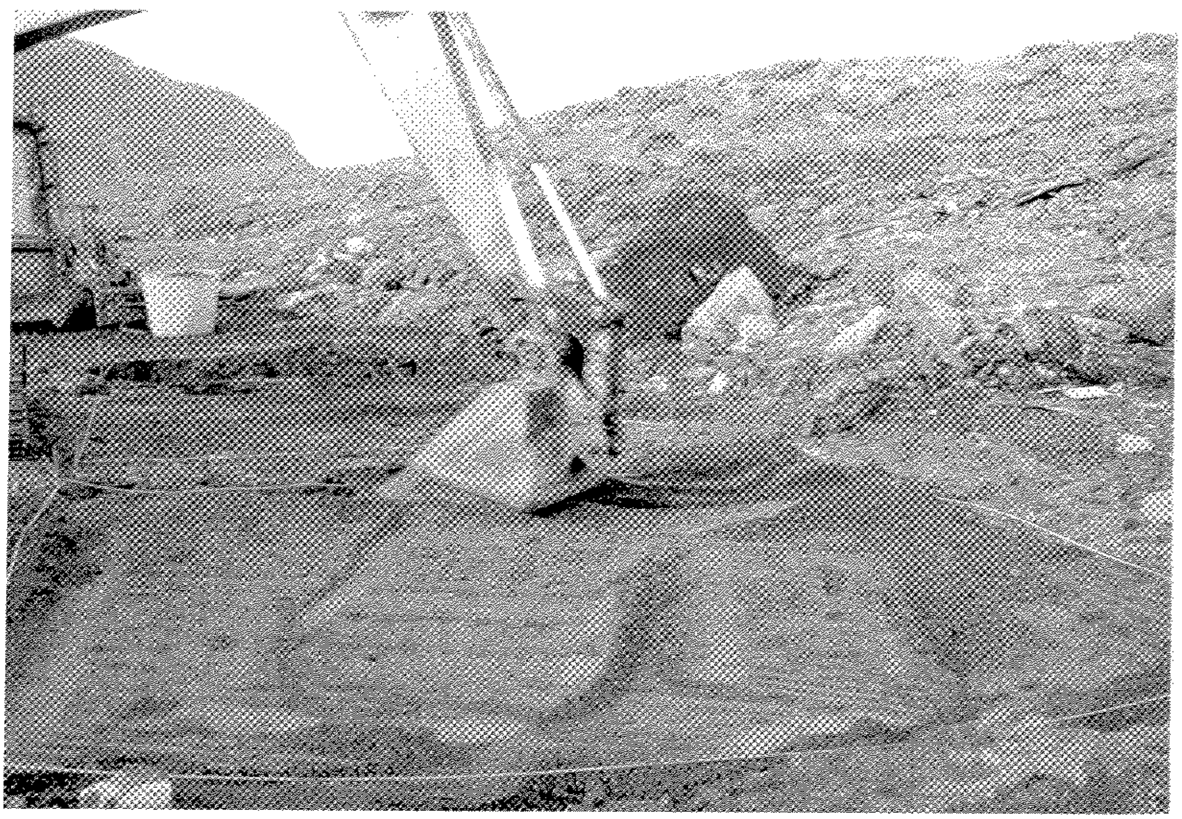
Photograph V-11: Excavating Plots For the In Situ Landfarm Experiment



Photograph V-12: Tamping Down the Soil in the In Situ Landfarm Plots

Table V-19: Results of Analyses of Soil Samples for TPH From the In Situ Landfarm

Plot Regime	TPH - Fuel (ug/g)	
	14 August 2005	18 August 2005
CP1-Control Plot 1	1160	820
CP1-Control Plot 1	760	890
CP1-Control Plot 1	830	1010
CP1-Control Plot 1	650	1150 (0-30 cm)
CP1-Control Plot 1	780	1060 (30-60cm)
CP2-Control Plot 2	1020	1480
CP2-Control Plot 2	820	1410
CP2-Control Plot 2	1180	1050
CP2-Control Plot 2	1160	1460 (0-30cm)
CP2-Control Plot 2	1000	690 (30-60 cm)
FAS-Fertilizer Added To Surface	670	210
FAS-Fertilizer Added To Surface	1040	1180
FAS-Fertilizer Added To Surface	740	570
FAS-Fertilizer Added To Surface	470	1260 (0-30 cm)
FAS-Fertilizer Added To Surface	960	450 (30-60 cm)
FAM – Fertilizer Added Mixed	930	950
FAM – Fertilizer Added Mixed	770	530
FAM – Fertilizer Added Mixed	870	650
FAM – Fertilizer Added Mixed	1640	830 (0-30 cm)
FAM – Fertilizer Added Mixed	920	880 (30-60 cm)
Average	**918 ± 250**	**926 ± 340**

H. Laboratory Landfarm Study

In order to gain a better understanding of the roles of aeration and bioremediation, laboratory studies were initiated in 2003 in order to mimic the field trial plots. The idea was that the experimental setup so developed could then be used to optimize parameters and conditions for rapid remediation of the diesel contaminated fuel at the site and elsewhere in the Canadian Arctic.

Eighty seven small reactors were constructed for the laboratory experiment. Each contained diesel contaminated soil from Resolution island in a closed vessel. Air was blown through the vessel and any TPH that evaporated was collected on charcoal tubes. Analysis of these charcoal tubes enabled the amount of TPH lost through aeration to be measured. The TPH level in the soil was determined periodically. This permitted the amount of TPH lost to both aeration and bioremediation to be determined. TPH degradation through bioremediation could therefore be calculated and this could also be observed by inspection of the C_{17}/Pr ratios.

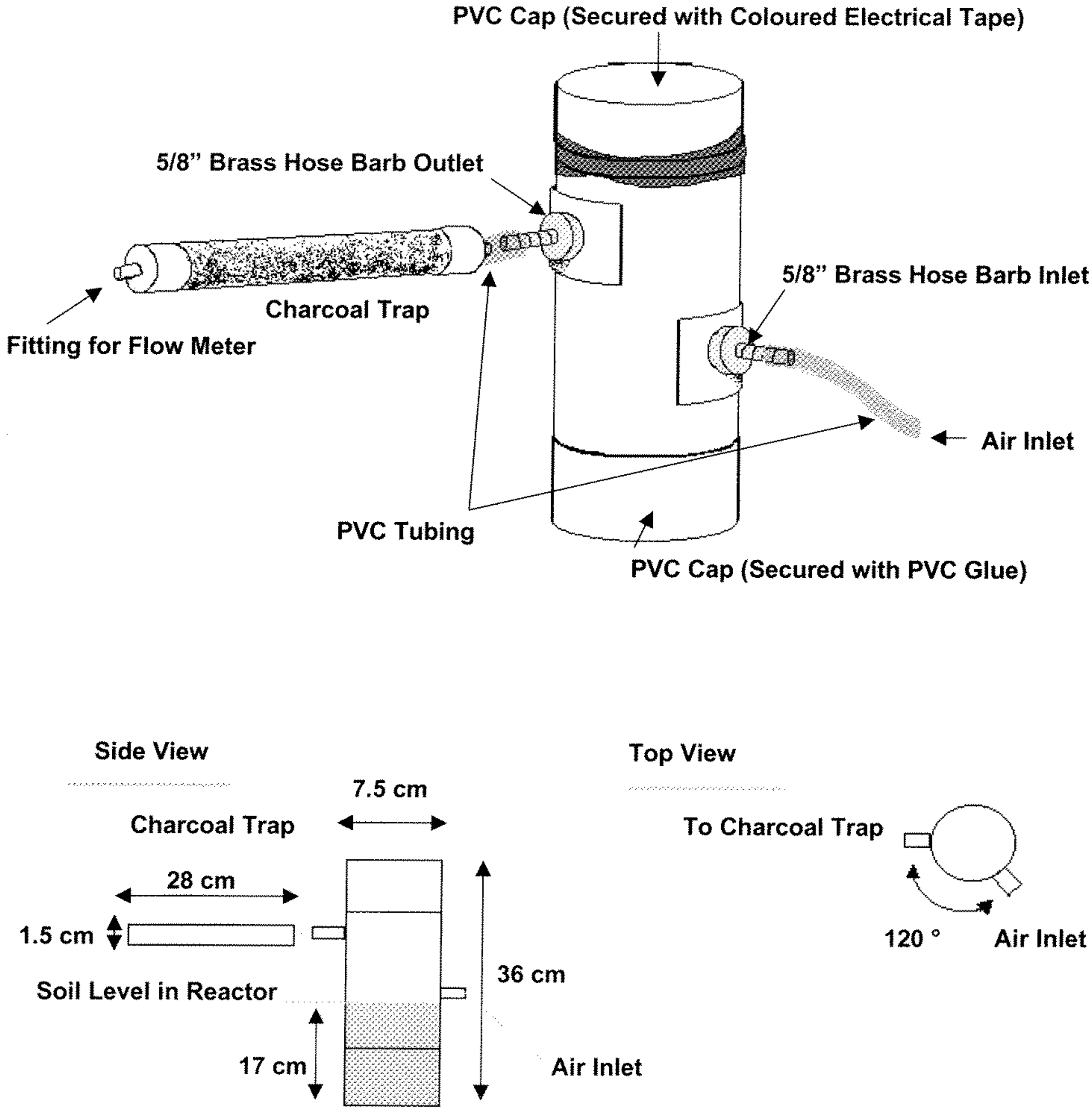
Three sets of reactors were kept at different temperatures and moisture levels were maintained.

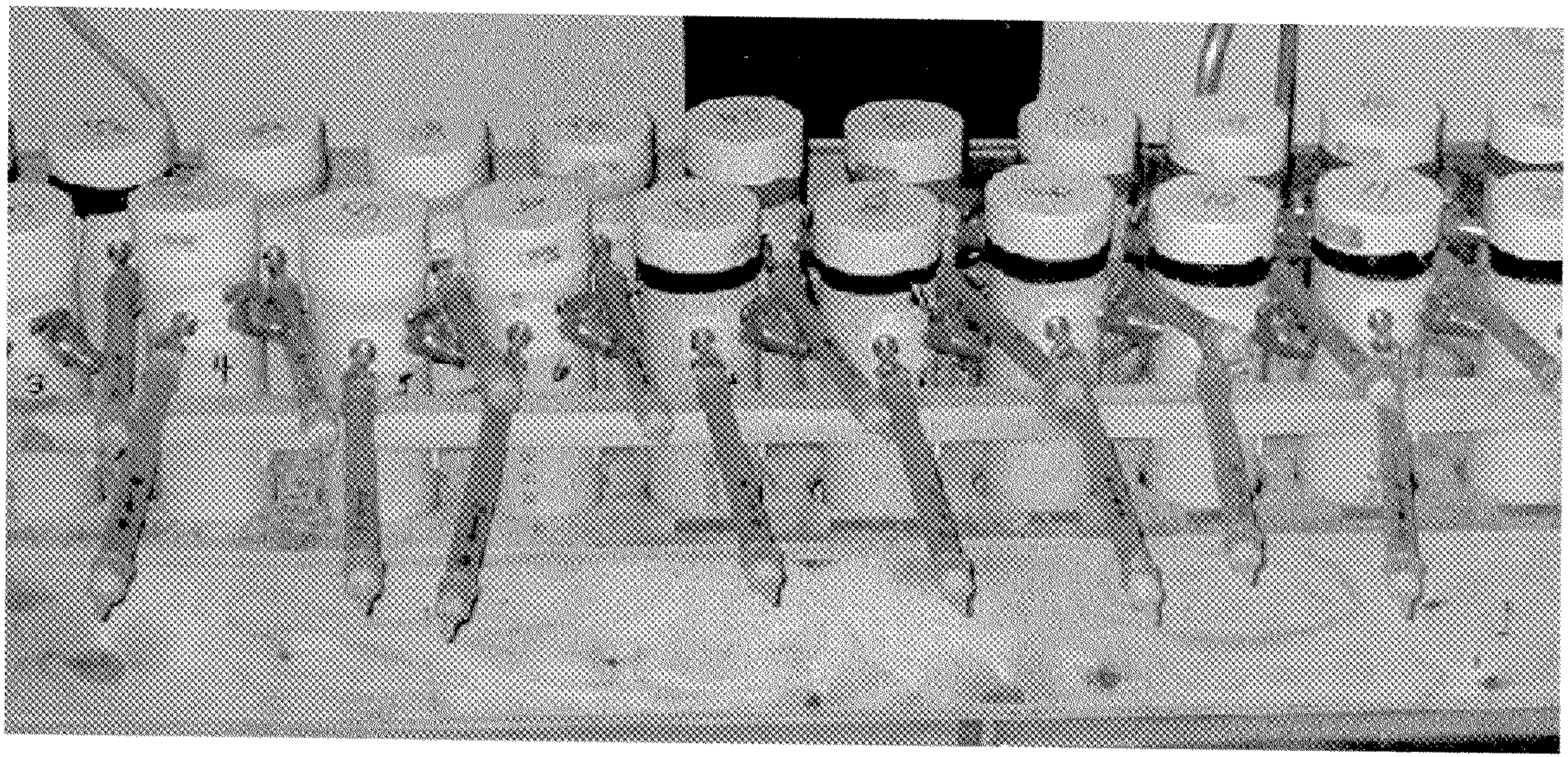
1. First Set of Reactors

This work is fully reported in the 2004 ASU Resolution Island report. The design and results are briefly described here for information and comparison with this year's work.

Three sets of 27 reactors were constructed so that the experiments could be carried out at the three temperatures of 18 °C, 8 °C, and 5 °C. Figure V-8 shows the individual reactors that were designed and constructed and Photograph V-13 one of the sets of reactors in operation.

Figure: V-8: Diagram of a Laboratory Reactor





Photograph V-13: Some of the Reactors in the Cold Room at 8 C

Each set of 27 reactors was composed as follows:

- Six reactors for a control set. These were not rotated.
- Six reactors that were rotated every day.
- Six reactors that were rotated every four days.
- Six reactors to which fertilizer was added and these were also rotated every four days. The amount of fertilizer added was 0.710 g of urea and 0.112 g of diammonium phosphate (DAP) per reactor.
- Three reactors to which silver nitrate was added and these were also rotated every four days. Silver nitrate was added to each tube for a final concentration of 0.3 %.

The amount of fertilizer added was based on the ratio of C:N:P of 100:7.5:0.5. Three had silver nitrate added to them. The silver inhibited bioremediation so that for these three reactors it was known that no bioremediation was occurring.

Results from this first set of experiments can be summarized as follows:

- the amount of TPH aerated increased as the temperature increased and also increased with the frequency of rotating the tubes
- the rate of TPH aeration decreased with time due to the decrease in TPH remaining and decrease in volatility of this remaining fraction
- The TPH levels generally decreased with time with the control samples, which were not rotated, showing the least decrease of the four regimes. The fertilized reactors clearly exhibited the largest decrease in TPH concentration over the course of the experiment for all temperatures.
- The fertilised reactors lost the largest mass of TPH with the daily aeration showing the next highest loss.
- The reactors clearly showed that by aerating every 4 days and fertilizing, the TPH contaminated soil could be remediated at all 3 temperatures. In

approximately 5 months, 78 % of the TPH had been remediated from the soil at 18 °C. The TPH in the soil at 8 °C and 5 °C was remediated 36 % and 51 % respectively. The remediation at these lower temperatures is important because it demonstrates that this regime is applicable to sites with colder temperatures than Resolution Island.

- The C_{17}/Pr ratios as presented in Figures V-9 and V-10 show that there was no change in the C_{17}/Pr ratio for any of the sets except the reactors to which nutrients were added. Also the decrease in the ratio increased with increasing temperature.

- The first set of experiments therefore show that TPH was lost in the fertilized reactors by both aeration and bioremediation while all other reactors only exhibit loss through aeration. These experiments clearly showed that both mechanisms were occurring even at temperatures as low as 5 °C and supported the results obtained in the field study at Resolution Island

Figure V-9: Change of C_{17}/Pr Ratio with Time for the 8°C First Reactor Set

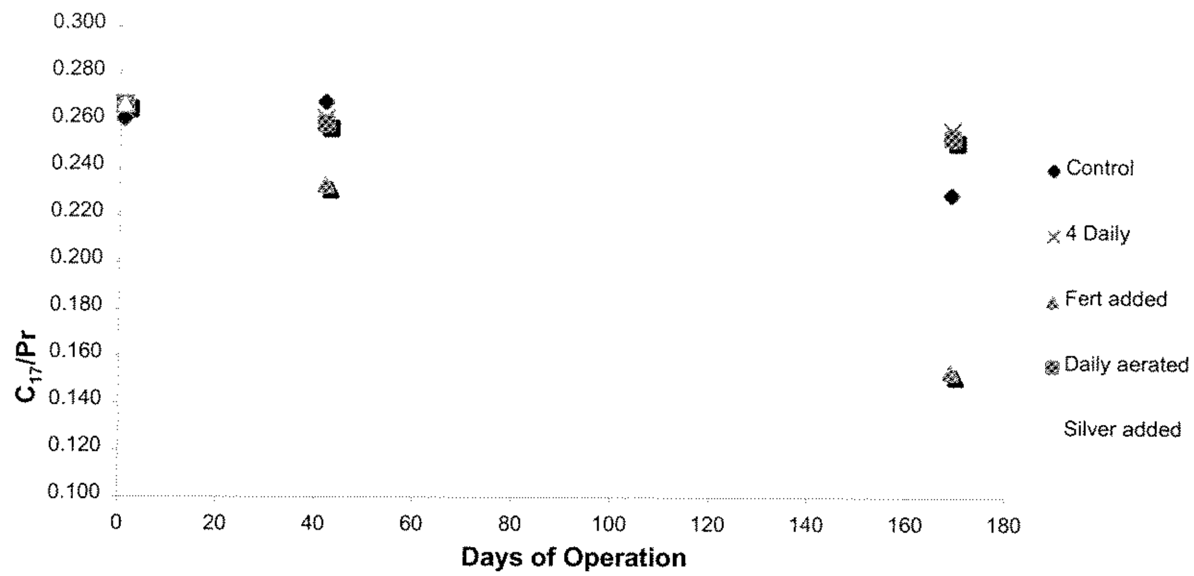
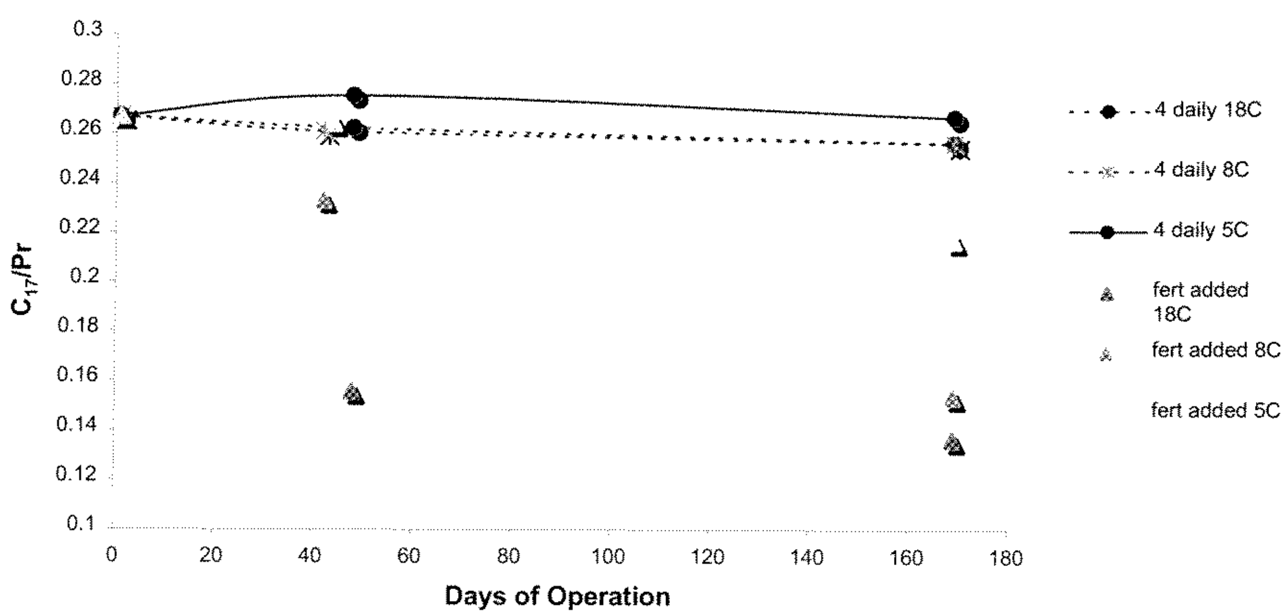


Figure V-10: Change of C_{17}/Pr Ratio with Time for Every Four Days and Fertiliser Added for the First Reactor Sets



2. Second Set of Reactors Experiments

The second set of laboratory reactor experiments were designed to confirm results found in the first set and to explore the possibility of in situ bioremediation. The sets of reactors were set up on 14 February 2005.

TPH contaminated soil was excavated from > 8000 ppm area near the imploded tank on 25 August 2004 and shipped back to the laboratory where it was stored at - 18 °C. In early January it was removed to an 8 °C cold room and allowed to thaw. On 9 February when the temperature in Kingston was near the freezing point, the soil was emptied into a robust child's paddling pool and thoroughly mixed. The reactors were then filled and the experiment initiated on 14 February 2005 at which time each was sampled. Results of the analyses of the 72 samples so obtained showed that the soil was relatively homogeneous and somewhat more contaminated than the first set with a concentration of 7200 ± 920 ppm TPH. The mass of soil in each reactor was 1350 g and therefore the average mass of TPH per reactor was 9720 mg. Nutrients were added to the soil in each reactor and thoroughly mixed. The amount of fertilizer added was 0.710 g of urea and 0.112 g of diammonium phosphate (DAP) per reactor.

Three sets of 24 reactors were attached to each of the three manifolds and set up in three different locations at 18 °C, 8 °C, and 5 °C. Each set of 24 reactors was composed as follows:

- Four reactors for a control set. These were not rotated. (CP)
- Four reactors with nutrients added but not rotated (FA-0D)
- Four reactors that were rotated every twelve days (A-12D)
- Four reactors with nutrients added and rotated every twelve days (FA-12D)
- Four reactors that were rotated every four days (A-4D)
- Four reactors with nutrients added that were rotated every four days (FA-4D)

As in the previous set of experiments, the air flow rate through the reactors was checked daily, the moisture content was maintained at between 10 % and 15 %, the GAC traps were replaced when it was deemed that they were approaching their maximum capacity to absorb TPH (before break through) and the TPH level in the soil was determined periodically.

a) GAC Traps

Results from the GAC traps gave similar results to the first set of experiments. The amount of TPH aerated increased as the temperature increased and also increased with the frequency of rotating the tubes. The rate of TPH aeration decreased with time due to the decrease in TPH remaining and decrease in volatility of this remaining fraction. In the reactors operated at 18□C, the rates of both aeration and bioremediation proceeded at a faster pace than at lower temperatures and thus trends can be more readily seen in this data.

In Table V-20, the rate of loss of TPH from the reactor decreased from the initial 30 day period from 29-51 mg/day to much lower rates by days 124-138. For the no aeration and no fertilizer added reactors the rate of 15 mg/day is much higher than for the other 5 sets (4-8 mg/day). Also the rates for the nutrient added reactors (4-6 mg/day) are less than those where no fertilizer was added (8-15 mg/day) as less TPH is present in them because of the additional loss by bioremediation. This is further evidenced in Table V-15 where the total mass of TPH lost is always higher in the non-fertilised reactors than their corresponding fertilized reactors. There is very little difference between the 8□C set and the 5□C set as can be seen by comparing Table V-21 with Table V-22 and columns 2 with column 3 in Table V-23. As regards aeration, more TPH was lost from the reactors that were rotated every 4 days than those rotated every 12 days and much more than those which were not rotated at all. This is most easily seen by comparing the rows in Table V-23. The largest amount of TPH (3790 mg) was lost from the aerated every 4 day reactors at 18□C while the lowest amount of TPH (960 mg) was lost from the 8□C set with no aeration and nutrients added. These two amounts correspond to losses of 38.6 % and 9.5 % respectively by volatilisation.

Table V-20: Mass of TPH Collected on Charcoal Traps in the Reactors at 18°C from the Second Set of Experiments

Reactor Type	Mass of TPH Collected per Day (mg)				
	Days from Start of Experiment				
	1-30	31-64	65-95	96-124	125-138
No aeration	30	11	15	17	15
No aeration, nutrients added	29	6	8	5	4
Aerated every 12 days	51	14	13	9	8
Aerated every 12 days, nutrients added	45	11	11	5	4
Aerated every 4 days	48	30	23	16	8
Aerated every 4 days, nutrients added	43	21	18	13	6

Table V-21: Mass of TPH Collected on Charcoal Traps in the Reactors at 8°C from the Second Set of Experiments

Reactor Type	Mass of TPH Collected per Day (mg)		
	Days from Start of Experiment		
	1-36	37-80	81-138
No aeration	20	8	5
No aeration, nutrients added	16	5	1
Aerated every 12 days	25	13	3
Aerated every 12 days, nutrients added	25	10	3
Aerated every 4 days	33	16	10
Aerated every 4 days, nutrients added	27	16	7

Table V-22: Mass of TPH Collected on Charcoal Traps in the Reactors at 5°C from the Second Set of Experiments

Reactor Type	Mass of TPH Collected per Day (mg)		
	Days from Start of Experiment		
	1-39	40-80	81-138
No aeration	16	6	4
No aeration, nutrients added	15	8	3
Aerated every 12 days	25	7	9
Aerated every 12 days, nutrients added	26	9	6
Aerated every 4 days	27	18	14
Aerated every 4 days, nutrients added	34	14	8

Table V-23: Summary of Total Mass of TPH Collected on Charcoal Traps in the Reactors From the Second Set of Experiments

	Total Mass of TPH collected on Charcoal Traps (mg)		
	18 °C	8 °C	5 °C
No aeration	2600	1330	1110
No aeration, nutrients added	1540	960	970
Aerated every 12 days	3150	1480	1940
Aerated every 12 days, nutrients added	2270	1590	1560
Aerated every 4 days	3790	2650	2610
Aerated every 4 days, nutrients added	3030	2240	2380

b) Soil TPH Levels

Table V-24 gives the TPH concentrations in the sets at the start and end (138 days) of the experiment. Table V-25 converts this data into the amount of TPH lost per reactor set during the experiment.

In Table V-25, bioremediation is clearly shown to be occurring as all the sets show a much higher reduction in TPH levels than their corresponding unfertilised counterparts. This is most pronounced in the 18°C set where levels dropped from 7210 ppm to between 870 and 1530 ppm. The amounts of TPH lost (5680-6040 mg) exceed the amounts lost by aeration (2450-4020 mg). The amounts of TPH lost by the 18°C sets with nutrients added corresponds to a loss of between 78 to 87 % of the TPH originally present by both bioremediation and aeration. For the 8°C and 5°C sets, the amounts of TPH lost during the experiment by both aeration and bioremediation ranged from between 44 and 77 %.

Table V-24: Summary of TPH Concentrations in the Reactors at the Start and End of the First of the Second Set of Experiments

	TPH Concentration in Soil in the Reactors (ppm)					
	18 °C		8 °C		5 °C	
	Start	End	Start	End	Start	End
No aeration	7210	4760	7210	5810	7210	5100
No aeration, nutrients added	7210	1530	7210	2830	7210	4030
Aerated every 12 days	7210	3830	7210	4030	7210	5570
Aerated every 12 days, nutrients added	7210	870	7210	1490	7210	2580
Aerated every 4 days	7210	3190	7210	3590	7210	5610
Aerated every 4 days, nutrients added	7210	910	7210	1630	7210	2920

Table V-25: Summary of Total Mass of TPH Lost From the Reactors During the Second Set of Experiments

	Total Mass of TPH Lost from the Reactors (mg)		
	18 °C	8 °C	5 °C
No aeration	2450	1400	2110
No aeration, nutrients added	5680	4380	3180
Aerated every 12 days	3380	3180	1640
Aerated every 12 days, nutrients added	6340	5720	4630
Aerated every 4 days	4020	3620	1600
Aerated every 4 days, nutrients added	6300	5580	4290

The mass of TPH lost through aeration is presented in Table V-23 and the mass lost through both aeration and bioremediation given in Table V-25. Table V-26 and Figure V-11 give the differences in these masses, which might be considered to represent the mass of TPH lost due to bioremediation. As in the previous set of experiments the precision of the data reflects the difficulty of obtaining representative samples. However the data show useful trends. For fertilized soils the amount of TPH lost through bioremediation generally exceeds that lost to aeration in these laboratory experiments. Furthermore, bioremediation worked well even with no aeration, showing that oxygen depletion was not a factor.

Table V-26: Calculated Masses of TPH Lost Through Bioremediation

Reactor Type	Calculated Difference in Mass of TPH From Total Mass Loss From TPH Soil Levels and Mass Collected on GAC Tubes (mg)		
	18 °C	8 °C	5 °C
No aeration	-150	70	1000
No aeration, nutrients added	4140	3420	2210
Aerated every 12 days	230	1700	-300
Aerated every 12 days, nutrients added	4070	4130	3070
Aerated every 4 days	230	970	-1010
Aerated every 4 days, nutrients added	3270	3340	1910

* negative numbers are left to show variability in TPH soil data

The C_{17}/Pr ratios confirm the findings discussed above. Figure V-12 gives the change in the C_{17}/Pr ratios with time for the 18 °C set while Figure V-13 shows the C_{17}/Pr ratios in fertilized reactors with no aeration and aeration every 12 days. In Figure V-12 there is clearly no bioremediation in the three reactors to which no nutrients were added whereas the C_{17}/Pr ratio quickly decreases in the nutrient added reactors due to bioremediation. In Figure V-13 the faster bioremediation in the aerated every 12 days over the non-aerated plots is demonstrated showing that aeration stimulated the bioremediation.

c) General Conclusions

The RS-2 rotation schedule was chosen to investigate the effect of longer times between rototilling on the rate of loss of TPH. In some cases it would be beneficial to operate a large scale landfarm with longer periods between aeration and this may be more practical in the case of remote, uninhabited Arctic sites. The results show that in these laboratory experiments with Resolution Island soils there was little benefit to aerating every 4 days as opposed to every 12 days.

However, the field experiment showed that aeration was as effective as bioremediation in reducing TPH levels and that every day aeration was better than 4 day aeration. Clearly the laboratory aeration scheme was not as effective as the climatic conditions at Resolution Island in removing TPH by aeration. Further work is needed to resolve this issue. Interestingly in similar experiments Ekalugad Fjord soils did show increased remediation when aerated every four days as opposed to every 12 days. The fact that some bioremediation took place effectively in the non-aerated reactors and at 5 °C holds great hope for in situ bioremediation.

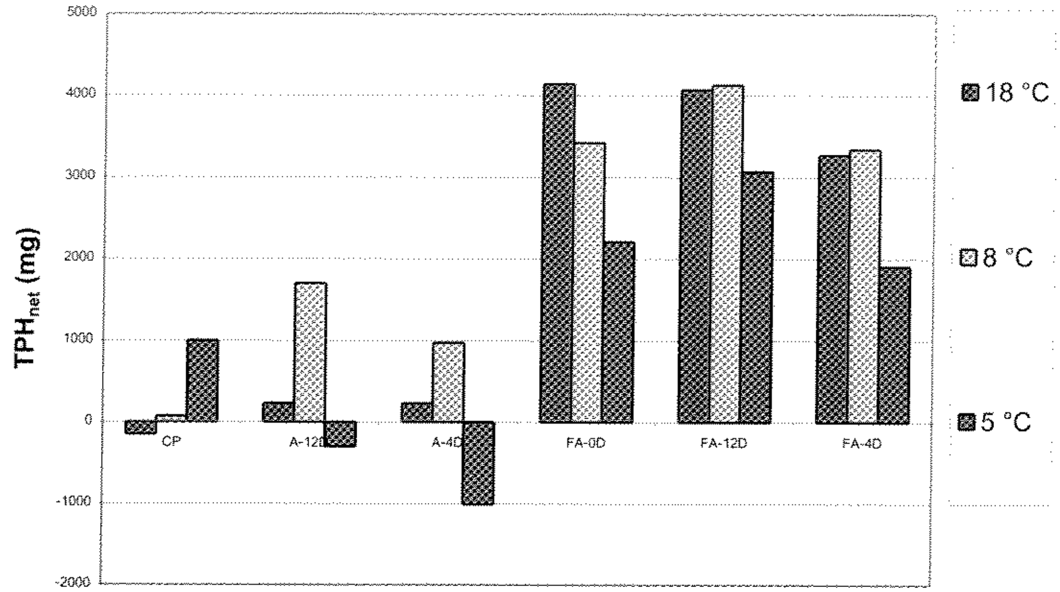


Figure V-11: Calculated Masses of TPH Lost Through Bioremediation

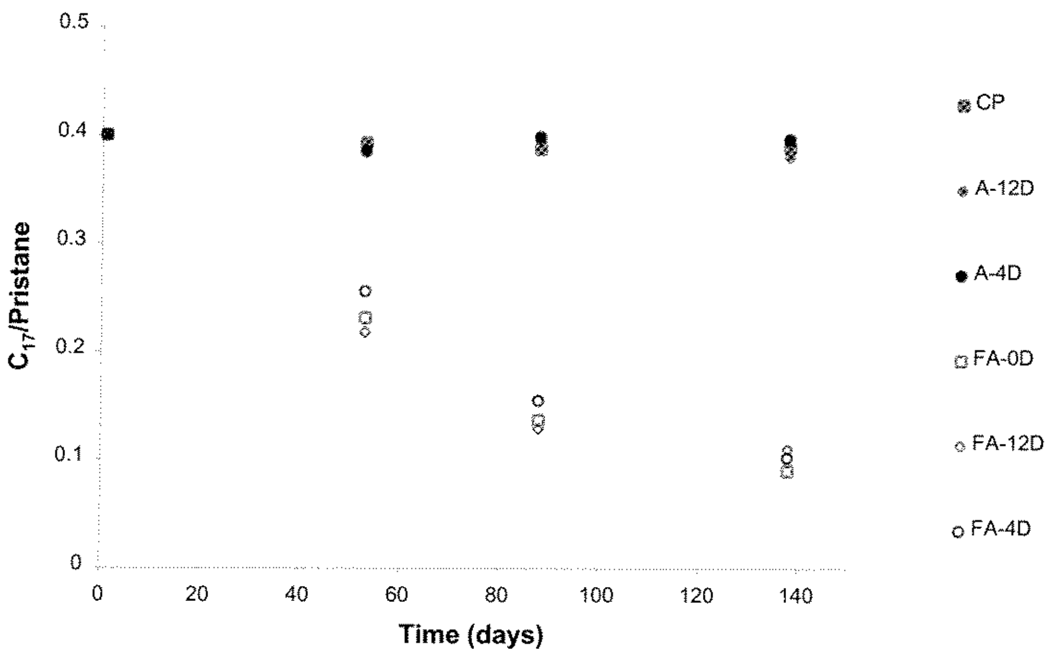


Figure V-12: C_{17}/Pr Ratios for the Reactors at 18 °C

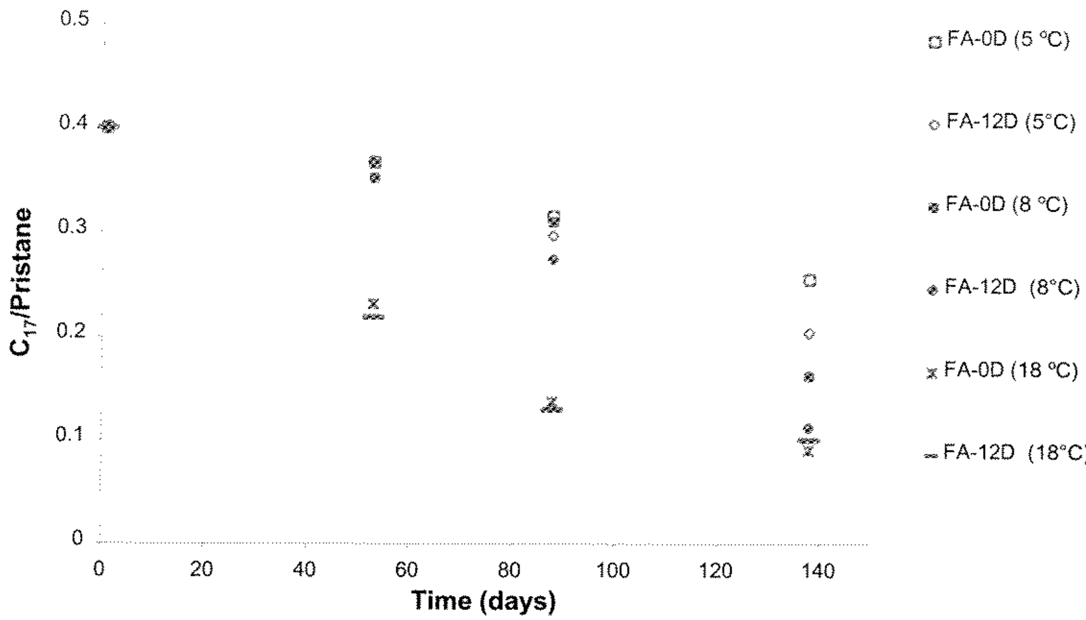


Figure V-13: C_{17}/Pr Ratios for the Reactors at Three Temperatures to Which Nutrients Were Added and Which Were Rotated Every 12 Days or Not at All

I. Rate Constant Calculations and Conclusions

In previous studies the TPH degradation has been modelled using first order rate constants in both unfertilized and fertilized soil systems[2,3]. For this system, the rate of loss of TPH is proportional to its concentration.

$$\frac{d[TPH]}{dt} = -k[TPH]$$

where [TPH] is the concentration of TPH in ppm and t is the time in days. Integration of above equation yields

$$\ln[TPH]_t = -kt + \ln[TPH]_0$$

$$[TPH]_t = [TPH]_0 e^{-kt}$$

where $[TPH]_t$ is the TPH concentration at time t and $[TPH]_0$ is the initial concentration of TPH in the system. The first order rate constant, k, is the slope of the line for a plot of the natural log of [TPH] with respect to time[4]. The fit of the line to the average TPH data can be described by the r^2 value, where a value of 1.0 indicates a perfect fit. The fit of the line gives an indication of the fraction of the variance in the slope of the line. A fraction of variance measured by the r^2 of less than 0.90 may be due to the large coefficient of variation, or irreducible error, associated with the average TPH in soil values (~20 %) used to calculate the first order rate constants.

The nature of the arctic climate, especially the extreme temperatures in the winter season, has led to the assumption that biodegradation exhibits a hiatus during the winter season when the soil is frozen[5]. However other models[6] and some studies[7,8,9] have shown

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[2] Zytner, R.G., Salb, A., Brook, T.R., Leunissen, M., Stiver, W.H., 2001. Bioremediation of diesel fuel contaminated soil. Canadian Journal of Civil Engineering 28, 131–140.

[3] Demque, D.E., Biggar, K.W., Heroux, J.A., 1997. Land treatment of Diesel contaminated soil Canadian Geotechnical Journal 34, 421-431

[4] Moore, J.W. and R.G. Pearson, 1981. Kinetics and Mechanism A study of Homogenous Chemical Reactions, Third Edition. John Wiley and Sons, Inc.

[5] Rike A.G., Børresen, M., Instanes, A., 2001. Response of cold adapted microbial populations in a permafrost profile to hydrocarbon contaminants, Polar Record. 37, 202, 239– 248.

that bioremediation sometimes occurs in the winter months but with significantly reduced microbial activity and no lower than in –5 °C temperatures[10].

Rate constants have been calculated for the experimental landfarm and discussed in Section G2 above. These are presented in Table V-27. For this determination it was assumed that remediation did not occur in the winter months. Therefore, the days where the landfarm was unmanaged (not aerated) were excluded for the rate calculation and a soil temperature of 9.3 °C applies. For the first and second laboratory sets rate constants have been calculated and are presented in Tables V-28 and V-29. The rate constants can be calculated in two ways – from the rate of loss of hydrocarbon to the charcoal traps (aeration only) or from the TPH concentration data. Both are given in Tables V-28 and V-29. Also included are the rate constants for bioremediation obtained by subtraction of the aeration only rate constant from the corresponding total rate constant.

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[6] Huesemann, M.H., Truex., M.J., 1996. The role of oxygen diffusion in passive bioremediation of petroleum contaminated soils. Journal of Hazardous Materials. 51, 93– 113.

[7] Zimov, S.A., Davidov, S.P., Prosiannikov, Y.V., Semiletov, I.P., Chapin, M.C., Chapin, F.S., 1996. Siberian CO_2 efflux in winter as a CO_2 source and cause of seasonality in atmospheric CO_2. Climatic Change 33, 111–120.

[8] Oechel, W.C., Vourlitis, G., Hastings, S.J., 1997. Cold season CO_2 emission from arctic soils. Global Biogeochemical Cycles 11, 163–172.

[9] Jones, M.H., Fahnestock, J.T., Welker, J.M., 1999. Early and late winter CO_2 efflux from arctic tundra in the Kuparuk River watershed, Alaska, USA. Arctic and Alpine Research 31, 187–190.

[10] Cline, J.S., Schimel, J.P., 1995. Microbial activity of tundra and taiga soils at sub-zero temperatures. Soil Biology and Biochemistry. 9, 1231–1234.