



PILOT-SCALE TRIAL OF BIOREMEDIATION ADDITIVES AND PRODUCTS

Summary of Results

UIO/G/PNPD



Objective

- A significant number of Companies have approached SPDC in connection with nutrient amendments and other remediation products they can provide to assist in the remediation of oil spills sites.
- The pilot trial was designed to measure the relative performance of these additives from different suppliers, as against controls, in the ex-situ land based bio remediation process used by SPDC.
- The Pilot Trial focussed on the remediation of:
 1. High crude oil impacted soil
 2. Medium crude oil impacted soil

Vendors Requirements

- The Vendors whose products were tested in the Pilot Trial were asked to comply with the following requirements as a condition to taking part in the trial:
 1. Provide the Product for Testing at no cost to SPDC.
 2. Provide a Method Statement for Product Application.
 3. Provide MSDS and Technical Specification of the Product.
 4. Provide evidence the products have already been approved by Regulatory Agencies, such as the DPR and NOSDRA.
 5. A total of 17 vendors were invited to take part in the Project, under the conditions stated, initially 7 Companies were brought on board for the pilot trial on the grounds that they accepted the terms and conditions of the trials.
- SPDC promised to keep the results of the trials Confidential and not to release the names of the vendors to 3rd Parties for commercial reasons.

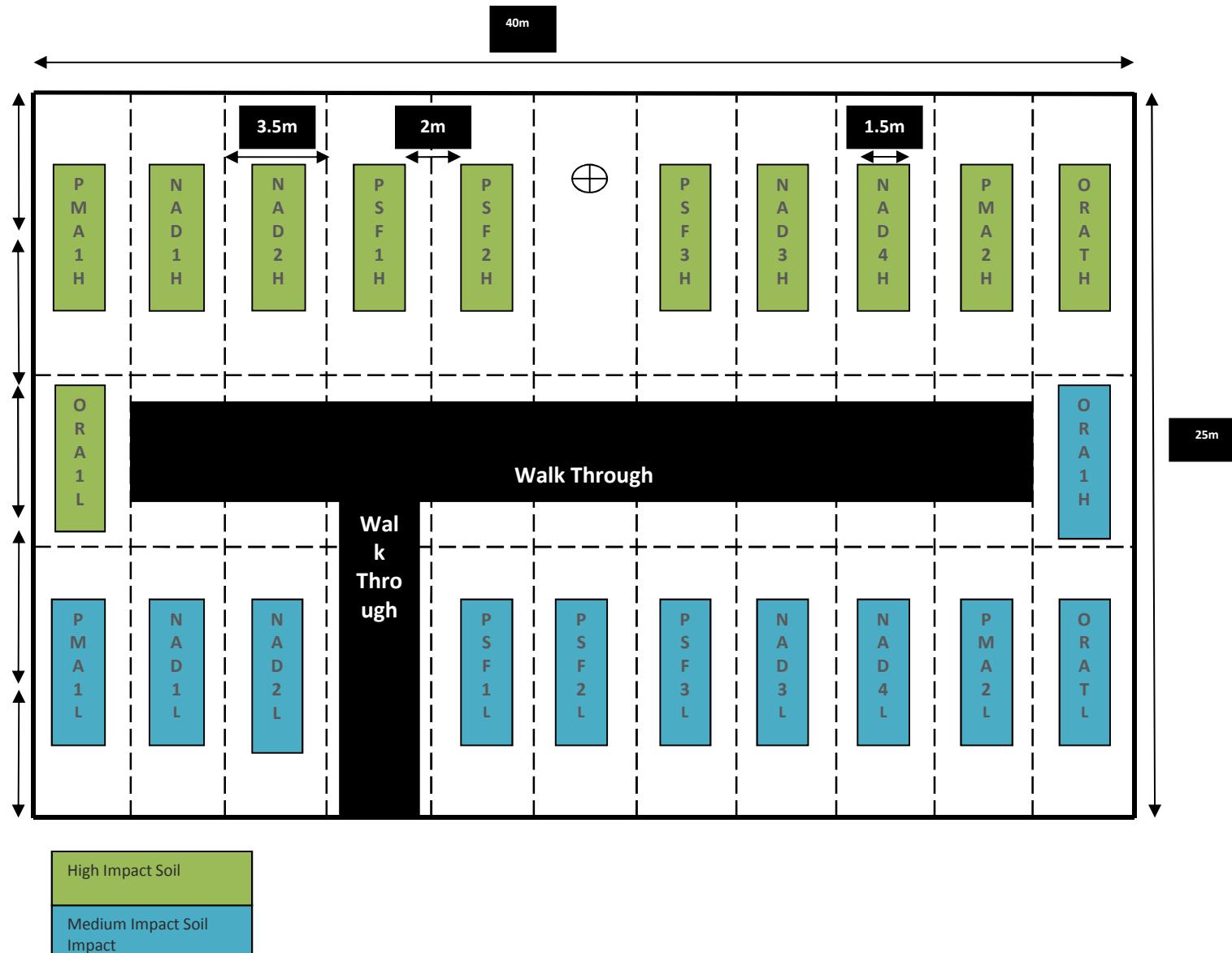
Pilot Trial Methodology

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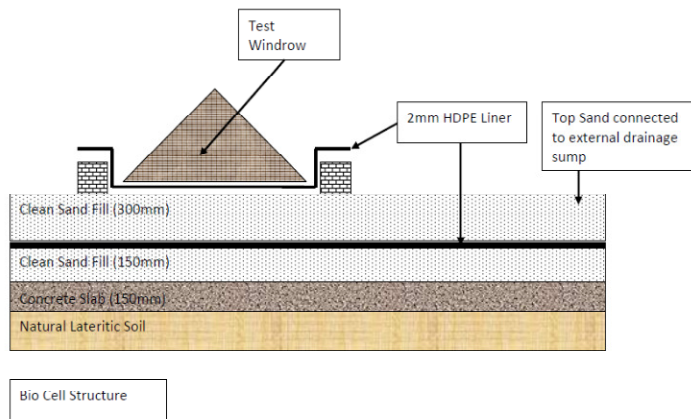
Pilot Trial - Methodology

- Initial Stockpile Soil Sieving – to remove large lumps of carbonized soil.
- Test Bed Volume Measurement – to ensure consistency between test beds.
- Soil/Crude Oil/Water Mixing – to create “contaminated soil”.
- Form Test Bed within HDPE liner – to prevent leachate migration.
- Initial Day 0 sampling.
- Product Application after initial sampling.
- Windrow Construction.
- Soil Sampling on fixed dates – composite sample of 10 grab samples to reduce variability.
- Windrow breakdown/reconstruction on sampling dates.
- Visits by Regulatory Bodies (NAPIMS, NOSDRA, DPR, RSMEnv)
- All analysis by Alcontrol Laboratory UK.
- Final Report Reviewed and approved by Shell Global Solutions.

Bio Cell Layout – Pilot Trial



Pilot Trial Pictures



■ Bio Cell Structure



■ Crude Oil - Delivery



■ Stockpile Soil Sieving



■ Test Bed Box - Volume control

Pilot Trial - Pictures



■ Test Bed Layout



■ Crude Oil Spiking of Sieved Soil



■ Product Application



■ Initial Sampling

Pilot Trial - Pictures



■ Visit by Shell Global Solutions Int'l



■ Visit by Regulatory Agencies



■ Product application



■ Visit by Regulatory Agencies

Pilot Trial Results

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Sieved Soil and Bioremediation Potential

Sieved Soil	pH	Total Organic Matter	Total Heterotrophic Bacteria	Total Heterotrophic Fungi
	7.59	66g/kg	2960000 (CFU/g)	500000 (CFU/g)

The high organic matter content, heterotrophic bacteria and fungi counts indicate the host sieved soil, prior to crude oil spiking, had more than sufficient microbial activity to support bio-degradation.

Carbon Dioxide and Oxygen

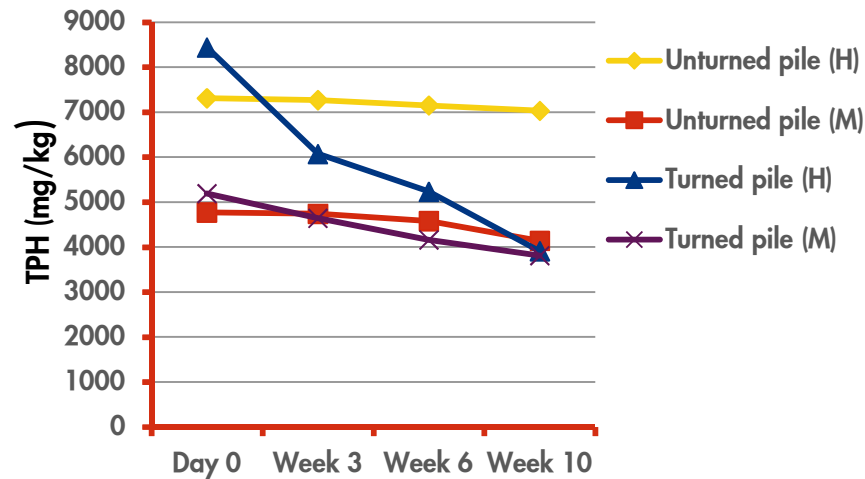
TEST CODE	Type	Average CO ₂ (%)	Average O ₂ (%)
NAD1	Nutrient Amendment	5.6	14.3
PMA1	Microbial additive	3.4	16.8
NAD2	Enzyme/Nutrient Additive	2.9	17
PSF3	Surfactant & Nutrient Amendment	2.4	17.4
PSF1	Surfactant & Nutrient Amendment	2.1	17.7
NAD4	NPK Fertilizer 2 (C:N:P 100:10:2)	1.7	18.2
NAD3	NPK Fertilizer 1 (C:N:P 100:48:11)	1.7	18.2
PSF2	Surfactant	1	18.8
PMA2	Microbial Stimulant	0.6	19.1
ORAT	Turned Control	0.5	19.3
ORA	Static Control	0.2	19.7

Environmental Parameters

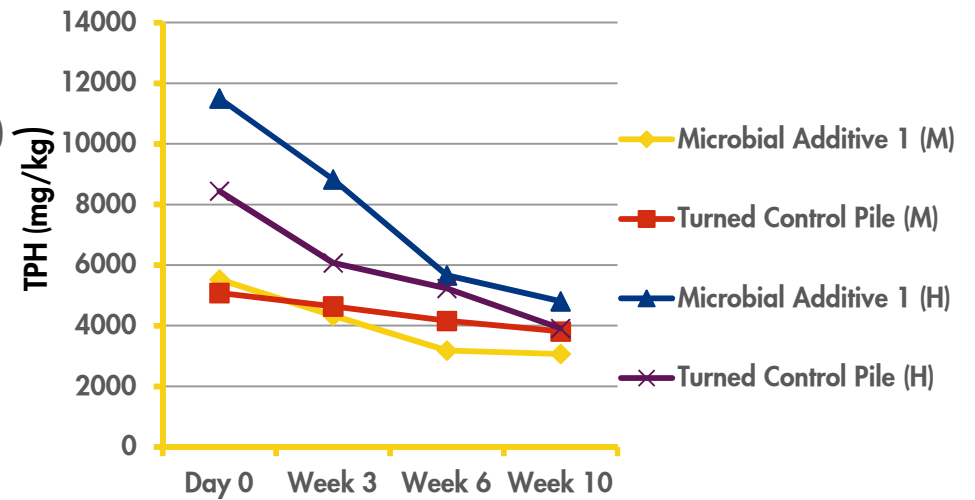
TEST CODE	Type	pH		Moisture Content (%)		Temperature (°C)	
		Average	Minimum - Maximum	Average	Minimum - Maximum	Average	Minimum - Maximum
PMA1	Microbial additive	7.62	7.33 - 8.08	13.91	9.7 - 19	30.08	26.7 - 35.6
PSF3	Surfactant & Nutrient Amendment	7.81	7.38 - 8.19	13.44	8.5 - 17.0	29.37	27.0 - 33.8
NAD1	Nutrient Ammendment	7.45	6.88 - 7.74	13.34	9.1 - 20.0	31.47	28.2 – 36.1
PMA2	Microbial Stimulant	7.63	6.58 - 8.69	16.19	12.0 - 20.0	29	26.0 - 32.8
NAD2	Enzyme/Nutrient Additive	7.57	7.16 - 7.91	14.6	8.7 - 18.0	29.5	26.7 - 33.2
PSF2	Surfactant	7.58	7.27 - 8.07	14.86	9.7 - 19.0	28.51	26.1 - 32.1
PSF1	Surfactant & Nutrient Amendment	7.32	6.34 – 8.12	15.13	11.0 - 19.0	29.65	26.0 - 34.5
NAD3	NPK Fertilizer 1 (C:N:P 100:48:11)	7.61	6.21 - 8.69	13.72	8.0 - 18.0	28.93	26.1 - 33.9
NAD4	NPK Fertilizer 2 (C:N:P 100:10:2)	7.42	7.1 - 8.07	15.59	9.4 - 20.0	29.81	23.8 - 35.7
ORAT	Control Turned	7.48	7.1 - 7.82	15.7	9.2 - 19.0	29.16	27.2 - 32.7
ORA	Static Control	7.64	7.02 - 7.91	15.14	7.3 - 20.0	28.88	26.0 - 32.7

Results – TPH Reduction

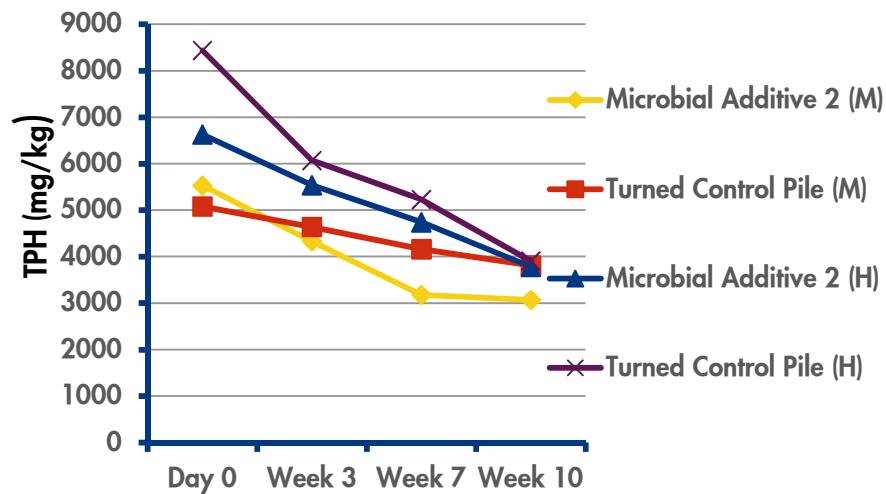
Control Piles (Turned v Static)



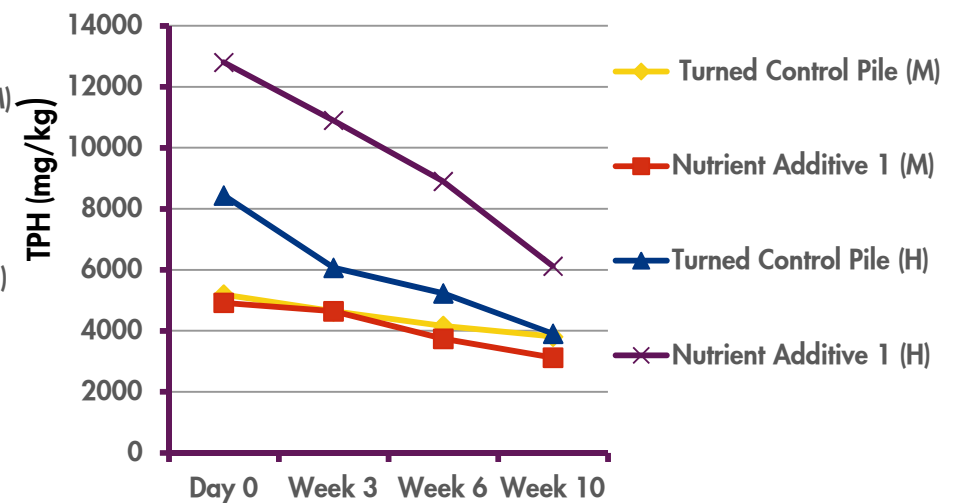
Microbial Additive 1 v Turned Control



Microbial Additive 2 v Turned Control

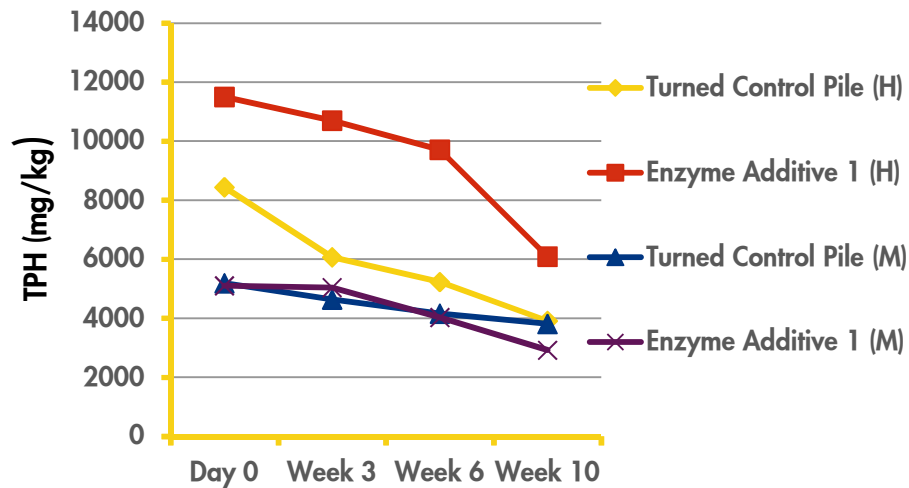


Nutrient Additive 1 v Turned Control

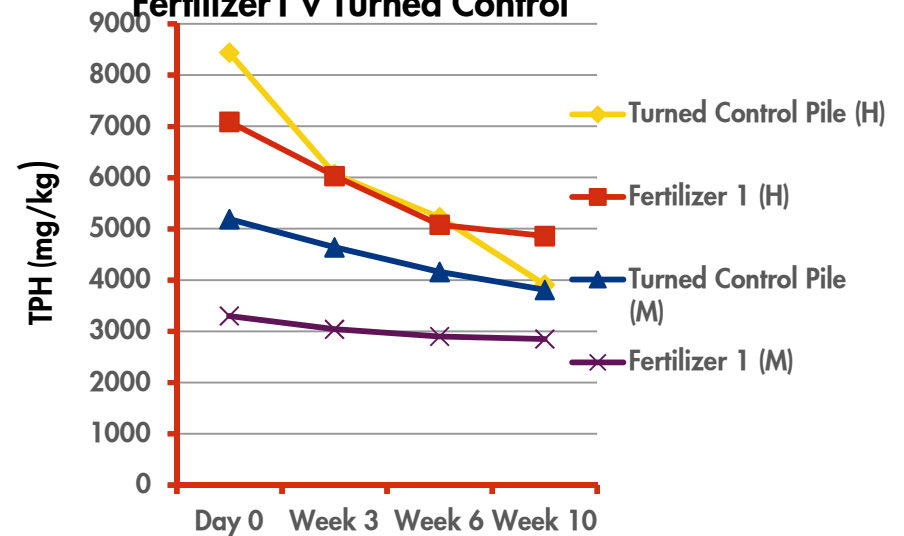


Results – TPH Reduction

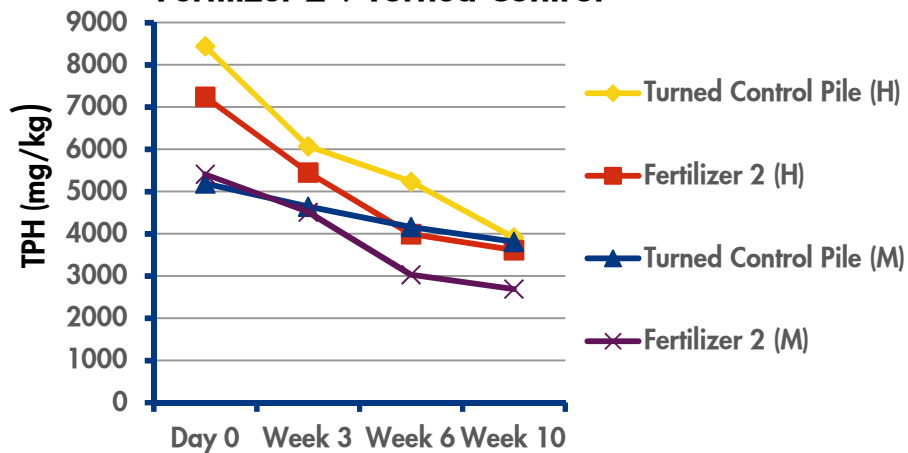
Enzyme Additive 1 v Turned Control



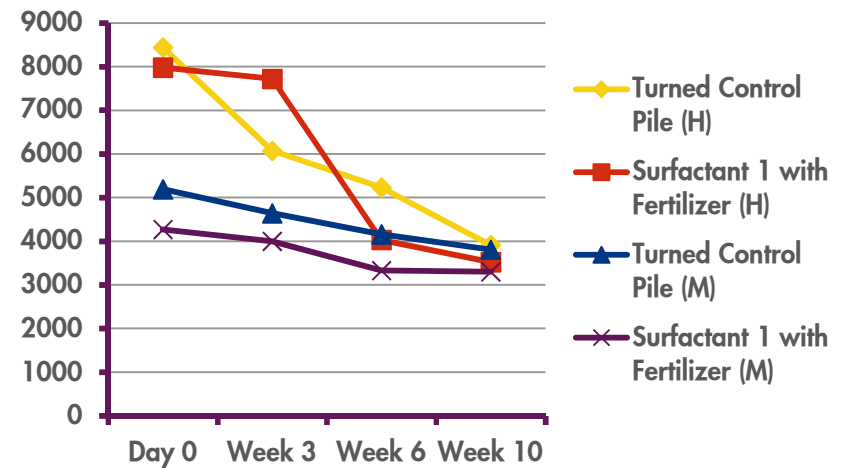
Fertilizer 1 v Turned Control



Fertilizer 2 v Turned Control

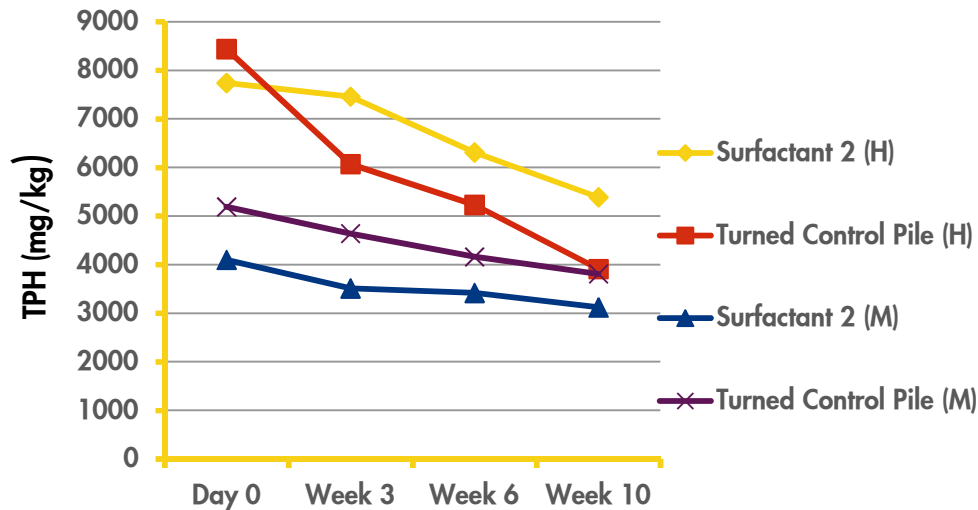


Surfactant 1 & fert. v Turned Control

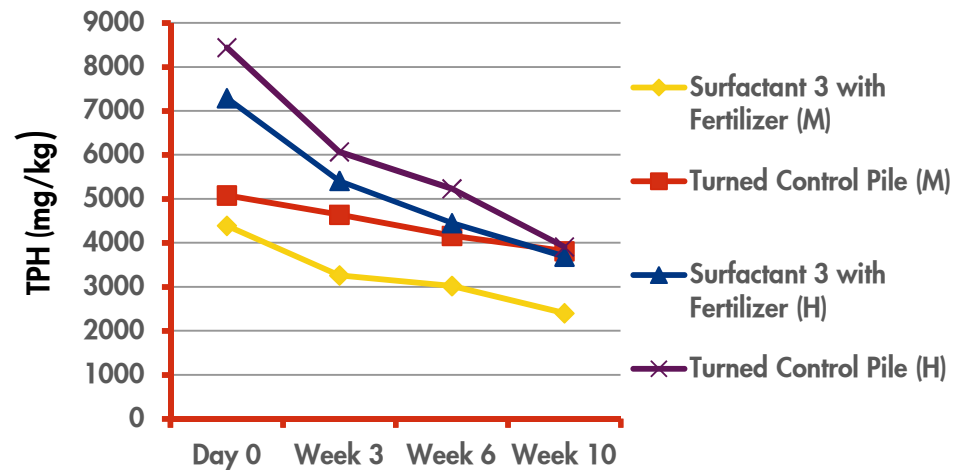


Results – TPH Reduction

Surfactant 2 v Turned Control



Surfactant 3 & fert. v Turned Control



Summary of Results

TEST CODE	Product	Performance ¹
NAD4	Fertilizer 2	11%
PMA1	Microbial additive 1	11%
PSF3	Surfactant 3 & Fertilizer	8%
NAD1	Nutrient Additive 1	5%
NAD2	Enzyme Additive 1	5%
PSF1	Surfactant 1 & Fertilizer	4%
ORAT	Turned Control (No Product)	0%
PMA2	Microbial Additive 2	0%
NAD3	Fertilizer 1	-9%
PSF2	Surfactant 2	-10%
ORA	Static Control (No Product)	-15%

1. Performance better than the Control Turned Test Bed.

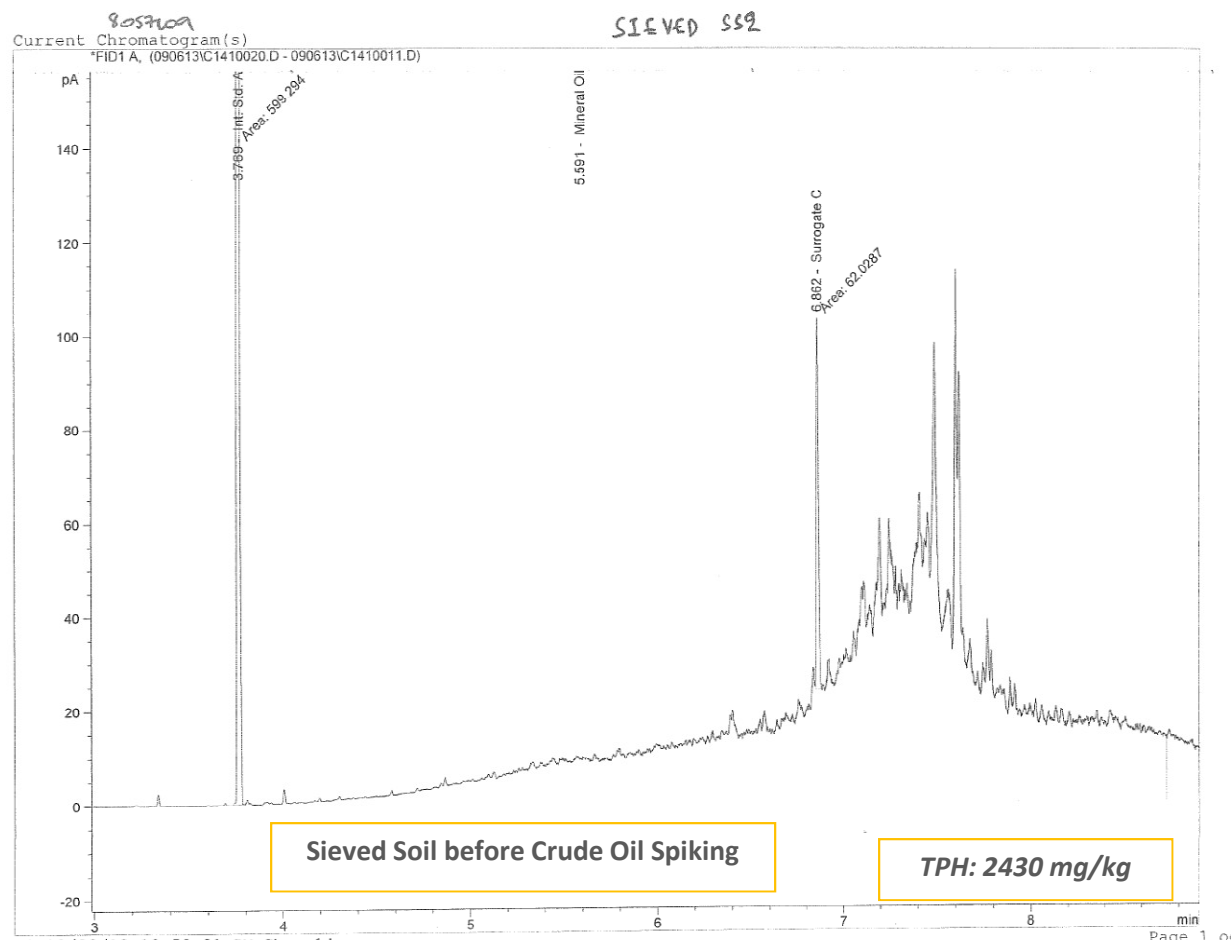
Crude Degradation Analysis

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Host Soil – Carbonized Sand



Host Sieved Soil – Before Crude Oil Spiking

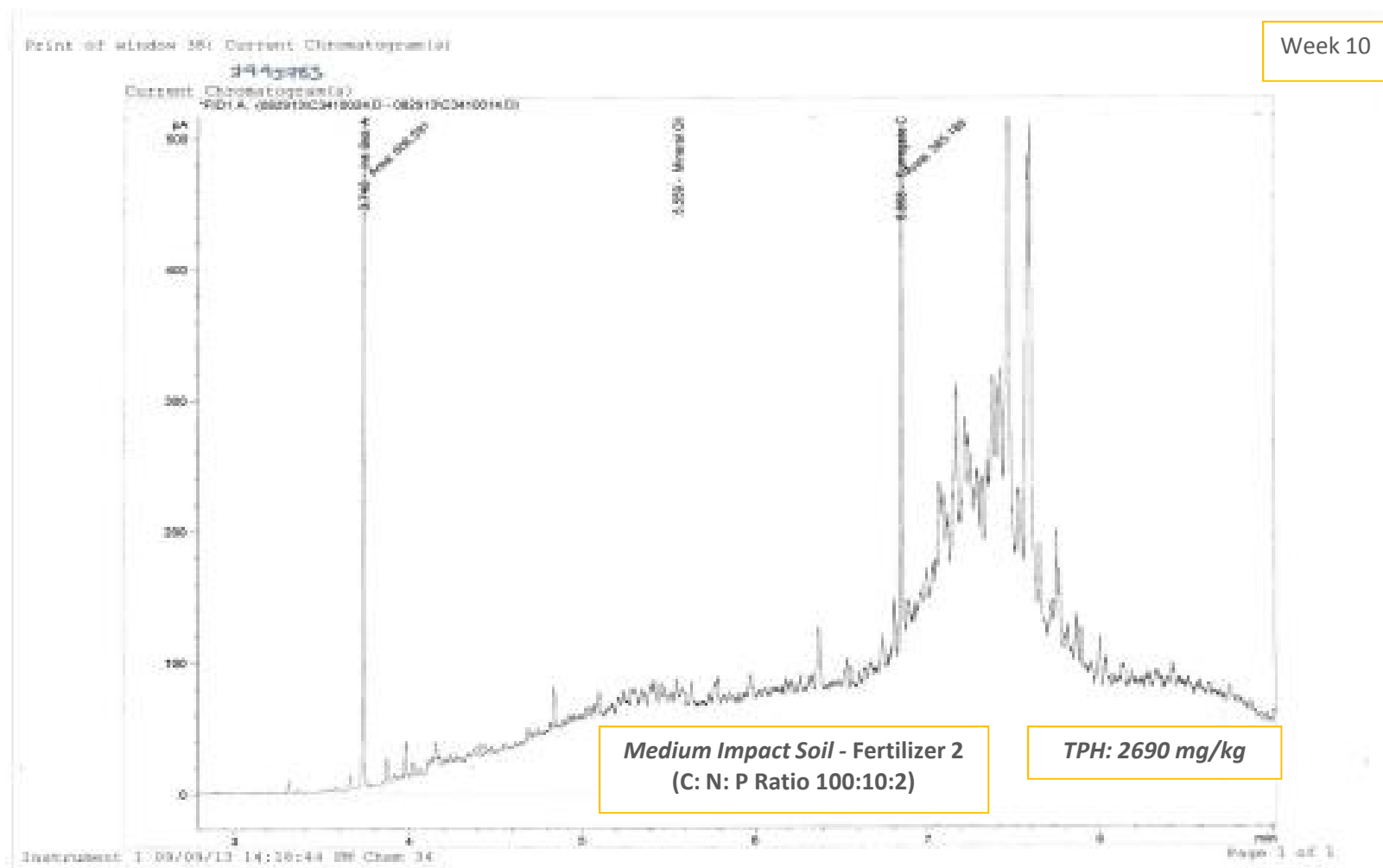


Fertilizer 2 Start of Test



Fertilizer 2 End of Test

Week 10



Cost v Benefit Analysis

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Cost v Benefit Analysis

- The objective of the trial was to determine the value add of new products to the existing land based bio-remediation techniques currently used by SPDC.
- After the technical performance of the products was shared with individual vendors, they were requested to provide indicative costs for supply of products.
- The cost benefit analysis was based on calculating the unit cost for removal of crude oil from soil via bio-remediation using the different additives and the land farming technique. This was based on the actual TPH reduction in each bed, and was not a relative measure.
- Costing were based on a typical 1 Hectare remediation site, using NAPIMS approved rates for land farming to provide the base cost, with no additives.
- The quantities of product to be used on a typical 1 Hectare remediation site was provided by the vendors, scaled up from the pilot trial quantities.

Product Requirements for Typical One Hectare Site

Unit Cost Rates				Product Requirement Medium Impact - 10,000m2 (0.3m depth) = 3000m3				Product Requirement High Impact - 10,000m2 (0.3m depth) = 3000m3			
Product	Nature of product	Indicative Price		Scaled up Total Product(s) requirement	Cost of Product required (USD)		Total Product Cost (USD)	Scaled up Total Product(s) requirement	Cost of Product required (USD)		Total Product Cost (USD)
		Cost Powder/Granules [USD]	Cost Liquid (Litres) [USD]		Powder/Granules	Liquid			Powder/Granules	Liquid	
Microbial additive 1	Powdery	\$12 per Kg		42.7 Tonnes	511992		511,992	84 Tonnes	1008000		1,008,000
Microbial Additive 2	Granules & liquid	\$2.3 per Kg	\$1.25 per litre	16.7 Tonnes & 133333L liquid	38331.8	166668	204,999	33.3 Tonnes & 333333L liquid	76668.2	416668	493,336
Nutrient Additive 1	Powdery	\$58.8 per Kg		15.2 Tonnes	893760		893,760	30.4 Tonnes	1787520		1,787,520
Enzyme Additive 1	Liquid		\$32.5 per litre	1333L		43355	43,355	4000L		130000	130,000
Fertilizer 1	Granules	\$1 per kg fertilizer		15.5 Tonnes	15466		15,466	46.7 Tonnes	46666		46,666
Fertilizer 2	Granules	\$1 per kg fertilizer		3.7 Tonnes	3734		3,734	11.2 Tonnes	11200		11,200
Surfactant 1 & Fertilizer	Liquid & fertilizer granules	\$1 per kg fertilizer	\$19 per litre	2000 L & 2.7 Tonnes NPK 30:10:10 fertilizer	2666	38000	40,666	6000 L & 8 Tonnes NPK 30:10:10 fertilizer	8000	114000	122,000
Surfactant 2	Liquid		\$14.25 per litre	13333 L		190010	190,010	13333 L		190010	190,010
Surfactant 3 & Fertilizer	Liquid &fertilizer granules	\$1 per kg fertilizer	\$4.03 per litre	12000 L & 2.7 Tonnes NPK fertilizer	2666	48360	51,026	18000 L & 2.7 Tonnes NPK fertilizer	2666	72540	75,206

Average Cost to Remove 1 Kg of Crude Oil

Product	CODE	Impact	Total Mass Oil Reduction (kg) per windrow	Calculated Total Mass Oil Reduction (kg) per Ha	NAPIMS Base Cost per Ha (F\$)	Product Cost per Ha (F\$)	Total Cost per Ha (F\$)	Unit Cost per Kg Mass Oil Reduction (F\$)	Av. Cost per Kg Mass Oil Reduction (F\$)
Fertilizer 2	NAD4	High	10.13	13504	68000	11200	79200	5.9	6
		Medium	7.59	10118	68000	3734	71734	7.1	
Turned Control	ORAT	High	12.64	16852	68000	0	68000	4.0	9
		Medium	3.54	4724	68000	0	68000	14.4	
Enzyme Additive 1	NAD2	High	15.09	20125	68000	130000	198000	9.8	12
		Medium	6.08	8110	68000	43355	111355	13.7	
Surfactant 3 & Fertilizer	PSF3	High	10.04	13392	68000	75206	143206	10.7	13
		Medium	5.55	7403	68000	51026	119026	16.1	
Surfactant 1 & Fertilizer	PSF1	High	12.44	16591	68000	122000	190000	11.5	21
		Medium	2.71	3608	68000	40666	108666	30.1	
Fertilizer 1	NAD3	High	6.22	8296	68000	46666	114666	13.8	32
		Medium	1.26	1674	68000	15466	83466	49.9	
Microbial Additive 2	PMA2	High	7.95	10602	68000	493336	561336	52.9	49
		Medium	4.52	6026	68000	204999	272999	45.3	
Surfactant 2	PSF2	High	6.56	8742	68000	190010	258010	29.5	50
		Medium	2.73	3646	68000	190010	258010	70.8	
Microbial additive 1	PMA1	High	18.67	24887	68000	1008000	1076000	43.2	53
		Medium	6.86	9151	68000	511992	579992	63.4	
Nutrient Additive 1	NAD1	High	18.64	24850	68000	1787520	1855520	74.7	109
		Medium	5.02	6696	68000	893760	961760	143.6	

Summary of Findings

- The current bio-remediation land farming method employed by SPDC for land spills is effective at reducing TPH concentrations.
- Six of the nine products being tested produced more degradation than the turned control, the rest the same or less degradation. The greatest additional degree of degradation over control was +11% the worst was -10%.
- Two products recorded 11%; these were a standard NPK fertilizer and microbial additive 1.
- For fertilizer nutrient amendment the proper C:N:P ratio is a critical factor and is TPH specific.
- In terms of cost benefit only the standard NPK fertilizer delivers real value to the standard remediation process, all other products add no value, just increased costs.

Fixation

Carbonized Soil

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Fixation of Carbonized Sand

■ Fixation Process

1. Carbonized gravel, cobbles and boulders crushed down to sand and fine gravel size particles.
2. Mixed carbonized sand in correct ratio with sand, cement and water.
3. Fix into blocks using molding machines
4. Take test cubes for analysis
5. Store blocks for curing

■ Testing Process

1. DPR- Crushing Strength $> 200\text{lb/in}^2$
2. DPR- Durability Testing – no loss in 10 cycles
3. DPR - Leachate Analysis

■ Results

1. All cubes passed DPR testing criteria

Carbonized Sand Fixation Test Results

Toxicity Characterisric Leaching Procedure Test (TCLP)					DPR Limit
Sample	A1	A2	B2	C3	
Chloride (mg/l)	1,273	1,826	1,716	1,882	5,000
Total Chromium (mg/l)	2.7	2.8	2.8	2.8	5
Cadium (mg/l)	0.2	<0.10	<0.10	<0.10	1
Lead (mg/l)	<1.00	<1.00	<1.00	<1.00	5
Zinc (mg/l)	<0.50	<0.50	<0.50	<0.50	50
Arsenic (mg/l)	<0.50	<0.50	<0.50	<0.50	5
Mercury (mg/l)	<0.50	<1.00	<1.00	<2.00	0.2
Silver (mg/l)	<1.00	<2.00	<2.00	<2.00	5
Barium (mg/l)	<2.00	<2.00	<2.00	<2.00	100
Selenium (mg/l)	<0.50	<0.50	<0.50	<0.50	1
Oil and Grease (mg/l)	<1.00	<1.00	<1.00	<1.00	100

STRENGTH TEST	Units	DPR Criteria	A1	A2	B1	C2	D1
Weight	Kg	-	5.992	6.014	6.232	6.302	6.358
Density	Kg/m ³	-	1775	1782	1847	1867	1884
Crushed	kN	-	200	200	270	260	215
Strength	N/mm ²	1.4	8.89	8.89	12	11.56	9.56
	lb/in ²	200	1271.27	1271.27	1716	1653.08	1367.08
Size of Cubes	mm	-	150*150*150	150*150*150	150*150*150	150*150*150	150*150*150

Fixation of Carbonized Soils



Fixing Carbonized Sand



Blocking Warehouse



Finished Blocks



Test Cubes



Back Up