



National Spill Control School

College of Science and Technology, Corpus Christi State University

September 28, 1993

Mr. John Miller
Resource Manager
Padre Island National Seashore
9405 South Padre Island Drive
Corpus Christi, Texas 78418

Dear John:

Enclosed is a report on the "Hydrocarbon Baseline Project" to date. All of the sampling for TPH has been done and the analytical results are included. We were able to sample a significantly greater number of sites than originally planned. Equipment problems have delayed the gas chromatograph analyses. However, we will analyze those samples showing significant hydrocarbon contamination by gas chromatography using those samples already collected where they have not exceeded the recommended holding time and resampling any that have exceeded the holding time. I am anticipating that this work will be done primarily during October and a final report on these samples can be turned in soon thereafter, but no later than December 31, 1993.

I am requesting that based on this report a payment of 85% of the total project funding be approved. This will allow us to meet expenses applicable to this project.

If you have any questions concerning the results or the remaining work on the project, please contact me.

Sincerely,

Steven S. Barnes
Director

**PADRE ISLAND NATIONAL SEASHORE
INVESTIGATORS ANNUAL REPORT - 1993**

Project Title:

Padre Island National Seashore Hydrocarbon Baseline Study
Report

Field of Study:

Geochemistry

Principle Investigator:

Dr. Steven S. Barnes
National Spill Control School
Texas A&M university - Corpus Christi
6300 Ocean Drive
Corpus Christi, Texas 78412

Co-investigators:

David Jensen
Roy Coons

Estimated Funding:

\$9500 National Park Service
\$3500 National Spill Control School
Texas A & M University at Corpus Christi

Date Started	Anticipated End	Percent Done
10/1/93	12/31/93	90 %

Project Objectives:

In the event of future oil spills it is essential for proper damage assessment to have a baseline of existing hydrocarbon concentrations in soils. This study is designed to provide that baseline for selected environments on Padre Island National Seashore.

Progress to Date:
On-going

Significant Findings:

Three samples were taken at each site and analyzed for Total Petroleum Hydrocarbons (TPH) by Method 9071 taken from EPA publication SW 846. A full listing of this method and the sampling methodology is attached as Appendix A.

A summary of results is given below.

LOCATION	% MOISTURE	Individual TPH mg/Kg	AVERAGE TPH mg/Kg
Yarborough Pass	18.55 %	348	356
	18.75 %	357	
	18.87 %	365	
Novilla Camp	20.46 %	334	360
	20.71 %	436	
	20.78 %	311	
Dagger Hill	20.78 %	340	318
	19.48 %	318	
	20.37 %	296	
1/4 mile south of Dagger Hill	19.43 %	328	324
	18.52 %	305	
	18.92 %	340	
1/2 mile south of Dagger Hill	23.08 %	350	319
	20.83 %	310	
	19.70 %	298	
3/4 mile south of Dagger Hill	17.69 %	341	667
	23.19 %	1660	
	20.55 %	93	
1 mile south of Dagger Hill	27.40 %	61	57
	22.45 %	52	
	30.20 %	57	
1 1/4 miles south of Dagger Hill	21.06 %	125	807
	22.74 %	990	
	20.58 %	1307	
1 1/2 miles south of Dagger Hill	25.00 %	1238	576
	22.98 %	341	
	21.28 %	150	
1 3/4 miles south of Dagger Hill	22.15 %	206	135
	22.26 %	136	
	23.10 %	63	
2 miles south of Dagger Hill	22.27 %	58	56
	21.49 %	59	
	22.07 %	51	
2 1/4 miles south of Dagger Hill	22.91 %	116	109
	20.59 %	95	
	20.93 %	117	
2 1/2 miles south of Dagger Hill	23.53 %	61	78
	20.41 %	93	
	21.54 %	81	

2 3/4 miles south of Dagger Hill	21.12 % 22.36 % 20.17 %	90 130 80	100
3 miles south of Dagger Hill	22.19 % 30.27 % 21.63 %	74 113 98	95
3 1/4 miles south of Dagger Hill	22.26 % 19.65 % 20.52 %	80 82 117	93
3 1/2 miles south of Dagger Hill	22.71 % 21.54 % 21.59 %	87 61 72	73
3 3/4 miles south of Dagger Hill	22.40 % 20.93 % 21.63 %	66 60 81	69
4 miles south of Dagger Hill	22.66 % 21.63 % 20.10 %	120 78 44	81
4 1/4 miles south of Dagger Hill	21.22 % 17.45 % 21.38 %	78 61 66	68
Chevron Site	14.67 % 12.78 % 14.45 %	35,415 37,275 36,605	36,431
4 1/2 miles south of Dagger Hill	20.51 20.68 20.09	96 101 60	86
4 3/4 miles south of Dagger Hill	20.70 22.26 20.25	56 55 51	54
5 miles south of Dagger Hill	20.77 54.02 77.63	51 81 323	152
5 1/4 miles south of Dagger Hill	72.76 69.96 24.02	201 289 52	181
5 1/2 miles south of Dagger Hill	20.07 20.50 21.75	66 72 76	71
1 mile north of Dagger Hill	28.49 25.31 22.40	66 71 16	51

2 miles north of Dagger Hill	23.16	407	170
	22.95	63	
	22.61	41	
3 miles north of Dagger Hill	23.81	31	30
	23.51	24	
	23.68	34	
4 miles north of Dagger Hill	22.24	27	44
	22.85	30	
	20.62	75	
5 miles north of Dagger Hill	20.34	41	47
	20.90	92	
	20.21	7	

Lowest values range from 30 to 135 mg/Kg dry weight. The Texas Natural Resource Conservation Commission requires that all contaminated sites be cleaned up to the 100 mg/Kg level. Therefore, this group of samples would appear to represent a good background level for TPH in the samples analyzed to date. There is another grouping of samples in the range of 320 to 360 mg/Kg which would appear to indicate moderate contamination is present at this time. The third group of samples with much greater contamination has average values ranging from 576 to 807. Individual samples show a much greater variability as the average concentration increases. This is attributed to an inhomogeneity in the samples with possibly the presence of small tar balls rather than analytical problems. The Chevron site is a known contaminated site and the results here are not surprising. The fact that all three samples are giving similar results tends to verify the methodology. All data is included in Appendix B.

All sampling and analyses were done by Mrs. Shari Hollyfield.

APPENDIX A

Sampling Procedure

Sampling Device

A glass bottle 9 cm deep was used. The bottle was cleaned and then rinsed in Freon. A piece of aluminum foil was placed over top to act as an inert barrier between sample and lid.

Sampling Procedure

Three individual samples were taken within a radius of approximately 25 cm at each site. The jar was placed on the top of the sediments and while exerting pressure, use a screwing motion until one sees the sediments in the bottom of the jar. Then scoop the sediments away along side of the sample bottle till the top is met and place finger over top and remove. Place the aluminum foil back over the top of jar and seal with lid tightly. Place immediately into an ice chest submerged in the ice. Upon return to laboratory place in freezer until time of extraction. Sample may be stored up to 14 days.

Analytical Method

The method used for the extraction of hydrocarbons from the sediment samples was from SW 846, 9071.

Reagents

1. Concentrated hydrochloric acid.
2. Magnesium sulfate monohydrate: To prepare $\text{MgSO}_4 \cdot \text{H}_2\text{O}$, spread a thin layer of MgSO_4 in a dish and dry overnight in an oven at 150°C .
3. Trichlorotrifluoroethane (1,1,2-trichloro-1,2,2,-trifluoroethane).
4. Silica gel, 100 to 200 mesh (dried at 110°C for 24 hours).

Sample collection, Preservation, and Handling

1. No plastic of any type should be used throughout the procedures and assemblies.
2. Samples were taken using glass bottles that extended to a depth of 8cm and were prepared by rinsing with trichlorotrifluoroethane and placing aluminum foil over the top of the bottle.
3. Immediately after obtaining the samples, they should be placed on ice and then transferred to a freezer for no longer than a 2 week period from the time of sample collection.

Procedure

1. Weigh out $20 \pm 0.5\text{g}$ of the wet sediment sample (with a dry solid content known) and place in a 250mL beaker.
2. Acidify sample to a pH of 2 by using approximately 0.3mL of concentrated HCl.
3. Then add 25g of prepared $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ stir with a glass rod until thoroughly combined. Then let stand until the substance has solidified, approximately 15 minutes.

4. Remove any solids and grind the sediments into fine powder using a mortar.
5. Carefully add the powder to the paper extract thimble.
6. Wipe the beaker and mortar with pieces of filter paper moistened with solvent and add to the thimble.
7. Place glass wool or glass beads in the thimble.
8. Extract in Soxhlet apparatus using trichlorotrifluoroethane at a rate of 20 cycles/hr for 4 hours.
9. When solvent returns to room temperature measure the volume and filter through silica gel.
10. Bring to 200mL volume by adding trichlorotrifluoroethane and rinsing the silica gel with this volume.
11. Sample is then stored in a amber glass bottle with a teflon coated lid, and sealed with parafilm until time of analysis.

IR Analysis

1. To set the baseline, trichlorotrifluoroethane was added to two each matched path length silica cuvettes and placed into the holders located in IR sample compartment.
2. Immediately scan from 3200 cm_1 to 2700 cm_1 on the 3 minute scan setting. A shield must be placed between the source and the sample compartment to retard possible vaporization of the extraction solvent in the cuvettes.
3. After flushing the sample cuvette with Freon solvent, fill with sample and scan again from 3200 cm_1 to 2700 cm_1 .
4. To measure the net absorbance a straight line over the scan range and measuring the transmittance of peak maximum and subtracting base-line transmittance at that point. Then the logarithm is taken of this sum to obtain the net absorbance.

Determination of percent moisture

1. Immediately after weighing the sample for extraction, weigh out 5-10g of the sample into a dry dish and place in an oven at 105° C overnight.
2. Allow sample to cool in a desiccator before weighing.
3.
$$\frac{\text{g of sample} - \text{g of dry sample}}{\text{g of sample}} \times 100 = \% \text{ moisture}$$

Calculations used

1. Beer-Lambert Law

$A = abc$ where,

A = absorbance

a = absorptivity(slope)

b = path length of cell

c = concentration

Through manipulation of this formula the concentration was obtained.

2. TPH

1 mL = concentration of sample

$$\text{TPH} = c(\text{mgmL}^{-1}) \times 200\text{ml}$$

3. Weight of the Water

$$\frac{\text{g of wet sample} \times \% \text{moisture}}{100 \%} = \text{g of H}_2\text{O}$$

4. Dry weight of the sample

$$\text{g of wet sample} - \text{g of H}_2\text{O} = \text{g of dry sample}$$

5. TPH dry weight

$$\frac{\text{mg of TPH}}{\text{kg of dry sample}} = \text{mg TPH kg}^{-1}$$

Detection limit is 10 ppm.

APPENDIX B

Sam- ple #	Absor- bance	Conc. mg/mL	TPH mg	Wet wt (g)	% Moi- sture	Dry wt (g)	TPH Drywt mg/kg
<u>2</u>	0.3366	0.0293	5.860	20.21	18.75	16.42	356.88
<u>3</u>	0.3462	0.0301	6.020	20.34	18.87	16.50	364.85
<u>4</u>	0.3149	0.0274	5.480	20.42	20.46	16.42	33.74
<u>5</u>	0.4053	0.0352	7.040	20.35	20.71	16.14	436.18
<u>6</u>	0.2895	0.0252	5.040	20.46	20.78	16.21	310.92
<u>7</u>	0.3139	0.0273	5.460	20.25	20.78	16.04	340.39
<u>8</u>	0.3001	0.0261	5.220	20.35	19.48	16.39	318.49
<u>9</u>	0.2773	0.0241	4.820	20.42	20.37	16.26	296.43
<u>10</u>	0.3079	0.0268	5.360	20.30	19.43	16.36	327.63
<u>11</u>	0.2914	0.0253	5.060	20.39	18.52	16.61	304.64
<u>12</u>	0.3230	0.0281	5.620	20.37	18.92	16.52	340.19
<u>13</u>	0.3149	0.0274	5.480	20.36	23.08	15.66	349.94
<u>14</u>	0.2885	0.0251	5.020	20.46	20.83	16.20	309.88
<u>15</u>	0.2829	0.0246	4.920	20.47	19.70	16.44	298.44
<u>16</u>	0.3261	0.0284	5.680	20.24	17.69	16.66	340.94
<u>17</u>	0.1199	0.0129	25.80	20.23	23.19	15.54	1660.23
<u>18</u>	0.0468	0.0075	1.500	20.29	20.55	16.12	93.05
<u>19</u>	0.0412	0.0045	0.9000	20.43	27.40	14.83	60.69
<u>20</u>	0.0379	0.0041	0.8200	20.39	22.45	15.81	51.87
<u>21</u>	0.0373	0.0040	0.8000	20.08	30.20	14.02	57.06
<u>22</u>	0.0931	0.0101	2.020	20.45	21.06	16.14	125.15

<u>Sam- ple #</u>	<u>Absor- bance</u>	<u>Conc. mg/mL</u>	<u>TPH mg</u>	<u>Wet wt (g)</u>	<u>% Moi- sture</u>	<u>Dry wt (g)</u>	<u>TPH Drywt mg/kg</u>
<u>23</u>	0.0712	0.0077	15.40	20.14	22.74	15.56	989.72
<u>24</u>	0.0985	0.0106	21.20	20.42	20.58	16.22	1307.03
<u>25</u>	0.0880	0.0095	19.00	20.47	25.00	15.35	1237.79
<u>26</u>	0.2455	0.0265	5.300	20.15	22.98	15.52	341.49
<u>27</u>	0.1105	0.0119	2.380	20.13	21.28	15.85	150.16
<u>28</u>	0.1498	0.0162	3.24	20.23	22.15	15.75	205.71
<u>29</u>	0.1001	0.0108	2.160	20.40	22.26	15.86	136.19
<u>30</u>	0.0458	0.0049	0.9800	20.32	23.10	15.63	62.70
<u>31</u>	0.0429	0.0046	0.9200	20.31	22.27	15.79	58.26
<u>32</u>	0.0435	0.0047	0.9400	20.29	21.49	15.93	58.26
<u>33</u>	0.0373	0.0040	0.8000	20.33	22.07	15.84	50.51
<u>34</u>	0.0843	0.0091	1.820	20.34	22.91	15.69	115.99
<u>35</u>	0.0715	0.0077	1.540	20.35	20.59	16.16	95.29
<u>36</u>	0.0868	0.0094	1.880	20.39	20.93	16.12	116.63
<u>37</u>	0.0435	0.0047	0.9400	20.19	23.53	15.44	60.88
<u>38</u>	0.2859	0.0309	618.0	20.45	14.67	17.45	35415.47
<u>39</u>	0.3060	0.0331	662.0	20.36	12.78	17.76	37274.77
<u>40</u>	0.2929	0.0317	634.0	20.25	14.45	17.32	36605.08
<u>41</u>	0.0358	0.0058	1.500	20.23	20.41	16.10	93.17
<u>42</u>	0.0399	0.0064	1.280	20.23	21.54	15.87	80.66
<u>43</u>	0.0442	0.0071	1.420	20.05	21.12	15.82	89.76
<u>44</u>	0.0636	0.0102	2.040	20.24	22.36	15.71	129.85

<u>Sam- ple #</u>	<u>Absor- bance</u>	<u>Conc. mg/mL</u>	<u>TPH mg</u>	<u>Wet wt (g)</u>	<u>% Moi- sture</u>	<u>Dry wt (g)</u>	<u>TPH Drywt mg/kg</u>
<u>45</u>	0.0405	0.0065	1.300	20.29	20.17	16.20	80.25
<u>46</u>	0.0368	0.0059	1.180	20.40	22.19	15.87	74.35
<u>47</u>	0.0489	0.0079	1.580	20.06	30.27	13.99	112.94
<u>48</u>	0.0479	0.0077	1.540	20.11	21.63	15.76	97.72
<u>49</u>	0.0389	0.0063	1.260	20.32	22.26	15.80	79.75
<u>50</u>	0.0415	0.0067	1.340	20.23	19.65	16.25	82.46
<u>51</u>	0.0587	0.0095	1.900	20.42	20.52	16.23	117.07
<u>52</u>	0.0421	0.0068	1.360	20.25	22.71	15.65	86.90
<u>53</u>	0.0306	0.0049	.9800	20.41	21.54	16.01	61.21
<u>54</u>	0.0353	0.0057	1.140	20.19	21.59	15.83	72.02
<u>55</u>	0.0322	0.0052	1.040	20.34	22.40	15.78	65.91
<u>56</u>	0.0296	0.0048	0.9600	20.12	20.93	15.91	60.34
<u>57</u>	0.0394	0.0064	1.280	20.23	21.63	15.85	80.76
<u>58</u>	0.0587	0.0095	1.900	20.44	22.66	15.81	120.18
<u>59</u>	0.0384	0.0062	1.240	20.33	21.63	15.94	77.79
<u>60</u>	0.0211	0.0036	0.7200	20.49	20.10	16.37	43.98
<u>61</u>	0.0363	0.0062	1.240	20.26	21.22	15.96	77.69
<u>62</u>	0.0299	0.0051	1.020	20.31	17.45	16.77	60.82
<u>63</u>	0.0315	0.0053	1.060	20.40	21.38	16.04	66.08
<u>64</u>	0.0455	0.0077	1.540	20.12	20.51	15.99	96.31
<u>65</u>	0.0482	0.0081	1.620	20.23	20.68	16.05	100.93
<u>66</u>	0.0289	0.0049	0.0980	20.38	20.09	16.29	60.16

<u>Sam- ple #</u>	<u>Absor- bance</u>	<u>Conc. mg/mL</u>	<u>TPH mg</u>	<u>Wet wt (g)</u>	<u>% Moi- sture</u>	<u>Dry wt (g)</u>	<u>TPH Drywt mg/kg</u>
<u>67</u>	0.0268	0.0045	0.9000	20.09	20.70	15.93	56.49
<u>68</u>	0.0253	0.0043	0.8600	20.23	22.26	15.73	54.62
<u>69</u>	0.0247	0.0042	0.8400	20.47	20.25	16.32	51.47
<u>70</u>	0.0242	0.0041	0.8200	20.39	20.77	16.15	50.77
<u>71</u>	0.0277	0.0038	0.7600	20.37	54.02	9.37	81.11
<u>72</u>	0.0439	0.0074	1.480	20.49	77.63	4.58	93.02
<u>73</u>	0.0326	0.0055	1.100	20.13	72.76	5.48	200.73
<u>74</u>	0.0526	0.0089	1.780	20.46	69.96	6.15	289.43
<u>75</u>	0.0237	0.0040	0.8000	20.29	24.02	15.42	51.88
<u>76</u>	0.0321	0.0054	1.080	20.48	20.07	16.37	65.97
<u>77</u>	0.0342	0.0058	1.160	20.31	20.50	16.15	71.83
<u>78</u>	0.0358	0.0061	1.220	20.40	21.75	15.96	76.44
<u>79</u>	0.0320	0.0048	0.9600	20.49	28.49	14.65	65.53
<u>80</u>	0.0359	0.0054	1.080	20.29	25.31	15.15	71.29
<u>81</u>	0.0085	0.0013	0.2600	20.36	22.40	15.80	16.46
<u>82</u>	0.2098	0.0315	6.300	20.13	23.16	15.47	407.24
<u>83</u>	0.0326	0.0049	0.9800	20.08	22.95	15.47	63.35
<u>84</u>	0.0215	0.0032	0.6400	20.09	22.61	15.55	41.16
<u>85</u>	0.0159	0.0019	0.4800	20.04	23.81	15.27	31.43
<u>86</u>	0.0127	0.0019	0.3800	20.40	23.15	15.60	24.36
<u>87</u>	0.0171	0.0026	0.5200	20.21	23.68	15.42	33.72
<u>88</u>	0.0138	0.0021	0.4200	20.32	22.24	15.80	26.58

<u>Sam- ple #</u>	<u>Absor- bance</u>	<u>Conc. mg/mL</u>	<u>TPH mg</u>	<u>Wet wt (g)</u>	<u>% Moi- sture</u>	<u>Dry wt (g)</u>	<u>TPH Drywt mg/kg</u>
<u>89</u>	0.0159	0.0024	0.4800	20.42	22.85	15.75	30.48
<u>90</u>	0.0406	0.0061	1.220	20.49	20.62	16.26	75.03
<u>91</u>	0.0220	0.0033	0.6600	20.29	20.34	16.16	40.84
<u>92</u>	0.0487	0.0073	1.460	20.12	20.90	15.91	91.77
<u>93</u>	0.0042	0.0006	0.1200	20.45	20.21	16.32	7.353

SAMPLE LOCATION

<u>LOCATION</u>	<u>SAMPLE NUMBERS</u>
Yarborough Pass	1,2,3
Novilla Camp	4,5,6
Dagger Hill	7,8,9
1/4 mile south of Dagger Hill	10,11,12
1/2 mile south of Dagger Hill	13,14,15
3/4 mile south of Dagger Hill	16,17,18
1 mile south of Dagger Hill	19,20,21
1 1/4 miles south of Dagger Hill	22,23,24
1 1/2 miles south of Dagger Hill	25,26,27
1 3/4 miles south of Dagger Hill	28,29,30
2 miles south of Dagger Hill	31,32,33
2 1/4 miles south of Dagger Hill	34,35,36
2 1/2 miles south of Dagger Hill	37,41,42
Chevron site	38,39,40
2 3/4 miles south of Dagger Hill	43,44,45
3 miles south of Dagger Hill	46,47,48
3 1/4 miles south of Dagger Hill	49,50,51
3 1/2 miles south of Dagger Hill	52,53,54
3 3/4 miles south of Dagger Hill	55,56,57
4 miles south of Dagger Hill	58,59,60
4 1/4 miles south of Dagger Hill	61,62,63
4 1/2 miles south of Dagger Hill	64,65,66
4 3/4 miles south of Dagger Hill	67,68,69
5 miles south of Dagger Hill	70,71,72
5 1/4 miles south of Dagger Hill	73,74,75
5 1/2 miles south of Dagger Hill	76,77,78
1 mile north of Dagger Hill	79,80,81
2 miles north of Dagger Hill	82,83,84
3 miles north of Dagger Hill	85,86,87
4 miles north of Dagger Hill	88,89,90
5 miles north of Dagger Hill	91,92,93