.5	<.5	1 700	46	240	51.7	<0.010	517	65
	2-Oct-12	8.1	<.5	600	732	<5	<5	1.610	49	252	56.9	< 0.015	56.9	76
	17-May-13	8.0	<5	564	688	<5	<5	1.490	48	181	40.9	< 0.015	40.9	71
	30-Sep-13	8.10	<5	671	818	<5	<5	1,790	31	285	64.4	< 0.015	64.4	77
	18-Nov-14	7.98	<5	632	771	<5	<5	1,630	15	200	45.2	< 0.01	45.2	80
	5-Jun-15		-	-		-	-	-	31	310	70.4	-	70.4	-
	22-Sep-15		-	-		-	-	-		242	54.7	< 0.01	54.7	-
	2-Dec-15	-	-	-	-	-	-	-	-	209	47.2	-	-	
09-MW07	16-Oct-09	7.85	< 5	506	617	< 6	< 5	1,020	3.8		0.07	< 0.005	0.07	102
	21-Jun-10	7.7	<5	492	600	<5	<5	955	3		0.136	<0.015	0.136	79
	28-Sep-10	8.2	<5	520	634	<5	<5	952	4		0.203	<0.015	0.203	85
	19-May-11	8	<5	489	597	<5	<5	875	4	0.7	0.158	< 0.015	0.158	82
	12-Oct-11	8.2	<5	476	580	<5	<5	921	4	0.6	0.136	< 0.015	0.136	90
	23-May-12	8.0	<5	480	585	<5	<5	884	3	1.0	0.226	< 0.015	0.226	5/
	2-Oct-12	8.3	8	560	664	10	<5	978	3	1.0	0.226	<0.015	0.23	/4
	17-May-13	8.2	<5 ~5	466	568	<5 ~5	<5	8/3	3	0.9	0.203	<0.015	0.20	60 70
	30-Sep-13	0.26 0.17	<0	SUS	616 E00	< 5 < F	<0	1,000	2		0.248	<0.015	0.25	/ 7 7 E
	5- lup-15	0.10	< 3	471	- 399	<5		9/9	12	6.4	1 45	<0.01	1.45	/3
MW15 01	2 Doc 15								4.2	- 0.4	1.45		1.45	
MW15-01	2-DeC-15									72.3	16.3		<u><u><u></u></u>Ctan</u>	
MW15-02	2-DeC-15	-	-	-	-	-	-	-	-		0.25		Stan	tec_
<u>MW15-03</u>	2-Dec-15	-	-	-	-	-	-	-	-	0.6	0.14		-	-

- Nitrate sources in groundwater
 - Natural nitrate sources
 - Geogenic sources (including desert-derived nitrate, lake evaporate deposits)
 - Soil organic nitrogen (including proteinaceous materials and heterocyclics)
 - Anthropogenic nitrate sources
 - Septic systems
 - Sanitary sewage effluent releases
 - Domestic animal wastes
 - Usage of nitrogen fertilizers including nitrate fertilizer, ammonium fertilizer, and urea



- Nitrogen and oxygen isotopic signature of nitrate were reported to be significantly different from natural or anthropogenic sources.
- Therefore, stable nitrogen and oxygen isotope data (¹⁵N and ¹⁸O) have been frequently used to estimate the origin of nitrate in groundwater
- Groundwater samples were collected from monitoring wells 05-MW02, <u>09-MW06</u>, and 09-MW07 for stable isotopic analysis of ¹⁵N and ¹⁸O of nitrate



 $\delta^{15}N$ (‰AIR) and $\delta^{18}O$ (‰VSMOW) of Nitrate in Groundwater

	δ ¹⁵ N Nitrate	δ ¹⁸ O Nitrate
05-MW02	34.96	11.87
09-MW06	10.40	-2.22
09-MW06-DUP	10.57	-2.47
09-MW07	24.30	6.61





- ¹⁸O=0.58¹⁵N-7.97
 - A slope of
 approximately 1 part
 δ¹⁸O to 1.7 parts δ¹⁵N
 (1/0.58)
- Occurrence of denitrification in groundwater



Original isotopic values of nitrate can be calculated by Rayleigh equation:

$$\delta_{S(t)} = \delta_{S(0)} + \varepsilon \ln(\frac{S_t}{S_0})$$

Where:

- ε = Isotopic enrichment factor (-40‰ to -5‰ for δ 15N and -18‰ to -8‰ for δ 18O)
- $\delta_{S(t)}$ = Isotopic compositions of the substrate at time t
- $\delta_{S(0)}$ = Isotopic compositions of the substrate at time 0
 - S_0 = Concentration of substrate at time 0 (mg/L)
- S_t = Concentration of substrate at time t (mg/L)
- Calculated original 09-MW06 δ15N and δ18O are: 2.5‰ to 9.4‰ for δ15N and -5.8‰ to -3.8‰ for δ18O





Elevated nitrate in 09-MW06 groundwater could be either from ammonium fertilizers (anthropogenic source) or soil nitrate (natural source)

Adapted from Kendall (1998)

Kendall, C. 1998. Tracing nitrogen sources and cycling in catchments. In: Kendall, C. and McDonnell, J.J., eds., Isotope Tracers in Catchment Hydrology, Elsevier Science B.V., Amsterdam, The Netherlands, 519–576.











- The biggest difference between the two possible nitrate sources (ammonium fertilizers and soil nitrate) is that ammonium fertilizers can be considered as anthropogenic source and soil nitrate can be considered as natural source
- Water quality consistency between 09-MW06 and 05-MW02 and nitrate concentration consistency prior to 2009 confirms that natural soil nitrate could not be the source for the recent increase of nitrate concentrations in 09-MW06 groundwater
- The source for the recent nitrate increase in 09-MW06 groundwater is likely related to the application of ammonium fertilizer



4 Conclusions

- Utilized fertilizers in the previous land farming practice were 11-48-0 (NH₄H₂PO₄) and 46-0-0 (CO(NH₂)₂)
- The source for the recent nitrate increase in <u>09</u>-MW06 groundwater is likely related to the excessive application of these ammonium fertilizers
- Therefore, soil remediation activities conducted at the Site may result in additional nitrate contamination in groundwater



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