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COMPOSTING OF SOILS CONTAMINATED WITH HEAVY PETROLEUM HYDROCARBONS

by
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A thesis
submitted under the supervision of
Dr. Leta Fernandes

for partial fulfilment of the
requirements for the degree of
Master of Applied Science
in
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To my wife, Shirley

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ABSTRACT

This project tested at the field scale, five on-site, non-proprietary bioremediation processes on weathered petroleum hydrocarbons from a fire fighter training area. Two bioremediation processes based on fungi (commercially produced white rot fungus, *Pleurotus ostreatus*, and aged, coarse wood chips, 'compost', with naturally occurring fungi) were applied with variations and compared to one control: a typical static biopile. An elevated-face compost turner was used to turn the soil in selected windrows for aeration. Statistically-based sampling was employed and quality control measures were enforced for sampling and analysis. The treatment options examined for the contaminated soil were:

- white rot fungus and compost,
- compost, poultry manure and turning,
- compost, synthetic nitrogen-phosphorous-potassium fertilizer, and turning,
- compost, the above synthetic fertilizer, and no turning, and
- the above synthetic fertilizer, and no turning (static biopile).

The compost and poultry manure process performed the best, remediating 35 tonnes of soil contaminated with 6000 mg/kg of mineral oil and grease (MOG) to the remediation criteria of 1000 mg/kg in 19 days and to less than 300 mg/kg in less than 56 days. The net rate of bioremediation was 100 mg/kg/day of MOG. The estimated cost of this process for commercial applications, excluding labour, excavation and site preparation, was \$18 to \$29 per tonne, depending on the cost of the poultry manure.

Key words: bioremediation, white rot fungus, compost, poultry manure, fire fighter training area, weathered petroleum hydrocarbons.

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GLOSSARY

This glossary has been developed primarily from the Canadian Soil Information System (CanSIS), the University of Arizona (Agriculture) Glossary of Terms Relating to Soils [of Arid Regions] (1997), and specific items from the References.

Actinomycetes. A family of microorganisms belonging to a group intermediary between bacteria and moulds (fungi), mainly resembling the latter because they usually produce branched mycelium: a form of filamentous, branching bacteria. Unicellular filamentous microorganisms that branch monopodially or more rarely dichotomously and form radiating colonies; mainly found in the soil, and cause of its characteristic odour.

Aeration, soil. The process by which air in the soil is replaced by air from the atmosphere. In a well-aerated soil, the soil air is similar in composition to the atmosphere above the soil. Poorly aerated soils usually contain a much higher percentage of carbon dioxide and a correspondingly lower percentage of oxygen than the atmosphere. The rate of aeration depends largely on the volume and continuity of pores in the soil.

Aerated Static Pile. Composting system using controlled aeration from a series of perforated pipes running underneath each pile and connected to a pump that draws or blows air through the piles.

Anaerobic: Conditions that are free of molecular oxygen. In soils this is usually caused by excessive wetness.

Available Water. The portion of water in a soil that can be readily absorbed by plant roots. Most workers consider it to be the water held in the soil against a pressure of up to approximately 15 bars. See also Field Capacity, Soil Moisture Tension

Batch Composting: All material is processed at the same time, without introducing new feedstock once composting has begun. Windrow systems are batch systems.

Biopile: A bioremediation process which involves heaping contaminated soil into piles, or "cells", and stimulating aerobic activity through aeration and/or the addition of minerals, nutrients, and moisture.

Aeration often is achieved by forcing air to be moved through the biopile by perforated piping placed throughout the pile.

Biopolymer: A natural polymer consisting of thousands of smaller molecules bound together to form very large molecules, like cellulose, lignin and cutin.

Bound Residue: Organic pollutant compounds in soil believed to become covalently bound with humus through the action of microbial enzymes that immobilizes and detoxifies the compounds and makes them highly resistant to biological and chemical attack.

Bulking Agent: Material, usually carbonaceous such as sawdust or woodchips, added to a compost system to maintain airflow by preventing settlement and compaction of the waste.

Compositing: The combining and homogenizing of samples (eg. soil) before performing an analysis of the composite sample.

Cellulose: Carbon component of plants, not easily digested by microorganisms. Cellulose is a polymer of the sugar glucose.

Controlled Dynamic System: Compost piles which receive forced aeration and periodic turning.

Decomposition: Conversion of organic matter as a result of microbial and/or enzymatic interactions; initial stage in the degradation of an organic substrate, characterized by processes of destabilization of the pre-existing structure.

Detoxification: Immobilization of toxic substances in soil and water, including sorption mechanics, so that they do not harm plants.

Dynamic Pile System: Compost piles which receive forced aeration and are not turned. (See also: Aerated Static Pile.)

Fertilizer: A material that is added to the soil to supply one or more plant nutrients (C, H, O, P, K, N, S, Ca, Mg, K, B, Mn, Cu, Zn, Mo, Cl, Co, Si, and F) in a readily available form so that they may be taken up

and utilized in sufficient quantities for plants to complete their life cycles. Fertilizer usually is manufactured to supply especially the macronutrients (N, P, K, S, Mg, Ca, Fe) that are needed in large amounts for plant growth.

Field Capacity, or Field Moisture Capacity: The total amount of water remaining in a freely drained soil after the excess has flowed into the underlying unsaturated soil. It is expressed as a percentage of the oven-dry soil.

Fungi: Simple plants that lack chlorophyll and are composed of cellular filamentous growth known as hyphae forming a mass called a mycelium. The fruiting bodies of many fungi, namely mushrooms and puffballs, are quite large. Fungi bring about cellulolysis and humification of the substrate during stabilization.

Gas chromatography/mass spectroscopy (GC/MS): A method for separating, identifying, and quantifying organic compounds. Compounds pass through a chromatographic column where the differences in their rates of travel form the basis for their separation, and their identification is based on both their retention time in the GC column and their mass spectral pattern. Quantification is achieved by measuring peak areas in the mass spectra.

Headspace: The empty volume in a container between the cap and the water, or soil, level of the sample.

Heavy Hydrocarbons: Organic compounds containing only hydrogen and carbon atoms which have 12 to 50 carbon atoms per molecule.

Hygroscopic Water: Water that is adsorbed onto a surface of a particle from the atmosphere.

Leaching: The washing out of material from the soil, both in solution and suspension.

Light Non-Aqueous Phase Liquids (LNAPL): Fluids that are lighter than water and are relatively insoluble in water.

Lignin: The organic polymer of wood responsible for its rigidity and binding together the cellulose fibres.

Low Temperature Thermal Desorption: Contaminated soils are heated to 93°C to 315°C to volatilize water and organic contaminants. The volatilized gases are transported to a secondary chamber where these gases usually are destroyed at high temperature.

Mesophilic Stage: A stage in the composting process characterized by bacteria that are active in a moderate temperature range of 20°C to 45°C (68°F; to 113°F).

Metabolism: Sum of the chemical reactions within a cell or whole organism, including the energy-releasing breakdown of molecules (catabolism), and the synthesis of complex molecules and new protoplasm (anabolism).

Method Detection Level: The method detection level (MDL) includes the number of calibration points determined for the instrumentation, the effects of sample dilution and the recovery of surrogates when a sample is processed through the complete analytical procedure. Rather than being specific to just the analytical instrument as for instrument detection level (IDL), MDL represents the complete analytical procedure. For a uniform matrix of water, the MDL is approximately four times higher than the IDL. (Cathum et al., 1996)

Microorganisms: A group of organisms consisting of bacteria, fungi, actinomycetes, and cyanobacterial.

Mineralization: The change of an organic compound by microorganisms to an inorganic substances, like carbon dioxide and water.

Moisture Content: The mass of water lost per unit dry mass when the material is dried at 103°C (217°F) for eight hours or more. The minimum moisture content required for biological activity is 12–15%; it generally becomes a limiting factor below 45 or 50%; expressed as a percentage, moisture content is water weight/wet weight.

Nitrification: The oxidation of ammonia to nitrite and nitrite to nitrate by microorganisms.

Nutrients. (See Fertilizer)

Obligate Aerobic (Anaerobic) Organisms: Can only grow in the presence (or, absence) of oxygen respectively.

Organic: Substances containing carbon, with the exception of carbon dioxide and carbonates.

Organic Contaminants: Synthetic trace organics, including pesticides, and polychlorinated biphenyls (PCB's) - a class of chlorinated aromatic hydrocarbons representing a mixture of specific biphenyl hydrocarbons which are thermally and chemically very stable; and some of which are proven carcinogens.

Organic Matter: That portion of the soil that includes microflora and microfauna (living and dead) and residual decomposition products of plant and animal tissue; any carbon assembly (exclusive of carbonates), large or small, dead or alive, inside soil space; generally consists primarily of humus.

Oxidation: Energy-releasing process involving removal of electrons from a substance for transfer to oxygen; in biological systems, generally by the removal of hydrogen (or sometimes by the addition of oxygen); chemical and/or biochemical process combining carbon and oxygen and forming carbon dioxide (CO₂).

Pesticides: Collective term for herbicides, insecticides, fungicides and rodenticides.

Phytotoxic: Detrimental to plant growth; caused by the presence of a contaminant.

Polycyclic Aromatic Hydrocarbons: The most stable form of hydrocarbons having low hydrogen-to-carbon ratios and are formed by the combustion of hydrocarbons under oxygen deficient conditions. The partial combustion of coal, which has a H:C ratio of less than 1, is a major source of PAH compounds.

Respiration: The oxygen dependent breakdown of carbohydrates to carbon dioxide.

Size Reduction: Generic term for breaking up solid waste or other materials into small pieces through crushing, chipping, shredding, grinding, etc.; the process makes wastes easier to separate and increases surface area for composting.

Soil. A three phase system of aggregate of minerals, water, microorganisms and other organic matter including humus. Soil includes the void space, typically 35%, which is filled with water and/or soil-gas. More than 50% of the material by volume must have a particle size of less than 2mm.

Soil-gas: The soil atmosphere, the gaseous phase of the soil, is the volume not occupied by solid or liquid.

Soil Moisture Tension: The measure of the condition whereby pore water rests at a pressure less than atmospheric.

Static Biopile System: An aerated static pile with or without a controlled air source.

Surfactant. A substance that breaks the natural surface tension of liquids

Test Pit: A shallow pit, made using a backhoe, to characterize the subsurface.

Volatilization: Gaseous loss of a substance to the atmosphere.

Abbreviations

ATP	Adenosine triphosphate
BTEX	Benzene, toluene, ethylbenzene, xylenes
C	Centigrade
CAEAL	Canadian Association of Environmental Analytical Laboratories
CCME	Canadian Council of Ministers of the Environment
CFB	Canadian Forces Base
CEC	Cation exchange capacity
DDT	Dichlorodiphenyltrichloroethane
DOEP	New Jersey Department of Environmental Protection
EPA	United States Environmental Protection Agency
GC/MS	Gas chromatography / mass spectroscopy
IDL	Instrument Detection Level
LNAPL	Light Non-Aqueous Phase Liquid
mg/l	milligram per litre

MDL	Method Detection Level
MISA	(Ontario) Municipal Industrial Strategy for Abatement
MOG	Mineral Oil and Grease
n/a	not available
N-P-K	Nitrogen:Phosphorous:Potassium
PAH	Polycyclic aromatic hydrocarbons
PCB	Polychlorinated biphenyls
PCP	Pentachlorophenol
QC	Quality Control
SOPs	standard operating procedures
TPH	total petroleum hydrocarbons
USA	United States of America
VOCs	Volatile organic compounds
WRF	white rot fungus

CHAPTER 1

INTRODUCTION

1.1 GENERAL

It has been common practice to use expired and out-of-specification fuels, old solvents and lubricating oils as the fuel for fire fighting practice at airports. These petroleum products were usually spread on bare ground at fire fighter training areas and set on fire so that fire fighting crews could practise their approach to and rescue of imaginary crew and passengers. What fuel was not consumed in the fire was volatilized or rapidly seeped into the ground. Although petroleum fuels usually consist of hundreds of compounds, the contamination in the fire fighter training areas is typified by the accumulation of a number of heavy petroleum hydrocarbons [also designated as weathered petroleum hydrocarbons, or mineral oil and grease (MOG) - the spectrum of heavy petroleum hydrocarbons typified by specific laboratory analytical procedures] and polycyclic aromatic hydrocarbons (PAHs). Fire fighter training areas exist at most major military and civilian airports and contamination migrating from these sites is becoming an environmental and public concern. As a result, new environmentally friendly methods and facilities are being developed to train fire fighters and the old fire fighter training areas are being decommissioned and remediated. The effectiveness and cost of remediation of these old fire fighter training areas is a concern.

1.2 EXISTING REMEDIATION METHODS

Historically, remediation of soil contaminated with light and/or heavy petroleum hydrocarbons consisted of hauling the contaminated soil to a landfill site for disposal and replacing the excavated soil with a clean fill. This was not only expensive, but it was disruptive to the continuing use of the site (Reisinger, 1995). Moreover, the contaminated soil was only moved to another site, it was not truly remediated. As landfills became scarce the trend to higher tipping fees was making this option more expensive and public concern for not remediating the contaminated soil were increasing. Where space and suitable separation from inhabited areas were available in non-attainment areas, landfarming was sometimes used. In this method, the contaminated soil is spread on a liner above ground to a depth of approximately 0.5 m, and may be tilled on a periodic basis. The sun and wind volatilize and remediate the organic contamination (Environment Canada, 1993). This method is usually limited to light petroleum hydrocarbons, costs \$20 to \$50 per tonne, and has highly variable degradation rates and efficiencies (Cyr and Spieles, 1995, St-Cyr et al., 1992).

A variety of technologies were developed to remediate contaminated soil such as: thermal desorption and incineration, soil washing, and bioremediation including bioventing, natural attenuation, and processes requiring the addition of inoculums, nutrients and/or surfactants. Many of these technologies are based on proprietary procedures and/or require large amounts of equipment. Performance claims for these processes were often made in isolation without comparison to other processes and it was difficult to evaluate their effectiveness in relation to non-proprietary methods. The large amount of equipment tended to raise the cost of such processes. Recent fire fighter training area remediation projects have been using low temperature thermal desorption (LTTD). Although LTTD can remediate a fire fighter training area in a matter of days or weeks (based on a process rate of 2 to 50 tonnes per hour depending on moisture content, friability, soil type, contamination type and concentrations, and equipment design output rates) to non-detectable concentrations of petroleum hydrocarbons, its cost were from \$95 to \$175 per tonne (CPPI, 1991), the organic fraction of the soil was destroyed and large amounts of fuel were used to drive off relatively small amounts of petroleum contamination. In fact, it is calculated that 500 or more litres of fuel are used to destroy 15 litres of fuel contamination in 20 tonnes of soil (refer to **Appendix B - Calculations**). In addition, LTTD incurred additional cost by government departments since a high degree of contract supervision was required to ensure that only soil which exceeded the remediation criteria was selected and processed.

Many of the bioremediation technologies were based on the large numbers of bacterial microorganisms naturally present in the soil. Under appropriate conditions, the microorganisms mineralize dissolved organic toxic compounds into harmless carbon dioxide and water. However, the large molecular weight organic contaminants, such as heavy hydrocarbons and PAHs, tended to be left alone by the soil bacteria and remain after bacterial-based bioremediation processes or landfarming have been completed (Leahy and Colwell, 1990, Boyle and Richardson, 1993). The large petroleum hydrocarbon and PAH molecules, as with lignin and cellulose, were often too large to pass through the microbial cellular walls. These heavy hydrocarbons became known as recalcitrant organics.

Fungi, another group of microorganisms, consume lignin and cellulose (dead tree matter) as a food source, or substrate. The cellulose and lignin are large complex polymer organic molecules, similar to those in human-made plastics. In order to break these biopolymers into a size suitable for absorption into the fungus, fungi exude peroxide-like enzyme substances. The cellulose and lignin are broken down by oxidation and enzymatic action into simpler and smaller molecules suitable for absorption and consumption by the fungus. It has been shown in laboratory experiments that in addition to cellulose and lignin, fungi act on a variety of other large organic molecules including MOG and PAHs in the same manner. Various laboratory experiments proved the remediation dynamics of fungi under carefully controlled laboratory

conditions. (Bumpus and Aust, 1987; Aust and Benson, 1993; Boyle and Richardson, 1993; Kaal et al., 1993; Liang and McFarland, 1994; Mougin et al., 1994; McFarland and Qiu, 1995; Yadav et al., 1995) However, the practicalities and costs of using fungi at the field scale had not been well established in projects.

1.3 **BASIS OF PROJECT**

It was proposed to the three federal government departments with a large stake in the remediation of the fire fighter training areas (National Defence, Transport Canada and Environment Canada) that a scientifically run, field scale project examine the fungal-based bioremediation of contaminated soil typical of old fire fighter training areas. The project would be aimed at proving the efficacy and low-cost of non-proprietary, robust fungal-based soil composting processes. The Department of National Defence agreed to the use of one of their old fire fighter training areas, at Canadian Forces Base (CFB) Trenton. Previous characterizations had shown this fire fighter training area to contain the typical weathered petroleum hydrocarbons that had been difficult to remediate.

The perspective of this project was the remediation of tonnes of soil on the macro scale at a typically contaminated site rather than the theoretical identification and analysis of the various microbial processes in grams of uniform soil in a laboratory culture flask on a micro scale. It was noted that in the microcosm of soil from a contaminated site, crumbs of soil greater than 6 mm in diameter have shown no oxygen in their centres, and as the effective pH changes at the surface of the soil particles, the availability or deficiency of soluble nutrients change (McLaren and Peterson, 1967). However, at the field scale such perturbations are not apparent. Therefore the project adopted the conceptual approach considered by Quastel (1946) whereby the soil as a whole was likened to an organ in a body to which various nutrients, plant material, rain and air were added and in which enzymatic reactions occurred. The perspective was more one of looking at what the microorganisms were doing in terms of the bulk concentrations of oxygen, moisture, pH, soluble nutrients, and contaminants rather than in the precise identification of the taxonomy, size, and shape of the microorganisms.

1.4 **PROJECT OBJECTIVE**

This project examined at the field scale, the performance of primarily two fungal-based bioremediation schemes on the remediation of soil contaminated with MOG and PAHs and compared their performance and cost with a typical control: a static biopile. The underlying principle in the design of the project was to develop a robust generic design for the rapid bioremediation of heavy molecular weight

petroleum hydrocarbon contaminated soils in small-scale projects so to reduce the design and operating costs and to reduce the time lag before remediation commences.

The bioremediation schemes had variations in the passive and active supply of oxygen, and in the addition of organic and synthetic nutrients. To examine the fungal-based bioremediation concept, five treatment options were evaluated and compared. Although at the field scale, many variables were present in a project of this nature, bioremediation treatment options were selected to identify the effect of selected variables of concern. These variables were the type of fungi, the types of nutrients and bulking agents, and the means of oxygen replenishment. Two sources of fungi were used: a commercially supplied monoculture, *Pleurotus ostreatus*, and naturally occurring fungi on aged, coarse wood chips, or 'compost'. Nutrients were in the form of synthetic fertilizer or poultry manure. The bulking agent primarily was coarse wood chips, but for the commercial white rot fungus, its sawdust and hay substrate was also a bulking agent. To replenish the oxygen used for microbial respiration, two windrows were turned with a compost turner on a regular basis, and others were left to passive aeration. The effect of other variables were constrained by requiring that the soil and ambient conditions for each option were as similar as possible. To ensure that the data would be meaningful, statistically-based sampling and good sampling and analysis quality controls were employed.

It was expected that the fungal-based processes in which elevated nutrient and oxygen concentrations were maintained (treatment windrows 1, 2A, and 2B) would perform better than those which lacked nutrients, oxygen and/or inoculation with fungi. Windrow 3A was expected to have an oxygen deficiency by not turning the windrow. Windrow 3B, typical of some biopiles, would have an additional problem with oxygen since in addition to no turning, it did not have a bulking agent to increase the soil's pore space, thus limiting its reservoir of oxygen-containing soil-gas. Moreover, since Windrow 3B would not be inoculated with fungi, it would have to depend on indigenous bacteria for bioremediation. The rates of remediation were expected to be ranked in the order of the sequence of the windrows.

CHAPTER 2

LITERATURE REVIEW

2.1 GENERAL

Soil is an aggregate of minerals, water, humus and microorganisms (McLaren and Peterson, 1967). Many soils can assimilate and neutralize pollutants through various chemical, photochemical and biochemical processes. Manahan (1994) explains the three processes as each including the following. The chemical phenomena include oxidation-reduction processes, hydrolysis, acid-base reactions, precipitation, and sorption based on diffusion concentration gradients, binding to colloidal and organic matters. Photochemical processes are more important to high vapour pressure compounds which can be lost from water or solids by evaporation. The biochemical processes include polymerization, consumption by microbial action and transformation by energy exchange with electron acceptors/donors. In addition, various transport mechanisms can move pollution from areas of concern to other areas. These mechanisms include volatilization and leaching of dissolved, suspended and colloidal solids. Although volatilization, leaching, aqueous diffusion, dissolution and binding cannot be termed remediation per se, these mechanisms, if applicable, can remove the pollutants from the target soil and result in a perceived remediation of the contamination. Therefore it is important to understand and account for such losses.

2.2 HYDROCARBONS AND OTHER ORGANIC CONTAMINANTS

Petroleum hydrocarbons span a wide range of hundreds of compounds. They generally can be classified as light, medium or heavy depending on the number of carbons atoms contained in the molecules. Light petroleum hydrocarbons (as in gasoline) contain from 1 to 10 carbon atoms per molecule (C1 - C10), medium petroleum hydrocarbons (as in diesel) contain C11 - C35 and heavy petroleum hydrocarbons (as in bunker oil, lubricating oil, hydraulic fluid, coal tar and aged residuals) C12 - C50. The latter are referred to as mineral oil and grease (MOG).

CFB Trenton advise that recently, the principal fuel used in fire fighter training areas has been jet fuel. This is highly refined kerosene consisting of petroleum hydrocarbon compounds from C6 to C16. However, before jet engines became common, aviation gasoline was the primary fuel used for fire fighter training. It contained compounds from C6 to C12. In addition, other products, notably solvents, vehicle gasoline, diesel, furnace oil and lubricating oils have been disposed of by mixing with these principal fuels. Since the lighter petroleum hydrocarbons were more volatile, they were the easiest to set on fire when spread on the ground for fire fighting purposes. If not consumed in the fire, the lighter petroleum

hydrocarbons were more prone to volatilization, aqueous dissolution and leaching over time than the heavier petroleum hydrocarbons.

Although PAHs are found to be naturally occurring in petroleum, the majority of PAHs in the environment were formed by pyrolytic processes such as forest fires and fossil fuel combustion (Winkelmann, 1992). Therefore, PAHs can be expected to be found in fire fighter training areas. Lantz et al. (1995) indicated that despite suitable environmental conditions, bioremediation of PAHs is more difficult as the size of the molecule increases beyond three fused rings. This is in part due to their low solubility in water and to their sorption to particulate surfaces. Therefore, it is important to determine the speciation of PAHs at the beginning and end of the project in order to determine whether the processes have mineralized especially the high molecular weight PAHs and to compare PAH concentrations to their relative remediation criteria.

2.3 REMEDIATION CRITERIA

The regulated criteria for the remediation of petroleum hydrocarbons are varied by federal and provincial jurisdictions. The federal Canadian objectives set by the Canadian Council of the Ministers of the Environment (CCME) only have a remediation objective for light petroleum hydrocarbons (CCME, 1991). Although gasoline and other light petroleum products may contain hundreds of compounds, detection of contamination from such compounds is usually characterized by analysis for benzene, toluene, ethylbenzene and xylene (BTEX). No total petroleum hydrocarbon (TPH) standard was established because no acceptable method could be agreed upon to blend the results from the three main analytical groups to derive a representative total.

A summary of the criteria of different Canadian jurisdictions (**Table 2.1 - Provincial Soil Remediation Criteria for Medium and Heavy Petroleum Hydrocarbons**) indicates the variety of interpretations of the impact of petroleum hydrocarbons on the environment. The ability of remediation technologies to meet these various standards should be considered. Fire fighter training areas, with their burnt, aged products which are largely mid to heavy molecular weight hydrocarbons, are caught in the middle of this lack of consensus on remediation objectives since they may contain petroleum hydrocarbons from recent jet fuel residuals to heavy petroleum hydrocarbons in the order of C50.

Table 2.1 Provincial Soil Remediation Criteria for Medium and Heavy Petroleum Hydrocarbons (mg/kg)

Province	TPH	MOG	Sensitivity I	Sensitivity II	Sensitivity III	Reference
Nova Scotia	✓		100	400	2000	NS DOE, 1994
PEI	✓		50	400	3000	PEI DOER
New Brunswick	✓		20	100		NB DOE, 1992
Quebec		✓	100	1000	5000	MENVIQ, 1988
Ontario		✓	1000	1000	1000	MOEE, 1996
Manitoba		✓	1000	5000	5000	MB Envir, 1992
Saskatchewan		✓	100	1000	5000	SK EPS, 1992
Alberta	✓		2000	4000	5000	Alberta, 1994
British Columbia		✓	100	1000	5000	MOE, 1992

Sensitivity refers to intended use of the site and/or nearby areas. Jurisdictions generally refer to residential (I), commercial (II) and industrial (III) site locations and may specify the minimum distance to users of the groundwater flowing from the contaminated site.

At the time of the field trials in this project, the Ontario remediation objectives were two percent (2000 mg/kg) for weathered oil, and one percent (1000 mg/kg) for fresh oil (MOE, 1989). This objective was revised in 1996 to 100 mg/kg for gas/diesel and 1000 mg/kg for heavy oils for all land uses (MOEE, 1996). For this project, the 1000 mg/kg concentration was selected as the more stringent of the MOG criteria. With respect to the remediation criteria for PAHs, the remediation criteria are directed to land use (industrial/commercial is cited) and specific species, such as: Naphthalene $C_{10}H_8$ - 4.6 µg/g, Acenaphthylene $C_{12}H_8$ - 130 µg/g, and Benzo(a)pyrene $C_{20}H_{12}$ - 1.9 µg/g (MOEE, 1996).

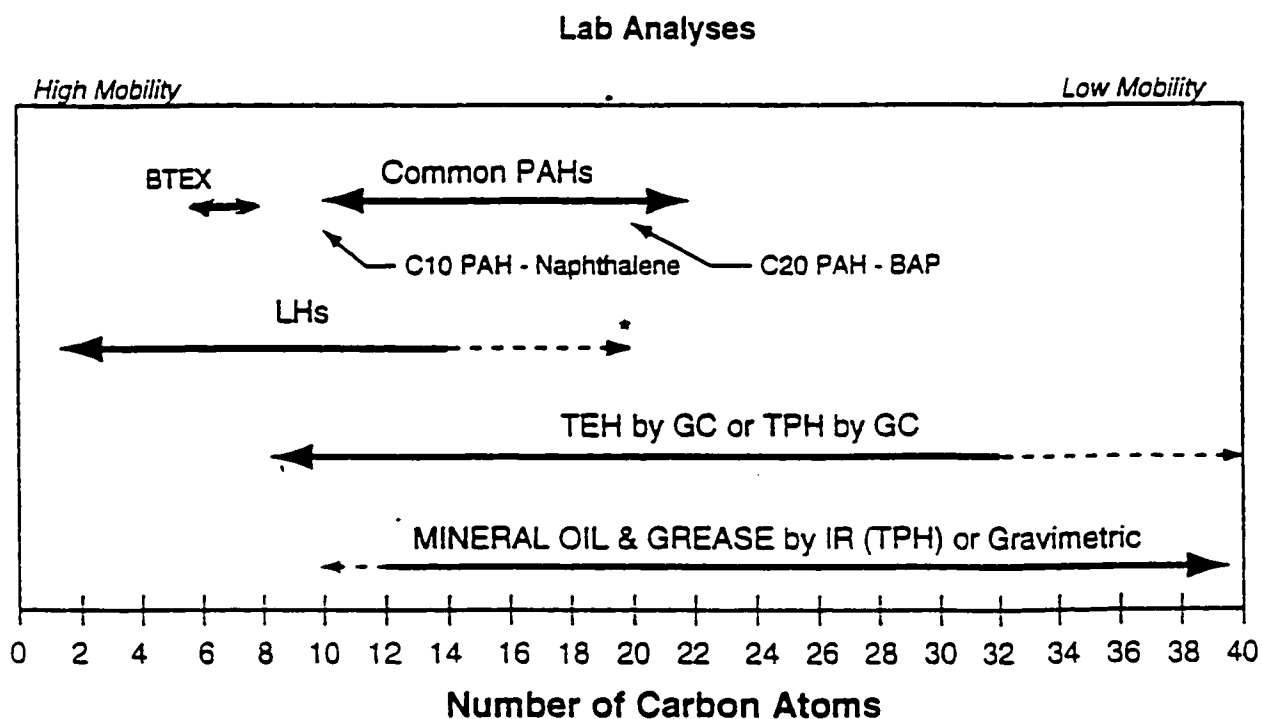
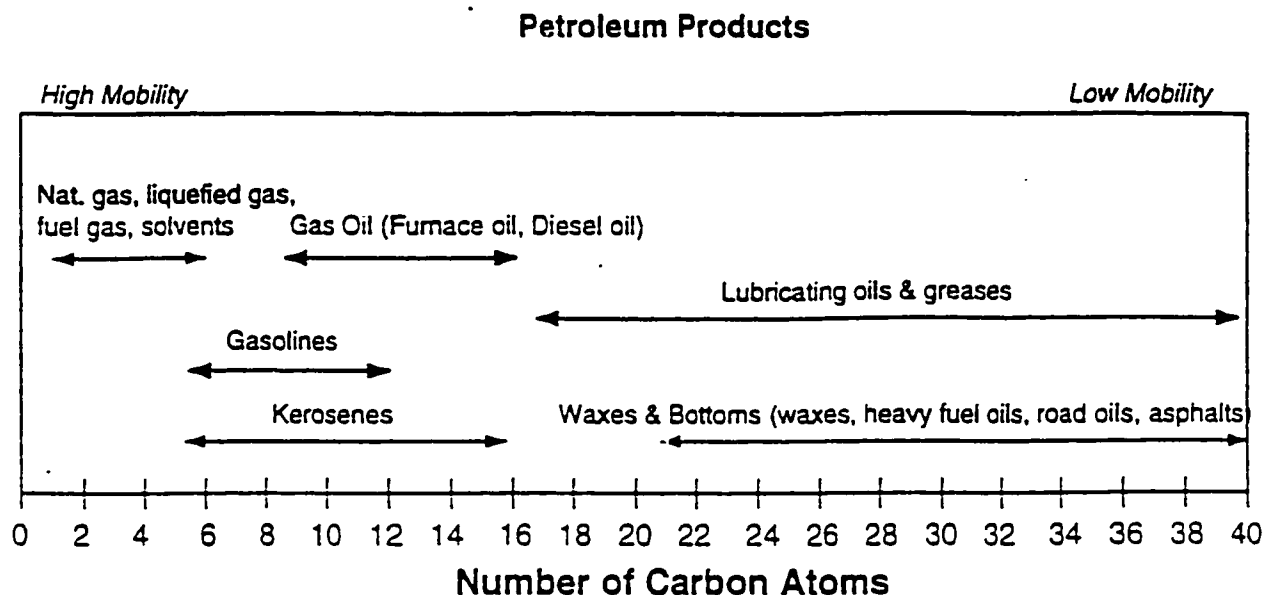
The ability to determine the fate of the residual and mobile contaminants is often governed by the ability to carry out truly representative sampling and analysis. Even then, the data will consist of only the compounds that are analytically accessible. There is not one specific laboratory analytical test method for TPH. The laboratory analysis recognized by the regulators for determination of petroleum hydrocarbons contamination levels in soils usually consists of any of a number of standard laboratory methods which place the petroleum hydrocarbons in three groups: hot extractables (also called purgeable hydrocarbons, or purge and trap), cold extractables, and MOG. The hot extractables analysis is aimed at petroleum compounds from C1 to C14 and is usually reported in individual concentrations of benzene, toluene, ethylbenzene and xylene, the cold extractables from C10 to C32, and MOG from C12 to C50. This overlap is illustrated in **Figure 2.1 - Petroleum Hydrocarbons Lab Analysis and Interpretation**. As can be seen from **Figure 2.1**, the three primary analyses overlap in the carbon spectrum from approximately C10 of C14 and from C12 to C32. Therefore if one simply adds the three laboratory analysis results together to portray the total petroleum hydrocarbons, some compounds would be double counted and would not really

Figure 2.1

PETROLEUM HYDROCARBONS

Lab Analysis and Interpretation

8



NOTE: Test recoveries are less efficient in these ranges. Do not rely upon these test results to measure hydrocarbon concentrations in these ranges.

Courtesy: Norwest Labs

represent the actual amount of product present. Depending upon the type and age of product being remediated, this could impose a varying standard of cleanup on sites which in turn can influence the cost of cleanup by hundreds of thousands of dollars since the remediation objective could double count the presence of some compounds (diesels) but only single count compounds in other spills (gasoline and lubricating oils). Therefore, although analyses of the three groups of petroleum hydrocarbons is preferable to gain an insight into the presence of these compounds, any project should secure the agreement of the regulators on how the data will be interpreted.

2.4 **BINDING OF ORGANICS**

Binding of hydrocarbons to organic matter was an area of concern, particularly since the project introduced an organic substrate for the white rot fungus, plant matter (wood chips) and manure into the contaminated soil. There is a general inverse relationship between the degree of sorption of organic compounds to their water solubility (Manahan, 1994) and heavy hydrocarbons are hydrophobic. Binding of non-polar organic compounds to colloidal matter, especially clay, humus and the less polar phases of plant materials such as membranes, starch, primary cell walls and lignin, is well recognized but is still the subject of research (Kohl and Rice, 1996; Tate, 1997; Davis et al., 1998). This binding may include ionic exchange, dipole-to-dipole interactions explained by van der Waals forces, and binding of neutral pesticides with the hydrogen ion to become bound as in their protonated positive form (Manahan, 1994). PAHs also are hydrophobic and bind strongly to the soil matrix, primarily the soil organic matter, thereby their availability to the microbial agents is reduced (Boyle and Richardson, 1994; Ghosh et al., 1995). As a result, bound residues are highly resistant to biological and chemical attack (Manahan, 1994; Kohl and Rice, 1996) and can be expected to be released only as the soil bacteria, for example, *Pseudomonas*, produce biosurfactants (Ghosh et al., 1995) or the substrate is destroyed. Experiments have shown varying ratios of sorption coefficients depending on the specific organic compound and the type of wood (Davis et al., 1998). Binding of the MOG and PAHs can be expected to occur as additional organic matter in the form of white rot fungus substrate (hay and sawdust), and compost, is added to the contaminated soil. The project's Environment Canada laboratory reported that bound residues are resistant to extraction in standard method laboratory sample preparations and therefore are hard to detect.

2.5 **FACTORS AFFECTING BIOREMEDIATION**

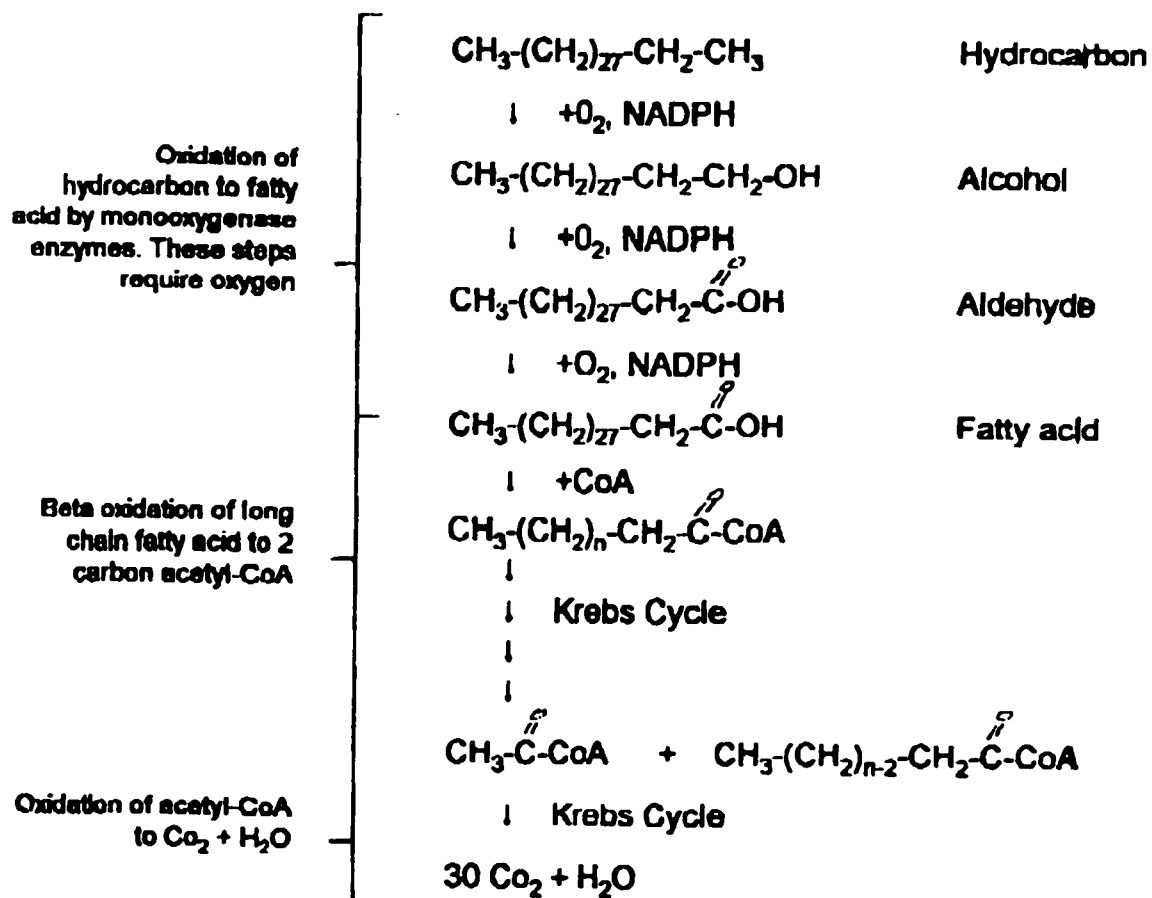
Young and Burns (1993) note that despite many exciting commercial developments, the wide application of microorganisms to the environment has been difficult outside of the laboratory or carefully monitored industrial reactors. This is due, in part, to the lack of knowledge by soil biologists of the multi

species dynamics and survival in natural soil microbial communities, and the lack of standardized techniques for counting and assessing the activities of introduced species. They also note that there is considerable public concern over safe use of microbes in the environment regarding human health, disruption to indigenous microbiota by the introduced species, and ethical concerns regarding the manipulation of the natural environment.

In general, microorganisms require carbon for the purposes of building cell mass (Bleckmann et al., 1995). In the remediation of fire fighter training areas, the carbon substrate is the petroleum hydrocarbon and PAH contamination. These compounds are mineralized through a series of steps, each involving the creation of intermediate breakdown compounds. Such a sequence in an aerobic environment is illustrated in **Figure 2.2 - Biodegradation of a C₃₀ Aliphatic Hydrocarbon**. Both aerobic and anaerobic processes can be involved in degradation of the hydrocarbons.

Microbial activity in soil is usually concentrated in the water film surrounding soil particles where there is a suitable interface of ingredients and conditions for microbial growth: moisture, oxygen, nutrients, temperature, pH and a carbon substrate. As certain metabolites are introduced into the "soil-organ", certain microorganisms are encouraged to multiply to synthesize these. A kind of steady state of microorganism species exists but only during each period of time as defined by concentrations of the metabolites in the soil, chemical setting, moisture conditions, and oxygen content (McLaren and Peterson, 1967, Reisinger, 1995).

Molecules of organic compounds in general are covalent, nonpolar compounds with relatively weak intermolecular forces. Therefore they are typically insoluble or only slightly soluble in water. (Manahan, 1994). In a fire fighter training area, the lighter compounds evaporate quickly due to their higher partial pressures (**Refer to Table 2.2 - Vapour Pressures and Solubilities of Selected Petroleum Hydrocarbons**) and are preferentially consumed by fire. Moreover, since their solubility is higher than the larger organic molecules (**Refer to Table 2.2**), they are dissolved in a greater ratio in the interstitial water film around the soil particles and are metabolized by the indigenous soil bacteria (Lantz et al., 1995, Ghosh et al., 1995, Wilson et al., 1995). Therefore, the residual lighter hydrocarbons are either absent or are in very small concentrations in fire fighter training areas.

Figure 2.2 - Biodegradation of a C₃₀ Aliphatic Hydrocarbon.

Summary: Aliphatic hydrocarbon is completely mineralized to carbon dioxide and water.

Courtesy of ESP Corp.

Table 2.2 - Vapour Pressure and Aqueous Solubility of Selected Petroleum Hydrocarbons

Petroleum Hydrocarbon	Formula	Carbon Number	Aqueous Solubility (mg/L at 25 °C)	Vapour Pressure mm Hg at 25 °C
n-Butane	C ₄ H ₁₀	4	6.12x10 ⁰¹	1.82x10 ⁰³
n-Pentane	C ₅ H ₁₂	5	3.8x10 ⁰¹	5.14x10 ⁰²
Benzene	C ₆ H ₆	6	1.79x10 ⁰³	9.52x10 ⁰¹
Toluene	C ₇ H ₈	7	5.26x10 ⁰²	2.84x10 ⁰¹
Ethylbenzene	C ₈ H ₁₀	8	1.69x10 ⁰²	9.6x10 ⁰⁴
m-Xylene	C ₈ H ₁₀	8	1.61x10 ⁰²	8.29x10 ⁰⁰
Napthalene	C ₁₀ H ₈	10	3.1x10 ⁰¹	8.5x10 ⁻⁰²
2-methylnapthalene	C ₁₁ H ₁₀	11	2.46x10 ⁰¹	5.5x10 ⁻⁰²
Acenaphthylene	C ₁₂ H ₈	12	1.61x10 ⁰¹	9.12x10 ⁻⁰⁴
Phenanthrene	C ₁₄ H ₁₀	14	1.15x10 ⁰⁴	1.12x10 ⁻⁰⁴
Pentadecane	C ₁₅ H ₃₂	15	2.87x10 ⁻⁰³	3.43x10 ⁻⁰³
Benzo(a)fluorene	C ₁₇ H ₁₂	17	4.54x10 ⁻⁰²	4.68x10 ⁻⁰⁶
Eicosane	C ₂₀ H ₄₂	20	1.9x10 ⁻⁰³	4.62x10 ⁻⁰⁶
Benzo(a)pyrene	C ₂₀ H ₁₂	20	1.62x10 ⁻⁰³	5.49x10 ⁻⁰⁹
Pentacosane	C ₂₅ H ₅₂	25	2.9x10 ⁻⁰⁸	1.51x10 ⁻⁰⁶
Octasane	C ₂₈ H ₅₈	28	8.84x10 ⁻¹⁰	9.76x10 ⁻¹⁴
Tricontane	C ₃₀ H ₆₂	30	8.58x10 ⁻¹¹	2.74x10 ⁻¹⁵
Tetracontane	C ₄₀ H ₈₂	40	6.96x10 ⁻¹⁶	2.49x10 ⁻¹¹

Reference: Howard and Meylan, 1997

Since the solubility of the heavier petroleum hydrocarbons is generally lower than the light petroleum hydrocarbons, they can not be dissolved as easily and therefore can not be made available in the aqueous environment of the bacteria. As discussed in the previous chapter, this left a residual contamination consisting of a high ratio of medium to heavy petroleum hydrocarbons in the fire fighter training areas which accumulated over the life of the facility. As a result, fire fighter training areas were hard to remediate by indigenous bacteria-based biological processes.

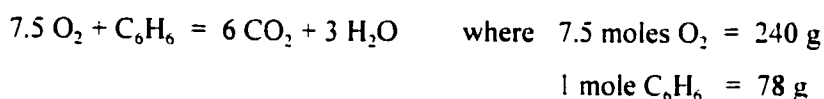
A major factor in limiting the rate of degradation [mineralization] of the organic contaminants for all microbial systems is the rate at which the contaminants and their breakdown products dissolve in the interstitial water film. This rate limiter can be overcome in part by the presence of other solutes in the water film which will assist in the dissolution rate (Rittmann, 1995). This dissolution can be augmented by the addition of surfactants which break up the pockets of pure product into smaller sizes to increase its surface area for improved microbial attack, and to change the solubility of the organic contaminants (Boyle

and Richardson, 1994). In some bioremediation schemes, surfactants were applied to make the heavy hydrocarbons available to the bacteria, but the surfactants increased the cost of the projects and care must be taken that the surfactant residuals do not become contaminants in themselves.

There are a number of factors which are important to successful use of bioremediation. The most significant environmental factors include terminal electron receptor, moisture, macronutrients, pH and temperature (Reisinger, 1995).

2.5.1 **OXYGEN**

Oxygen is used by the microorganisms as the terminal electron receptor by choice to provide the energy for reaction (Weidemeier et al., 1994, Reisinger, 1995). Aerobic processes are much faster than anaerobic processes for the mineralization of organic contaminants because aerobic pathways require less free energy for initiation and yield more energy per reaction (Reisinger, 1995). Oxygen is the most critical factor during bioremediation of hydrocarbons and the rate of biodegradation is proportional to the rate of oxygenation (St-Cyr et al., 1992). Typically, aerobic bioremediation processes can consume 2 to 20 mg of contamination (organic substrate) per kg of soil per day (Hinchee, 1994). The large amounts of oxygen for bioremediation are evident from the stoichiometric consumption of benzene: three kilograms of oxygen are required for the of one kilogram of benzene (Lee et al., 1995, Rifai, 1994).



$$\text{or, O}_2 : \text{benzene} = 240/78 = 3:1$$

The pore space in soil usually occupies 30 to 45 percent and varies in water and air content (McLaren and Peterson, 1967). The greater the air filled pore space, the greater the amount of oxygen in the soil. A common limiter to bioactivity is a deficiency of oxygen. The oxygen concentration of soil-gas is often related to the amount of biological activity in the soil and if the concentrations decrease too far, anaerobic pathways will dominate (Weidemeier et al., 1994). This is usually overcome by naturally ventilating the pile, forcing air through the pile, or turning the pile occasionally (windrowing). Natural ventilation can occur as a result of the effects of diurnal pumping, atmospheric pressure changes and wind. Diurnal pumping causes a movement of soil-gas between the soil and atmosphere as temperature changes throughout the day cause the air to expand and contract. Atmospheric pressure changes also cause the soil-gas to expand and contract as low and high pressure systems move through area. Winds cause a pressure/vacuum effect which is typical on any obstruction and therefore create an infiltration, or movement of soil-gas, in response the different pressure zones. The energy in the wind increases at the

cube of its speed as shown by the formula below (Hackleman, 1974). Therefore high winds will have significantly more ability to infiltrate atmospheric oxygen into the windrows.

$$P = \frac{1}{2} \rho A V^3 E$$

where, P = power
 ρ = air density
 A = perpendicular area of obstruction to the wind
 V = wind velocity
 E = efficiency of receptor

2.5.2 **MOISTURE**

Another common requirement for successful bioremediation operations is adequate concentrations of moisture. The moisture content is not as critical to the rate of biodegradation as is the oxygen supply (St-Cyr et al., 1992). The total amount of water in a soil will depend greatly on the water held in the capillary pore space. Therefore small particle-sized soils like clays and humus will hold more water than silt and sand. Waterlogged soils have their pore space almost completely occupied by water whereas air-dry soils may only have a water film around each particle and virtually none in the pore space. Although the latter may have a higher oxygen content, microorganisms cannot grow in the absence of water. It has been demonstrated that different microorganisms have different optimum moisture requirements (McLaren and Peterson, 1967). Since bioremediation relies on a large variety of microorganisms, the specific makeup of which is constantly changing, and soil composition that is different from one contaminated site to another, it is difficult to relate the moisture requirements of different species to the macro scale. Therefore, moisture concentrations are usually desired between a range of 40 to 60 percent of field capacity (Maat, 1993). Moisture in biopiles and windrows can be altered by a variety of means, e.g., by heaping the windrows to shed water, flattening them to absorb precipitation, covering them with a plastic membrane to prevent the infiltration of precipitation or, during hot, windy weather, the evaporation of moisture, and adding water by spraying or trickling hoses.

2.5.3 **NUTRIENTS**

The macro nutrients of nitrogen and phosphorous are very important to the stimulation of microbial populations. The supply of nutrients is not as critical to the rate of biodegradation as is the supply of oxygen, but it is important to provide the threshold level (St-Cyr et al., 1992). Young and Burns (1993) note that a problem in adding inoculants to many soils is that the nutritional and energy resources are already fully exploited by the indigenous microbiota and therefore, colonization by introduced microorganisms is more difficult. Graham et al. (1995) found that the optimum biodegradation rates differ

for different chemical subcomponents of contaminant spills not only due to the innate different biodegradability of the different compounds but also due to the absolute quantities and ratios of nitrogen and phosphorous. The addition of additional nutrients is a means of overcoming this problem. When constructing a biopile, the addition of synthetic nitrogen fertilizer and phosphorous can utilize the traditional nutrient ratios of: 100 parts hydrocarbon contamination to 10 parts of nitrogen to 1 part of phosphorous (Hayes et al., 1995, Frankenberger, 1988).

Nitrogen is an essential component of proteins and nucleic acids (Farabaugh, 1996). Nitrogen is not only an important microbial component, but when the dissolved oxygen has been depleted, nitrite and nitrate may be used as the alternate electron acceptor under anoxic conditions (Wiedemeier et al., 1994). Through the nitrification process, organisms oxidize ammonium to obtain energy to support their growth. The nitrite so produced is further oxidized to become nitrate. As a result of the higher energy of ammonium, microorganisms use it in preference to nitrates. Lasdin and O'Neill (1993) also note that ammonia is the preferred source of nitrogen for the bioremediation of hydrocarbons but note that since there are no reliable soil tests for nitrogen, nitrogen nutrients should be added to the soil in an amount that assumes there was no nitrogen in the soil before the amendment. Since ammonium has a positive charge, it is attracted to the negatively charged soil particles and organic matter in the soil thus reducing its susceptibility to leaching (O'Leary et al., 1997). Inorganic nitrogen from synthetic fertilizers is very soluble and most is lost to leaching (Manahan, 1994). Relative to synthetic fertilizers, organic fertilizers have shown to stimulate bacterial productivity to the greatest extent (Lee et al., 1995). Previous field level experiments have shown that the addition of five percent poultry manure in lieu of synthetic nitrogen fertilizer appears to work very well (BioCycle, 1995). The poultry manure provides not only a source of nitrogen, phosphorous and potassium, but also additional microbes. Poultry manure contains approximately six percent nitrogen, with 30 to 50 percent of the total nitrogen in the forms of ammonium and uric acid (Nicholson et al., 1996). **Table 2.3 - Nitrogen Oxidation States** is arranged in descending order typical of nitrification and indicates the oxidation state of the different nitrogen compounds/ions (Markwell, 1998).

Table 2.3 Nitrogen Oxidation States

Oxidation State	Form	Name
+5	NO_3^-	Nitrate ion
+3	NO_2^-	Nitrite ion
+1	$\text{N}_2\text{O}_2^{2-}$	Hyponitrite ion
0	N_2	Nitrogen gas
-1	NH_2OH	Hydroxylamine
-3	NH_3	Ammonia

Phosphorous is an essential component for microorganisms and usually must be available in some form of orthophosphate ion (Manahan, 1994). Phosphorous is used in the production of ATP (adenosine triphosphate) which is the carrier of metabolic energy (Farabaugh, 1996). Poultry manure contains approximately two percent phosphorous (Nicholson et al., 1996).

2.5.4 **pH**

The pH of the matrix can have a significant effect on the survivability of microbial species, the availability of nutrients and chemical conditions. As noted earlier, within the bulk pH of the matrix, the varying pH in the microcosm on the soil and organic matter particles can cause a change in the availability of soluble nutrients (McLaren and Peterson, 1967). Tchobanoglous and Burton (1991) note that when the pH is greater than 7, the NH_3 - NH_4^+ equilibrium changes and ammonia is formed. This ammonia gas is subject to loss from the matrix with the movement of the soil-gas. When the pH is less than 7, nitrate is formed which is subject to loss by leaching. However, other factors also impact the balance of the ammonia and nitrate such as soil type, moisture and level of organic matter (Mahanan, 1994). Bioavailability of orthophosphate is the greatest at pH values near neutrality (Manahan, 1994). Fungi normally grow well in a pH range from near neutrality to acidic conditions of 4.5 (EPA, 1994, Leahy and Colwell, 1990)

2.5.5 **TEMPERATURE**

Aerobic microbial activity is exothermic which causes a rise in the temperature of the surrounding matrix (Manahan, 1994). Since microbes have a preference for functioning in specific temperature ranges (Keene, 1995b), there will be a change in the types of active microorganisms as matrix temperatures change. Nonetheless, from the organ-body perspective, despite the rise and fall of specific populations, matrix temperatures elevated above the ambient are a good indication of aerobic bioactivity and therefore degradation of the organic contaminant. Moreover, since elevated temperatures promote

increased bioactivity (Leahy and Colwell, 1990) and therefore increased remediation rates, it is preferred to maintain matrix temperatures above the ambient, but below the thermal death point of the microbes. Thus monitoring the change in bulk temperature of a matrix will be a good indication of the rate of change of microbial activity.

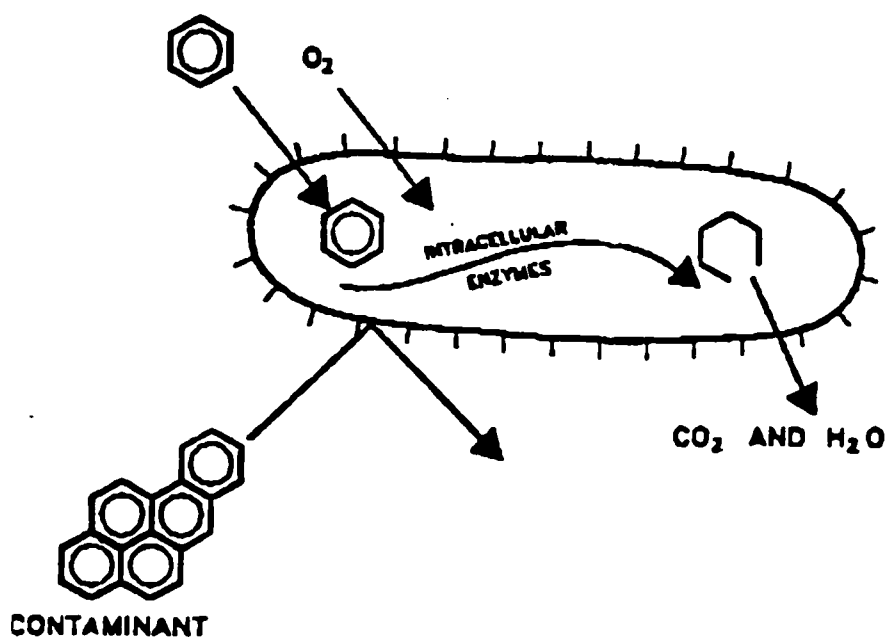
2.6 FUNGAL BIOREMEDIATION OF LARGE ORGANIC MOLECULES

2.6.1 **BACKGROUND**

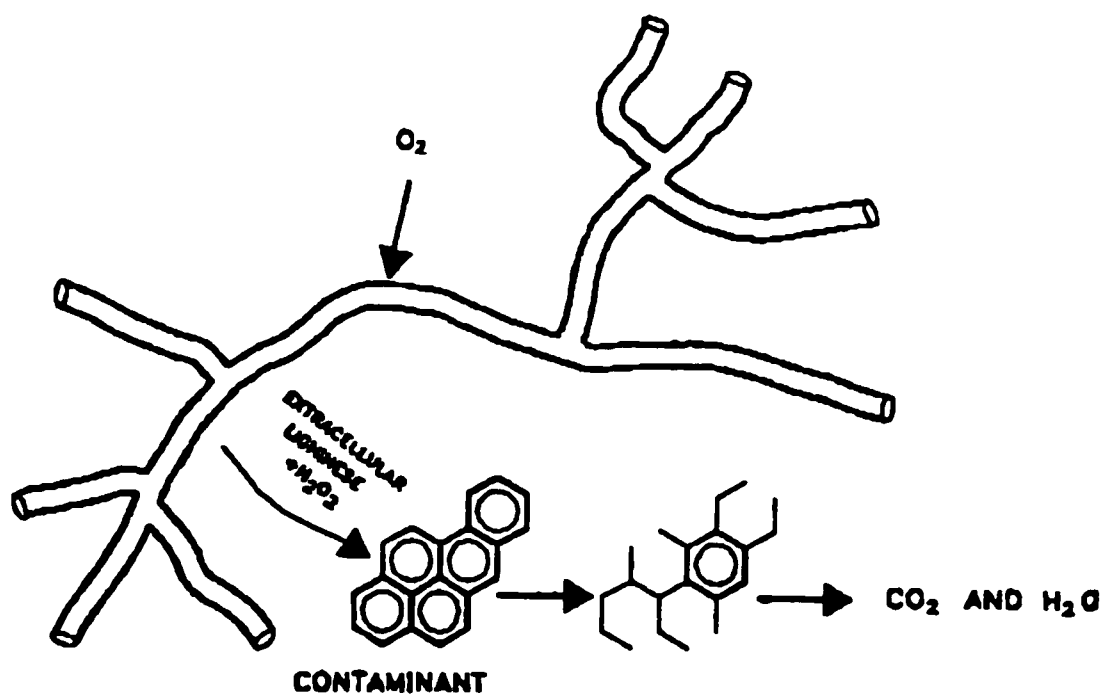
For the last decade, science has been intrigued with, and recent bioremediation symposia have been heralding, the potential for white rot fungus to breakdown and mineralize recalcitrant organic molecules, including heavy hydrocarbons. Research has demonstrated that white rot fungus is highly competitive, nonspecific and can degrade a wide variety of recalcitrant high molecular weight organic environmental pollutants such as Atrazine, Chlordane, chlorobenzene, DDT, dioxin, lindane, PCBs, PCP, PAHs, and toluene, some of which are toxic to most life forms (Bumpus and Aust, 1987; Aust and Benson, 1993; Boyle and Richardson, 1993; Kaal et al., 1993; Liang and McFarland, 1994; Mougin et al., 1994; McFarland and Qiu, 1995; Yadav et al., 1995). Lantz et al. (1995) note that the biotransformation of high molecular weight PAHs in contaminated soil is more difficult than for the low molecular weight PAHs.

Generally, white rot fungus is commonly found on fallen trees and branches in forests, on any other decaying wood and on the soil surface. Analysis of natural composts indicate a greater presence of fungi (Golueke, 1977). The fungus uses cellulose as a food source, or nutrient. Since the cellulose is wrapped by lignin, nature's plastic (Aust and Benson, 1993), fungus has a complex mechanism to degrade lignin. The white rot organisms are predominantly members of the basidiomycetes which attack both lignin and some cellulose and hemicellulose. They are different from brown rot fungus which disintegrate wood by removing the structural polysaccharide elements, leaving a residue of relatively unchanged lignin (Ferrey et al., 1995). The process of lignin degradation in the natural timber environment where proteins, carbohydrates and other micro-floral populations abound may be quite different from that of the single white rot fungus organism interaction with a lignin substrate. However, it appears that by secreting soluble enzymes such as peroxidases and phenoloxidases which act on the insoluble substrates such as cellulosic debris, and soil organic matter, the white rot fungus catalyzes the oxidation of the lignin, converting it to smaller molecular weight compounds. These smaller compounds are then taken up by microorganisms for an energy substrate (McLaren and Peterson, 1967). Although actinomycetes and bacteria are present, white rot fungi are the only microorganisms that can efficiently break all the chemical bonds in lignin (Boyle and Richardson, 1994). Refer to **Figure 2.3 - Bacterial Versus Fungal Bioremediation** (Maat, 1993).

Figure 2.3 - Bacterial Versus Fungal Bioremediation



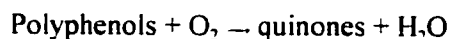
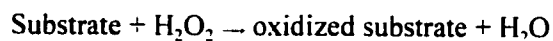
BACTERIAL BIOREMEDIATION



FUNGAL REMEDIATION

2.6.2 **WHITE ROT FUNGUS LIGNIN DEGRADING MECHANISMS**

The white rot fungus decay system is based upon an external broadcast of lignin-degrading substances. The organic pollutants which are included in this broadcast area are also degraded by the same oxidizing mechanisms. The reaction catalyzed by fungi-produced peroxidase enzymes and polyphenol oxidases are as follows (McLaren and Peterson, 1967):



The nonspecific nature of the mechanisms used by white rot fungus allows them to cometabolize a wide variety of complex organic pollutants to carbon dioxide while it is metabolizing larger amounts of the lignin/cellulose substrate. Unlike bacteria, the fungi do not require a preconditioning to the particular pollutant (Winkelmann, 1992; Barr and Aust, 1994). Whereas bacteria will stop using an organic contaminant when its concentrations are below that which it will adapt to, fungi tend to degrade pollutant chemicals to the non-detect concentrations because those chemicals are not involved in the fungus-cellulose/lignin cycle (Bishop, 1993).

White rot fungi normally do not exist in large numbers in the soil since they are an above ground microbe (Holroyd and Caunt, 1995; Keene, 1995a). They live on the surface where there is a plentiful supply of atmospheric oxygen, moisture and food. To effectively use fungi to remediate petroleum hydrocarbon contaminated soil, the fungi must be introduced into the soil in large numbers and appropriate conditions must be maintained in the soil matrix to foster their continued growth. When the fungi are in an anoxic or high temperature environment, they cease producing the peroxidase enzyme emitting mycelium and reproduce by sporulation (Keene, 1995a). Keene (1995a) recommended that the white rot fungus be used in a composting situation in order to provide the necessary plant-derived substrate and an oxygen-rich environment.

McFarland and Qiu (1995) noted that when carbon nutrient was limited, the peroxidase activity of *Phanerochaete chrysosporium* was severely inhibited and pointed out that the addition of ample amounts of compost and coarse sawdust-hay are important. For cultivated white rot fungus, straw and coarse sawdust are used as the substrate. For naturally occurring white rot fungi, compost is used. Traditional yard waste compost already has a variety of naturally occurring fungi, actinomycetes and bacteria (Golueke, 1977). The compost would not only be active with fungi, but the wood chips themselves act as a bulking agent to produce an oxygen-rich environment in the soil by increasing the soil's void space.

Once well established on the substrate, the fungi with substrate are mixed into the contaminated soil. Particular attention must be paid to maintaining good oxygen, moisture and temperature conditions.

The natural process of the fungi exuding the peroxidase enzyme continues to break down the cellulose and lignin in the substrate. However, when these oxidants come in contact with the petroleum hydrocarbons, these contaminants are also broken down. Now in their simpler molecular form, the intermediate products of the organic contaminants become a food source for the fungi and other microbes.

2.6.3 ***CULTIVATING WHITE ROT FUNGUS***

The white rot fungus can be supplied to the site either as a spore culture or as a substrate. Depending on the size of the project and the ability of the site personnel to maintain the necessary controlled conditions, it may be economical to cultivate the culture on-site. Keene (1995a) recommended that the preparation of white rot fungus for a soil composting project follow a sequence of events based on the concern that preparation of a spawn required controlled conditions and careful supervision :

- a. Concentrate. On the supplier's premises, the fungal spores from the desired culture are harvested, mixed with water and added to a growth media, for example, malt extract or some other form of glucose under controlled conditions of temperature, moisture and pH;
- b. Spawn. The concentrate is cultivated on a suitable material, for example, rye, again under tightly controlled conditions to activate it to produce the spawn for use in an approximate amount of 10 percent (w/w) spawn to substrate;
- c. Substrate. On-site, the white rot fungus spawn is then combined with a lignocellulose substrate to acclimatize it to a lignin source. There are a number of possible substrates. A study demonstrated that although there were many inexpensive amendments to promote the growth of white rot fungus in soil, alfalfa had the greatest growth promoting effect yet the least effect on pH (acidification) (Boyle and Richardson, 1993).
- d. Windrow. The inoculated substrate is mixed with the contaminated soil 20 percent (v/v) along with another 20 percent (v/v) of wood chips (of a standard 'chipper' product size) to the contaminated soil.

2.6.4 ***MAINTAINING GOOD FUNGAL GROWING CONDITIONS***

The wood chips and substrate not only provide the lignin-based medium to encourage further growth of the white rot fungus, but they also act as a bulking agent to hold the soil structure open to provide the oxygen-rich environment required by the white rot fungus. Tests have shown that white rot fungus cultures flourish better in oxygen rich mediums and static versus shaken matrices (Yadav et al., 1995). This latter point is further reinforced by observations by Morgan et al. (1993) in which his experiments showed a decrease in organic compounds [contaminants] when the mycelium are in their

growing phase and by Aust and Benson (1993) in their observation that very little or no mineralization occurred during the first three days despite the appearance of a mycelial mat, but that substantial mineralization began after this period and peaked somewhere between day 3 and days 12 to 18. Oxygen is rapidly used up by the respiration of the soil microorganisms and should anoxic conditions and/or high temperatures high occur, sporulation will occur. The optimum range for biodegradation with lignin-degrading fungus is from 30 to 38°C (EPA, 1994) and the general thermal death point is considered to be 60°C (Golueke, 1977). Since in the microcosm of the pore space, oxygen concentrations could be much lower than the bulk in-windrow soil-gas readings indicate, it is preferred to keep the windrow oxygen concentrations above five percent to maintain sufficient oxygen concentrations for the microbial processes (Downey and Hall, 1994) and enzymatic action of fungi ceases below five percent oxygen (EPA, 1994).

There are two schools of thought on whether additional nitrogen should be added. Experiments by Yadav et al. (1995) indicate that the fungi flourish and mineralization of contaminants proceed well in a high nitrogen environment. On the other hand, the US Environmental Protection Agency (EPA) suggest that a nitrogen deficient environment is required to stimulate the fungal enzyme production systems (EPA, 1994).

Soil moisture concentrations must also be maintained to the optimal range of 50 percent of field capacity, for the fungi to flourish and to mineralize the contaminants (Keene, 1995a).

Remediation usually takes 1 to 2 months to reach regulated target concentrations. However, the aqueous solubility of the contaminants and their breakdown products, the types of chemical bonds within a particular chemical structure, the molecular size (Brubaker, 1992), the density of microbial colonies, and the conditions within the matrix affect the ability and rate of degradation. There are reports that white rot fungus mineralization rates slow considerably after the initial 50 to 60 day treatment period even though contaminant concentrations have not possibly reached their target concentrations and that only the addition of more substrate can increase the rates (Morgan et al., 1993). However, reports indicate that what was attributed to contaminant removal of benzo(a)pyrene was mainly due to formation of a bound residue (Morgan et al., 1993; McFarland and Qiu, 1995) and that surfactants, which are not toxic to the microbes, should be considered to move the organics into the soil aqueous phase so that they become available to the microbial treatment systems (Boyle and Richardson, 1994). It has also been noted that the initial stages of treatment are predominantly chemical removal processes during which microbial acclimatization is occurring (McFarland and Qiu, 1995).

2.7 MONITORING BIOREMEDIATION.

The rate of bioremediation can be monitored by a variety of means. As indicated above, windrow temperature and soil-gas oxygen are two such indicators. Temperature can be measured directly by stem and electronic thermometers, and by buried thermocouples. Oxygen is often measured by electrochemical cells through which the soil-gas is passed and the change in resistance of iron wire being oxidized is measured. Another indicator of bioremediation is carbon dioxide, a product of aerobic microbial respiration. Hand-held monitors measure the carbon dioxide content of the gas passing through the device by non-dispersive infrared detection. However, it is not as reliable an indicator of bioactivity since the carbon dioxide in the soil-gas goes into solution forming carbonate in alkaline soils (Hinchee, 1994, Downey and Hall, 1994). Another means of monitoring bioactivity is by measuring the rate of change in soil-gas volatile organic compound (VOC) vapours. Portable detectors based on photo ionization (PID), flame ionization (FID), and concentrations of combustibles in a gas, can be used but they all experience nonuniform interferences and variable sensitivities to different organic substances (HNu, Century, Gastech operating manuals). Refer to **Appendix D - Field Monitoring Equipment** for further details. MOEE Guidance (1996) advise that soil-gas VOC measurements are primarily to be used as a screening technique to determine the extent of contamination and must be followed up with laboratory analysis. Vapour readings can be from different portable units such as the Gastechtor (combustibles), TIP (PID), NHu (PID), and various FID portable detectors, and are generally not comparable (MOEE Guidance, 1996). Still yet another means of monitoring bioactivity is by measuring the actual microbial counts over time. A test for the presence of living microorganisms in soil can follow various processes (McLaren and Peterson, 1967). If the microorganisms are known, then they can be cultured on an appropriate substrate so that a count can be made. There are no reliable methods to enumerate all bacteria potentially present and the results should be considered qualitative (CCME, 1994) and the use of different media and nutrients, and of different extractants or extraction methods can give a completely different range of species and results (Lei, 1995). Moreover, plate counts do not distinguish between active and dormant bacteria, and in the presence of the nutrient-rich agar, dormant bacteria germinate and produce colony-forming units (Young and Burns, 1993). Therefore, biological analysis should be considered only optional (Weidemeier et al., 1994) and qualitative.

2.8 CASE STUDIES

Although the reasons are not always understood, bioremediation of hydrocarbon-contaminated soils have not been successful for reasons related to unfavourable oxygen, temperature, moisture conditions, soil permeability, and the unavailability of hydrocarbons due to binding, and nitrogen and

phosphorous nutrient conditions (Graham et al., 1995). Introduced populations of bacteria have shown declines by one or two orders of magnitude per week in loamy soil due to physical conditions such as soil type, temperature, water content, oxygen and pH (Holroyd and Caunt, 1995). They also note that since bacteria are specific to certain chemicals or chemical groups, the mixed contaminants found at most polluted sites limit their effectiveness, especially when many of the waste concentrations are toxic to metabolic activity.

Attempts to directly inoculate contaminated soil with *Phanerochaete chrysosporium* have had only limited success due to the unnatural soil habitat for the fungi and competition from other soil microorganisms (Holroyd and Caunt, 1995). In typical fungal composting operations, the contaminated soil is excavated and mixed with wood chips and the white rot fungus substrate, and the mixture is placed in an above-ground windrow. Recently, a few soil remediation projects have used white rot fungus on the field scale. Some projects do not fully succeed due to the fungi lignin-degrading system not functioning in a soil matrix rather than in their normal environment of lignocellulose (Boyle and Richardson, 1994). A 1992 project in Finland treated 6,000 m³ of soil contaminated with 40 to 200 mg/kg of chlorinated phenol, especially dioxins and furans, using *Phanerochaete chrysosporium* and the naturally present soil and substrate microorganisms. The white rot fungus was cultivated on a mixture of lignocellulosic material, mixed well into the contaminated soil which had been screened to 2 mm and placed in series of 30 m x 50 m x 2 m treatment beds with forced ventilation from pipes under the cells. Degradation of 71 to 86 percent of the contamination was recorded after 13 weeks.

2.9 QUALITY CONTROL

Unlike the USA, Canada has very few regulations that stipulate the analytical methods to be used (Thomson, 1994). Since a parameter can be analysed by a variety of standard laboratory methods (CCME, 1993) and different methods will yield different results, this lack of stipulated standard methods makes it difficult to provide representative data that will be acceptable to the regulators (Thomson, 1994) and to the clients upon which to base remediation decisions that may potentially involve hundreds of thousands of dollars. Therefore in any project it is important to make a conscious selection of standard laboratory methods to represent the contamination. Moreover, although no standard report format is commonly used by the different environmental laboratories in Canada, there are various references available. These include: CSA Standard Z753-95, *Requirement for the Competence of Environmental Laboratories*, and the New Jersey Department of Environmental Protection, *Field Analysis Manual*, (DOEP, 1994).

General principles that apply to the design of the quality control plan should consider:

- Careful selection and preparation of the contaminated soil to ensure that the soil for all treatment options is uniformly contaminated and that all windrows have a similar dimension for access to atmospheric oxygen, precipitation and solar energy.
- Careful control of all sampling procedures so that sampling procedures in and between events are consistently applied and common sampling errors such as cross-contamination and faulty operation of equipment are avoided.
- Sample selection is representative of the whole population and takes into consideration the heterogeneity of soil, the non-uniform distribution of a contaminant in a soil matrix, and the limitation on particle size which can be dealt with by laboratory analytical processes. To ensure that sampling is representative of the soil, periodic samples for each treatment option should be taken from generally the same locations and consist of at least three composites, each of at least three grab samples.
- Samples should include blind replicates, spikes, background matrix and inter-laboratory replicates. Spikes should use certified reference material in a representative matrix.
- Preservation of samples so there is minimal change in the parameters between the time the sample is obtained and the time it is analysed.
- Sample control and chain-of-control documentation to track the samples from collection to analysis.
- Laboratory methodologies based on standard laboratory methods, or where such do not exist, on rigorously tested methods developed by recognized bodies which have been used by a variety of laboratories and have been examined for MDLs, interferences, and biases.
- Laboratory analyses follow standard laboratory quality control procedures which include proper sample preparation, cleaning, maintenance and calibration of analytical equipment to minimize cross-contamination and faulty operation, competency and consistency in analysis techniques through training and use of the same analysis personnel.
- Contaminated site investigations should use the method detection level (MDL) as recommended by the MOEE (1996). Rather than being specific to just the analytical instrument as for IDL, the MDL represents the complete analytical procedure.
- Laboratory reports should include, as a minimum, the client-laboratory agreed requirements based on CSA Standard Z753-95. The laboratory quality control report should include the project data, the quality control data and the evaluation of the data by the performing and senior chemists. The quality control data should report on the sample storage conditions, sample analysis date and the continual results of in-laboratory

calibrations, surrogate recovery rates, replicates, spikes and blanks performed during the analysis of the samples submitted. Due to the large number of petroleum hydrocarbon compounds usually present and the inability to easily quantify them in their totality, analysis results should specify which analysis procedure was used (Thomson, 1994).

- Data analysis should examine the data for outliers and other gross errors and should follow standard statistical procedures.

Even with a carefully planned and controlled sampling and analysis plan, it can be expected that there will be a greater degree of uncertainty in obtaining data representative of the bulk and peak contamination levels in a soil rather than in water. The Ontario Ministry of Environment and Energy recognize the high degree of variability encountered in soils and strongly recommend that sampling soil for analysis of potential contaminants other than volatile organics should be a composite of representative samples taken from locations no more than four metres apart (MOEE Guidance, 1996). Environment Canada (1993) recommends that for characterization of soil volumes of 5 l to 100 m³, two composite samples are required, each consisting of three representative grab samples. The Quebec Ministry of Environment recommend that for soil volumes of less than 100 m³, three composite samples are required, each consisting of three representative grab samples (Orban, 1991). The variety of the above requirements is an indication of the difficulty in obtaining representative data from soil. This uncertainty can be minimized somewhat by careful sampling and analysis procedures and by the application of statistical methods to the analysis of the data. Nonetheless, it is expected that the greatest error in the overall uncertainty will be introduced during the field sampling processes (Cathum et al., 1996). For a given number of observations in a sample, this uncertainty is increased as the particle size of the matrix increases and, when there is a composite sample consisting of different sized particles, as the difference between particle sizes increases (Cathum et al., 1996). Therefore the ideal would be that each sampling event of a soil include a large number of observations. Due to the limitation of sample size by economics, a method is required to indicate whether the data truly represent the overall population. For a selected level of confidence, Student's *t*-statistic can be used to indicate the range that would likely include the true mean of the population. For small sample sizes, this statistic considers the size of the sample and the standard deviation of the range of its observations (Chao, 1969). This range can then be examined with respect to the range and mean of the sample to gain an insight into the latter's validity.

2.10 SUMMARY

Composting with white rot fungus (commercial or native species) offers an attractive technology for single-use sites. The design of the project should take into consideration the following:

- The combination of white rot fungus and soil bacteria form a particularly effective symbiosis to breakdown and mineralize a variety of large organic molecules, including heavy petroleum hydrocarbons as found in weathered petroleum products. The final concentrations of heavy petroleum hydrocarbons should be lower than processes depending on bacteria only and should reach asymptotic levels within 60 days.
- A remediation objective of 1000 mg/kg MOG should be established as the goal for this project. The objective for PAH contamination should be based on speciation analysis of PAHs during the project.
- Determination of starting concentrations of contamination should be carried out only after the soil has been excavated, screened and mixed with compost, where applicable, to ensure that losses due to volatilization through soil handling and binding to amendments are not be attributed to the remediation processes.
- Since the process for destruction of large organic molecules involves their breakdown to smaller intermediate compounds, completion testing should include testing for light petroleum hydrocarbons to determine what concentrations, if any, of these lighter organics remain in the soil.
- The chipped yard waste to be used in the project should be coarse and aged so that it will act as a bulking agent and have a well established population of naturally occurring fungi.
- The windrows should be maintained in aerobic conditions for ensure high rates of biodegradation. Forced soil aeration systems or turning will be required when the soil-gas oxygen concentrations fall below five percent.
- Moisture should be monitored during the project and adjustments carried out to maintain a moisture concentration of approximately 50 percent field capacity. Excess moisture should be prevented so to prevent leaching of nitrates from the windrows.
- Determination of bulk bacterial and fungal counts should be carried out during the initial phase of the project to determine the rate of increase of these populations, however, the data should only be considered as qualitative.

CHAPTER 3

EXPERIMENTAL MATERIALS AND METHODS

3.1 GENERAL

In order to demonstrate that soil composting with white rot fungus or naturally occurring fungi are suitable for remediation of sites contaminated with heavy petroleum hydrocarbons, the project was carried out at the field scale. Moreover, this project was designed to be a comparative examination of not only these two primary bioremediation systems with treatment variations, but to compare their effectiveness, rates of remediation and costs to a typical biopile control.

3.2 PROJECT DESIGN CONCEPTS

3.2.1 *REMEDIATION DYNAMICS*

The determination of which variables to examine started with an analysis of the remediation dynamics likely to be encountered in this project. Because heavy petroleum hydrocarbons have a low vapour pressure and low solubility, volatilization at ambient temperatures and leaching are not significant transport mechanisms to be considered for in-situ or on-site bioremediation schemes. Since the selected site had been contaminated for a long time, it can be assumed that any reaction of the petroleum hydrocarbons with the chemicals in the soil and with the infiltrated precipitation would have occurred long ago and that the present contamination concentrations reflect a state of equilibrium in these processes. Since the project was to be undertaken in ambient air, there was not a significant change in temperature or infiltration of precipitation as a result of outside influences. Therefore, destruction of petroleum hydrocarbons by chemical or thermal processes was ignored.

3.2.2 *MATERIALS AND CONDITIONS AFFECTING THIS PROJECT*

3.2.2.1 OXYGEN.

Since maximum remediation rates were being sought, good aerobic conditions were required. Three factors to improve the replenishment of oxygen lost to microbial respiration were assessed in the project:

- a. Passive ventilation from diurnal pumping, atmospheric pressure changes and wind.
- b. Bulking agents to increase the pore-space and to improve the movement of soil-gas due to natural ventilation, and

c. Periodic windrow turning.

Temperature, precipitation and wind records were obtained from the CFB Trenton airport and are summarized in **Appendix A - Data**. This information was used in the analysis of the results.

3.2.2.2 WHITE ROT FUNGUS.

To keep the cost of remediation projects low, a general method to apply the white rot fungus technology was sought. Therefore any tailoring of this project to optimize it for site specific conditions was avoided where possible. In line with this concept, samples of the Trenton fire fighter training area soil were not sent to the white rot fungus supplier, Intech 180, for identification and bench-scale testing for the most suitable white rot fungus species. (Such biofeasibility studies normally add in the order of \$8,000 to \$12,000 to a project.) Whereas *Phanerochaete chrysosporium* appeared to be a fairly fragile organism (Keene, 1995a), the supplier recommended the strain of white rot fungus, *Pleurotus ostreatus*, for the project. It is an edible mushroom and was selected for its proven record of remediating petroleum contaminated soils, its ability to function in a variety of soil types, its tolerance for temperatures above its optimum upper 20°C range, and its active persistency in soils for up to 3 years (Keene, 1995b).

Since the carefully controlled conditions for cultivating the white rot fungus on the spawn could not be controlled on-site as required, it was decided that this first stage would be carried out at the supplier's site. It was recommended that for a nominal 100 tonnes of contaminated soil, 1800 kg of white rot fungus spawn cultivated on substrate of 2 tonnes of mould-free wheat straw and 18 tonnes of moistened coarse sawdust, to provide an approximately 20 percent (v/v) substrate to contaminated soil (Keene, 1995a). He recommended that the white rot fungus be cultivated for approximately two weeks until an adequate mycelium mat was visible before it was introduced into the windrow. Morgan et al. (1993) noted that this substrate had shown to be very good for fungal growth. Keene (1995a) recommended that the cultivation piles not be too thin since they would dry out. He recommended that they be about 0.6 to 0.75 metres thick. Refer to **Appendix E - Figures** for a photograph of the on-site cultivation.

The white rot fungus was delivered to the site in time for it to be cultivated and ready for mixing with the soil on Day 2 so that all treatment processes would commence simultaneously. Unfortunately, within five days, windrow temperatures approached 60°C, exceeding the 40°C thermal death point of the *Pleurotus ostreatus* fungus, killing the fungi in the centre of the piles. The windrows were then reduced to a depth of 0.2 m. This depth seemed to strike a reasonable balance between maintaining the heat of bioactivity and moisture to reach the desired 25 to 30°C range, while radiating sufficient heat so that the piles would not overheat. The cultivation period was extended to Day 22 to allow time for an adequate redevelopment of a mycelium mat. Although in hind sight, the majority of the MOG contamination had

already been degraded by Day 22, this was not known at the time since none of the laboratory MOG results had been received by that date.

The supplier requested that once the white rot fungus was introduced into the contaminated soil, the soil not be turned any further and that the target moisture concentration be approximately 50 percent of field capacity. To limit the number of variables in this project, no synthetic or organic fertilizer was added to the white rot fungus windrow since the EPA found that elevated nitrogen levels had a negative effect on the enzyme-producing stage of the white rot fungus.

3.2.2.3 COMPOST.

CFB Trenton had been stockpiling chipped yard waste for over a year. It consisted of mostly coarse chips and tree branch segments, ranging in length of 20 mm to 100 mm and cross-section of 5 to 25 mm. Visual inspection of the stockpile indicated that a white mycelial mat typical of fungi growth was present. Since sufficient quantities existed for the 20 percent (v/v) requirements in Windrows 1, 2A, 2B and 3A, this material was used for the compost requirements. The compost had a field density of 557 kg/m³.

3.2.2.4 POULTRY MANURE.

Five hundred kilograms of poultry manure was acquired from a local farmer for the project. Analysis of the nitrogen content of the poultry manure indicated that it contained 156 µg NO₃⁻ as N per gram (dry weight). Since the sample was accidentally dried before analysis, it was not possible to determine the ammonia concentrations. Therefore, the total nitrogen in the poultry manure could not be determined. The total phosphorous was not determined. The nominal value of six percent N and two percent phosphorous from literature was used for calculations in the project. Refer to **Appendix B - Calculations** for the calculations supporting the application rate of 5 kg/m³. The poultry manure had a field density of 732 kg/m³.

3.2.2.5 SYNTHETIC FERTILIZER.

Two hundred and fifty kilograms of a locally available, slow release synthetic fertilizer was purchased. It had a formulation of 48:8:2 nitrogen-phosphorous-potassium (N-P-K) with 40 percent slow release nitrogen. Refer to **Appendix B - Calculations** for the calculations supporting the application rate of 1.5 kg/m³.

3.2.2.6 MOISTURE.

Since the soil moisture holding capability is related to particle size, a grain size analysis was carried out by sieve and hydrometer analysis. The analysis indicated that the soil contained 5 percent gravel, 59 percent sand and 36 percent silt/clay. (Refer **Appendix B - Calculations**). This soil would be classified for Ontario contaminated site remediation criteria purposes as medium/fine textured (MOEE, 1996).

Two field methods of measuring moisture content of the soil, soil suction and dielectric, were trialed in the project and compared to the laboratory's gravimetric moisture analysis. A tensiometer reading of zero soil suction indicates that the soil is saturated, that is, field capacity equals 100 percent. The actual amount of water in a soil matrix at this point depends on the pore space. The dielectric properties of the soil are related to not only the amount of moisture which would promote or restrict the flow of electricity, but the amount of salts dissolved in the water. In both of the above, the readings given by the instruments are site specific and would have to be calibrated to each site. In this project, there was no consistent correlation of the instrument readings to each other or to the apparent moisture conditions as seen visually. Refer to **Appendix D - Field Monitoring Equipment** for further discussion on the results of moisture measurement in this project. The readings were not calibrated to field capacity or to total moisture capacity since there was no correlation in the data.

3.2.3 ***SELECTION OF TEST VARIABLES AND WINDROW TREATMENT OPTIONS***

As many variables as possible were constrained so that the comparative analysis would be based on the chosen variations in treatment options. The possible variables included starting concentration and type of contamination, soil type, windrow size and orientation to the sun, atmospheric conditions, windrow temperature, pH and moisture, and soil-gas oxygen concentrations. Selected windrows were turned every week to ensure that the in-windrow conditions remained as aerobic as possible. This was to ensure that technologies with rapid rates of remediation would not be artificially slowed by the lack of oxygen and therefore allow slower technologies to catch up.

Since the soil contamination had persisted for a long time and the excavated soil was mixed before the windrows were formed, only one gas chromatography/mass spectroscopy (GC/MS) analysis of the contaminated soil in the windrows was carried out to reduce project costs. The analysis showed that the primary contaminant was typical of motor oil (C17 - C24). Refer to **Figure 3.1 - Gas Chromatogram of Trenton FFTA Soil** and, for comparison, to **Figure 3.2 - Gas Chromatogram of Crude Oil** and **Figure 3.3 - Gas Chromatogram of Diesel Fuel**. The gas chromatogram of the fire fighter training area soil clearly shows a preponderance of heavy hydrocarbons as predicted. Since the contaminated soil for all

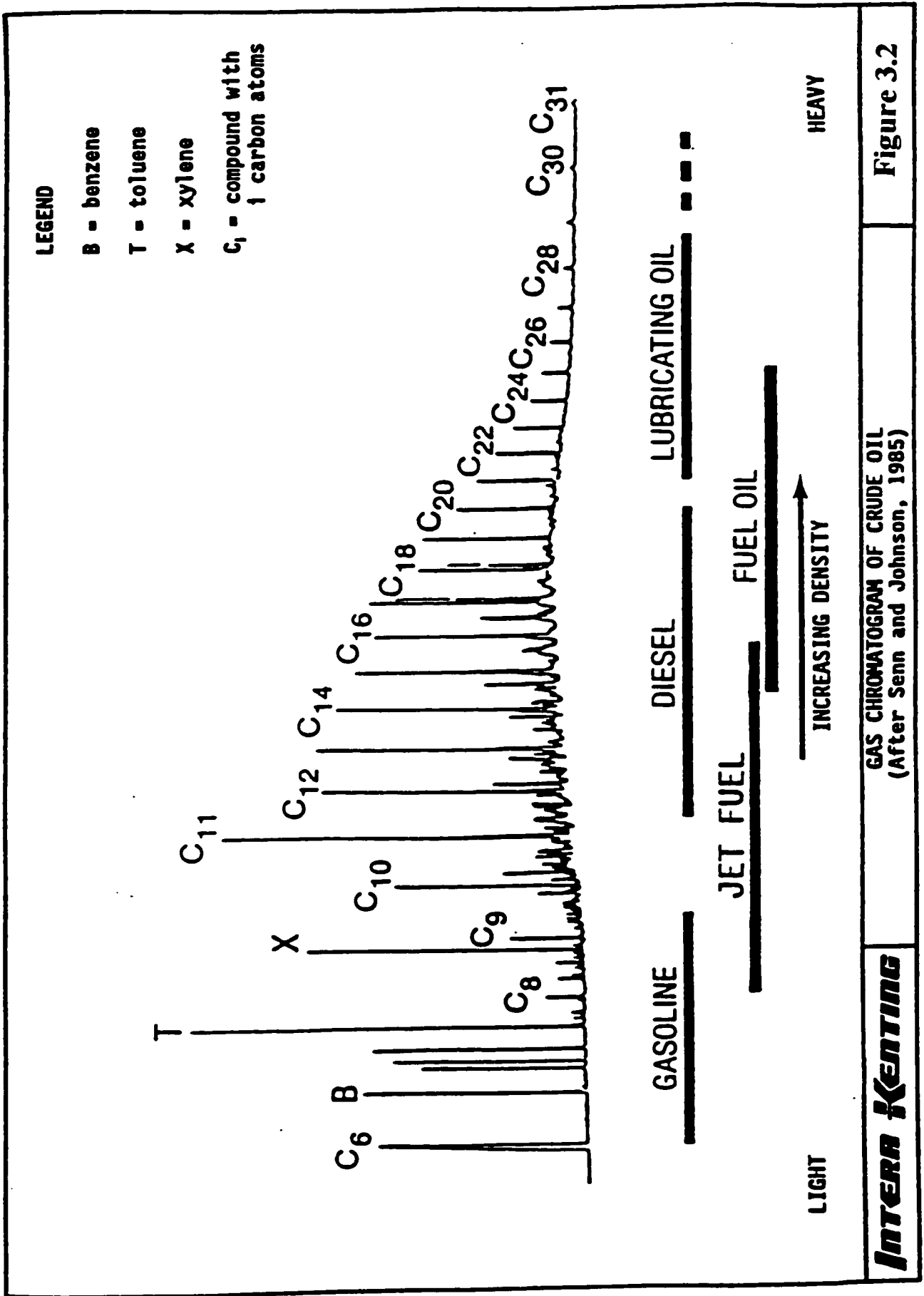
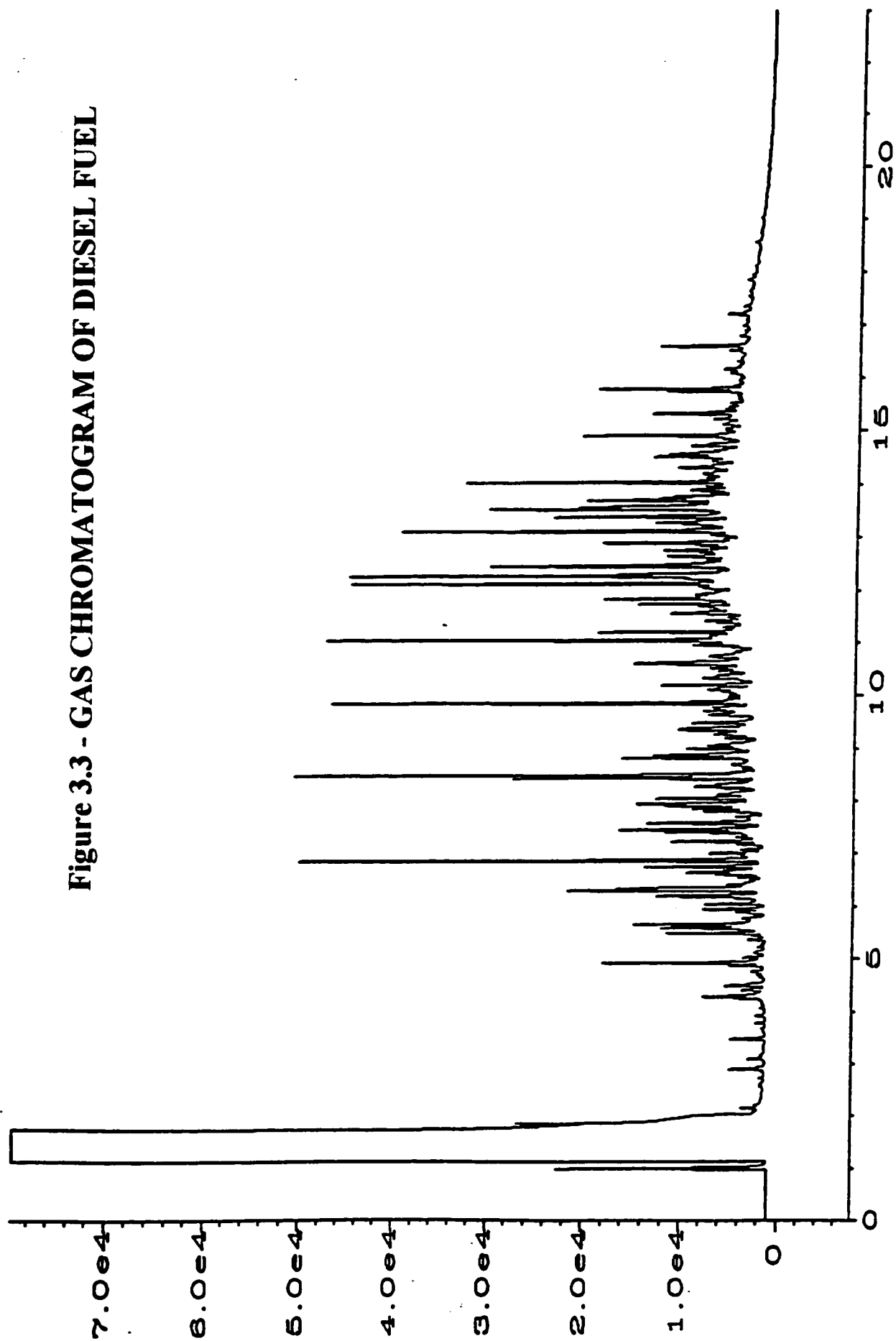


Figure 3.3 - GAS CHROMATOGRAM OF DIESEL FUEL



Sig. 1 in C:\HPCHEM\1\DATA\PETRO\002F0101.D

windrows came from the same 10 by 15 m excavation and was mixed after excavation, it can be assumed that the type of contamination in the other windrows was generally typical of the heavy hydrocarbons found in the contaminated soil that was tested. Rowe (1995) noted that most peaks above C28 were likely due to naturally occurring organic compounds, with the PAHs as the likely components of the C19 - C31 peaks and that the peaks below C18 - C20 were characteristic of jet fuel. Since motor oil is used as one of the surrogates for calibrating the GC/MS equipment, it should be noted that laboratories report such contamination as motor oil, when in fact other petroleum hydrocarbons, such as weathered petroleum products, have a similar signature.

Soil treatment options were chosen to compare the efficacy of cultured fungus versus naturally occurring fungus. The white rot fungus was applied in accordance with the supplier's recommendations for a ratio of spawn to substrate (10 percent v/v), substrate to soil (20 percent v/v), and wood chips to soil (20 percent v/v). In the case of naturally occurring fungus, there were a number of potential factors which could influence the rate of contaminant reduction. Therefore, variations were selected in an effort to discern what, if any, effect the variables of type of nutrient and maintenance of soil-gas oxygen concentrations would have on contaminant reduction rates. Since it is common practice to add nutrients to the bioremediation process, the effect of an organic fertilizer was compared to a synthetic fertilizer in different windrows. Rather than assess different concentrations of nutrient applications, for cost reasons standard application rates were selected. The static biopile was constructed in the same configuration as the other windrows. Typical of static biopiles only nutrients were added. No bulking agent or fungus was added to the biopile. The selected treatment options are summarized in **Table 3.1 - Project Treatment Options**.

Table 3.1 - Project Treatment Options.

Option	Windrow Designation	Microbial Inoculation	Nutrient Additions	Bulking agent	Oxygenation
1.	1	- White rot fungus - Compost	Nil	Sawdust, compost	Limited turning.
2.	2 A	- Compost	Poultry manure	Compost	Weekly turning.
3.	2 B	- Compost	Synthetic fertilizer	Compost	Weekly turning.
4.	3 A	- Compost	Synthetic fertilizer	Compost	Nil
5.	3 B (Biopile)	Nil	Synthetic fertilizer	Nil	Nil

Legend: White rot fungus = *Pleurotus ostreatus*.
Compost = Naturally occurring fungi on aged coarse wood chips.

To restore the concentration of oxygen in the windrow matrix to near atmospheric concentrations Windrows 2A and 2B were turned on a weekly basis, except when the compost turner was

not available on Day 35. Although oxygen concentrations were being monitored and it would have been possible to take corrective action on a case-by-case basis if windrows were becoming anoxic, some windrows were not turned to confirm the effect of a lack of oxygen. It should be noted that one of the objectives of the project was to find a low cost approach. Therefore, since turning incurred cost, it was important to confirm the theory that turning was required for the rapid bioremediation of the soil and to determine at what reduced oxygen concentrations the bioactivity was being negatively influenced. On the advice of the white rot fungus supplier, the turning of the Windrow 1, with white rot fungus, was not carried out after the supplement, compost and soil were blended on Day 22. However, to determine whether turning would have a noticeable effect on the white rot fungus and its rate of remediation, the windrow was turned on Days 28 and 42.

3.3 SITE BACKGROUND

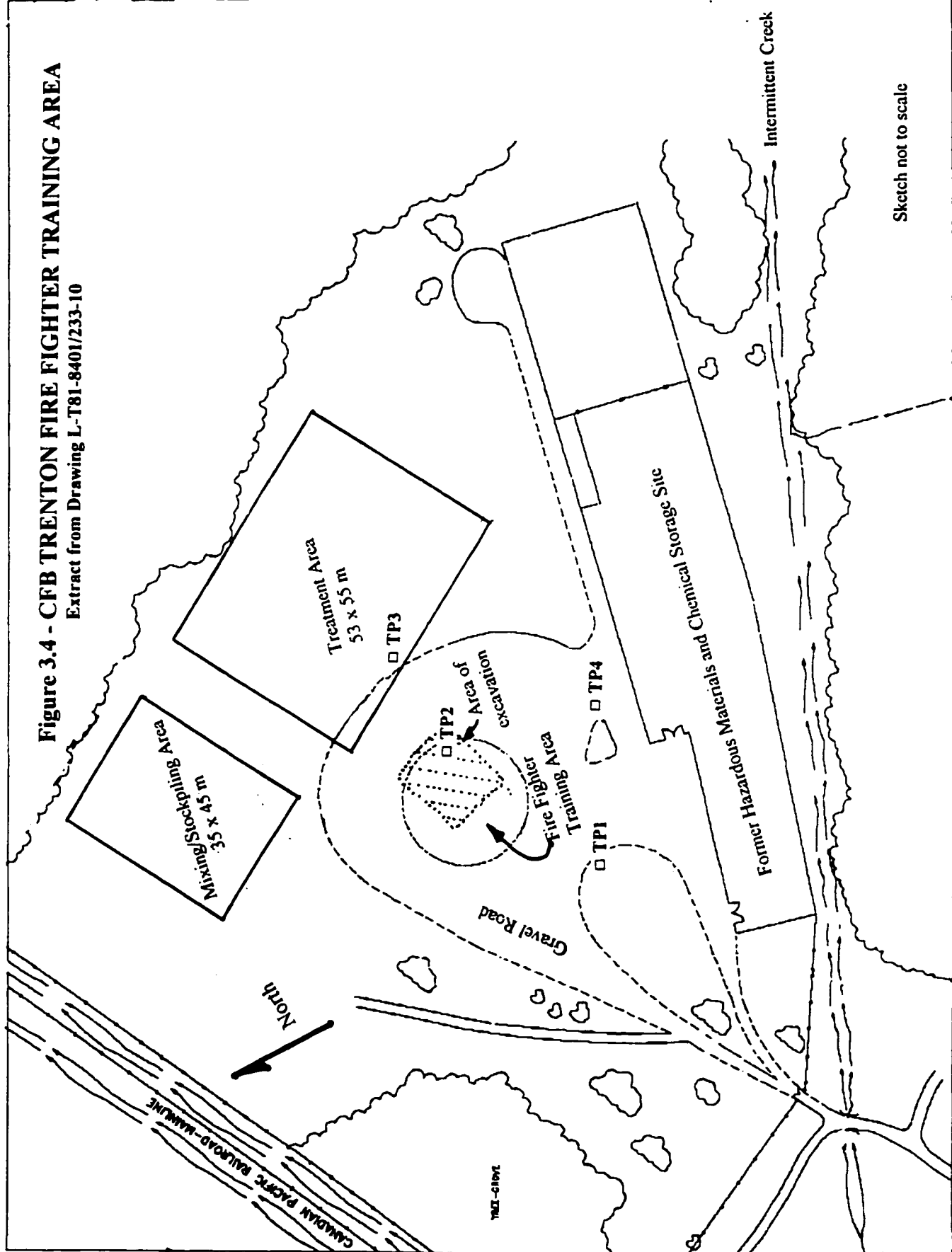
The old fire fighter training area at CFB Trenton in Ontario (Refer to **Figure 3.4 - CFB Trenton Fire Fighter Training Area**) was used to train personnel in the fighting of aircraft fires since the 1960s. In close proximity to the northeast of the site there was an uncontrolled landfill which was used for disposal of aircraft maintenance products, including plating wastes, cyanide and chromic acid. To the south, there was a hazardous materials and chemical storage site with building and to the northwest, there was an explosive ordnance disposal area. Since contamination was expected in the area, a number of environmental site investigations were carried out over the years. The contamination was generally found to be localized and not migrating off-site. From these studies, a general understanding of the topography of the site and its contamination was derived. In summary, the upper metre (approximate) was fill consisting of washed gravel, ash, and possibly coal cinder. Below the fill were narrow intrusions fine sand, silt and clay to a limestone bedrock which was at a four to six metre depth. In 1992, a soil analysis of just southeast of the fire fighter's mock-up showed 2,240 mg/kg TPH along with light petroleum hydrocarbons concentrations of benzene and xylene, and propylene glycol. Since the studies were mainly concerned with the potential for off-site migration of the petroleum hydrocarbons, they focussed on groundwater sampling rather than contamination of the soil. As a result, they did not delineate the soil contamination.

3.4 SELECTION OF CONTAMINATED SOIL

To confirm the type and concentration of contamination, and location of the more contaminated areas in the fire fighter training area, a soil-gas survey and test pitting program was carried out. A soil-gas survey of oxygen at a depth of approximately 0.9 metres was carried out on a grid over the area to find the areas of highest contamination for digging confirmatory test pits. Since the site consisted of a top cover of

Figure 3.4 - CFB TRENTON FIRE FIGHTER TRAINING AREA

Extract from Drawing L-T81-8401/2333-10



compacted gravel, the soil-gas probe could not be driven into the ground. Instead, the holes first had to be augered out then sampled for the target gas. Unfortunately the results were not reliable since the soil-gas was diluted with atmospheric air as the auger was withdrawn. Four test pits were then dug at locations shown on **Figure 3.4** for the background soil and in areas deemed to be high contamination from earlier site characterizations. The results of the analysis of soil samples from the test pits are shown in **Table 3.2 - Preliminary Test Pit Results**. After the test pits had been filled in, the author used a portable PID and a portable FID to determine the soil-gas VOC concentrations in the backfill. These results are also indicated in Table 3.1. There was only an approximate correlation between the PID and FID and as expected, no correlation with the laboratory MOG analysis since the latter was based on petroleum hydrocarbons of low vapour pressure.

Table 3.2 - Preliminary Test Pit Results [mg/kg]

Location	Purg HC (Recvy 66%)	CE HC (Recvy 114%)	MOG	PAHs	PID Reading	FID Reading
TP1 (W of centre)	nd	nd	599	nd	17	100
TP2 (Centre of site)	nd	nd	594	nd	50 - 60	900
TP3 (E of centre)	nd	nd	798	nd	70	225
TP4 (S of centre)	nd	nd	1589	nd	4	25
Bkgrd (wood line)	nd	nd	598	nd		

Legend:

Purg HC = purgeable hydrocarbons (C1 - C10)

CE HC = cold extractable hydrocarbons (C10 - C35)

MOG = mineral oil and grease (C12 - C50)

Bkgrd = background

nd = not detected

recvy = % recovery of surrogate.

3.5 MIXING AND TREATMENT PAD DESIGN AND CONSTRUCTION

Factors which were important for the design of the site included placing the mixing and treatment pads near the fire fighter training area to reduce transportation requirements, controlled access to the site to prevent unauthorized access, prevention of runoff of potentially contaminated precipitation to the surrounding area, and access to water for washing equipment and, if required, irrigating the windrows. The treatment pad was designed on cost effective principles to demonstrate the likely cost for it in typical field projects, with the spacing between windrows being only sufficient to allow passage of the compost turner towing equipment. At the end of the windrows, 13 m were allowed for equipment turning. However, for this project the space between windrows was increased to 4 m to avoid possible cross contamination between windrows. Therefore the overall dimension of the treatment pad, including berm, was 53 by 55 m.

The CFB Trenton heavy equipment section prepared the site. The mixing and treatment pad sites were graded to provide a level, smooth surface free of sharp rocks and with sufficient gradient to minimize ponding of precipitation. This area was then bermed with soil to a height of 0.3 m around the perimeter to retain any accumulation of water. Since the surface materials were sandy loam, the designed sand sub-base for the pad membranes was not required. A 0.3 mm (12mil) plastic sheeting (consisting of a sheet of reinforcing scrim laminated between polyethylene), factory welded to the required sizes of 35 x 45 m and 53 x 55 m were laid and held in place with sandbags along the edges (Refer to **Appendix E - Figures** for photographs of the operation). On the treatment pad membrane, 150 mm of sand was placed on top to act as a ballast to prevent the membrane from being affected by wind and to protect the membrane from damage by heavy equipment. Due to delays and the necessity to keep the project on schedule, the mixing pad did not have the sand ballast placed on it. Tearing of the mixing pad membrane by heavy equipment became obvious. In the case of the treatment cell, the action of the heavy equipment building the windrows and the operation of the compost turner did not have any apparent negative effect on the membrane. There was no apparent effect of UV radiation on the plastic.

3.5.1 ***CONTAMINATED SOIL PREPARATION.***

In order to test the technologies at a field scale where soil volume versus windrow surface area would be typical for commercial scale projects, each 3 m by 25 m by 1.5 m high windrow (1, 2A and 2B, 3A and 3B) was designed to contain approximately 100 tonnes of soil, based on an estimated 1.9 tonnes per cubic metre of soil. Windrow 2A was connected to 2B, and 3A to 3B since their turning programs were the same. Refer to **Table 3.3 - Planned Windrow Dimensions.**

Table 3.3 - Planned Windrow Dimensions (average dimensions, estimated weight)

Windrow	Width (m)	Length (m)	Height (m)	Volume (m ³)	Weight (tonnes)
1	3	25	1.5	55	100
2A	3	12.5	1.5	27.5	50
2B	3	12.5	1.5	27.5	50
3A	3	12.5	1.5	27.5	50
3B	3	12.5	1.5	27.5	50

The site selected for excavation was visually based on the soil with the greatest staining in the area of highest probable use of petroleum hydrocarbons. This was in the centre of the fire fighter training area where the fire fighter's mock up was located, and just to the east of it. To obtain the required

contaminated soil, the excavation was approximately 10 by 15 m to an approximate depth of 2 to 2.5 m, as indicated in **Figure 3.4** and **Appendix E -Figures**. Clean overburden was set off to the side of the excavation. The excavation itself was a confined space with potentially hazardous vapours and personnel were not permitted to enter it to take soil-gas readings at the excavation floor and walls. Therefore, excavation was guided by the staining of the soil - the more heavily stained soil being selected. Soil was mixed to blend the types of soil and contaminant concentrations, screened to 150 mm to remove large rocks and debris and placed into windrows.

To assist in mixing the excavated soil, the soil was carried to the mixing pad by dump truck and randomly placed in various piles. From these piles, a front end loader randomly picked soil for loading into the shaker. (Refer **Appendix E -Figures**) After screening, it was randomly stockpiled again to assist in mixing the soil as much as possible. From the mixing cell, over a period of three days the soil was randomly selected from the piles and placed in windrows in the treatment cell.

In typical remediation projects the contaminated soil could be excavated and placed directly in the treatment windrows. However, in this case, to achieve a degree of uniformity in soil type and contamination, the soil was excavated, placed into holding piles in such a manner so to mix the soils from one area with those of another then processed through a 150 mm mechanical screen to remove large debris and to further mix the soil. Ideally it was planned to place the soil alternatively in the various windrows, again to achieve more mixing. Project delays in the construction of the mixing and treatment pads, required that the windrows were sequentially constructed as the soil came out to the screening process. Therefore, an additional stage of mixing did not occur.

3.5.2 ***WINDROW CONSTRUCTION AND AMENDMENTS***

Windrow construction consisted of a front end loader putting down the layer of screened soil then placing the compost and nutrients, as applicable, in layers on top. An open, elevated faced compost turner was selected since it was fairly tolerant to debris in the soil and would not chew up the bulking agent. Two passes on each side of the windrow by the compost turner were sufficient to provide a good mixing of the different components. (Refer to **Figure 3.5 - Treatment Area Layout**, and photographs in **Appendix E - Figures**). The amendments were placed on the windrows by reckoning in accordance with the plan. As indicated in **Table 3.4 - Final Windrow Dimensions**, over the duration of the project, the turning tended to lengthen and widen the windrows with a corresponding reduction in the height.

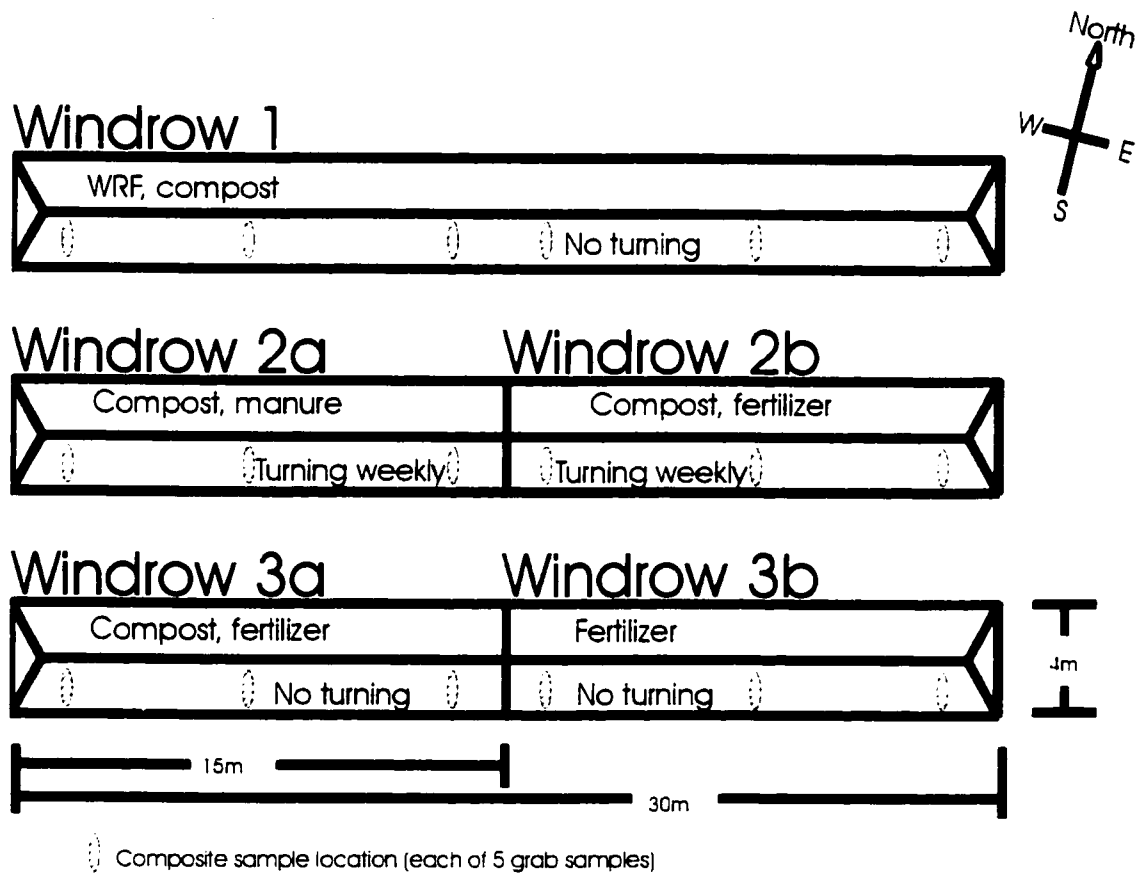
Figure 3.5 - TREATMENT AREA LAYOUT

Table 3.4 - Final Windrow Dimensions (average dimensions, estimated weight)

Windrow	Width (m)	Length (m)	Height (m)	Volume (m ³)	Weight (tonnes)	Bulking Agent
1	4.2	29.5	1.6	95	97	sawdust, compost
2A	3.5	15.25	1.2	30	37	compost
2B	3.5	15.25	1.2	30	37	compost
3A	4.4	14.25	1.2	35	43	compost
3B	4.4	14.25	1.2	35	49	nil

Note: volume and weight includes bulking agents.

3.5.3 **COMPOST TURNING OPERATION AND EQUIPMENT.**

If turning of windrows proves to be important, selection of a compost turner can have a significant effect on the cost of remediation. Most compost turners use a system of internal augers to pick up and mix compost and deliver it to a conveyor belt to be discharged from the rear of the machine. These machines require well screened material which is free of cobble and large debris. Moreover, they are designed to chew up the compost and reduce its size. This would have a negative effect on the bulking agent used in this and similar soil remediation projects. Therefore, a compost turner was sought which could handle cobble and debris, and would "fluff" up the windrows to improve the air volume in the windrows to provide more oxygen to the microbes without chewing up and reducing the size and effectiveness of the bulking agents.

As mentioned earlier, an open, elevated face towed unit with a face width of 1.8 m (6 ft) was selected. Its action provided good bulk mixing action by inverting the surface material in the windrow to the centre of the windrow. One pass on each side of the windrow was required to turn a windrow.

3.6 **WINDROW MONITORING AND SAMPLING**

Table 3.5 - Chronology of Windrow Events, summarizes the general chronology of events during the remediation period. Shading of even-numbered weeks is provided for clarity of events occurring in each week.

3.6.1 **MONITORING**

Field monitoring of the windrow conditions was done every week. The effects of oxygen infiltration, moisture gain/loss, and radiation of heat tend to be influenced by the shortest distance from the point of concern in the windrow matrix to the windrow-air interface. This is the perpendicular distance to the two windrow faces of approximately 2.3 m in length. Apart from such surface effects, the collected gas

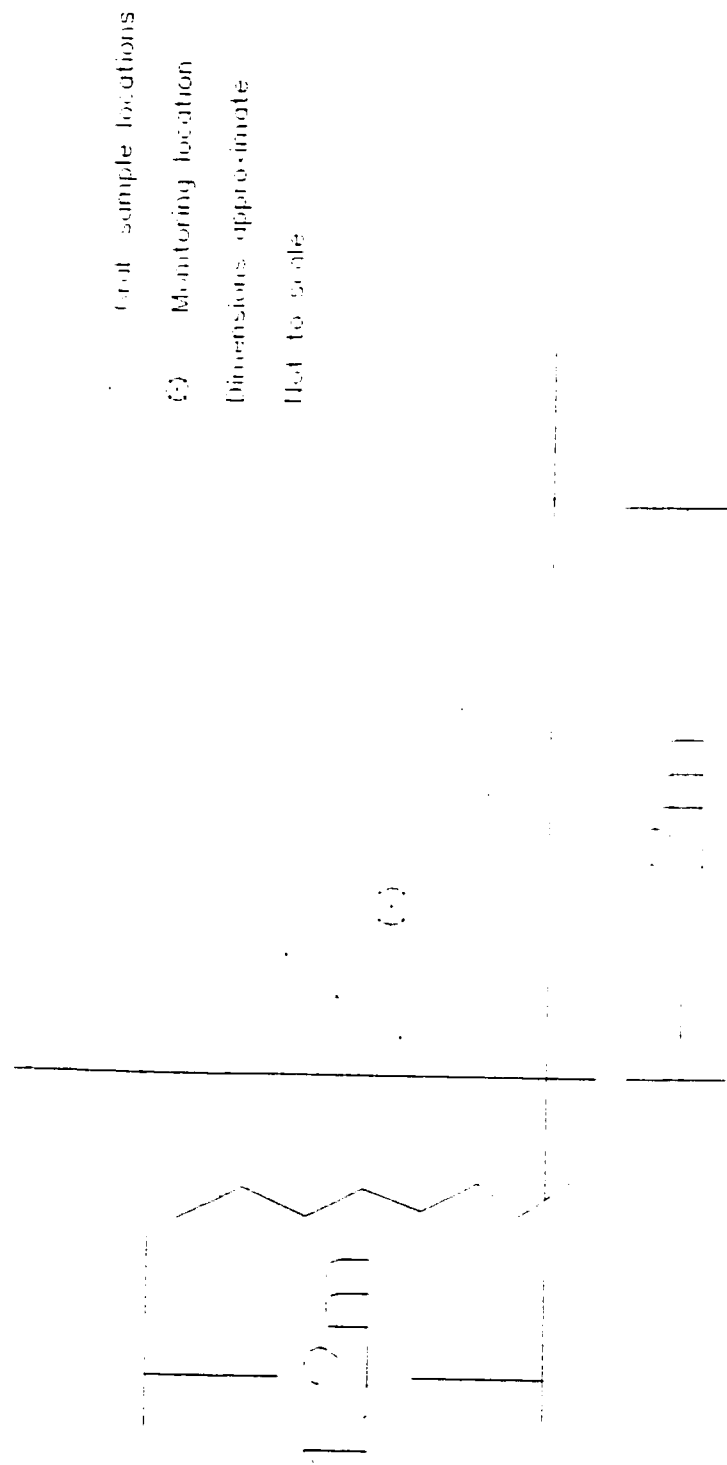
Table 3.5 - Chronology of Windrow Events

Day	Week	Event			Remarks
		Monitoring	Sampling	Turning	
-3	0	(✓)			Commence excavation and screening, and initial monitoring of some windrows.
0				✓	
1		✓	✓		Initial chemical and biological analyses
6	1	✓			
7				✓	
13	2	✓	✓		Progress chemical and biological analyses
14				✓	
21	3	✓			
22				✓	WRF mixed into Windrow 1
27	4	✓	✓		Progress chemical and biological analyses
28				✓	
34	5	✓			
41	6	✓	✓		Progress chemical analyses
42				✓	
48	7	✓			
49				✓	
56	8	✓	✓		Completion chemical analyses

Note: Turning on Day 35 (Week 5) was not carried out due to the unavailability of the compost turner.

sample can represent the average chemistry of approximately a cubic metre or more compared to the chemistry of a discrete soil sample (Downey and Hall, 1994). Therefore, such effects are viewed primarily in a two-dimensional context which is independent of the length of the windrow. However, at the exterior end of the 15 m windrow and at the peak of the windrow, there are additional surface effects due to the proximity of more than one surface. Therefore monitoring was not carried out within 2 m of the end of the windrows nor near the top of the windrow. The monitoring points were approximately at the centre of the windrow half cross-sectional plane in three zones - one near the exterior end and two representing in-windrow conditions as shown in **Figure 3.6, Windrow Cross-Section and Grab Sample Locations**. In-windrow conditions were monitored for temperature, moisture and soil-gas concentrations of oxygen, carbon dioxide and VOCs. When soil sampling occurred, windrow conditions were monitored in the same cross-sectional plane as the sampling locations. (Refer to photographs in **Appendix E - Figures**) In order to sample the soil-gas at its potentially lower concentrations of oxygen and undisturbed concentrations of VOCs and carbon dioxide, the monitoring was carried out using an AMS sealed retractable tip sampling probe (refer to illustration in **Appendix E - Figures**) the day before the windrows were turned. With respect to VOCs, although Downey and Hall (1994) report that an FID detector is a more accurate

Figure 3.6 - Window Cross-section and
Grab Sample Location



indicator of fuel hydrocarbons in the soil-gas, they also found that platinum catalyst detectors were acceptable and reportedly easier to use in the field. For in-windrow soil gas analysis, this project used the GasTech GT408 four-gas detector (Refer to **Appendix D - Field Monitoring Equipment** for a description of this instrument).

3.6.2 **STATISTICAL SAMPLING REQUIREMENTS**

Every second week, five grab soil samples were collected in a plastic bag from each windrow cross-section, mixed to form a composite sample of approximately one litre, and used to fill the sample jars for the laboratory analyses and quality control samples. As described above for monitoring, the perpendicular distance to the two sloped windrow surfaces was the predominant factor for oxygen infiltration, moisture gain/loss, and microbial heat radiation which in turn was predicted to have a significant effect on the rate of bioremediation. Again, these effects would be independent of the length of the windrow. Therefore representative grab sampling locations were selected in a two dimensional cross-sectional plane of the windrows to represent the outer, intermediate and inner matrix conditions. The outer 0.15 m of soil was avoided due to the assumed pronounced surface effects. Three composite samples were selected along the length of the windrow as shown in **Figure 3.5**.

Initial and completion testing was extensive and included: pH, moisture, purgeable hydrocarbons, cold extractable hydrocarbons, MOG and PAHs. Although progress sampling would not be required for commercial field projects since only the starting and completion concentrations are of concern, in this project, it was necessary to determine the relative performance of the different bioremediation methods. A weekly sampling would have been preferred, however, due to considerations of costs, sampling was carried out only every two weeks. Therefore, every second week, soil samples were taken and analysed in the laboratory for pH, moisture, and MOG.

The selection of sample size was based on statistics and economics. The Student's *t*-statistic for a sample size of three ($n = 2$), with a 2-tailed test for a 90 percent confidence level ($\alpha = 0.05$) is 2.920. This is the minimum size sample with any statistical significance. At this level, it is impossible to double resolution. An infinite number of samples would still only produce a *t*-statistic of 1.645. A sample size of four would increase the resolution to 2.353, or by only 20 percent. To improve the resolution to 1.812 or 40 percent would require an increase of sampling effort of over 400 percent (sample size of 13) - a prohibitively expensive undertaking considering the number of sampling events, number of parameters to be tested and number of windrows involved. Hence, it was decided that the minimum economically and statistically significant sample size will be three. These samples were taken from near each end of the windrow and in the middle, so to reduce as much as possible, differential effects of the wind, solar

incidence and differing concentrations of amendments and inoculants/bulking agents throughout the windrow.

3.6.3 ***LABORATORY ANALYTICAL METHODS.***

Although lighter petroleum compounds, if present, would be degraded preferentially by microbial action, and would be mineralized first, they could still be present as a residual or as breakdown products from incomplete mineralization of the heavy hydrocarbons. Therefore, three laboratory methods were required to identify the full range of petroleum hydrocarbons. Although PAHs were initially found at low concentrations, since the white rot fungus had demonstrated a capability of mineralizing these organics, laboratory analysis was also required for them. Since this was a comparative evaluation of different bioremediation technologies, biotesting was required to provide information on each of the processes so to assist in the evaluation and explanation of the results. In addition to these parameters, laboratory methods were required to determine moisture and pH.

Due to the number of laboratory methods and the number of samples to be analysed, the laboratory analysis was contracted out to two laboratories: Environment Canada's River Road Laboratories in Nepean, ON performed the chemical analyses, and Integrated Explorations of Guelph, ON carried out the biological analysis and inter-laboratory quality control comparisons for MOG replicates. The choice of laboratory methods for each of the parameters was largely determined by the capability of the laboratory, but efforts were made to ensure that standard laboratory methods were used. As a result, the following laboratory methods, with brief summary, were selected:

3.6.3.1 River Road Laboratory Methods.

- a. Sample preparation. After soil is removed for purgeable hydrocarbons analysis, the remaining soil is spread out on a tray, clods broken down and air dried for 48 hours. It is then gently ground and sieved to 2 mm before its use for the other analyses.
- b. pH: Mix soil with a 0.01 M CaCl₂ solution (to reduce sodium interference) and read settled solution with a pH metre.
- c. Total moisture (gravimetric). Air dry a weighed sample for 24 hours and reweigh to determine weight loss (moisture).
- d. Purgeable Hydrocarbons (Light petroleum hydrocarbons: C1 - C10): (EPA Method 5030). To minimize the loss of VOCs, wet soil is weighed directly and is subsequently corrected to equivalent dry weight. After large twigs and stones have been removed, the wet soil is further mixed with water, and then an inert gas is bubbled through the suspension to

- vaporize the hydrocarbons. These vapours are sorbed in a trap, heated in the gas chromatograph and detected with a gasoline calibrated FID (GC/FID).
- e. Cold extractable Hydrocarbons (Medium petroleum hydrocarbons: C10 - C35): Pentane is added to the soil sample and refrigerated for 24 hours. The extract is then injected into a GC/FID which has been calibrated with diesel.
 - f. MOG (Heavy petroleum hydrocarbons: C12 - C50): (Gravimetric). Petroleum hydrocarbons are extracted with Freon 113 or dichloromethane to separate the MOG from the soil. The solution is left for 24 hours for the solvent to evaporate and the residue is weighed. Dichloromethane has stronger solubilizing properties for greases and oxygenated derivatives of mineral hydrocarbons (Thomson, 1994). Freon is the reported solvent of choice since it is less toxic than organic solvents, insoluble in water, has a relatively low boiling point and is transparent to infrared spectrum in which hydrocarbons are measured. However, there is intense pressure to stop using this chlorofluorocarbon since it causes upper atmospheric ozone depletion (Thomson, 1994).
 - g. PAH: (EPA Method 8100, using EPA 610 PAH mixture as a reference). PAH is extracted from the soil with the solvent mixture (acetone, dichloromethane, hexane), cleaned and injected into GC/MS.

3.6.3.2 Integrated Explorations Laboratory Methods

Quantification of microbial populations in contaminated soil is very vulnerable to the selection and concentrations of nutrients and a wide variation in the range of species (Lei, 1995). As a result, the absolute microbial count for the following may vary widely from one laboratory to another, and one technician to another. Therefore, it is more important to carefully follow standardized procedures and use the same persons throughout. In this fashion, the trends rather than the absolute numbers of colony forming units gain a higher degree of confidence. Secondly, since high microbial activity rates were expected at the outset of the project, it was determined that analysis of nutrients would be targeted to those forms that would be immediately available to the microbes rather than the total nutrients.

- a. Fungal count. (HPB Methods, 1991): Phosphate buffered water is added to the soil from which different dilutions of suspensions are spread onto different petri plates. A dextrose nutrient is mixed with each plate and incubated for five days at room temperature. Colonies are then counted if there are between 30 and 100 colonies.

- b. Bacterial count: (per Fungal Count, above): Preparation and nutrient addition as per the fungal counting method. Incubation is for 48 hours at 35°C.
- c. Fungal laccase enzyme, (Boyle, 1995): The soil is extracted with a potassium chloride solution, centrifuged to produce a clear extract. One ml of extract is incubated with catalase, then reacted with a peroxidase substrate for 10 minutes at which time the reaction is stopped and the absorbance read against a reagent blank at 405 nm.
- d. Nitrates, (McKeague, 1976; Bremner, 1965): McKeague notes that MOG interferes with the Standard Method of nitrate analysis (soil is extracted with a potassium chloride solution, filtered and analysed colorimetrically by cadmium reduction). Therefore, a special nitrate method recommended in the latter reference was used. A soil extract is prepared with potassium chloride, placed in a microdiffusion apparatus and treated with magnesium oxide and titanous sulfate to reduce the nitrate to ammonia. The latter is diffused into a boric acid-indicator solution which is titrated to measure ammonia content.
- e. Ammonia, (McKeague, 1976; Bremner, 1965): It is noted that due to the soil constituents the extract background colour interferes with the Standard Method of ammonia analysis. (Soil is extracted with a potassium chloride solution, filtered and analysed colorimetrically by reaction with hypochloride and phenol to form an intensely blue compound). This requires that the background colour be compensated for by an appropriate blank. Therefore a special ammonia method was recommended in the second reference for a more robust and reliable result. A soil extract is prepared with potassium chloride, placed in a microdiffusion apparatus and treated with magnesium oxide alone to release ammonia. The latter is diffused into a boric acid-indicator solution which is titrated to measure ammonia content.
- f. Available phosphate, (Agri-Food, 1995): Soil is slurried with 0.5 N sodium bicarbonate, pH 8.5, filtered and analysed colorimetrically for orthophosphate.

Standard laboratory quality control protocols were followed for both laboratories. These included the calibration of all laboratory equipment with standard reference materials and the determination of matrix effects from the recovery of surrogates. The laboratories corrected all raw concentration results for the surrogate recovery and corrected purgeable hydrocarbons for moisture.

Since there is no universal laboratory report format standard, agreement with the laboratory was required on the content of the laboratory report. It included laboratory procedures used, surrogate recovery

rates, correction factors, MDL, certificates of analysis and of quality control, and assessment by the laboratory supervisory personnel of laboratory quality control and data quality.

The laboratory analyses schedule was based on the analysis of total matrix samples and size-screened samples (10 mm) for the initial and final round of samples, and on the analysis of progress samples with only screened samples so that the effect of removing the oversized material could be determined. It was felt that testing only screened samples would potentially result in higher concentrations being reported in relation to the total matrix since the contamination per unit mass of stones would be less in relation to soil. During the initial round of analyses it became evident that prior to sample analyses, the laboratory was removing considerable material (stones, wood chips, etc) from the matrix before it was rolled to break down clods, ground by mortar and pestle and sieved to 2 mm for analysis. The laboratory reported that this resulted in approximately 40 to 90 percent of the sample being removed prior to analysis, with approximately 5 to 15 percent of it consisting of metal fragments, carbonaceous, and yellow, "sulphur-like" particles. Evidently, the concept of testing the total matrix was not viable. However, most environmental analyses of contaminated sites use only screened samples. Therefore it was decided that the data to be available for this project would be representative of data being used by the environmental regulators for other contaminated site projects.

Another area of concern with the removal of the oversized material was the potential removal of contamination bound to the oversized organic matter. Whether this bound contamination would result in a higher or lower contamination per unit mass of the total matrix is still unknown. However, since such contamination is strongly bound to the organic material, it would not be mobile or toxic in the natural environment and therefore would be of only academic interest.

3.7 **QUALITY CONTROL.**

It was important that the data obtained be objective and statistically significant. Therefore a quality control program was established. The quality control program included both field and laboratory quality control requirements. Refer to **Appendix C - Project Quality Control and Standard Operating Procedures** for a summary of results from the quality control program.

3.7.1 ***FIELD QUALITY CONTROL.***

As provided in **Appendix C**, Standard Operating Procedures (SOPs) for field monitoring and sampling were developed to standardize efficient windrow monitoring and sampling procedures and to ensure that appropriate quality control measures were instituted.

3.7.2 **LABORATORY QUALITY CONTROL.**

The following were included in the preparation of samples to be sent to the laboratory and for laboratory analysis:

- labelling of sample jars with random serial numbers, the analysis protocol required and the sampling date,
- preparing triplicate samples for MOG analyses from one composite sample for each sampling event,
- preparing duplicate samples for inter-laboratory MOG analyses,
- preparing blind samples of a specified background soil sample,
- spiking 500 mg of background soil samples with 100 ml spike prepared by the Environment Canada laboratory consisting of 1042mg/kg MOG, 255 mg/kg PCBs and 457 mg/kg PAHs,
- spiking 500 mg of background soil samples with a locally prepared lubricating oil spike (0.5 gm of new SAE 20-50 lubricating oil was mixed with 100 ml of naphtha and added to a 500 ml background soil sample, stirred well and left to evaporate overnight.)
- refrigerating samples before and after use.
- requiring standard laboratory quality control procedures including the use of in-laboratory surrogate standards, blanks, standards and spikes.

3.8 **ANCILLARY OPPORTUNITIES**

Due to the nature of the project, there were a number of opportunities to examine other technologies, techniques and equipment. Although not directly related to the efficacy and cost of the fungal remediation processes examined in this thesis, nonetheless, valuable information was gained. This additional information is presented in **Appendix D - Field Monitoring Equipment.**

CHAPTER 4

RESULTS AND DISCUSSION

4.1 OVERVIEW

It was expected that Windrows 1 and 2A with the white rot fungus, and indigenous fungi-compost-manure would be the best performing processes. The other windrows were set up to assess the variables of oxygen supply, and organic versus synthetic nitrogen fertilizer, and to compare the results with a typical static biopile control. In comparison to laboratory projects, this field project was not as thorough in mixing the contaminated soil to obtain a uniform concentration of contamination across the windrows, nor as precise in measuring the amendments to the different windrows. This resulted in different starting conditions, in a variability in the usage rates of nutrients and oxygen, and potentially in irregular analysis, as different amounts of oversized materials were removed from the composite samples before laboratory analysis.

The nature of the contaminated soil made it difficult to obtain truly representative bulk data of the parameters of concern since:

- a. the soil was heterogenous mixture of different particles each with different chemical and physical properties,
- b. contamination was distributed in a typically nonuniform manner, and
- c. amendments were of varying particle sizes, most of which were too large to be involved in the samples to be processed by the laboratory analytical equipment.

To reduce this variability as much as possible, each sample was a composite of five grab samples, testing varying depths and conditions of the windrow: one near the lower windrow surface, one near the upper windrow surface, one at mid-depth near the top, one at mid-depth near the side and one in the middle of the windrow. Refer to **Figure 3.6**. Grab samples for each composite sample were collected from the cross-sectional areas where the monitoring had just taken place, and placed in a large, clean plastic bag. Large stones and wood were removed and the soil was mixed in the bag.

4.1.1 *INITIAL AND FINAL MOG CONCENTRATIONS AND RATES OF REMEDIATION*

As seen in **Table 4.1 - Initial and Final MOG Concentrations and Rates of Remediation**, it is apparent that the compost and poultry manure process was the fastest for remediating the MOG contamination. As stated earlier, typical soil bioremediation rates are 2 to 20 mg/kg/day (Hinchee, 1994). Only the compost and manure or fertilizer, with frequent turning, significantly exceeded these rates. It is

also important to note that the compost-manure with turning achieved the lowest residual concentration. Since this process involved only materials that were locally available, it is expected that public concern about the process would be less than for other processes that introduced foreign microbes and/or surfactants into the soil.

Table 4.1 - Initial & Final MOG Concentrations and Rates of Remediation

Row	Treatment	Mean MOG [mg/kg]			Time to Criteria [days]	Regression Equation Day 1 - 27 (Note 1)	Day 255 [mg/kg] (Note 2)
		Day 1	Day 56	Rate [mg/kg/d]			
1	WRF, compost, limited turning	2438	627	32	24	$y = 2800 x^{-0.34}$	439
2A	Compost, manure, turning	6005	270	102	20	$y = 6700 x^{-0.75}$	290
2B	Compost, fertilizer, turning	6071	528	99	22	$y = 6900 x^{-0.68}$	528
3A	Compost, fertilizer, no turning	1500	660	15	21	$y = 1650 x^{-0.20}$	738
3B	Fertilizer, no turning	1567	428	20	17	$y = 1660 x^{-0.24}$	327

Notes: 1. Regression equations analyse only the period of major degradation and have been rounded off.
2. Day 255 was a follow up sampling after the spring thaw, to determine further cleanup gains.

Considering that this soil had remained contaminated for many years, all windrows achieved remediation to MOG criteria in about the same time, an impressive 17 to 22 days. However, starting concentrations of contamination of the different windrows were not uniform. As indicated by the different rate coefficients, had the initial contamination concentrations been more uniform, one may well have seen more divergent results in the time to reach remediation criteria. The other remediation processes would still have to prove that their rates can match the 100 mg/kg/day if their starting contamination concentrations had been 6000 mg/kg. The rate coefficients in this study were determined from the observed mean mass loss over the first 27 days. The range of the individual windrow rate coefficients from highest to lowest are:

- Windrow 2A - 0.75,
- Windrow 2B - 0.68,
- Windrow 1 - 0.34,
- Windrow 3B - 0.24, and
- Windrow 3A - 0.20.

An opportunity arose the following spring to conduct another round of sampling (Day 255) to determine whether the microbial processes had started again after the winter and to observe any further remediation of the contamination. Although this sampling was outside the project period and was not included in the detailed analysis, it was a useful indicator of ongoing bioremediation. When the data from

Day 255 were examined, it was apparent that by Day 56 the white rot fungus process at 627 mg/kg, had not reached its asymptotic MOG concentration since it had declined by another third in May, to 430 mg/kg. However, the May MOG concentration for the white rot fungus windrow, or the others, were not as low as achieved by the compost-manure-turning process by Day 56, 270 mg/kg. If remediation to less than 1000 mg/kg or even 500 mg/kg was required, there was only one remediation process that proved itself being capable of reaching the lower concentration with a margin of safety, the compost-manure-turning process. This is in line with literature which indicates that fungi are able to take contamination concentrations to lower levels than bacteria. However, the other fungal process, based on commercially supplied white rot fungus with compost, did not achieve such low remediation concentrations by the time the project ended.

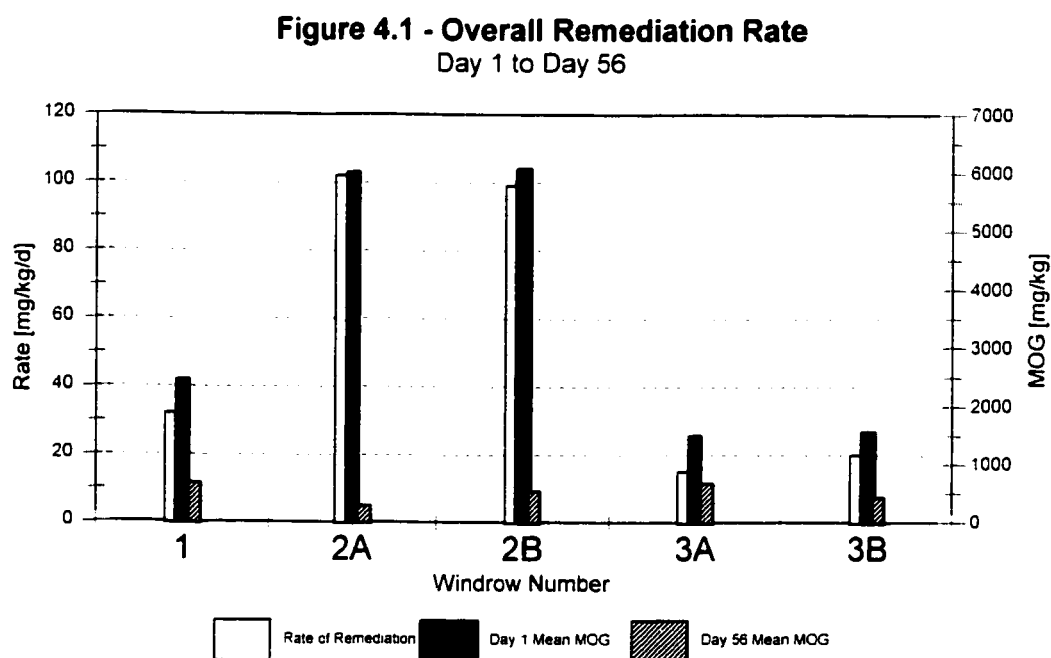
Windrow 1 benefited from the same amount of compost active with natural fungi as Windrow 2 and it was expected that both windrows would have similar initial results up to when the white rot fungus was added. However, the rate of remediation and final concentration of MOG in this windrow was not as good as for Windrows 2A or 2B. It should be noted that Windrow 1 did not have any fertilizer added to it, and the windrow was not turned as frequently. This latter point had both beneficial and negative aspects and is discussed in more detail in the individual windrow results.

The decline of MOG in Windrow 3B, which had negligible amounts of fungi, indicated that the fire fighter training area soil apparently had a natural population of bacteria that was adapted to using petroleum hydrocarbons, including MOG, as a substrate. Since in this project the MOG was degraded under aerobic conditions, these bacteria were aerobic and would have benefited from the excavation and aeration of the contaminated soil. These bacteria would also have been present in the other windrows so that the primary MOG reduction in all windrows was a combination of the introduced fungi and these indigenous bacteria. Competition between these bacteria and the inoculants may account for some of the lack of uniformity of the fungal counts in other windrows and even in the remediation rates, but as stated earlier, from the organ-body concept, the objective was to provide good bioremediation conditions to rapidly degrade the heavy petroleum hydrocarbons and not be too concerned about the taxonomy in the matrix.

It should be remembered that the regression equation could not properly account for the addition of the white rot fungus part way through the project and therefore the rate coefficient for Windrow 1 is not a valid indication of the white rot fungus process. Many laboratory and field studies have developed first-order rate constants for a variety of contaminants, but they are not readily transferable to other sites due to variations in electron acceptors (Rifai et al, 1995). Therefore, perhaps the most important aspect of the determination of the rate coefficients is the indication of bioremediation rate rankings for this project.

There appeared to be a very close relationship between the initial MOG concentration and the rate of remediation. This is in agreement with observations in the aquatic environment where the rate of mineralization by microbial populations of many [soluble] organic compounds is proportional to the concentration of the compound (Leahy and Colwell, 1990). They also note that for petroleum hydrocarbons of C12 or greater with solubilities of less than 0.01 mg/l, the rate of biodegradation is limited not by the concentration but by the rate of the hydrocarbon solubility. In soil, they state that oxygen, nutrient concentrations, moisture and pH are the predominant biodegradation rate factors. Refer to

Figure 4.1 - Overall Remediation Rate. Since some windrows started at a contamination concentration of 6000 mg/kg and others started at only 1500 mg/kg, it appears that the higher the concentration of contamination (but not to exceed toxic concentrations), the more organic contaminant is utilized by the microorganisms. Therefore where more substrate is available to the microorganisms and if conditions for their growth are appropriate, there will be a faster population growth of the microorganisms resulting in a greater rate of mineralization of the organic contaminant. Although in fungal remediation, the cellulosic material is the substrate, not the organic contamination, the fungi would still benefit from the availability of the hydrocarbon's breakdown products.



4.1.2 **INITIAL AND FINAL PAH CONCENTRATIONS**

By virtue of their large molecular structures, PAHs have been difficult to bioremediate. Based on the history of white rot fungus being able to mineralize these compounds, it was a useful option to determine the initial and final concentrations of PAHs in the soil from this fire fighter training area. Refer to **Table 4.2 - Initial and Final Mean Concentrations of PAHs**. As expected, the commercial and indigenous white rot fungus processes showed that they were effective in mineralizing these contaminants. However even windrow 3B, which had no white rot fungus or compost with indigenous fungus, demonstrated that the PAHs were destroyed. The mechanisms that produced these results should be the subject of another project to determine the field conditions necessary to ensure destruction of PAHs by simple aerobic bioremediation schemes.

Table 4.2 Initial and Final Mean Concentrations of PAHs [mg/kg]

	Criteria	1	2A	2B	3A	3B
Mean initial PAH	130	24	21	16	44	16
Mean final PAH	130	3	1	2	1	1

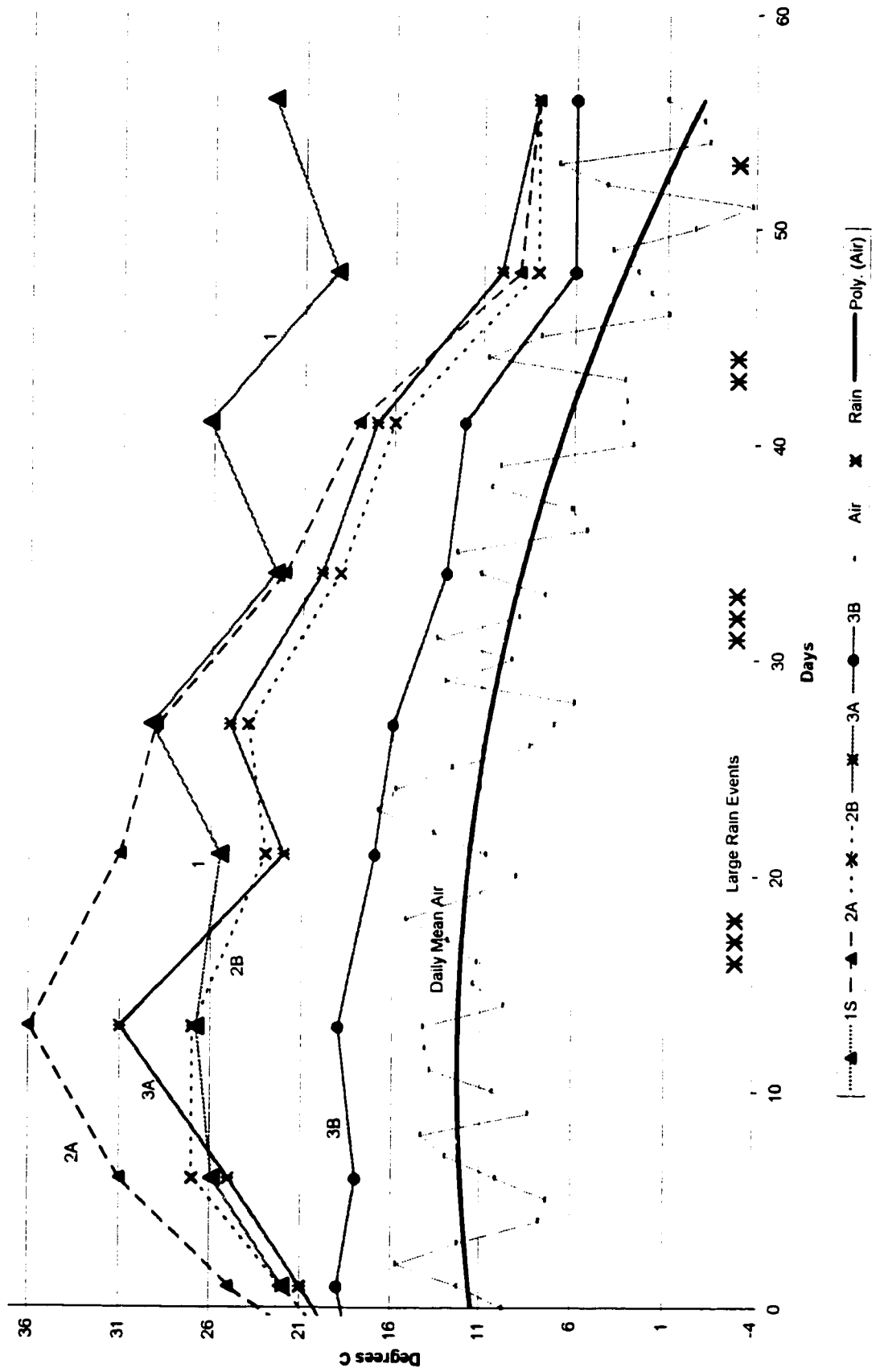
Notes: PAH criteria are compound specific. Acenaphthylene criteria selected since it was the most prevalent in the final PAH testing (MOEE, 1996).

4.1.3 **WEATHER CONDITIONS**

Figure 4.2 - Comparative Windrow Temperatures, indicates the daily mean air temperatures and the windrow temperatures during the project. As seen by the regression analysis of the air data, the polynomial line indicates that there was a relatively even net air temperature for the first 20 days, after which there was a cooling trend with the approach of winter. In comparison to the individual windrow temperatures, there appears to be a parallel cooling of the windrows. However, examination of the individual windrow conditions at the time indicates that the bioactivity had been able to raise the windrow temperatures by up to seven degrees Centigrade per week, despite relatively uniform ambient temperatures. By the time the windrows started to cool, the organic contamination had been largely mineralized and bioactivity was subsiding. Therefore, the cooling trend of the windrows was due primarily to the reduction of bioactivity and not the loss of heat from the windrows to the air.

An examination of the effect of solar incidence on the heating effect on the windrows was carried out. An earlier biopile project examined this variable and found that it had a negligible effect (McNicoll and Baweja, 1995). Although no data were gathered on the solar incidence, this project based its assessment on the correlation with rain - cloud cover and solar incidence. Therefore major rain events are also indicated on **Figure 4.2**. Although the comparison of windrow temperature profiles with the rain

Figure 4.2 - Comparative Air/Windrow Temperatures



events shows that there was some correlation between these cooling rain events and windrow temperature, examination of specific windrow oxygen concentrations provides a more compelling reason for the windrow cooling. Therefore, it is concluded that the rain and solar incidence correlation is insignificant for these windrows which had high rates of bioactivity.

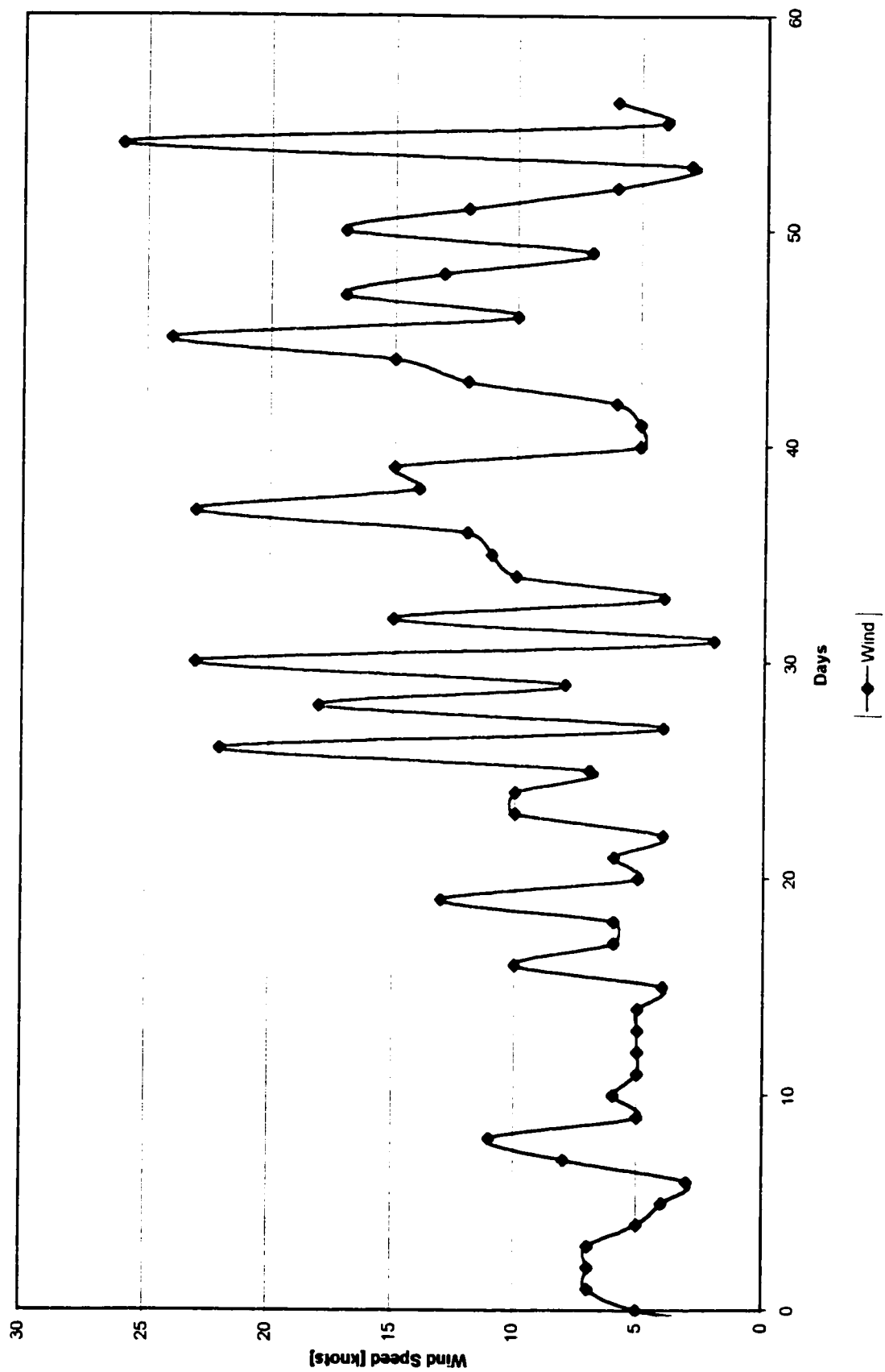
Figure 4.3 - Daily Winds, indicates the daily wind information during the project based on surface winds recorded at 1300 hours each day at the CFB Trenton airfield. As discussed earlier, since the energy in the wind increases at the cube of the wind speed, the higher the winds, the more pronounced will be the infiltration of atmospheric air into the windrows. There were high winds on Days 26 to 30, Day 36, Day 44 and Day 54. This information is not portrayed on the individual windrow graphs since they would become too cluttered. However, the effect of these high winds on specific windrow oxygen concentrations is discussed under each of the windrows. From field data and observations, it appears that the winds had no significant effect on drying out the windrows.

4.1.4 ***PREAMBLE TO INDIVIDUAL RESULTS.***

In the following discussion on individual results, the sequence of discussion commences with an examination of the validity of the data, the apparent trends of different parameters and finally a regression analysis which is compared to statistical conclusions about the mean MOG concentrations. Raw data for the project are provided in **Appendix A - Raw Data**. It should be noted that for optimum clarity of charts, the x and y axes have been expanded as applicable to illustrate the data with the maximum clarity. Therefore, direct comparison between graphs should carefully note the axis range on each graph. Also of note is the divergence of MOG readings in a given windrow's sampling event, and even among field replicates. This underscores the normal lack of precision and accuracy in sampling heterogenous soil.

Throughout the discussion of results, windrows are identified by windrow number and/or title. The titles are for identification purposes and do not accurately reflect the constituents of the windrows. For example, above, all windrows were identified as having a component of indigenous bacteria. However, for brevity of title, these are not mentioned in the titles. Moreover, the compost used in the project is identified with having a population of naturally-occurring white rot fungus. Although literature supports this assumption, general fungal counts indicated that significant fungal populations existed on the compost, and that a white mycelial mat was visually observed on the compost, no speciation was carried out to confirm that the fungi were, in fact, white rot fungi. The counting of bacteria and fungi was ceased after 27 days for cost reasons when it was apparent from windrow temperatures that bioactivity was declining. Although such counts are indicated in **Appendix A** to 2 significant figures, it should be noted that microbial counts are difficult, especially due to the filamentous nature of fungi, and in such a heterogenous matrix as the

Figure 4.3 - Daily Winds



soil/compost windrows. Therefore this microbial data should be considered as qualitative only since the error in such data is commonly one to two orders of magnitude.

4.2 ***WINDROW 1 - WHITE ROT FUNGUS, COMPOST.***

This windrow tested the use of commercially supplied white rot fungus. Since a medium to fine soil was expected, a bulking agent in the form of compost was added. It also acted as an inoculant. Approximately 20 percent (v/v) white rot fungus on a substrate and 20 percent compost (v/v) was added to the soil. Until the white rot fungus was added on Day 22, the windrow was turned twice. Thereafter it was turned on Days 28 and 42.

Windrow 1 initially consisted of only contaminated soil and compost and was turned on Day 7 so to further blend the soil and compost. On Day 22 the white rot fungus was sufficiently cultivated on its substrate of straw and sawdust, and was added to the windrow and mixed in with the compost turner. The windrow was again turned on Days 28 and 42 to see what effect this would have on the disruption of the mycelium and on the resulting bioactivity of the fungi and bacteria.

a. **START - FINISH PETROLEUM HYDROCARBON CONCENTRATIONS.**

The initial testing for light petroleum hydrocarbons was sufficient to determine whether there were significant starting concentrations of these compounds to influence the bacterial populations. As seen in **Table 4.3 - Start-Finish Petroleum Hydrocarbon Concentrations Windrow 1**, the initial concentrations of 40 and 30 mg/kg of purgeable and cold extractable hydrocarbons were below the Ontario remediation objectives of 100 mg/kg for gas/diesel. Although the observed concentrations of light petroleum hydrocarbons normally would not be of concern in a typical remediation project, it still was intended to determine the effect of this process on their destruction and to see if there was any accumulation of intermediate breakdown products which would have shown up as light and medium petroleum hydrocarbons at the end of the project. The final testing for light petroleum hydrocarbons would be sufficient to determine whether all these light petroleum hydrocarbons and intermediate breakdown products of lighter petroleum hydrocarbons had been consumed by the end of the project. However, due to the ice storm, final determination of the light petroleum hydrocarbons was not carried out. **Table 4.3** shows that no data were available for the light petroleum hydrocarbons.

The initial MOG concentration of approximately 2400 mg/kg exceeded the remediation criteria of 1000 mg/kg for heavy oil. This validated the project intent to only

monitor the MOG concentrations during the project as being the significant indicator of the change in petroleum hydrocarbon contaminant concentrations. **Table 4.3** shows that the MOG was remediated to below criteria.

The initial test for PAHs showed a combined total of 24 mg/kg. **Table 4.3** shows that the PAH were remediated to near non-detect levels.

Table 4.3 - Start-Finish Petroleum Hydrocarbon Concentrations Windrow 1 (mg/kg)

Hydrocarbon	Criteria	Start	Finish
Purgeables	100	40	n/a
Extractables	100	30	n/a
MOG	1000	2438	627
PAH	130	24	1

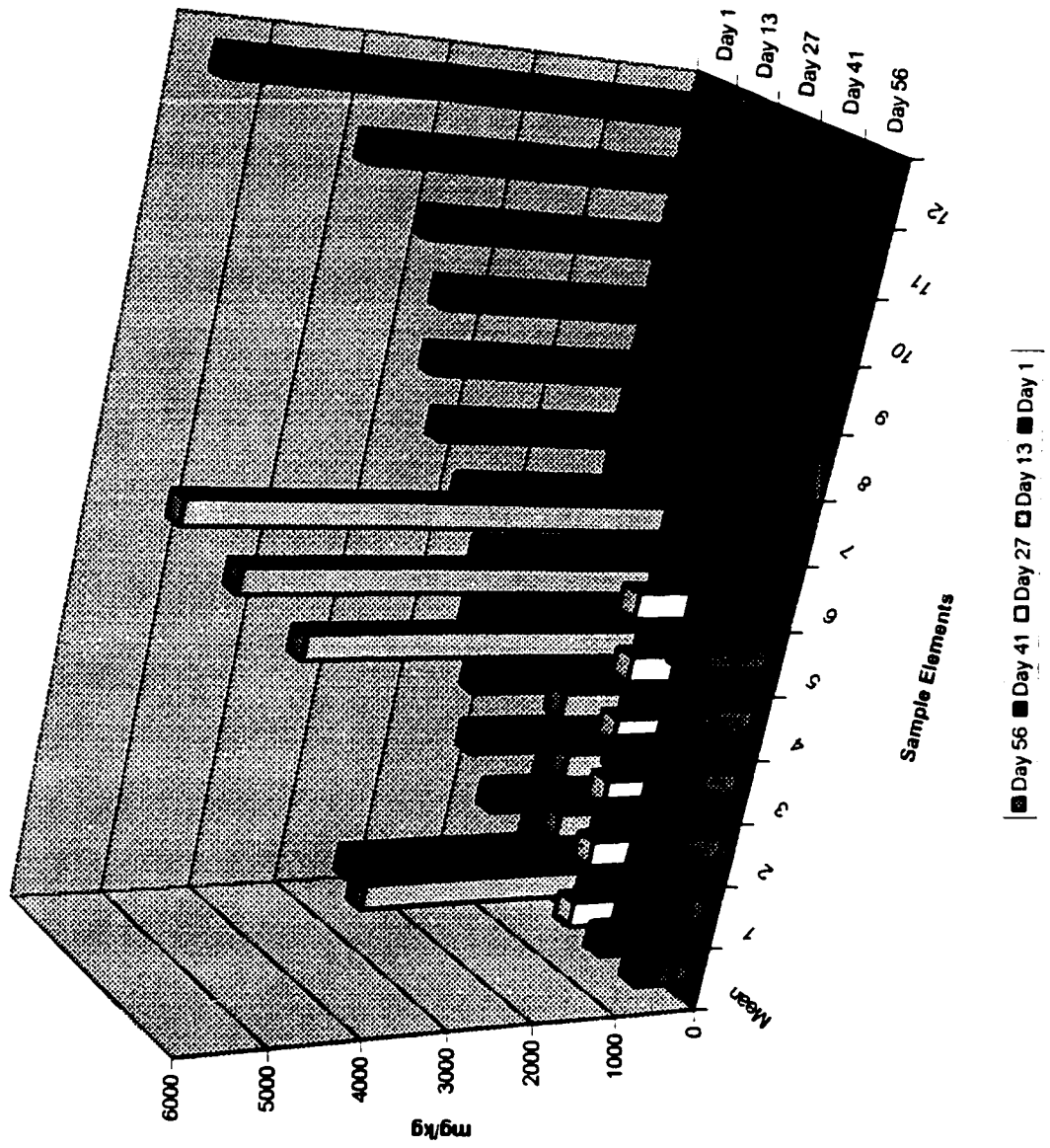
Note: Final MOG concentration adjusted.

b. DISTRIBUTION OF MOG OBSERVATIONS.

Figure 4.4 - MOG Sample Mean and Range illustrates the scatter in the observations comprising each composite soil sample for MOG. Most sampling events showed a relatively even distribution of observations. Although the size of samples was not sufficient to realize a normal distribution of data, theory would support that such a distribution could exist if sufficient data had been gathered during the sampling events.

Figure 4.4 illustrates that the MOG concentrations of the 12 samples analysed for Day 1 were spread evenly across the range from 761 to 5677 mg/kg with a mean concentration of 2438 mg/kg. The large number of samples resulted from six composite samples being collected from this windrow with duplicates of each being sent to the laboratory to establish a baseline of the variability of the MOG analysis. Although the standard deviation of the sample is 1364 mg/kg, or approximately half the mean, this represents a typical range of data in a heterogenous mixture of soil and amendments, and the manner in which light non-aqueous phase liquid (LNAPL) contaminants move unevenly through soil. Day 13 shows a very large scatter of the 6 data elements with a range from 431 mg/kg to 5620 mg/kg and a distribution that is strongly weighted towards both extremes. The mean is 2696 mg/kg and the standard deviation of 2395 mg/kg is almost equal to the mean. Despite it being deemed that such scatter could occur in a heterogeneous soil sample, the indication that the mean concentration increased from the Day 1 value of 2438 mg/kg to 2696 mg/kg is improbable. Since no observations should be

Figure 4.4 - MOG Sample Mean and Range - Windrow 1
Mean MOG and Individual Sample MOG Analyses Shown for Each Sampling Event



deleted as outliers caused by sampling, analysis, and/or data entry errors and it can be presumed that some remediation did occur, it will be conservatively assumed for the analysis of the data that the Day 13 mean MOG is the same as Day 1 mean, that is, 2438 mg/kg, but with larger standard deviation of the two sampling events, 2395 mg/kg.

The means for Days 27, 41 and 56 were 544, 627 and 665 mg/kg respectively. An analysis of these three sampling events generally show an even distribution of concentrations over the range of each event except for Day 41. The tighter range of the observations with time probably reflects the improved mixing as a result of the additional turning during the project. Although the Day 41 sample has one very low reading and two higher (43, 865 and 973 mg/kg), this skewing is overshadowed by the low concentrations with respect to the MDL of 500 mg/kg.

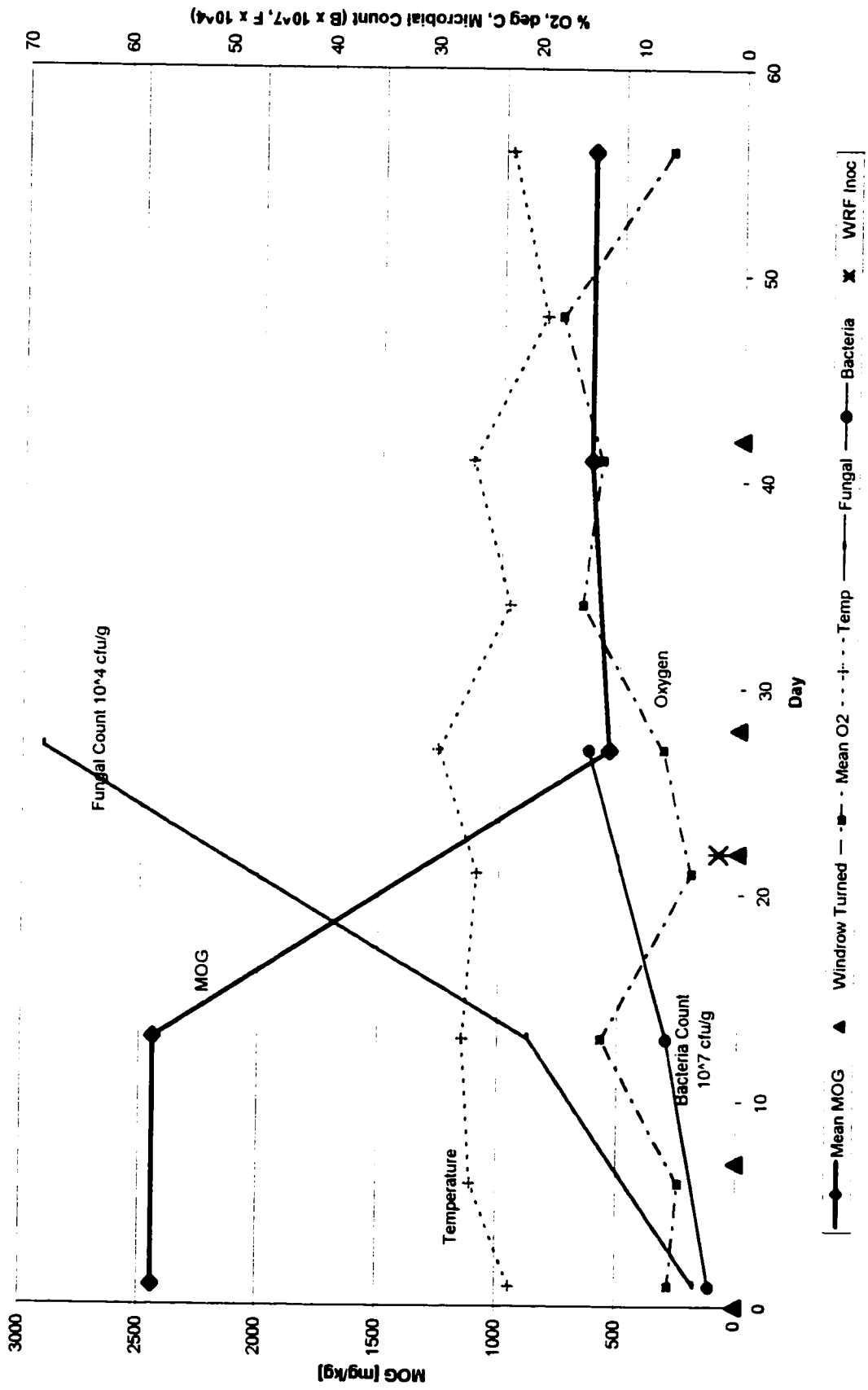
With the addition of 10 percent white rot fungus and substrate on Day 22, considerable organic matter was mixed into the contaminated soil at this point. Due to the binding of organic compounds to organic material, it must be assumed that some of the MOG would have become bound to the straw and sawdust. Since the bound residue resists desorption even during chemical analysis, some of the subsequent reduction of MOG could be attributed to this effect rather than its mineralization, however, the ratio can not be determined.

Although the MOG contamination concentrations are shown to be rising for the last three sampling events, this is probably due to the variability in sampling and analysis rather than an actual increase that could only be due to rebound or leaking oil from the heavy equipment. In this project, the potential for diffusion of petroleum hydrocarbons from contaminated particles was not determined. The heavy equipment was examined for oil leaks and none were found. It was assumed that the MOG concentrations approached their asymptotic concentrations around Day 27 and declined slightly thereafter. Therefore, it was conservatively assumed that the Day 41 mean MOG of 627 mg/kg could be ascribed to Day 56, but with Day 41's larger standard deviation of 509 mg/kg to indicate the adjustment. In summary, all data were counted as valid except with the adjustment on Day 13 and Day 56.

c. MEAN MOG, OXYGEN, TEMPERATURE AND MICROBIAL ACTIVITY.

Figure 4.5 - Mean MOG, Oxygen, Temperature and Microbial Activity versus Time, compares the mean MOG concentrations over time with the weekly

Figure 4.5 - Mean MOG, Oxygen, Temperature, Microbial Activity vs Time
Windrow 1 - Compost, WRF, Limited Turning



results of monitoring in-windrow oxygen and temperature, and for the first four weeks, the biweekly analysis of microbial counts. The effect of inoculating the contaminated soil with the compost and aerating it would have activated the indigenous microorganisms. Both microbial populations increased from Day 1 to Day 13 (fungi count increased from 4×10^4 to 20×10^4 colony forming units /gram (cfu/g), and bacterial count increased from 3×10^7 to 7×10^7 cfu/g). By Day 27, fungal counts soared to approximately 70×10^4 cfu/g as a result of the addition of the white rot fungus and the continued growth of native fungi. Bacterial populations continued to increase to 15×10^7 cfu/g.

On Day 6 when the daily mean ambient temperatures were only 11 to 13°C (refer to paragraph 4.1.3 summarizing weather conditions) windrow temperatures were 26°C. By Day 27, windrow temperatures had risen further to 29°C due to the increased oxygen from the Day 22 mixing/turning. After Day 27 windrow temperature began to subside. The Day 56 windrow temperature of 23°C had risen from the previous week's 19°C. There was a high degree of confidence in the temperature readings since a simple stem thermometer was used and its measurement of ambient temperatures each monitoring event correlated well with meteorological records.

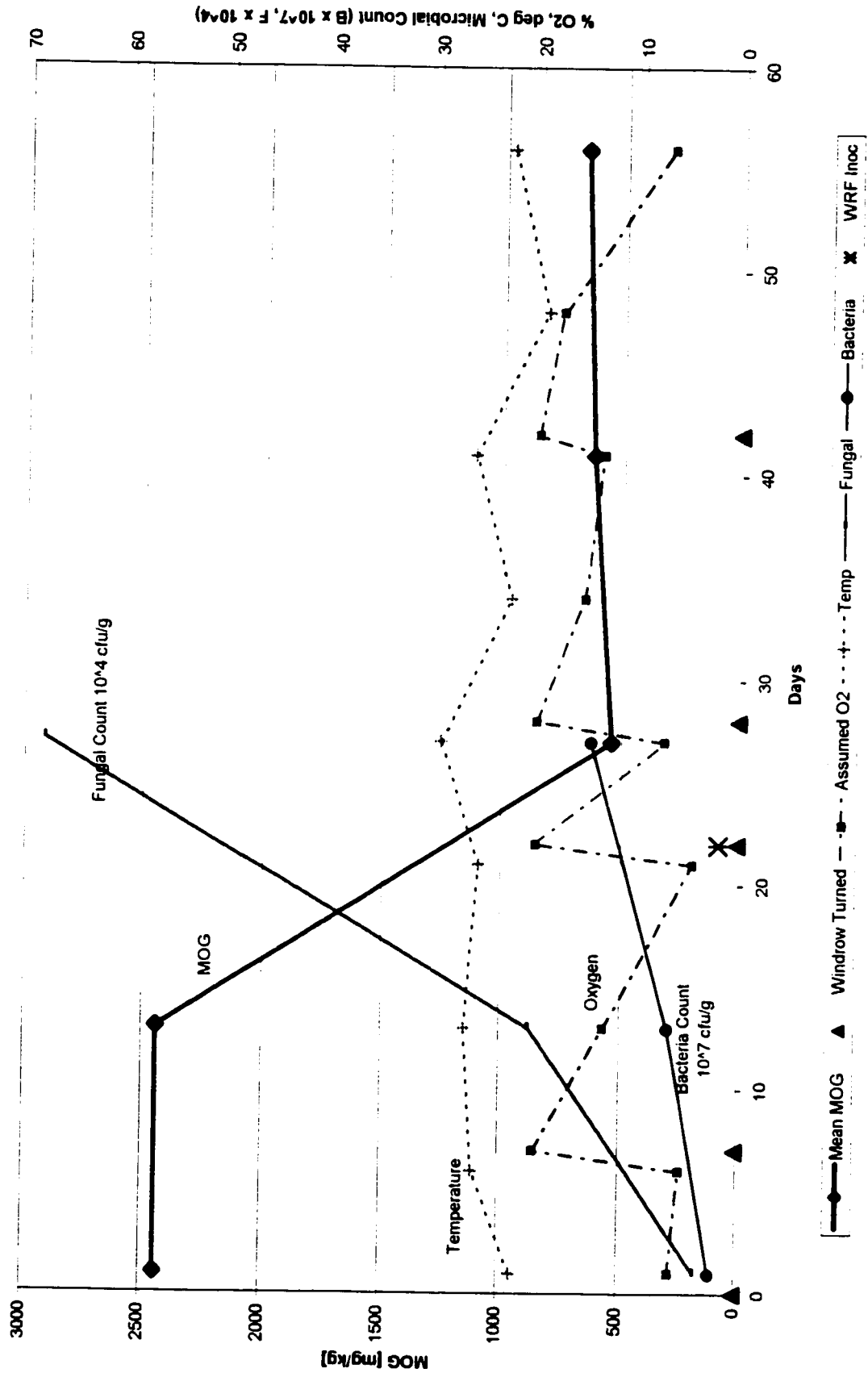
Oxygen concentrations were already depressed to seven percent on Day 1 from the near atmospheric concentrations the day before when the windrow was constructed. By Day 6, the concentration had declined further to six percent. The turning of the windrow on Day 7 restored oxygen concentrations to atmospheric concentrations of approximately 21 percent. By Day 21, the bulk concentration of oxygen had again decreased to approximately five percent with the lowest data element in the range being only 0.5 percent. As before, oxygen concentrations were restored to near atmospheric concentrations by the turning when the white rot fungus was mixed in on Day 22, and by Day 27 had declined to seven percent. A turning on Day 28 caused the oxygen concentrations to rise to near atmospheric concentrations but to fall to 14 - 15 percent concentrations by Day 34. On Day 42, the windrow was turned and soil-gas conditions restored to near atmospheric oxygen concentrations. By Day 48 the oxygen concentration had again fallen to 18 percent. The oxygen concentration on Day 56 decreased to 7 percent, however this value was questionable since the oxygen detector's operation was erratic in the 1°C air temperature. Although throughout this chapter, restoration to atmospheric oxygen concentrations may be interpreted as being to 21 percent, the action of the compost turner could not completely expose all soil pore spaces to fresh air. Therefore

when the windrows were reformed during the turning, it can be assumed that in the small particles of soil some soil-gas remained at its original lower oxygen concentrations or was only partially diluted with fresh air. No actual measurement of the soil-gas was made after turning to determine what the net increase to soil-gas oxygen was since time would be required for the oxygen concentrations to equalize and by then, microbial activity would have already started depleting the oxygen concentrations again. However, it is estimated that the ratio of micro pore volume unaffected by the turning would be very small to the macro pore space volume exposed to fresh air. Therefore, it is assumed that the net oxygen level upon turning would have been 20 percent. This assumption is incorporated into a version of Figure 4.6 wherein the oxygen levels as measured during the monitoring events and those calculated upon turning are indicated, **Figure 4.5a - Mean MOG, Temperature, Microbial Activity and Calculated Oxygen versus Time**. This graph illustrates more clearly, the apparent consumption of oxygen throughout the project.

The relationships among bioactivity, temperature and oxygen levels are readily seen in this windrow. By Day 6, the microbial activity of the increasing microbial populations resulted in elevated temperatures of the windrow and in decreasing oxygen levels. The turning of the windrow on Day 7 restored oxygen concentrations to atmospheric concentrations and fostered the continued growth of the microbial population. This was reflected in continued elevated temperatures, and depletion of oxygen to 13 percent by Day 13. Without any further turning, the oxygen continued to be depleted to a mean concentration of five percent on Day 21 with one point in the range being 0.5 percent. Anaerobic conditions may have existed in the microcosm of some soil particles. A decline in temperature indicated that this level of oxygen was having a negative effect on the level of bioactivity. Since population counts are only general and the sampling bracketed this period, there is no indication of the daily microbial populations during this period of reduced oxygen.

The turning/mixing on Day 22, restored atmospheric oxygen levels in the windrow, and by Day 27 microbial populations and temperatures were higher but with a corresponding decline in oxygen to seven percent. The turnings on Days 28 and 42 restored atmospheric oxygen concentrations in the windrow but despite the ample oxygen, windrow temperature declined. This reflected a negative effect the turning had on the mycelium, which in both cases, caused the biological activity to subside for approximately one week despite oxygen levels being adequate for microbial activity, that is, above five

**Figure 4.5a - Mean MOG, Temperature, Microbial Activity, Calculated O₂ vs Time -
Windrow 1 - Compost, WRF, Limited Turning**



percent over the period. It is concluded that to maintain optimum levels of bioactivity turning should only be performed when soil-gas concentrations fall below five percent. The four observed periods of temperature increase, from Days 1, 21, 34 and 48, showed similar rates of temperature increase, namely 3 to 4 °C, indicating that throughout the project, whether the bioactivity was negatively impacted by a lack of oxygen or disruption of the mycelium, once good composting conditions were restored (oxygen concentrations above five percent, and undisturbed matrix), the rate of increase in bioactivity and generation of heat due to the bioactivity was similar despite the decline in concentrations of light petroleum hydrocarbons and MOG, and the low mean daily ambient temperatures of 3 to 5 °C (refer to paragraph 4.1.3) towards the end of the project. This indicates that the substrate of the white rot fungus (natural and/or commercial) was primarily the cellulosic material and not the petroleum hydrocarbons. However, the breakdown products of the petroleum hydrocarbons would have been available to all microbes and would have contributed to an increase in their bioactivity. It should also be noted that the matrix temperature on Day 56 was still 23 °C. This indicates that there is still bioactivity in the windrow despite freezing ambient conditions.

From Day 27 onwards, rate of oxygen concentration declines were not as rapid as earlier. Over the project, the infiltration of air would have continued into these windrows of small cross-section, due to their porosity, oxygen diffusion gradients and the effects of diurnal pumping and atmospheric pressure changes. However, it can also be noted from analysis of the effect of winds (paragraph 4.1.3) that there were times of high winds around the periods of Days 26-30, 36, 44 and 54. The net effect is that in relation to microbial activity, the replacement of soil-gas oxygen by natural infiltration of oxygen produced a net gain in soil-gas oxygen concentrations. The consumption of oxygen was indicative of bioactivity continuing up to the end of the project (Day 56).

The growth curves of both fungi and bacteria are typical of an initial acclimatization period and then growth in line with the availability of substrate. It must be remembered that the microbial population initially consisted of the naturally occurring fungi on the compost and the indigenous bacteria readily available in the soil. Since the light petroleum hydrocarbons were only at 40 mg/kg, the bacterial population did not experience the typical explosive growth as seen under laboratory conditions when such bacteria are exposed to immense amounts of a suitable substrate under favourable growing conditions.

d. VOC CONCENTRATIONS.

VOC concentrations were measured in the soil-gas at a depth of approximately 0.5 m by the GT408 hand held monitor. The VOCs showed a five-fold decrease in the first week from 2800 mg/kg to 700 mg/kg and slowly decreased thereafter to 400 mg/kg. (See **Figure 4.6 - Mean VOCs, MOG, Oxygen, Temperature versus Time.**) Since the turning operations would have liberated any methane which resulted from anaerobic decomposition while the soil was in its original location, it can be assumed that readings on the GT408 are the result of only other organic vapours. Since the vapour pressure of MOG compounds is low in relation to that of light petroleum hydrocarbons, it appears that the VOCs detected are as a result of light petroleum hydrocarbons in the soil. It is evident that despite the considerable manipulation of the soil by excavation, screening, mixing and windrow construction, there was still some higher vapour pressure organic compounds present at the outset. There are no apparent relationships of VOCs to temperature, oxygen concentrations or bioactivity for Windrow 1. The VOC readings indicate that the initial VOC vapours were rapidly consumed by bacterial action and/or volatilized into the atmosphere and subsequently very few VOCs were generated due to:

- the low starting concentrations of light petroleum hydrocarbon indicated in **Table 4.3;**
- the rapid consumption of these light petroleum hydrocarbons by bacterial action, and
- the negligible accumulation of light breakdown products as a result of the fungal-bacterial symbiotic action on MOG breakdown products.

Since light and medium hydrocarbons were not tested at the end of the project, no quantitative data are available to prove that the intermediate breakdown products of the heavy hydrocarbons were consumed. However, the reducing concentrations of VOCs in the soil-gas suggested that such was the case.

e. NUTRIENT CONCENTRATIONS.

In **Figure 4.7 - Nutrients, Microbial Activity, Oxygen, Temperature versus Time**, the concentrations of the available macro nutrients are indicated.. There was a dramatic drop in mean ammonium concentrations from 36 to 1 $\mu\text{g/g}$ in the first 13 days whereas the nitrates increase from 6 to 12 $\mu\text{g/g}$ on Day 13 to again decrease to 4 $\mu\text{g/g}$ on Day 27. It is speculated that the decrease in ammonium can be explained in part by the

Figure 4.6 - Mean VOCs, MOG, Oxygen, Temperature vs Time
 Windrow 1 - Compost, WRF, Limited Turning

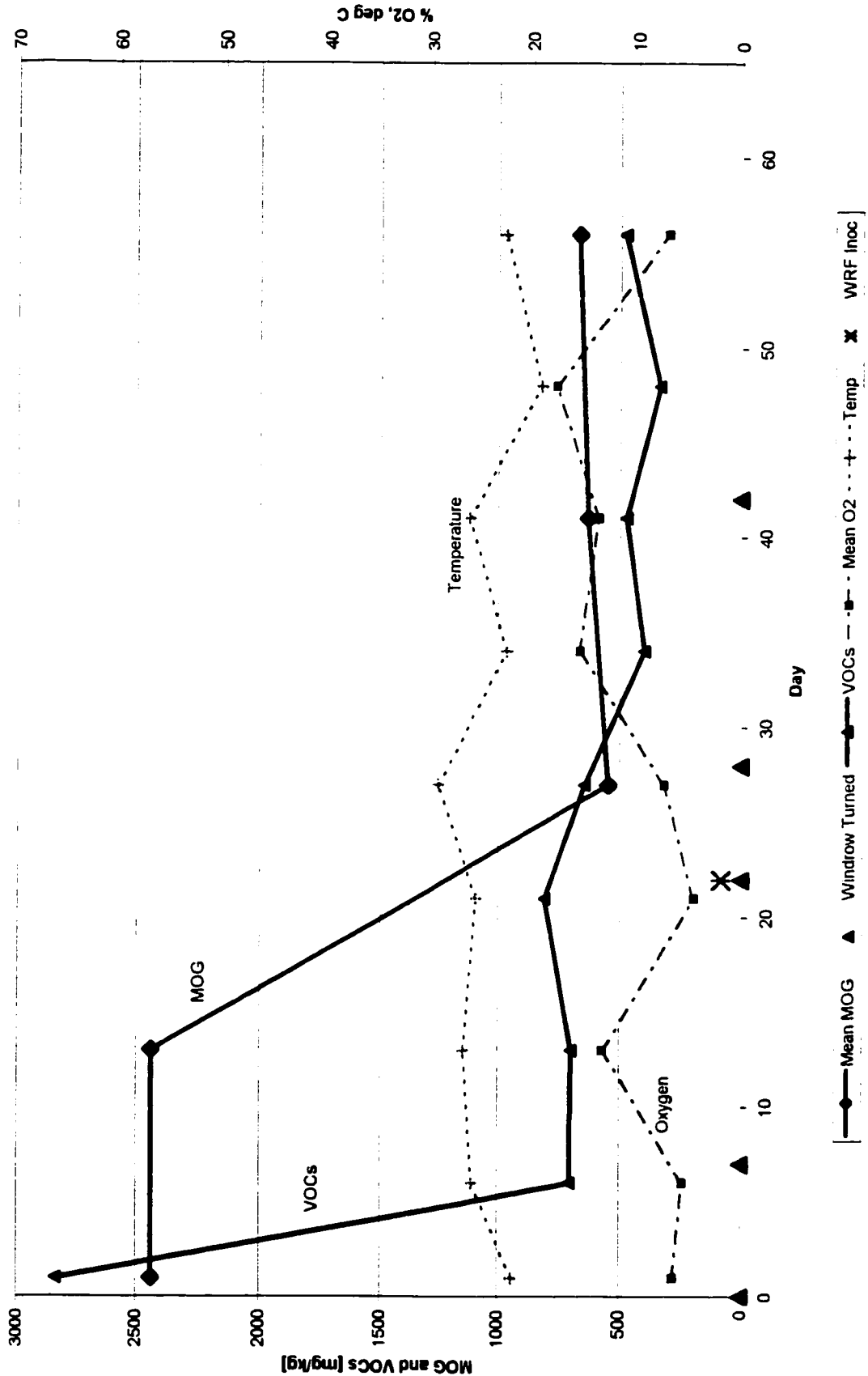
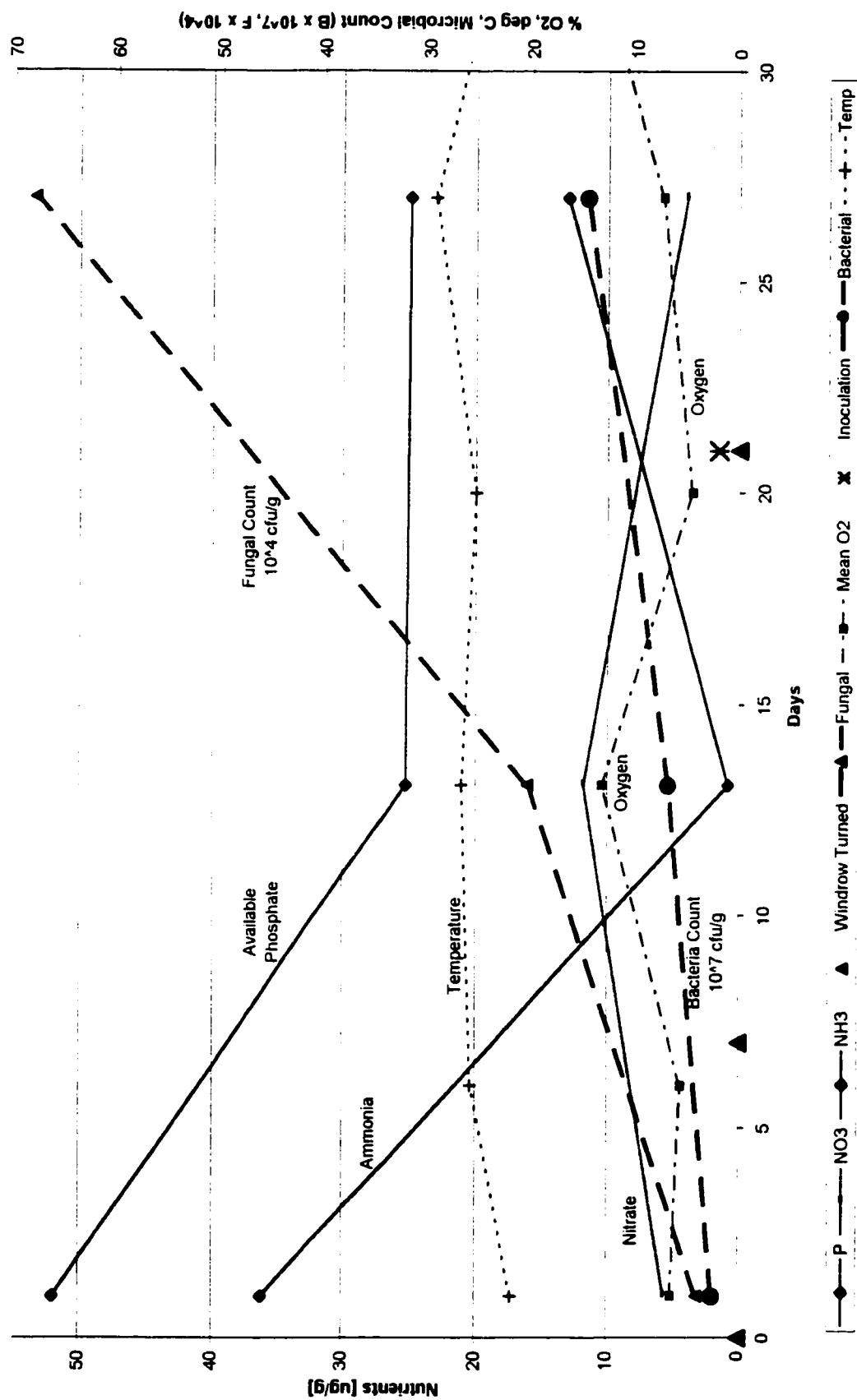


Figure 4.7 - Nutrients, Microbial Activity, Oxygen, Temperature vs Time
Windrow 1 - Compost, WRF, Some Turning



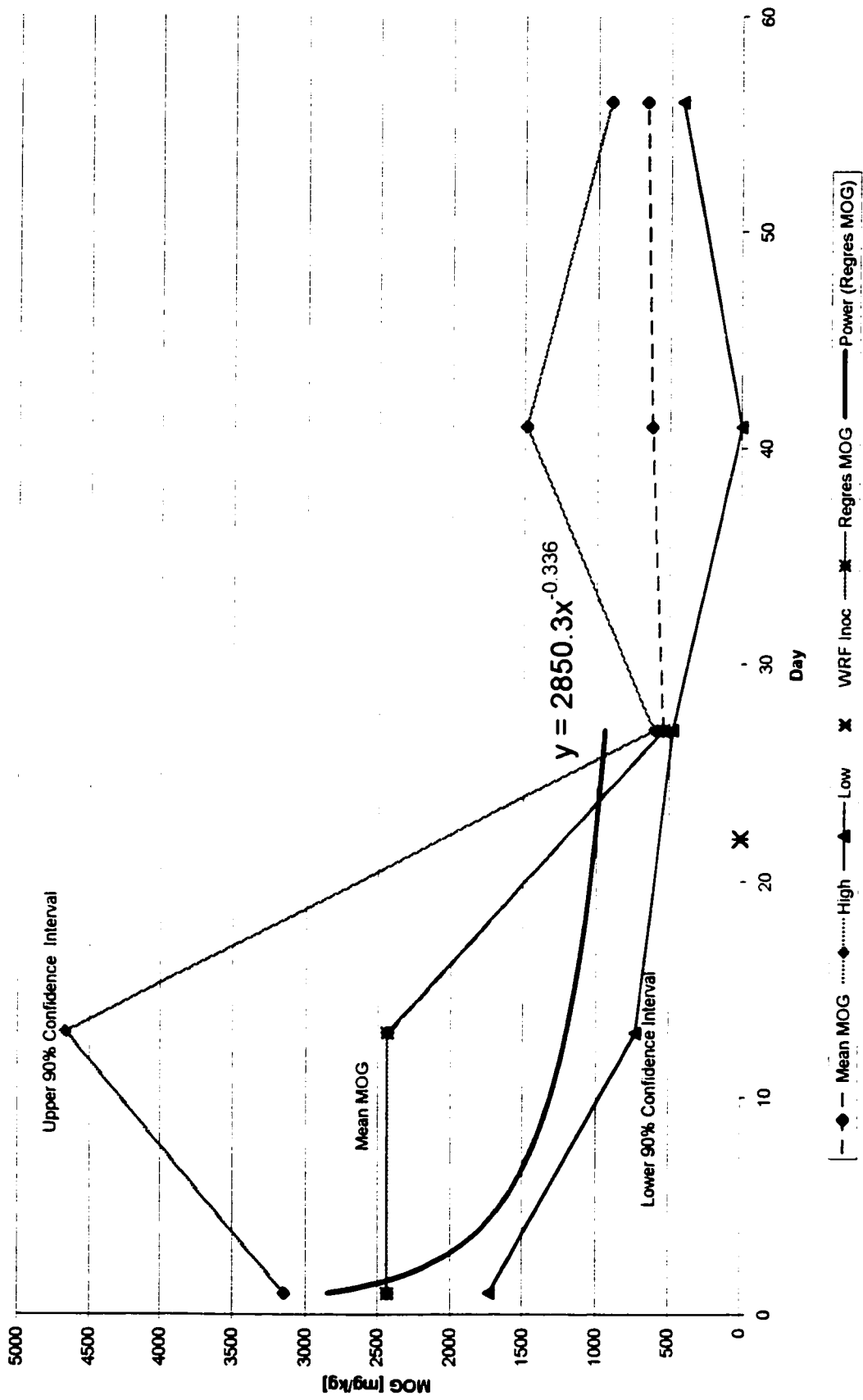
preference of microorganisms for utilizing ammonium rather than nitrates. On Day 13 since the mean pH of the windrow was approximately 7.4, there would not have been a significant shift of ammonium to ammonia and subsequent ammonia off-gas lost from the windrow during this period. The increase in ammonium to 13 $\mu\text{g/g}$ after Day 13 reflects the conversion of organic nitrogen to the inorganic form. However, since total nitrogen was not determined, any loss of ammonia through volatilization could not be ascertained. The nitrates initially showed an increase since nitrifying bacteria are slow growers and dependent on conditions of pH, temperature and ammonium. Approximately on Day 13 after the ammonium was largely depleted, the microorganisms began to use the nitrates as a nutrient and, since anaerobic conditions may have existed in areas of the microcosm, the nitrate could have been used as an electron acceptor.

Phosphates are recycled in the metabolic energy transfer cycle for the production of ATP and associated enzymes. The concentration of total phosphates should be stable throughout. However, the analysis for phosphates only determined bioavailable orthophosphates. As the microbial population increased, greater quantities of soluble phosphates would be consumed. This traditional relationship is portrayed well in this graph.

f. STATISTICAL SIGNIFICANCE AND REGRESSION ANALYSIS.

Figure 4.8 - MOG True Mean Range (90% Confidence), examines the statistical significance of the mean MOG data. Student's *t*-test for small samples was selected as a method of representing the true mean of the population, that is, of the actual bulk MOG concentrations in the windrow. A 2-tailed test with a 90 percent confidence interval was used since this reflects the variability in analysis of a heterogeneous material like soil and since the MOEE uses the 90th percentile analytical concentration criterion for determination of background conditions (MOEE, 1996). Regression analysis was carried out to portray the relationship between mean MOG concentrations and time during the rapid degradation phase. The resulting exponential trend line was based on the best least squares fit through the mean MOG data points. Given that there was a 90 percent confidence that the true mean of the MOG contamination in the windrows lay between the high and low intervals, it was apparent that an exponential decrease in the concentration of MOG was certainly possible.

Figure 4.8 - MOG True Mean Range (90% Confidence)
 Windrow 1 - Compost, WRF, Some Turning



It showed good correlation with Student's *t*-statistic analysis except for Day 27. This aberration was likely caused by the wide range for the Day 13 data (range: 431 to 5620 mg/kg, mean: 2696 mg/kg and standard deviation: 2395 mg/kg). Therefore allowances should be made for the Day 13 data scatter and the introduction of a major new variable on Day 22, inoculation with white rot fungus, which could not be factored into the regression analysis. Although the small range of data for Day 27 (485 to 654 mg/kg) would indicate a high confidence in a windrow MOG contamination concentration of say 500 to 600 mg/kg, one must remember the wide variance in data of other sampling events and the MDL of 500 mg/kg. Therefore this apparent precision may be considered as a chance occurrence that is not truly representative of the range of contamination concentrations in the windrow. Hence, it was decided not to weight the third sampling event so to have the exponential curve pass through its high/low confidence interval. It can be assumed that the exponential trend line provides good characterization of the net MOG reduction. Whereas the mean MOG concentration indicates that the remediation criteria was reached on Day 24, the trend line indicates that this concentration was nominally reached on Day 22. Nonetheless, it would be fair to conclude that the windrow concentration of MOG contamination had declined to below 1000 mg/kg by the third sampling event, Day 27, two and a half weeks after commencement of treatment. Since the white rot fungus was added only on Day 22, it is assumed that probably the majority of the remediation in this treatment option was as a result of the naturally occurring fungi on the compost which was added when the windrow was initially constructed.

g. EFFECTS OF TURNING ON THE WHITE ROT FUNGUS.

As evidenced by the drop in bulk windrow temperature after the Day 28 and 42 turning, the turning disrupted the mycelium and apparently caused a reduction in bioactivity of the fungi. Continuing oxygen consumption was indicative of bioactivity still on-going up to the end of the project (Day 56). Turning should only be done when soil-gas oxygen concentrations fall below five percent.

4.3 ***WINDROW 2A - COMPOST, MANURE, WEEKLY TURNING.***

This windrow tested a common method of stimulating microorganisms used in biopile remediation processes by the use of poultry manure as an organic fertilizer. Since a fine soil was expected and contamination with large organic molecules, compost was added as a bulking agent and fungal

inoculant. Approximately 5 kg poultry manure per m³ and 20 percent compost (v/v) were added to the soil. The windrow was to be turned weekly.

This general windrow design was expected to be very effective in remediating heavy petroleum hydrocarbons and other large molecular organic compounds. The organic fertilizer, poultry manure, was expected to stimulate the microbial population to a greater extent than the synthetic fertilizer used in other windrows. Although there were no written guidelines nor literature describing the effect of varying ratios of compost to soil, it was assumed that the heavier the soil, the more bulking agent would be required to maintain an open pore space in the matrix. In view of apparent fine soil, 20 percent v/v compost was added to the contaminated soil. In anticipation of a high rate of microbial activity, the turning of the windrow was scheduled every week to be sure that the maximum aerobic conditions would persist throughout the project.

a. START - FINISH PETROLEUM HYDROCARBON CONCENTRATIONS.

As seen in **Table 4.4 - Start-Finish Petroleum Hydrocarbon Concentrations Windrow 2A**, the starting concentrations of light petroleum hydrocarbons of 98 and 70 mg/kg of purgeable and cold extractable hydrocarbons were below the Ontario remediation criteria of 100 mg/kg for gas/diesel. The MOG contamination of 6005 mg/kg exceeded the Ontario remediation criteria of 1000 mg/kg for heavy oil. Combined PAHs of 21 mg/kg were below the Ontario criterial for the most prevalent PAH, Acenaphthylene, in the final testing. As described earlier, only MOG and PAH were tested at the conclusion of the project. These had been remediated to 270 and 1 mg/kg respectively, well below the remediation criteria.

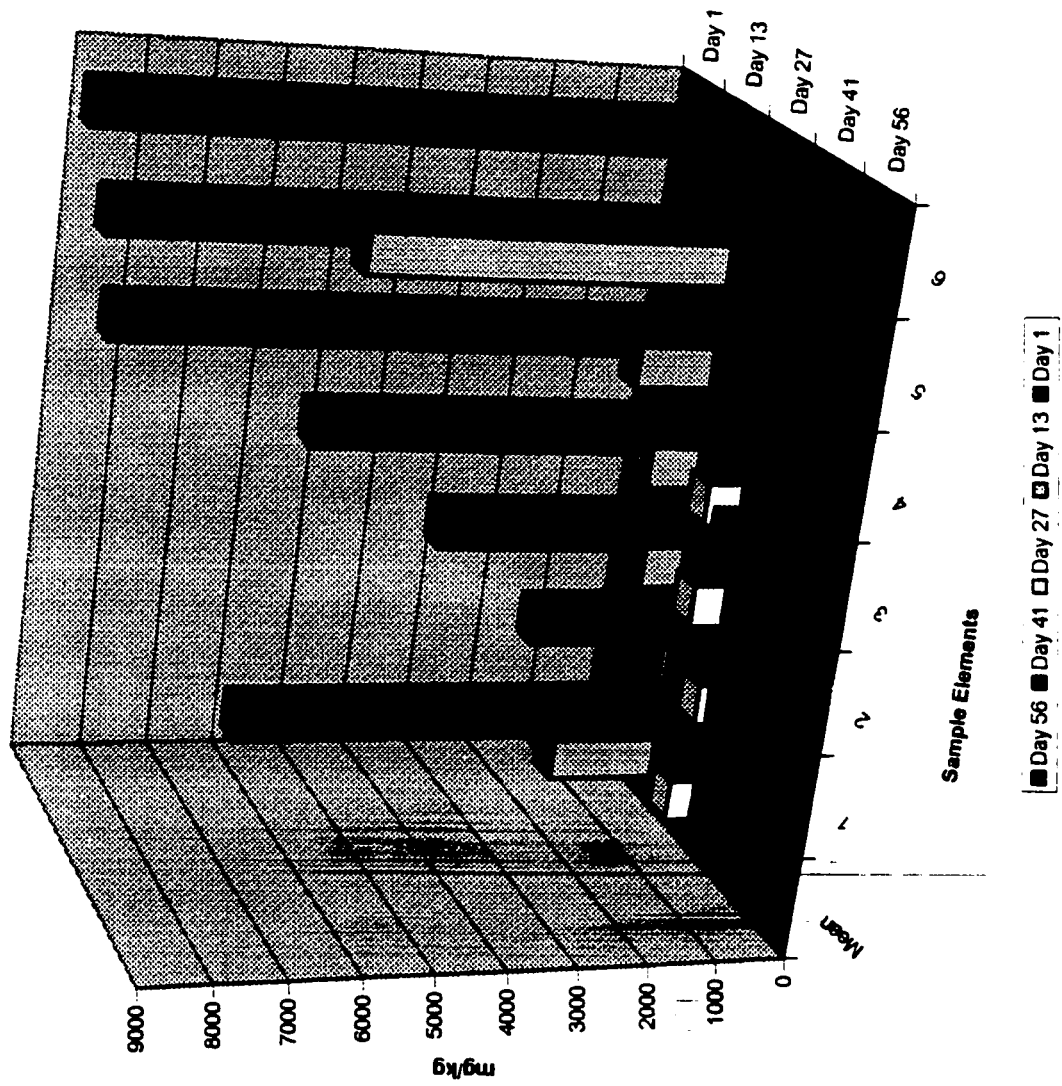
Table 4.4 - Start-Finish Petroleum Hydrocarbon Concentrations Windrow 2A (mg/kg)

Hydrocarbon	Criteria	Start	Finish
Purgeables	100	98	n/a
Extractables	100	70	n/a
MOG	1000	6005	270
PAH	130	21	1

b. DISTRIBUTION OF MOG OBSERVATIONS.

Figure 4.9 - MOG Sample Mean and Range - 2A. illustrates the distribution of observations within each sample. Of the six Day 1 samples, one half of the observations

Figure 4.9 - MOG Sample Mean and Range - Windrow 2A
 Mean MOG and Individual Sample MOG Analyses Shown for Each Sampling Event



were at the heavy end of the range of 1531 mg/kg to 8940 mg/kg which caused some skewing over what could be expected to be a population with a normal distribution. One sample and its duplicate were 8940 and 3207 mg/kg. This reflects a considerable imprecision in the MOG analysis. The mean was 6005 mg/kg and the standard deviation was 2523 mg/kg. Although only three composites were collected for Day 1, duplicates of each sample were analysed by the laboratory. The Day 13 samples, with two blind replicates, showed one sample of 5350 mg/kg which was three times the mean of an otherwise compact range of 108 mg/kg to 1150 mg/kg for a mean of 1598 mg/kg. Again this skewed the mean to the high side. The Days 27, 41 and 56 samples had reasonable distributions of observations with their means of 387, 332 and 270 mg/kg respectively and probably reflected the improved mixing as a result of the additional turning during the project. Due to the heterogeneity of the soil-amendment mixture and the low level of accuracy of the MOG analysis no data were deemed to be outliers and removed from the analysis.

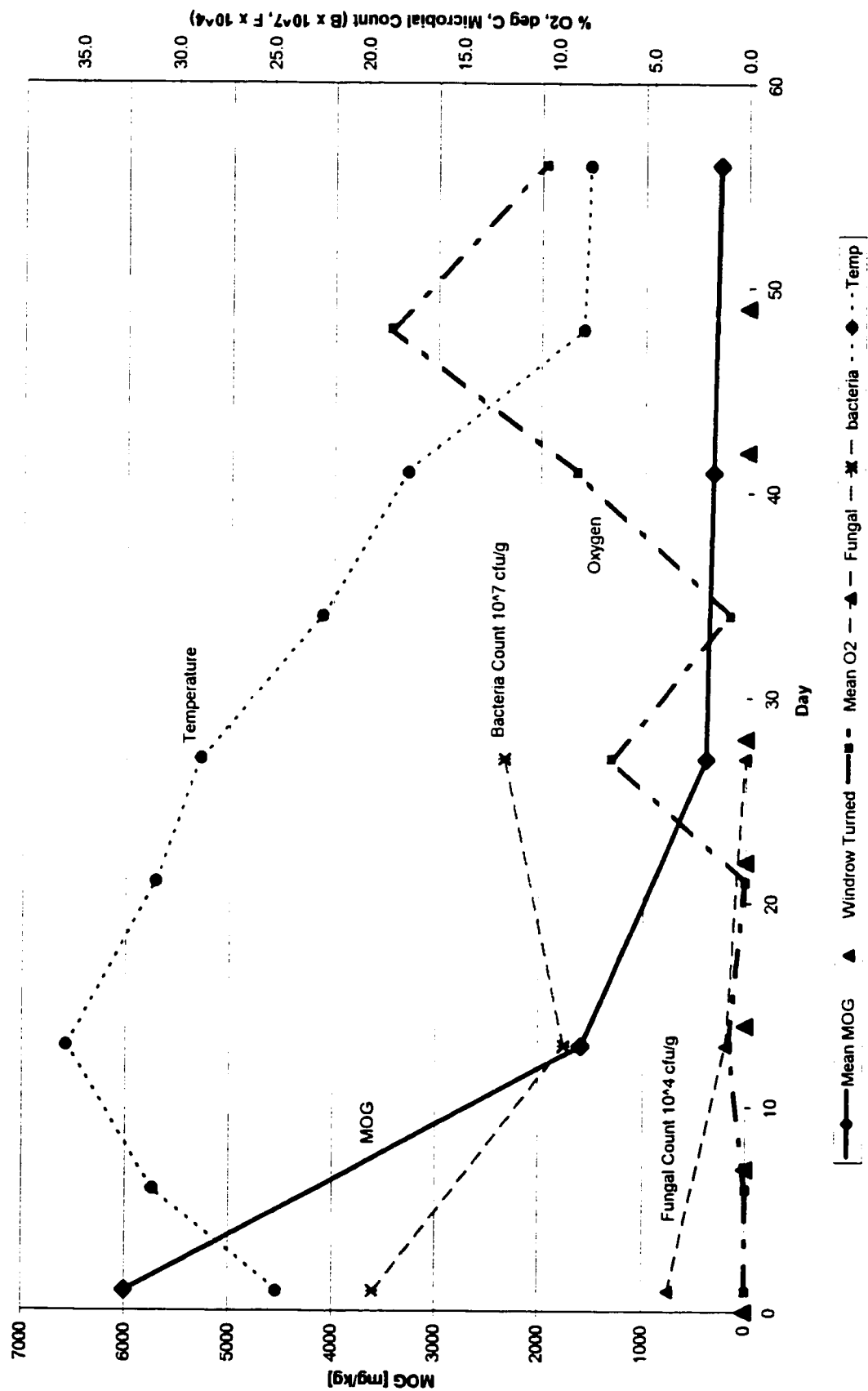
c. MEAN MOG, OXYGEN, TEMPERATURE AND MICROBIAL ACTIVITY.

Figure 4.10 - Mean MOG, Oxygen, Temperature and Microbial Activity versus Time. examines the mean MOG concentrations over time with oxygen, temperature and for the first four weeks, the microbial counts. Due to the addition of the compost and especially the poultry manure, the windrow had a high inoculation of bacteria. Starting bacterial count of 20×10^7 cfu/g was approximately seven times that of Windrow 1 whereas the fungal count of 4×10^4 cfu/g was the same as Windrow 1. By Day 13, both the bacterial and fungal counts had declined to 10×10^7 and 1×10^4 cfu/g respectively. By Day 27, the bacteria had recovered to 13×10^7 cfu/g but the fungi declined further to 0.1×10^4 cfu/g.

Windrow temperatures rapidly rose from 18 °C on Day 1 to the highest recorded windrow temperature in the project, 36°C, on Day 13 when the ambient temperature was only 11 to 13°C. This represented an increase of 6 to 7°C per week for the first three weeks for the 37 tonnes of soil and compost, the highest rate of rise of any of the windrows. After this date the temperatures steadily fell to 8°C at the end of the project.

The windrow oxygen was already depleted by Day 1 despite a turning on Day 0. The weekly indications of oxygen concentrations portray a general anoxic state for the first three weeks, however the effect of the weekly turnings and restoration of soil-gas to near

Figure 4.10 - Mean MOG, Oxygen, Temperature & Microbial Activity vs Time
Windrow 2A - Compost, Manure, Turning



atmospheric oxygen concentrations must be remembered. The windrow remained in a depleted oxygen state with only natural infiltration providing additional oxygen until the Day 7 turning restored the soil-gas to near atmospheric concentrations. This was followed by a rapid consumption of oxygen which despite the weekly turning and associated restoration of soil-gas to atmospheric concentrations, continued to be depleted to almost zero for most of the first five weeks. On Day 27 an oxygen concentration of seven percent was realized. By Day 34, oxygen concentrations had again fallen to near anoxic concentrations. The oxygen concentrations rose to nine percent on Day 41 and the turning on Day 42 restored the concentrations to 21 percent to again decline to 19 percent by Day 48. The final oxygen reading on Day 56 is not valid since the GT408 was experiencing problems in the cold weather.

The anoxic state from Day 1 to Day 7 would have been sufficient to cause the aerobic microorganisms to start becoming dormant and perhaps anaerobic bacteria to become active, however, no testing for changes to the anaerobic electron acceptors was carried out. As evidenced by the rising temperature, there was still significant bioactivity during this period. Later as the windrow returned to an aerobic condition, the microbial populations began to grow in line with the microbial counts data. The steady decline in temperatures after Day 13 indicated a net reduction in bioactivity. By Day 27 the lower bioactivity, as indicated by the reducing temperature, coupled with the turning and natural infiltration of atmospheric oxygen (including a period of high winds (refer to paragraph 4.1.3)) resulted in an oxygen concentration of seven percent. By Day 34, without the incremental effect of the high winds, oxygen concentrations had again fallen to near anoxic concentrations. However, as seen by the windrow temperatures now falling to the 20°C range, it is assumed biological activity was using less oxygen than was being infiltrated, especially by the high winds leading up to Day 41 which brought the oxygen concentrations up to nine percent.

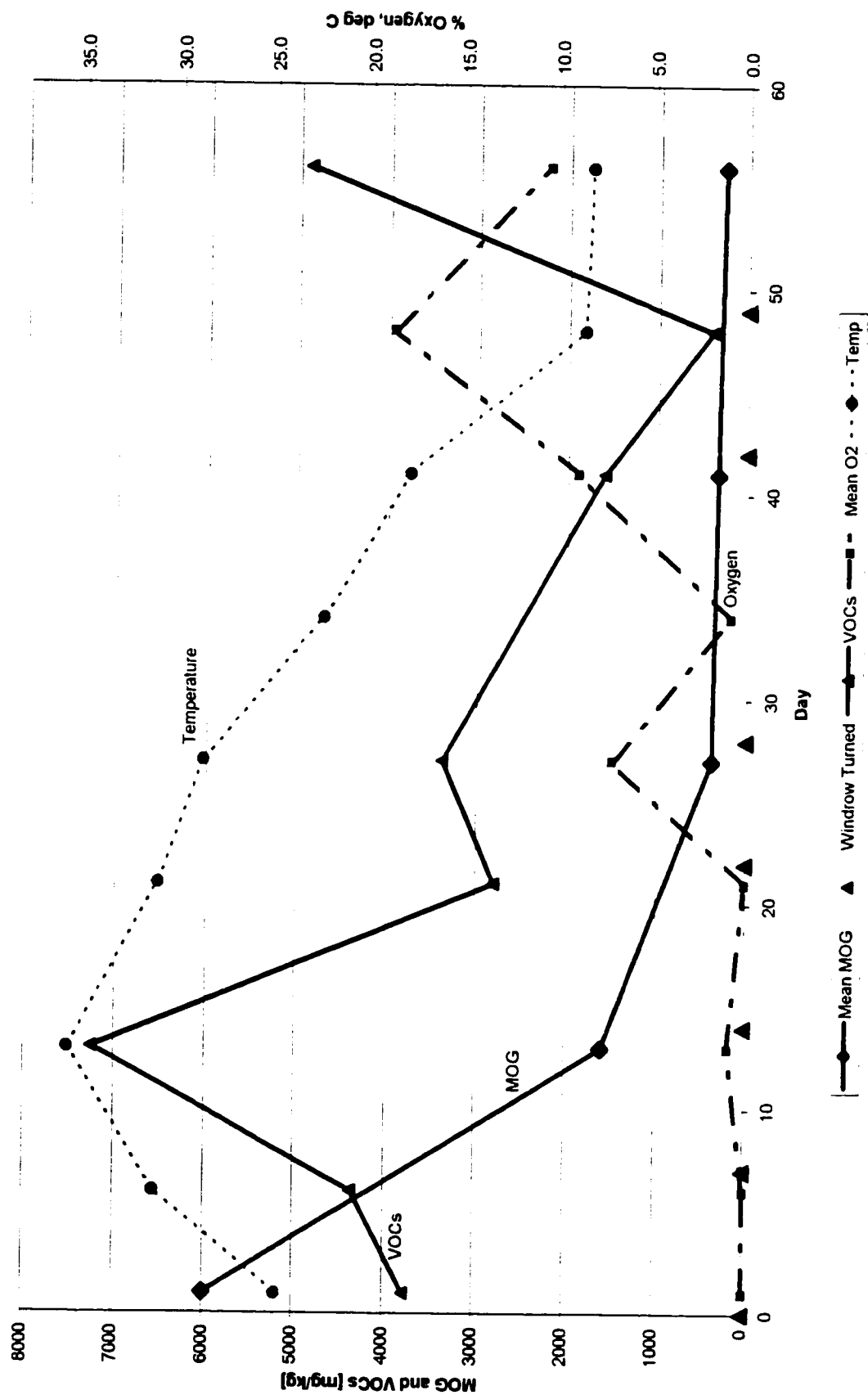
Since the overall level of bioactivity in the windrow was a combination of fungi, actinomycetes, and bacteria, it is difficult to assess whether the frequent turning had a disruptive effect on the growth of the natural fungi on the compost. However, it should be noted that this windrow exhibited the highest peak temperatures. This would support the assumption that the bioactivity in this organ-body was the highest of them all. Oxygen concentrations and temperatures correlated well to and were good indicators of the microbial activity.

The initial bacteria count was approximately one order of magnitude greater than the other windrows. This would be attributed to the biologically active poultry manure addition. The initial fungal population was similar to the other windrows. The drop in bacterial and fungal populations in the first 13 days indicates that some bacteria in the poultry manure could not adapt to the soil conditions and/or competition between the indigenous bacteria and inoculums were causing a decline in both bacteria and fungal populations, or they were very susceptible to the anoxic conditions which existed from Days 1 to 7. This was the only windrow that demonstrated a significant decline in bacteria and fungus counts in the first two weeks. By Day 27, the bacteria had adapted and populations were growing. However, the fungi still stayed at low populations, the lowest population of all windrows on this date. Although ample cellulosic substrate still existed at this time, the lack of fungal population growth may indicate that the poultry manure was toxic to the fungi introduced on the compost or the two further excursions to near anoxic conditions were having a devastating effect on their growth. By this time, the bulk of the MOG had been remediated so the loss of the fungi population would not have been evidenced by a decrease in remediation rate of the heavy petroleum hydrocarbons.

d. VOC CONCENTRATIONS.

As indicated in **Figure 4.11 - Mean VOCs, MOG, Oxygen, Temperature versus Time**, the VOC concentrations were quite erratic. The mean starting concentration of 3773 mg/kg climbed by Day 13 to 7247, almost double the Day 1 concentration. It is theorized that this may have been due to the Day 13 temperature of 36 °C volatilizing more semi-volatile organic compounds (SVOC) from the poultry manure and petroleum hydrocarbons and/or intermediate petroleum hydrocarbons breakdown products being present from the degradation of the MOG. After this date, the concentrations fell to a level of approximately 400 mg/kg on Day 48. Although the concentration on Day 56 showed a ten-fold increase to 4880 mg/kg, the windrow temperature was only 8 °C and the GT408 was experiencing problems on that day. Therefore, this reading is assumed to be faulty and should be ignored. There does not appear to be any clear relationship of the VOC concentrations with oxygen concentrations, temperature or bioactivity. Since light and medium hydrocarbons were not tested at the end of the project, no quantitative data are available to prove that the intermediate breakdown products of the

Figure 4.11 - Mean VOCs, MOG, Oxygen, Temperature vs Time
 Windrow 2A - Compost, Manure, Turning



heavy hydrocarbons were consumed. However, the reducing concentrations of VOCs in the soil-gas suggested that such was the case.

e. NUTRIENT CONCENTRATIONS.

In **Figure 4.12 - Nutrients, Microbial Activity, Oxygen, Temperature versus Time**, the starting ammonia concentrations of 1000 $\mu\text{g/g}$ were 30 times higher than in Windrow 1. This was due to the high concentration of ammonia in the poultry manure. Despite the high levels of bioactivity, there was very little decline in ammonia concentrations in the first 13 days. Since the pH was 7.4 which would indicate that little ammonium was being transferred to ammonia, this may be an indication that these elevated concentrations of ammonia were far in excess of the microbial requirements and/or there was a continuous breakdown of organic nitrogen in the manure to ammonia. After Day 13, ammonia started to show a decline to 560 $\mu\text{g/g}$ on Day 27. This was still 15 times more than the starting concentration in Windrow 1. As a result of this obviously ample supply of ammonia, nitrates were not utilized. At 330 $\mu\text{g/g}$, available phosphate concentrations were very high compared to Windrow 1 since the poultry manure would have been a good source. The soluble phosphates were in sufficient concentrations that microbial use and transformation into insoluble polyphosphates and other intracellular compounds did not reduce the concentrations with the growing microbial populations.

f. STATISTICAL SIGNIFICANCE AND REGRESSION ANALYSIS.

Figure 4.13 - MOG True Mean Range (90% Confidence) - 2A, plots the Student's 90 percent confidence intervals for the MOG true mean and a regression analysis of the mean MOG. The exponential trend line is a good fit since all points are within the confidence intervals. Whereas the mean MOG crossed the 1000 mg/kg criteria concentration on Day 20, the regression line indicates that the reduction to criteria concentration nominally occurred on Day 13.

4.4 ***WINDROW 2B - COMPOST, FERTILIZER, WEEKLY TURNING.***

This windrow tested a common method of stimulating microorganisms used in biopile remediation processes by the use of synthetic fertilizer. Since a fine soil was expected and contamination with large organic molecules, compost was added as a bulking agent and an inoculant. Approximately 20

Figure 4.12 - Nutrients, Microbial Activity, Oxygen, Temperature vs Time
Windrow 2A - Compost, Manure, Turning

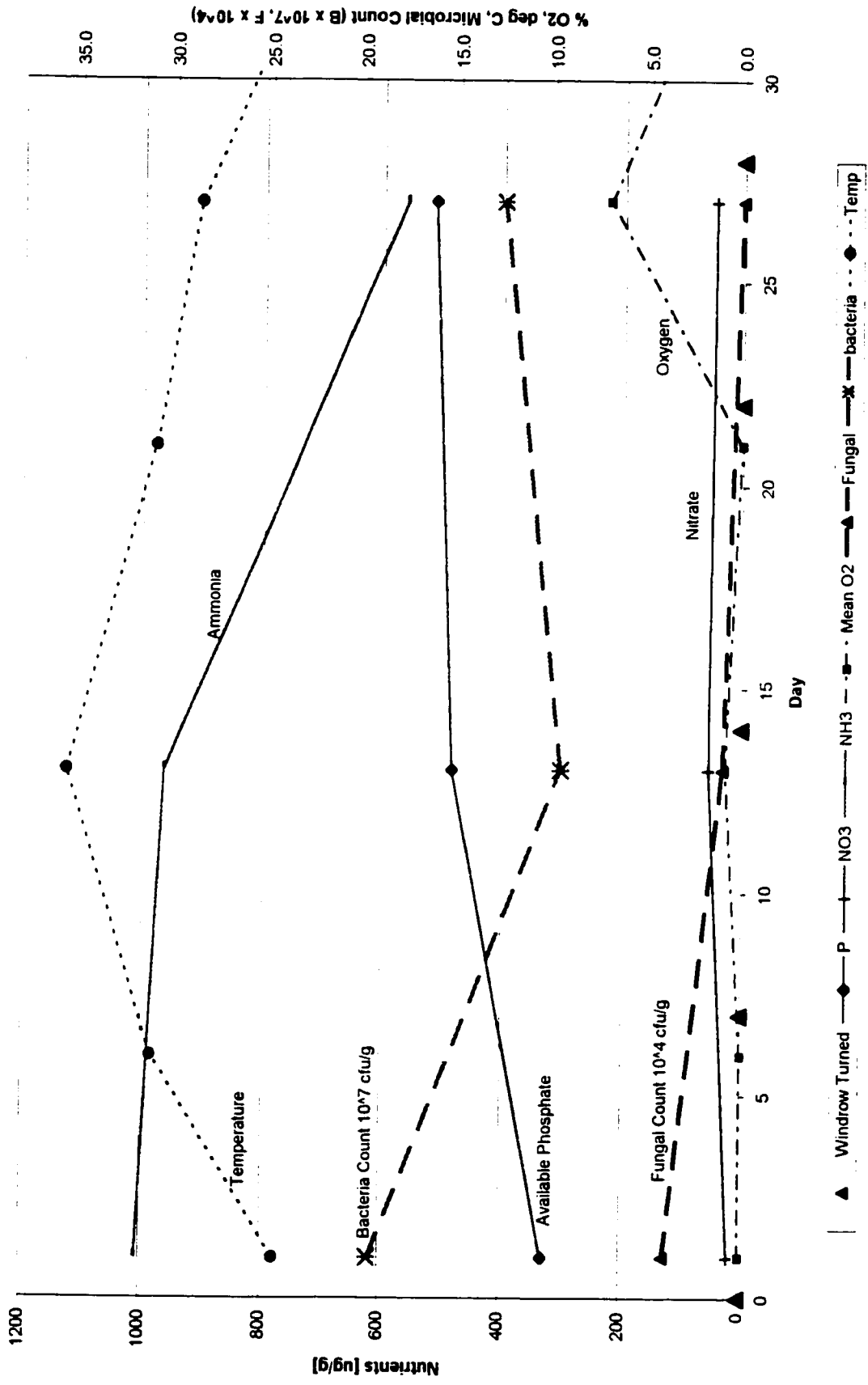
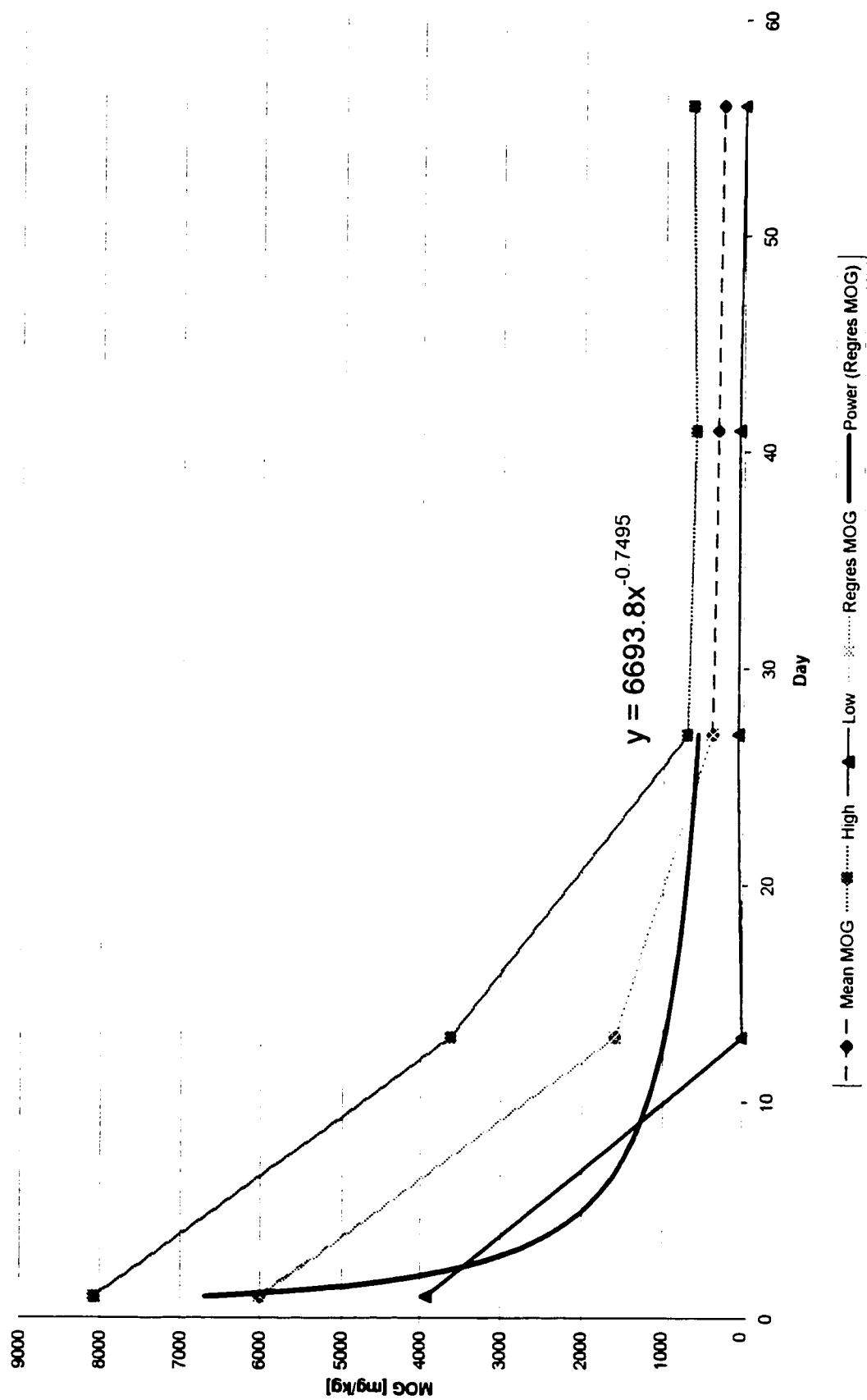


Figure 4.13 - MOG True Mean Range (90% Confidence)
 Windrow 2A - Compost, Manure, Turning



percent compost (v/v) and 1.5 kg/m³ of 48:8:2 slow release synthetic fertilizer was added to the soil. It was planned that the windrow would be turned weekly.

a. START - FINISH PETROLEUM HYDROCARBON CONCENTRATIONS.

As in **Table 4.5 - Start-Finish Petroleum Hydrocarbon Concentrations**

Windrow, the starting concentrations of light petroleum hydrocarbons of 27 and 5 mg/kg of purgeables and extractables were below the Ontario remediation criteria of 100 mg/kg. the starting concentration of MOG contamination was similar to Windrow 2A at approximately 6071 mg/kg, considerably above the Ontario remediation criteria of 1000 mg/kg for heavy oil. The combined PAHs of 16 mg/kg were below the Ontario criteria for the most prevalent PAH found in the final testing, Acenaphthylene. As described earlier, only MOG and PAH were tested at the end of the project. They were remediated to 528 and 3 mg/kg respectively, well below the remediation criteria.

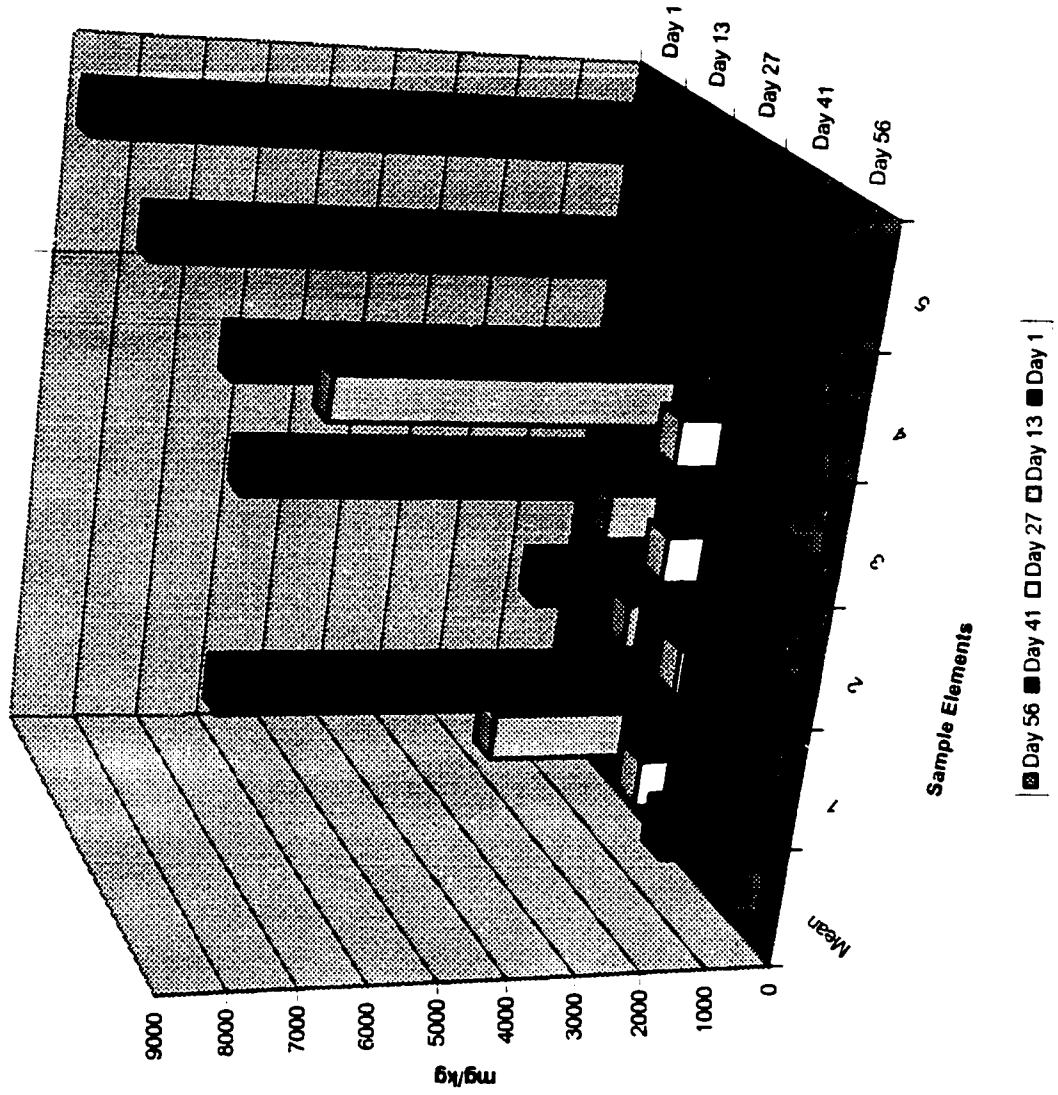
Table 4.5 - Start-Finish Petroleum Hydrocarbon Concentrations Windrow 2B (mg/kg)

Hydrocarbon	Criteria	Start	Finish
Purgeables	100	27	n/a
Extractables	100	5	n/a
MOG	1000	6071	528
PAH	130	16	3

b. DISTRIBUTION OF MOG OBSERVATIONS.

Figure 4.14 - MOG Sample Mean and Range, illustrates the distribution of observations within each sample. In a range of 988 to 8966 mg/kg, the five Day 1 observations had all but one at the high end of the range and one very low concentration of less than 1000 mg/kg. The mean was 6071 mg/kg with a standard deviation of 3069 mg/kg. The low concentration observation would have caused some skewing of the mean to the low side of the range of observations. There was another observation at 46,000 mg/kg which was deemed to be either a laboratory error or resulted from the inclusion of a pure product nodule in the sample being analysed. This observation was deleted as an outlier. Day 13 showed one sample of 5457 mg/kg which was ten times the mean of the other two observations. This would skew the mean to the high side. The mean was 2160 with a standard deviation of 2871. Had the one large observation on Day 13 been

Figure 4.14 - MOG Sample Mean and Range - Windrow 2B
Mean MOG and Individual Sample MOG Analyses Shown for Each Sampling Event



removed/modified, the drop in MOG would have been even faster. The standard deviation for Day 41 of 661 mg/kg was almost equal to its mean of 779 mg/kg due to one observation being approximately four times the mean of the other four samples. The samples on Days 27 and 56 had reasonable distributions of observations. The means for Days 27 and 56 were 471 and 528 respectively. Due to the heterogeneity of the soil-amendment mixture and the low level of accuracy of the MOG analysis no data were deemed to be outliers and removed from the analysis except for the observation of 46,000 mg/kg.

c. MEAN MOG, OXYGEN, TEMPERATURE AND MICROBIAL ACTIVITY.

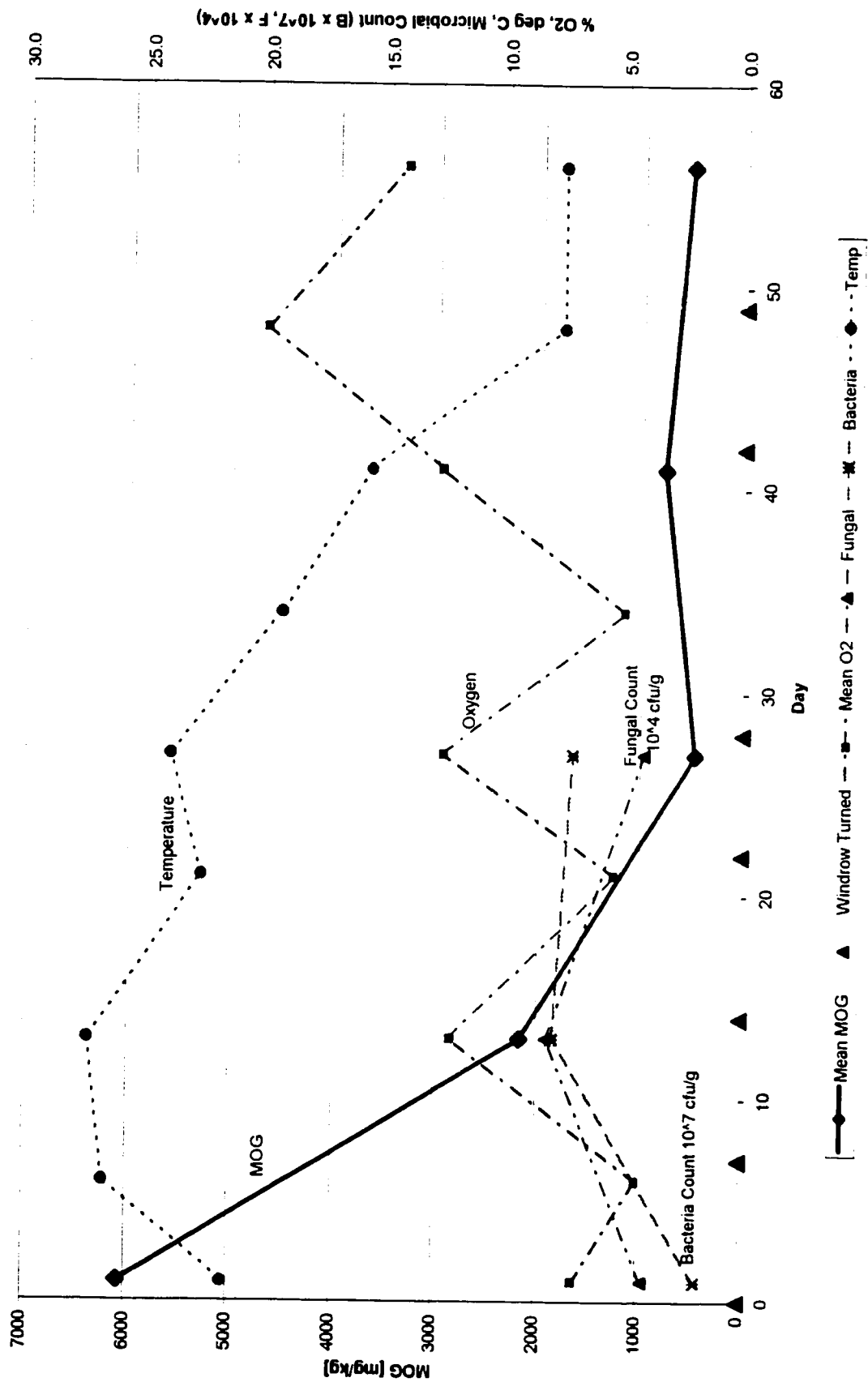
Figure 4.15 - Mean MOG, Oxygen, Temperature and Microbial Activity versus Time, examines MOG concentrations over time with oxygen, temperature and for the first four weeks, the microbial counts. Due to the addition of the biologically active compost, the windrow had initial fungal counts of 4×10^4 cfu/g which is similar to Windrows 1 and 2A. The bacteria counts of 2×10^7 cfu/g are similar to Windrow 1 since it too had only compost added by Day 1. By Day 13 the fungal count had doubled to 8×10^4 cfu/g and the bacterial count had quadrupled to 8×10^7 cfu/g. On Day 27 the fungal count declined to near its starting level whereas the bacteria only slightly declined to 7×10^7 cfu/g.

The windrow temperature on Day 1 was 22°C. The bulk windrow temperature quickly climbed to a peak of 27°C on Days 6 and 13 when the ambient temperatures were in the 11 to 13°C range then they slowly subsided to 8°C by the end of the project.

Unlike Windrow 2A, the windrow did not go anoxic in the first few days. Oxygen concentrations started at seven percent, and fell to 4.4 percent on Day 6, its lowest concentration in this windrow during the project. From there the oxygen concentrations varied between atmospheric concentrations when the windrow was turned and five percent on Days 21 and 34. There was only one apparent sustained period at the five percent concentration, from Day 0 to Day 7. Oxygen concentrations reflected microbial respiration, turning and natural infiltration of atmospheric oxygen much as described for Windrow 2A. As for Windrow 2A, oxygen concentrations did not sustain higher levels until towards the end of the project when temperatures were falling to the 20°C range.

Because the oxygen was not depleted as in Windrow 2A, both the bacterial and fungal populations grew when the windrow was established. The temperature profile

Figure 4.15 - Mean MOG, Oxygen, Temperature & Microbial Activity vs Time
Windrow 2B - Compost, Fertilizer, Turning



shows that when the MOG concentration reached asymptotic concentrations, the temperature slowly subsided. As the hydrocarbons were mineralized, the bacterial and especially fungal populations started to decline. Although the wood substrate was still present, it appears that the fungi may have also been deriving a beneficial effect from the presence of the organic contamination (a phenomena that has not been proven). There was a close correlation between the consumption of oxygen and temperature as indications of bioactivity. Oxygen consumption did not overtake the replenishment by turning and natural infiltration and concentrations were kept above the desired five percent for good aerobic activity.

d. VOC CONCENTRATIONS.

As portrayed in **Figure 4.16 - Mean VOCs, MOG, Oxygen, Temperature versus Time**, VOC concentrations rapidly declined from 6850 mg/kg almost seven-fold in the first week and stayed at low concentrations of approximately 1000 mg/kg until Day 41 at which time they moved to the a range of 500 mg/kg and less. As with the other windrows, it can be assumed that this was a result of initial concentrations of light petroleum hydrocarbons in the soil. These were quickly mineralized. Since light and medium hydrocarbons were not tested at the end of the project, no quantitative data were available to prove that the intermediate breakdown products of the heavy hydrocarbons were consumed. However, the reducing concentrations of VOCs in the soil-gas suggested that such was the case. There is no apparent relationship between VOCs and oxygen, temperature or bioactivity.

e. NUTRIENT CONCENTRATIONS.

As portrayed in **Figure 4.17 - Nutrients, Microbial Activity, Oxygen, Temperature versus Time**, the nutrient concentration of ammonia of 514 $\mu\text{g/g}$ was one half that of Windrow 2A which had compost and poultry manure, but 15 times that of Windrow 1 which had compost but no fertilizer. As a result of the ample supply of the preferred ammonia for microbial requirements and/or the continuous breakdown of organic nitrogen, the ammonia levels did not drop in the first two weeks. The ammonia concentrations only dropped significantly after Day 13, and by Day 27 were approximately 100 mg/kg. It is speculated that this may be due to microbial consumption, since the pH was in the range of 7.4 to 7.6 and there would have been no significant loss of

Figure 4.16 - Mean VOCs, MOG, Oxygen, Temperature vs Time
 Windrow 2B - Compost, Fertilizer, Turning

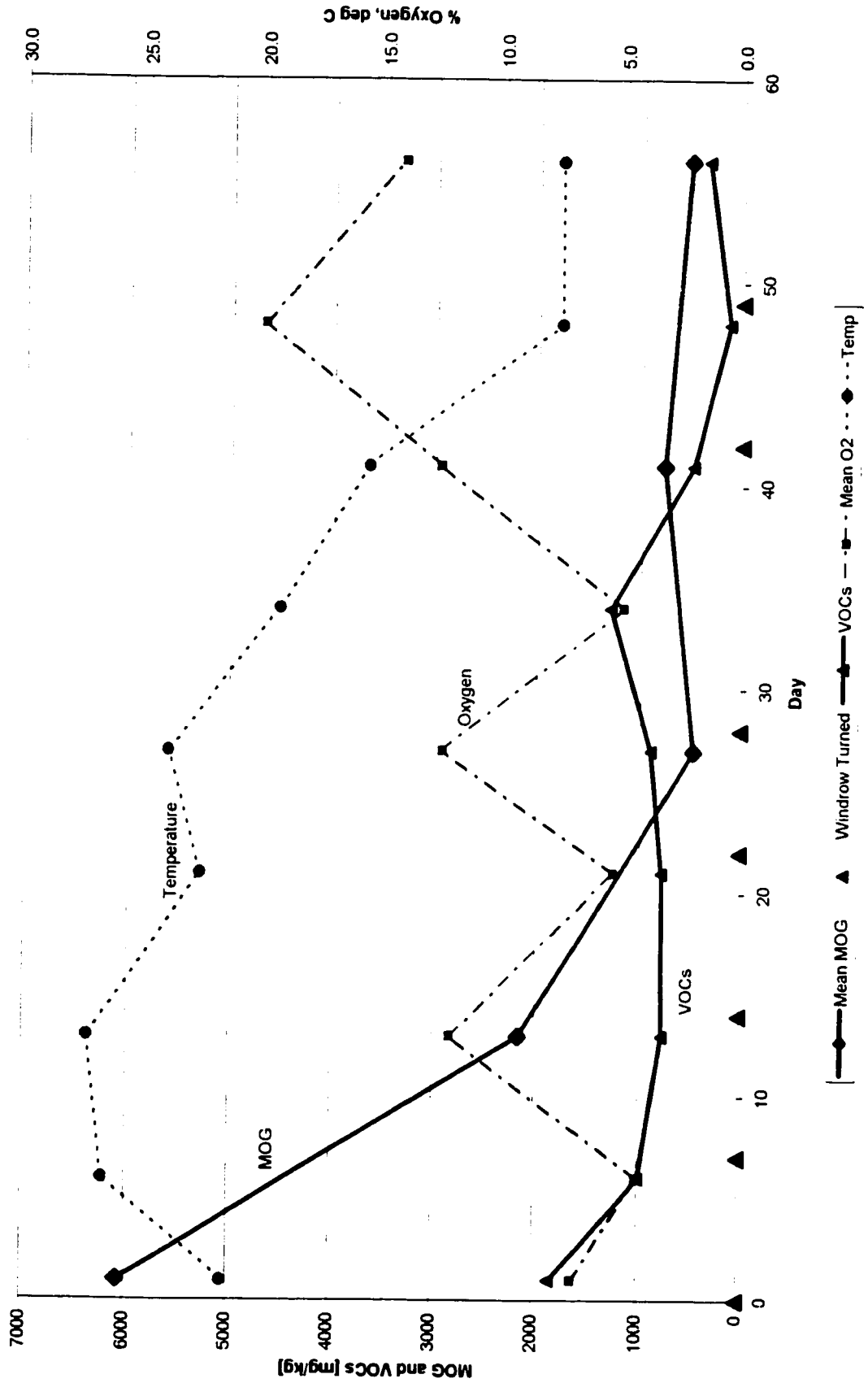
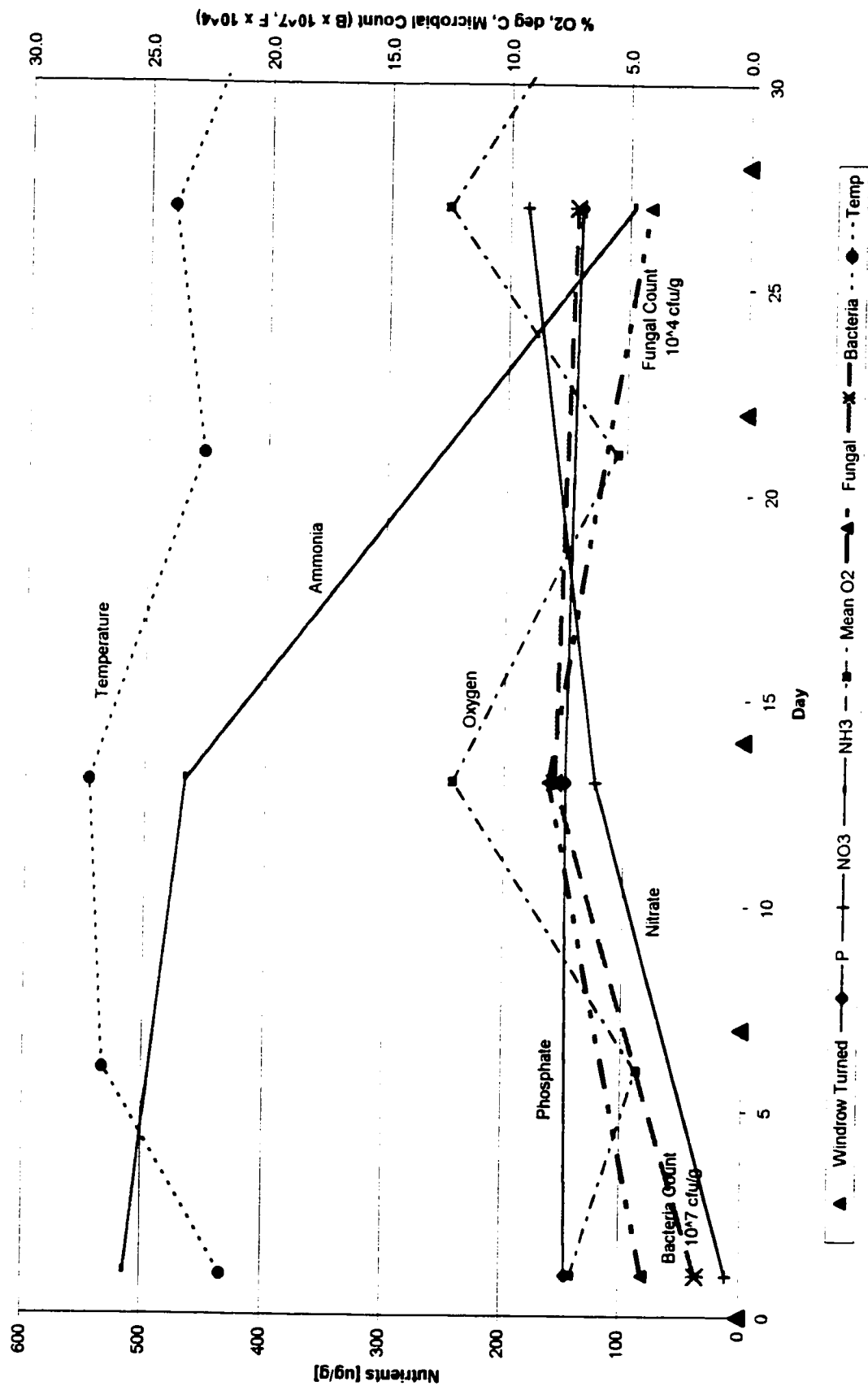


Figure 4.17 - Nutrients, Microbial Activity, Oxygen, Temperature vs Time
Windrow 2B - Compost, Fertilizer, Turning



ammonium as ammonia gas. However, since total nitrogen was not determined, loss of ammonia to volatilization cannot be ruled out. The increase in nitrate resulted from the nitrifying bacteria activity and since sufficient amounts of ammonia existed for the microbial requirements and adequate oxygen resources were available as an electron acceptor throughout the period the nitrates were not being used as an electron acceptor.

Available phosphate concentrations remained at relatively stable concentrations of 150 $\mu\text{g/g}$ which indicated that sufficient quantities of soluble phosphorous existed the period of analysis. Fertilizer provided an ample supply of the major nutrients for stimulating the microbial populations.

f. STATISTICAL SIGNIFICANCE AND REGRESSION ANALYSIS.

Figure 4.18 - MOG True Mean Range (90% Confidence). plots Student's 90 percent confidence intervals for the MOG true mean and a regression analysis of the mean MOG. The exponential trend line is a good fit since all points are within the confidence intervals. Whereas the mean MOG crossed the 1000 mg/kg criteria concentration on Day 22, the regression line indicates that the reduction to criteria concentration nominally occurred on Day 17.

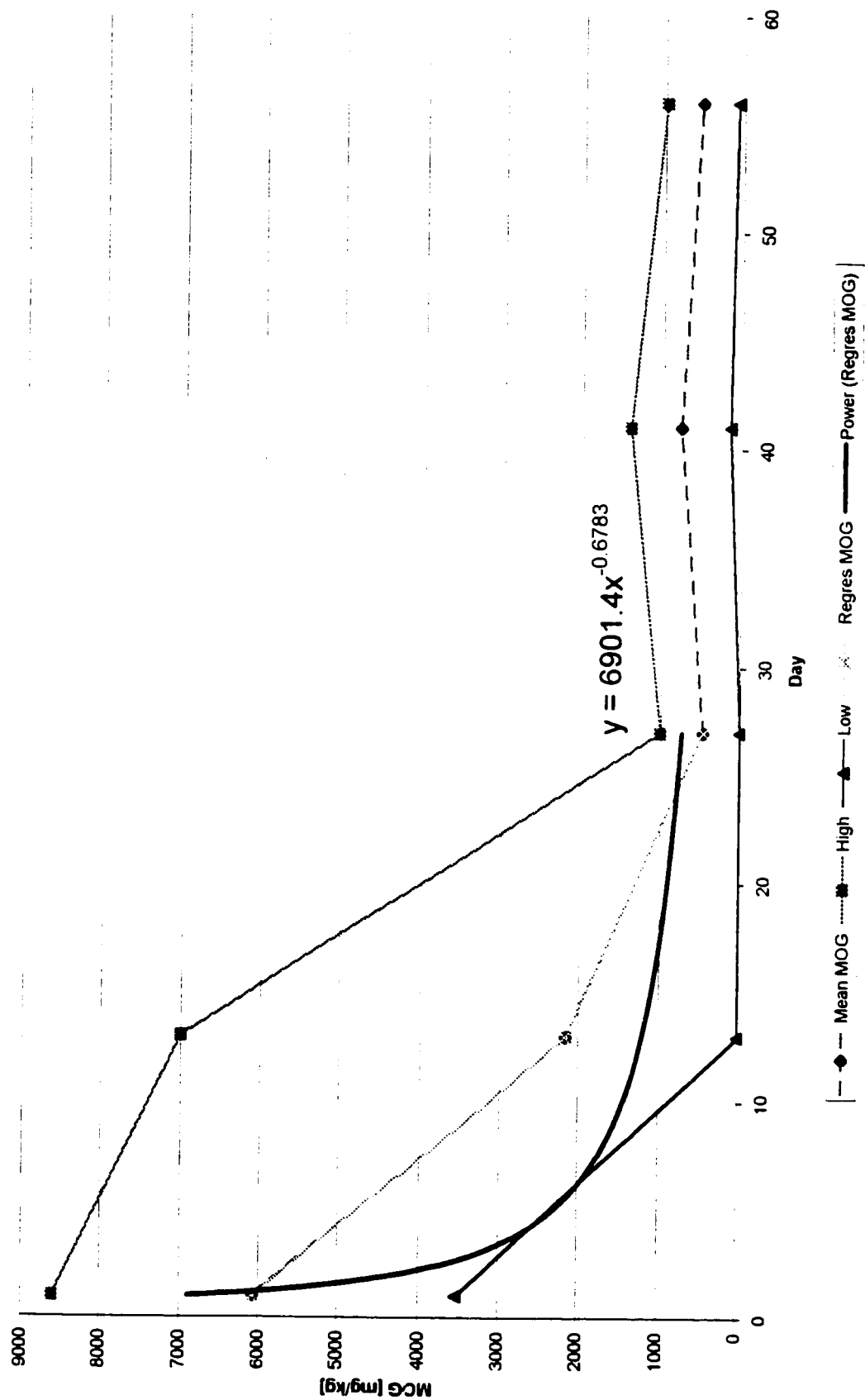
4.5 ***WINDROW 3A - COMPOST, FERTILIZER, NO TURNING.***

The composition of this windrow was a duplicate of Windrow 2B using synthetic fertilizer and compost. However, in order to determine the effect of aeration on the rate of remediation, it was not turned. Twenty percent compost and 1.5 kg/m³ of 48:8:2 slow release synthetic fertilizer were added to the soil. The windrow was turned in error on Day 22.

a. START - FINISH PETROLEUM HYDROCARBON CONCENTRATIONS.

As for the other windrows and as seen in **Table 4.6 - Start-finish Petroleum Hydrocarbon Concentrations Windrow**, starting concentrations of light petroleum hydrocarbons of 95 and 46 mg/kg purgeable and cold extractable hydrocarbons were below the Ontario remediation criteria of 100 mg/kg for gas/diesel. The mean MOG contamination was only 1500 mg/kg exceeded the Ontario remediation criteria of 1000 mg/kg for heavy oil. Since Windrow 3B was also found to be at this low concentration, it is concluded that the contamination concentration is representative of the true MOG concentration and reflects a poor mixing of contaminated soils during the excavation.

Figure 4.18 - MOG True Mean Range (90% Confidence)
WIndrow 2B - Compost, Fertilizer, Turning



screening and windrow construction process. The combined PAHs were 44 mg/kg were below the Ontario criterion for the most prevalent PAH, Acenaphthylene, in the final testing. As described earlier, only MOG and PAH were tested for at the conclusion of the project. These had been remediated to 660 and 1 mg/kg respectively, well below the remediation criteria.

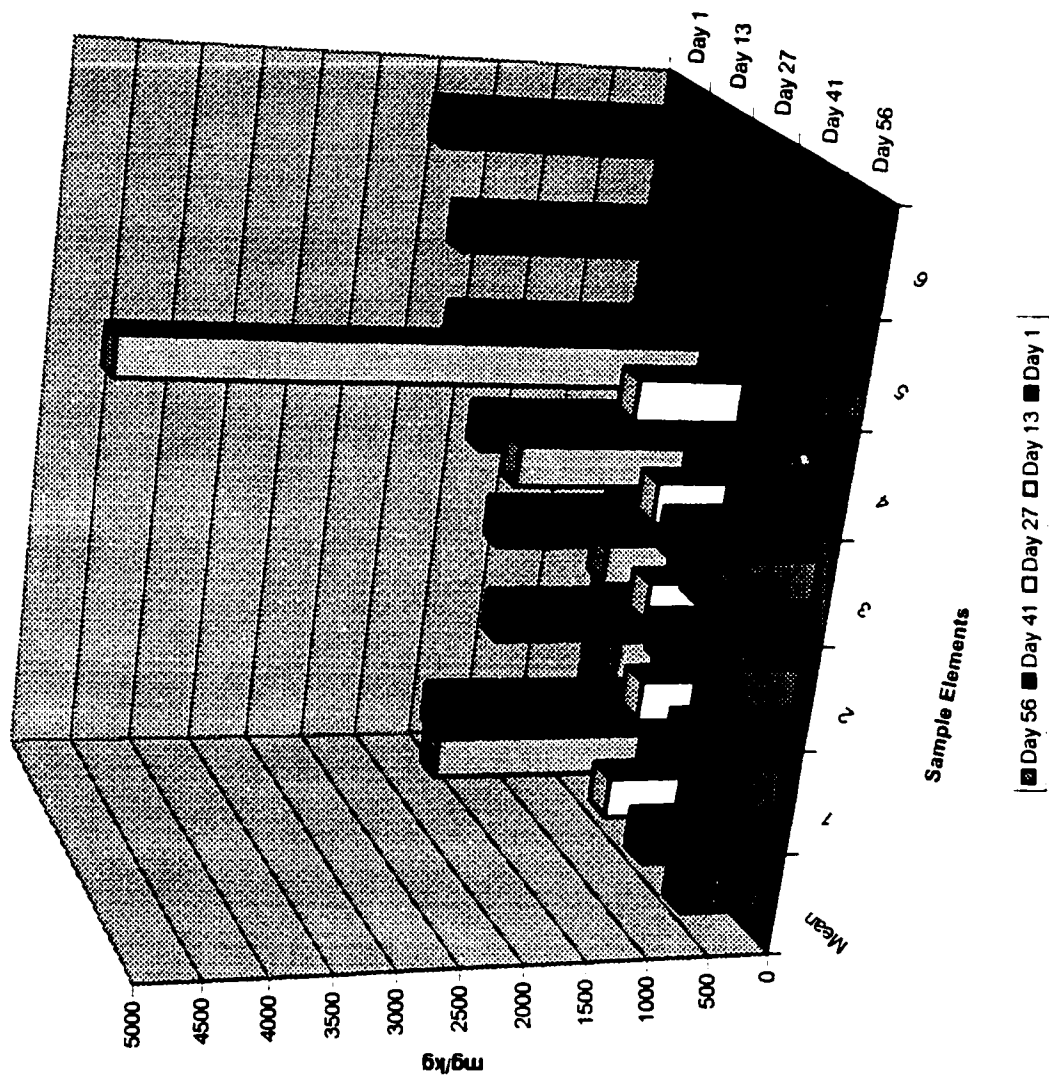
Table 4.6 - Start-Finish Petroleum Hydrocarbon Concentrations Windrow 3A (mg/kg)

Hydrocarbon	Criteria	Start	Finish
Purgeables	100	95	n/a
Extractables	100	46	n/a
MOG	1000	1500	660
PAH	130	44	1

b. DISTRIBUTION OF MOG OBSERVATIONS.

Figure 4.19 - MOG Sample Mean and Range, illustrates the distribution of observations within each sample. Day 1 had a very even range of six observations from 1061 to 2096 mg/kg with a mean of 1500 mg/kg and a standard deviation of 428 mg/kg. Day 13 had one sample of 4830 mg/kg which was seven times the mean of the other three observations. This skewed the mean to the high side. The mean was 1786 with a standard deviation of 2085. It is doubtful that the Day 13 mean was higher than the Day 1 mean. This serves to point out the approximation of the sampling and analysis methods, especially for MOG analysis of such a heterogeneous matrix with a blend of large and small particle sizes. Since it was deduced above that the starting concentration data are correct, it will be assumed that on Day 13 the mean concentration of MOG was at least the same as Day 1, or lower. The value of mean MOG for Day 13 will be conservatively assumed to be that of Day 1, namely 1500 mg/kg. The other samples had reasonably tight ranges of observations. Due to the heterogeneity of the soil-amendment mixture and the low level of accuracy of the MOG analysis no data were deemed to be outliers and removed from the analysis. The mean MOG concentration for Day 13 was adjusted to 1500 mg/kg.

Figure 4.19 - MOG Sample Mean and Range - Windrow 3A
Mean MOG and Individual Sample MOG Analyses Shown for Each Sampling Event



c. MEAN MOG, OXYGEN, TEMPERATURE AND MICROBIAL ACTIVITY.

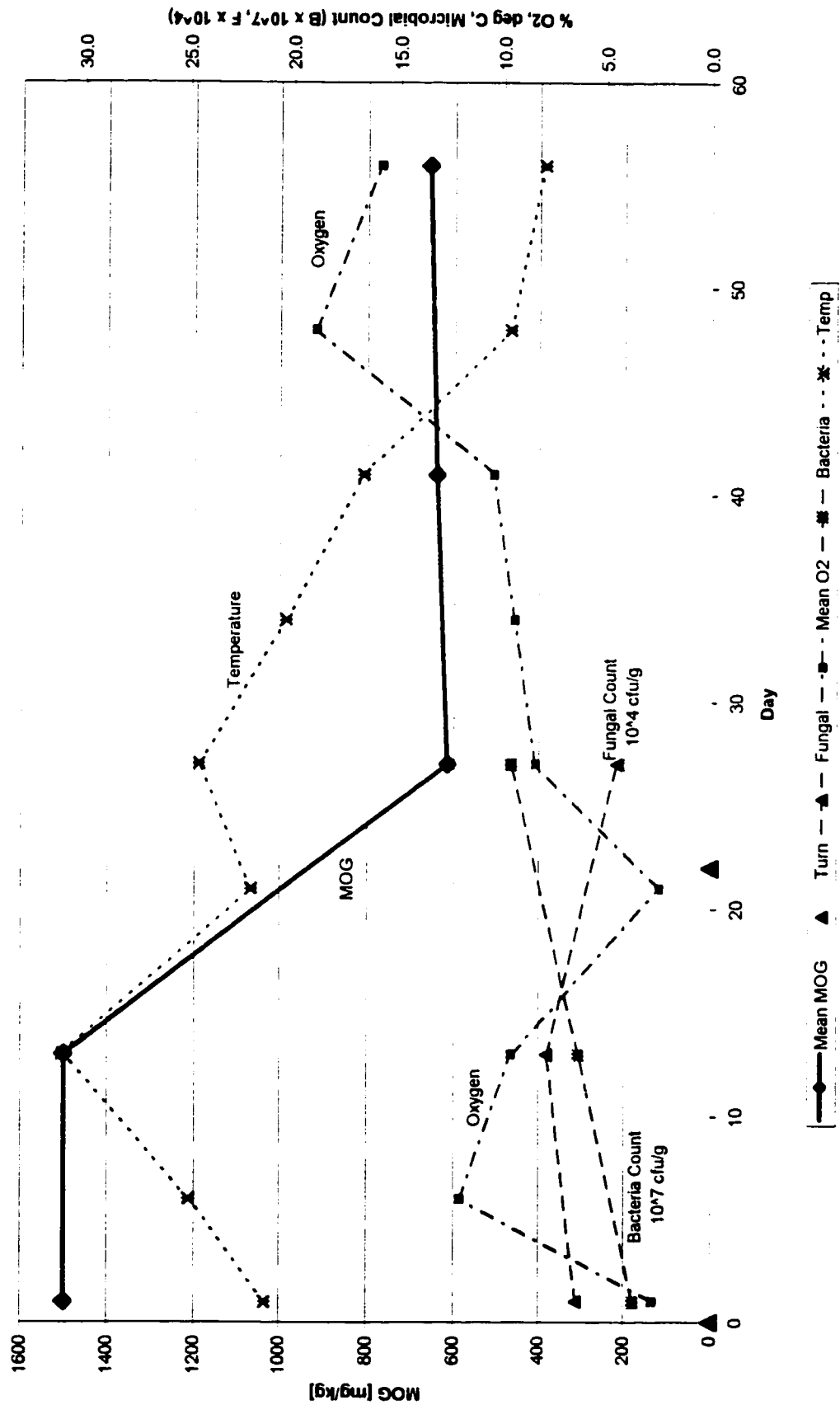
Figure 4.20 - Mean MOG, Oxygen, Temperature and Microbial Activity versus Time. compares the mean MOG concentrations over time with the weekly results of monitoring in-windrow oxygen and temperature and for the first four weeks, and the biweekly analysis of microbial counts. The starting fungal count was 6×10^4 cfu/g and bacterial count 4×10^7 cfu/g. These were slightly higher than Windrow 2A which had the same starting conditions. On Day 13 the fungal count had risen to 8×10^4 cfu/g and the bacterial to 6×10^7 cfu/g. By Day 27 the fungal had decreased to 4×10^4 cfu/g and the bacterial had increased to 10×10^7 cfu/g.

The Day 1 temperature was 21 °C. It rose to 25 °C on Day 6 and to 31 °C on Day 13. Thereafter, the temperature started a gradual decline with one minor increase from 22 °C on Day 21 to 25 °C on Day 27. On Day 56, the temperature was 8 °C.

The turning of the windrow on Day 0 restored oxygen concentrations in the soil-gas to near atmospheric concentrations, however, by Day 1 it had fallen to three percent. On Day 6, the windrow oxygen concentrations were 12 percent from where it declined to 10 percent on Day 13. By Day 21, the bulk concentration of oxygen had further decreased to approximately 2.5 percent. An accidental turning on Day 22 restored the oxygen levels to near atmospheric concentrations. By Day 27 it had declined again to eight percent. From then it rose to near atmospheric concentrations on Day 48. On Day 56, the oxygen level was shown to be falling again, however, due to faulty operation of the detector on this date, this reading will be ignored.

When the windrows were formed, the windrow consisted of contaminated soil, compost and slow release synthetic fertilizer. The effect of excavating and aerating the contaminated soil and inoculating it with the compost and synthetic fertilizer would have activated the indigenous microorganisms. The increasing populations of fungi, actinomycetes and bacteria would have resulted in increasing temperatures and decreasing oxygen through microbial activity on the compost and organic contaminant substrates. However, the oxygen levels increased from 3 percent on Day 1 to 12 percent on Day 6. The same phenomena occurred in Windrow 3B at this time. Since turning was not possible, and there were no high winds during this period, no explanation can be offered for the increase. Thereafter the oxygen concentration declined to Day 21. This had an apparent negative effect on the microbial populations since the windrow temperature started to decline after Day 13. When the windrow was turned on Day 22, the oxygen

Figure 4.20 - Mean MOG, Oxygen, Temperature & Microbial Activity vs Time
 Windrow 3A - Compost, Fertilizer, No turning



concentration would have risen to near atmospheric concentrations. Bacterial populations continued to increase in response to the growing availability of substrate in the form of breakdown products from the fungal activity on the complex organic hydrocarbons and lignin/cellulose molecules. The decline in fungal population indicates that they were more susceptible to the oxygen limited conditions after Day 13.

After Day 27 when MOG concentrations had reached approximately 600 mg/kg, the temperature started to decline and the oxygen concentrations started to rise, continuing the trend to the end of the project (Day 56). The natural rise in oxygen and decline in bulk windrow temperature indicated that microbial activity was still present, but at an ever reducing rate up to the end of the project. Bulk oxygen concentrations dipped below the desired five percent on two occasions, but did not remain there for long in either case.

d. VOC CONCENTRATIONS.

By **Figure 4.21 - Mean VOCs, MOG, Oxygen, Temperature versus Time**, the VOC concentration of 7067 mg/kg started at the highest concentration of all windrows. This could be explained as an error in reading or the probe being inserted into a nodule of heavily contaminated soil since when the soil-gas monitoring equipment was being set up the day before (Day -1), the soil-gas VOC reading was 3800 mg/kg. By Day 6, the VOC concentrations had fallen to a concentration of 1700 mg/kg and continued to decrease to concentrations of less than 500 mg/kg by the end of the project. As with the other windrows, it can be assumed that the high initial reading was as a result of the light petroleum hydrocarbons in the soil. When these were mineralized, no VOCs reappeared. Since light and medium hydrocarbons were not tested at the end of the project, no quantitative data are available to prove that the intermediate breakdown products of the heavy hydrocarbons were consumed. However, the reducing concentrations of VOCs in the soil-gas suggest that such is the case. There is no apparent relationship between VOCs and oxygen, temperature or bioactivity.

e. NUTRIENT CONCENTRATIONS.

As portrayed in **Figure 4.22 - Nutrients, Microbial Activity, Oxygen, Temperature versus Time**, the nutrient concentration of ammonia of 380 $\mu\text{g/g}$ was comparable to the other two windrows with synthetic fertilizer, albeit at slightly lower concentrations. This can be explained by the coarse manual application method of the

Figure 4.21 - Mean VOCs, MOG, Oxygen, Temperature vs Time
Windrow 3A - Compost, Fertilizer, No turning

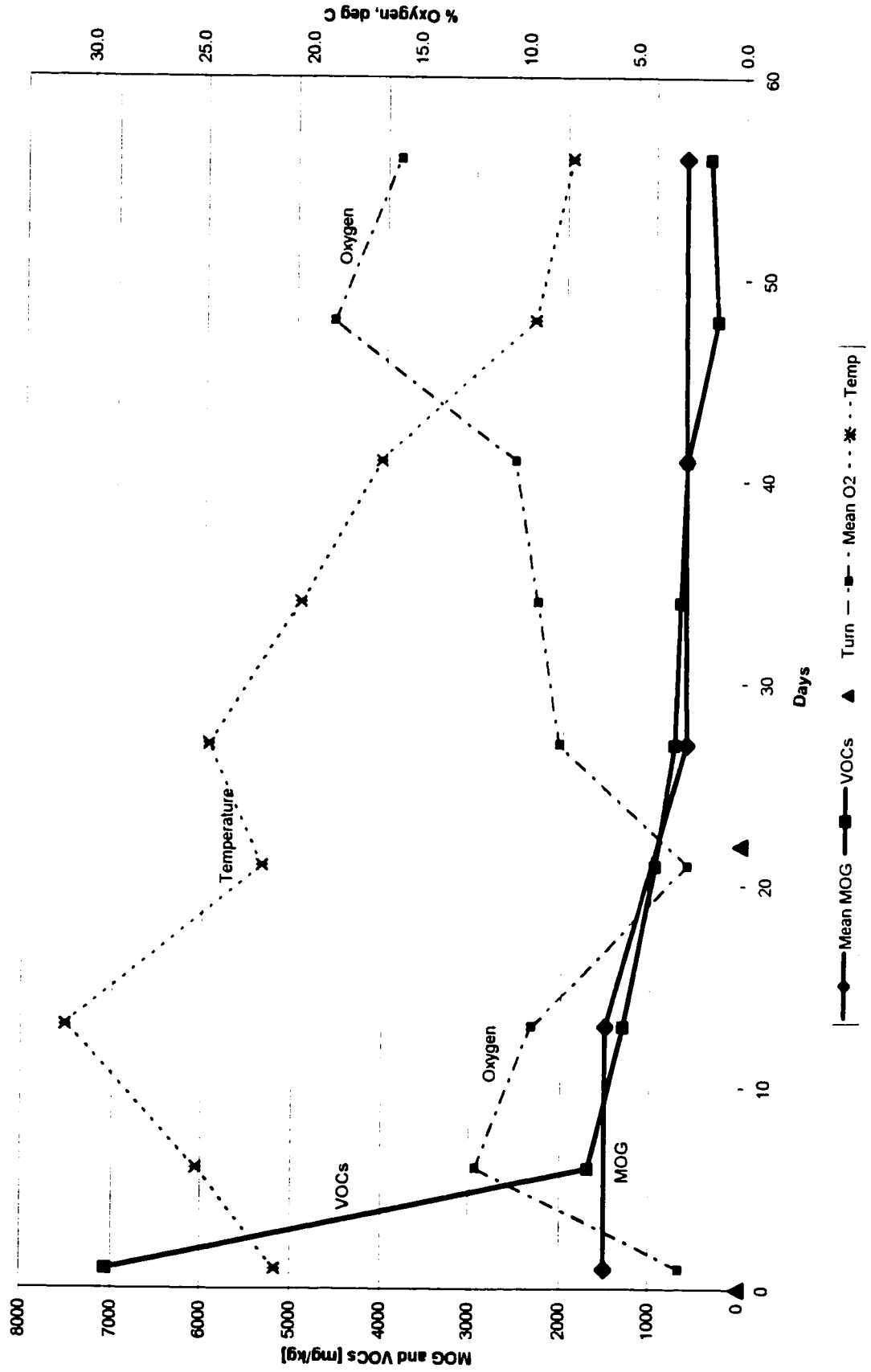
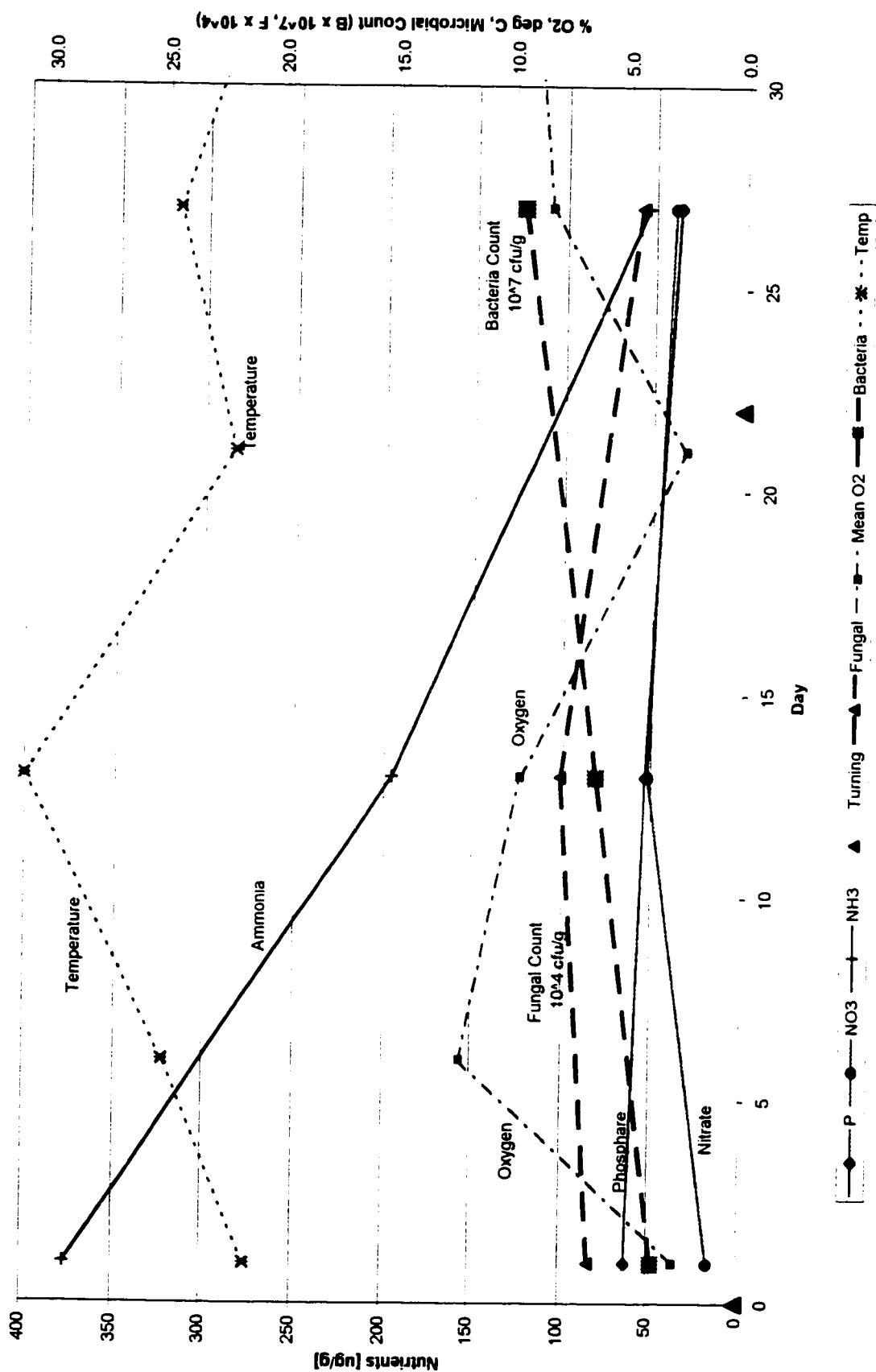


Figure 4.22 - Nutrients, Microbial Activity, Oxygen, Temperature vs Time
Windrow 3A - Compost, Fertilizer, No turning



fertilizer to the windrows. Since the initial pH was in the 8.0 range and fell to 7.4 by Day 6, it is speculated that not much ammonium was transformed to ammonia gas and lost to the atmosphere. Like the other fertilized windrows, the ammonia concentrations dropped significantly, in this case by approximately 300 mg/kg by Day 27 apparently in response to the microbial requirements for nitrogen. However, since total nitrogen was not determined, ammonia losses to volatilization cannot be ruled out. As a result of the lower supply of ammonia, the accumulation of nitrate in the synthetic fertilizer did not appear to occur to the same extent. It appears that for the level of microbial activity, the initial concentration of ammonia was at its critical concentration causing the microorganisms to start consuming the nitrates too. The low initial available phosphate concentrations declined by half to 36 mg/kg, indicating that there was microbial utilization of the soluble phosphate but that sufficient concentrations existed so that it was not depleted. Since total nitrogen and phosphorous were not measured, the above nutrient analysis can only be viewed as speculative reasoning since losses such as precipitation, volatilization and leaching cannot be confirmed or disallowed.

f. STATISTICAL SIGNIFICANCE AND REGRESSION ANALYSIS.

Figure 4.23 - MOG True Mean Range (90% Confidence). plots Student's 90 percent confidence intervals for the MOG true mean and a regression analysis of the mean MOG. The exponential trend line is a good fit since all points are within the confidence intervals. Whereas the mean MOG crossed the 1000 mg/kg criteria concentration on Day 21, the regression line, which started at the lowest initial concentration, indicates that the reduction to criteria concentration nominally occurred on Day 12.

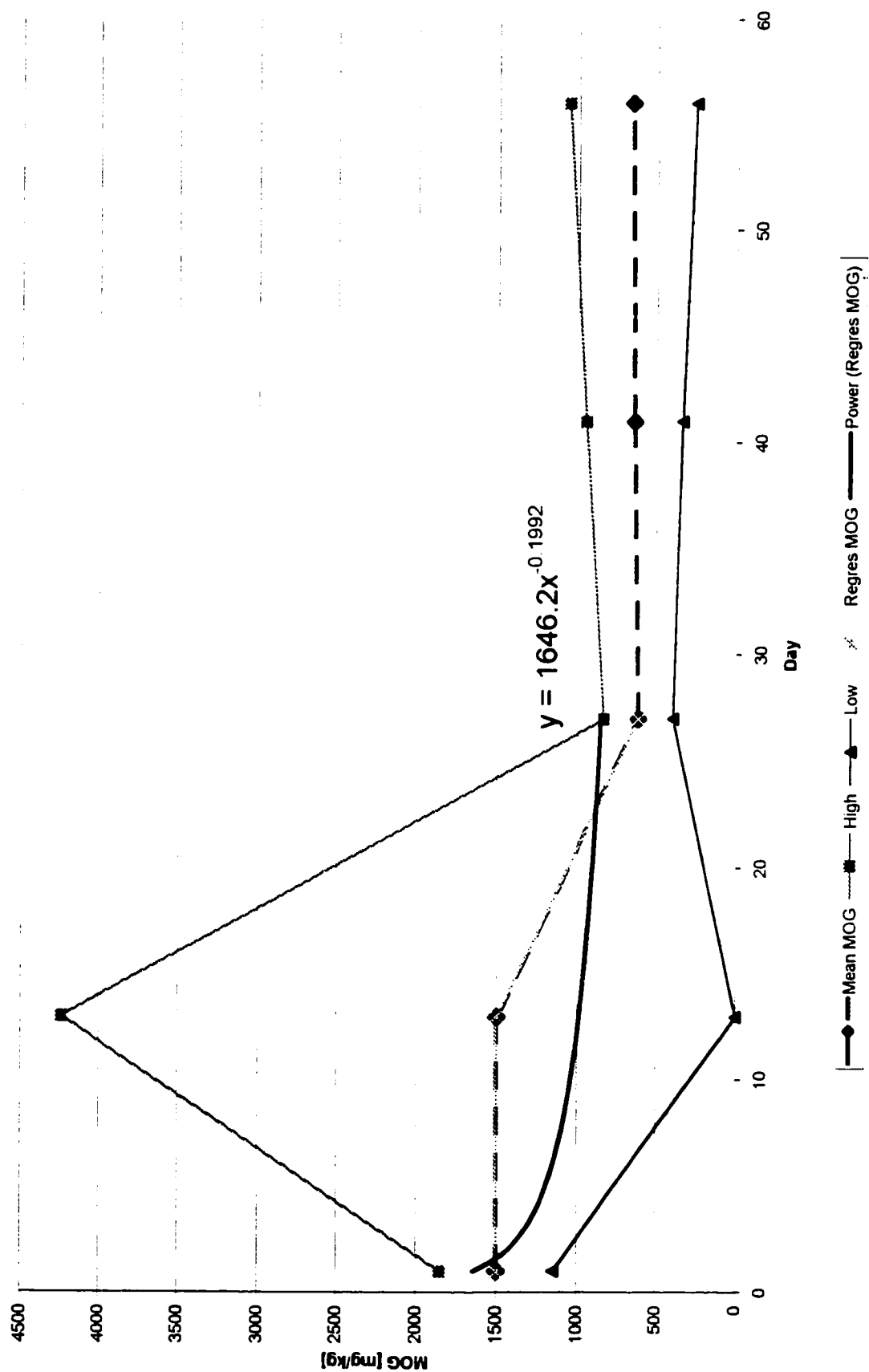
4.6 ***WINDROW 3B - FERTILIZER, NO TURNING.***

This windrow was a control which used only synthetic fertilizer and no aeration by turning. In order to determine the effect of compost as a bulking agent and inoculant, no compost was added to this windrow. The same 48:8:2 slow release fertilizer was added at the rate of 1.5 kg/m³ of soil. The windrow was turned in error on Day 22.

a. START - FINISH PETROLEUM HYDROCARBON CONCENTRATIONS.

As seen in **Table 4.7 - Start-finish Petroleum Hydrocarbon Concentrations Windrow**, the starting concentrations of light petroleum hydrocarbons of 73 and 34 mg/kg

Figure 4.23 - MOG True Mean Range (90% Confidence)
 Windrow 3A - Compost, Fertilizer, No turning



for purgeable and cold extractable hydrocarbons were below the Ontario remediation criteria of 100 mg/kg for gas/diesel. The mean MOG contamination of 1567 mg/kg exceeded the Ontario remediation criteria of 1000 mg/kg for heavy oil. Since Windrow 3A was also found to be at this low concentration, it is concluded that the contamination concentration is representative of the true MOG concentration and reflects a poor mixing of contaminated soils during the excavation, screening and windrow construction process. The combined PAHs of 18 mg/kg were below criteria of 130 mg/kg for the most prevalent PAH, Acenaphthylene, found in the final testing. As described earlier, only MOG and PAH were tested at the conclusion of the project. These had been remediated to 428 and 1 mg/kg respectively, well below the remediation criterias.

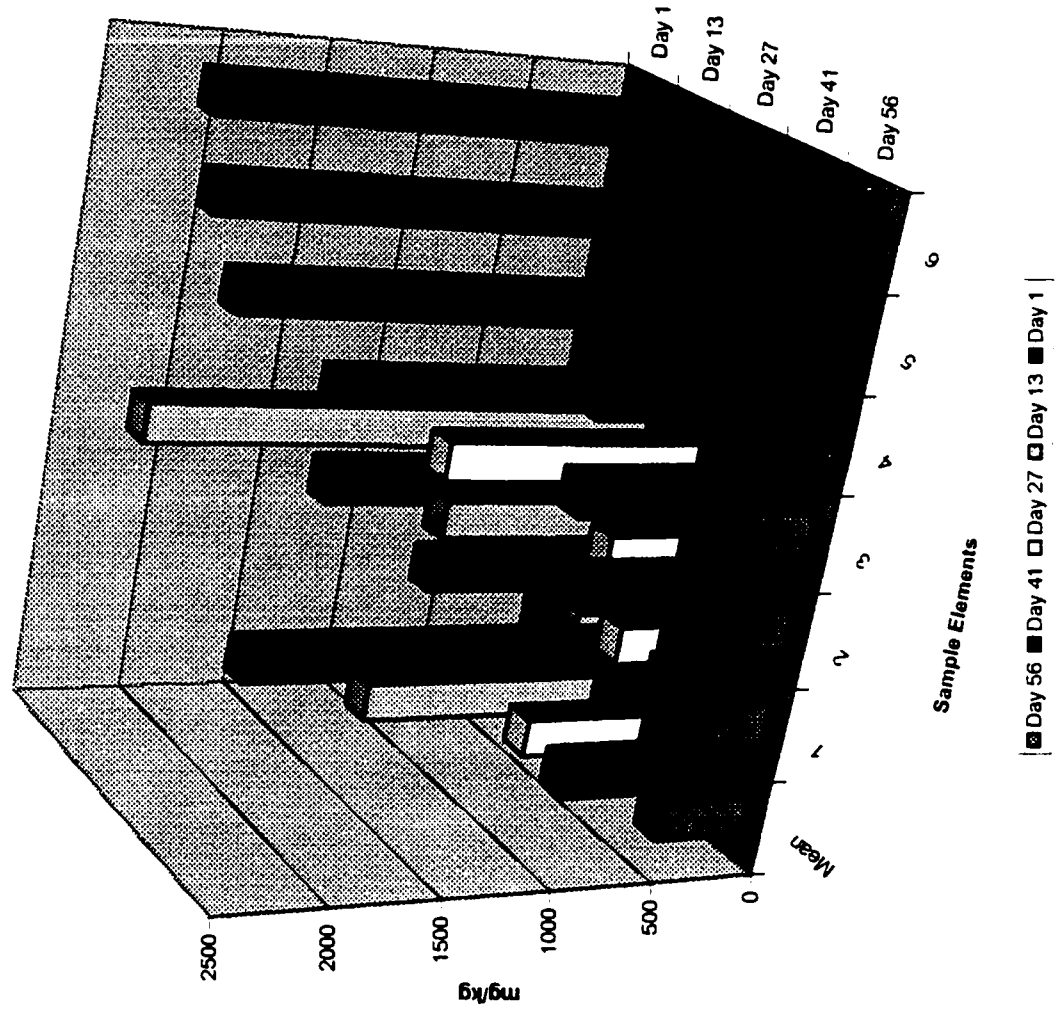
Table 4.7 - Start-Finish Petroleum Hydrocarbon Concentrations Windrow 3B (mg/kg)

Hydrocarbon	Criteria	Start	Finish
Purgeables	100	73	n/a
Extractables	100	34	n/a
MOG	1000	1567	428
PAH	130	18	1

b. DISTRIBUTION OF MOG OBSERVATIONS.

Figure 4.24 - MOG Sample Mean and Range, illustrates the distribution of observations within each sample. The Day 1 sample had a fairly even distribution of observations in its range from 715 mg/kg to 2121 mg/kg. Its mean was 1567 mg/kg and standard deviation was 528 mg/kg. Day 13 exhibited a wide scatter of the three observations (161, 952 and 2406 mg/kg) with a mean of 1173 mg/kg. The standard deviation of 1139 mg/kg was roughly equal to mean. Day 27 had one very high observation of 1245 mg/kg which was five times the mean of the other two observations. The mean was 605 mg/kg with the standard deviation of 559 mg/kg was roughly equal to the mean. Day 41 had one very light observation in the range of 217 to 844 mg/kg. The mean was 660 mg/kg. The Day 56 sample had good tight range of observations from 356 to 474 mg/kg, a mean of 428 mg/kg and a standard deviation of 63 mg/kg. Due to the heterogeneity of the soil-amendment mixture and the low concentration of accuracy of the MOG analysis (MDL was 500 mg/kg) no data are deemed to be outliers and removed from the analysis.

Figure 4.24 - MOG Sample Mean and Range - Windrow 3B
Mean MOG and Individual Sample MOG Analyses Shown for Each Sampling Event



c. MEAN MOG, OXYGEN, TEMPERATURE AND MICROBIAL ACTIVITY.

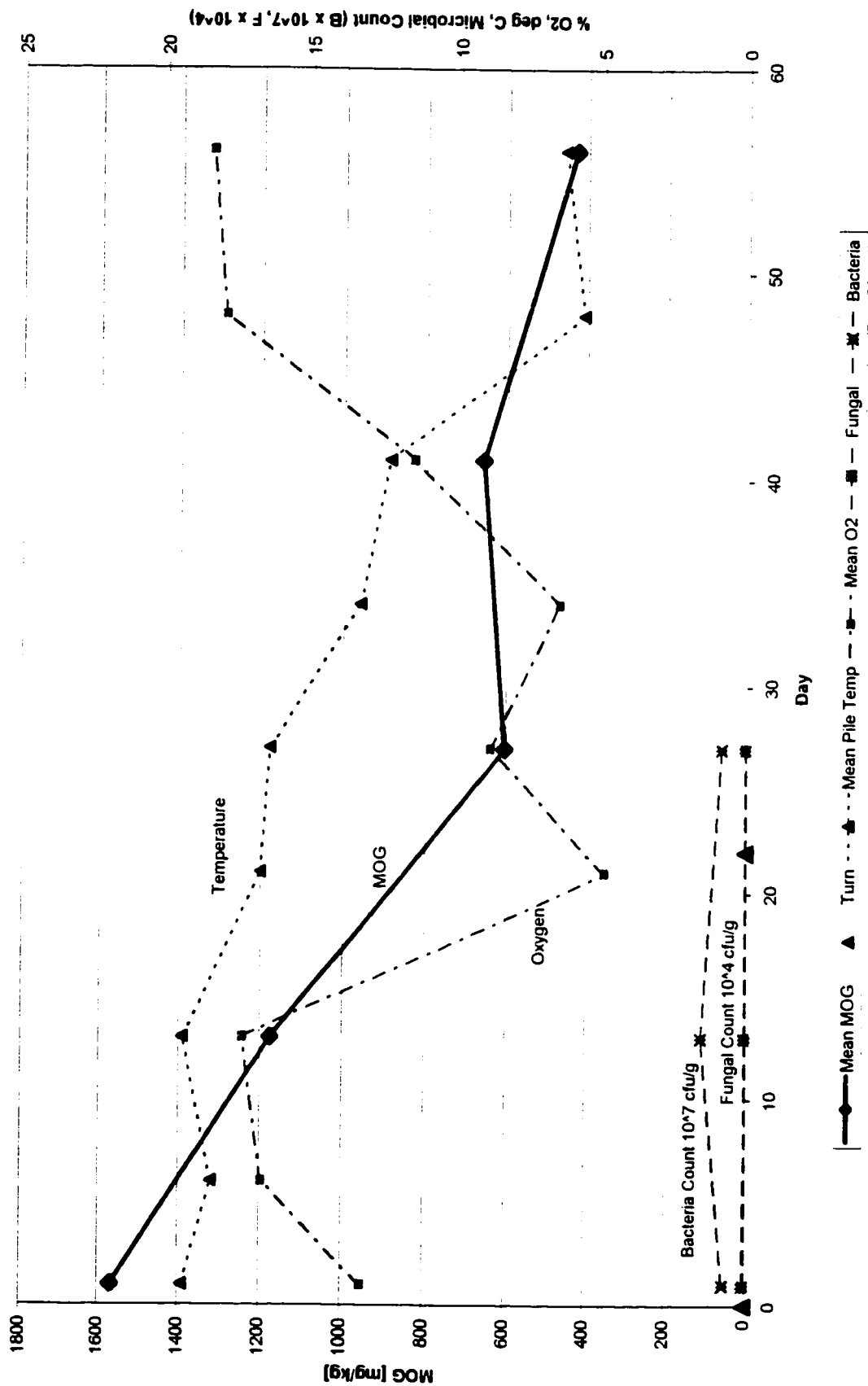
Figure 4.25 - Mean MOG, Oxygen, Temperature and Microbial Activity versus Time, compares the mean MOG concentrations over time with the weekly results of monitoring in-windrow oxygen and temperature and for the first four weeks, the biweekly analysis of microbial counts. Without the compost, the initial fungal count was very low. The centre and east ends showed counts of 0.08 and 0.03×10^4 cfu/g. The west end of the windrow which abutted Windrow 3A with compost, appears to have some compost incorporated into the composite sample since its fungal count was 8×10^4 cfu/g. Similarly subsequent observations at west end of the windrow showed a significant deviation from the other two composites. Therefore all three sampling events ignored the observation from the west end as a sampling error. The corrected initial mean fungal count was 0.05×10^4 cfu/g. The Day 13 mean fungal count was 0.04×10^4 cfu/g and the Day 27 fungal count was 0.04×10^4 cfu/g. The bacteria counts were 1, 1.5 and 1×10^4 cfu/g. The initial level was the lowest bacterial counts of all the windrows.

From a Day 1 temperature of 19°C , the temperature remained between 18°C and 19°C up to Day 13 at which time it began to steadily decline to a temperature of 6°C by the last two weeks of the project.

The turning of the windrow on Day 0 provided atmospheric oxygen concentrations to the soil-gas. By Day 21, the bulk concentration of oxygen had decreased to approximately five percent. An accidental turning on Day 22 restored the oxygen to near atmospheric concentrations and by Day 27, it had fallen to nine percent, with a further decline to six percent on Day 34. Oxygen concentrations rose after this to approach atmospheric concentrations by the end of the project.

The lack of fungi in this windrow without any compost is a clear indication that the compost used in the other windrows was active with fungi. The presence of bacteria indicate that this contaminated soil from an old fire fighter training area had soil bacteria already in it. Although no compost was added when the windrows were formed, there would have been an effect from aerating the contaminated soil and stimulating of indigenous microorganisms with the oxygen and fertilizer. Since the temperature profile shows that there was not a significant elevation in the temperature up to Day 13, there obviously was not a significant effect of the aeration due to the initial soil handling. The Day 21 concentration of oxygen of approximately five percent correlated with a corresponding decline in temperature. This lack of oxygen apparently had a negative effect

Figure 4.25 - Mean MOG, Oxygen, Temperature & Microbial Activity vs Time
Windrow 3B - Fertilizer, No turning



on the bacterial activity since the windrow temperature started to decline after Day 13. After Day 27 when MOG concentrations had reached approximately 600 mg/kg, oxygen concentrations started to rise and the temperature started to decline. The natural rise in oxygen and decline in bulk windrow temperature to the end of the project (Day 56) indicated that microbial activity was still present, but at ever reducing rates. Bulk oxygen concentrations dipped below the minimum desired five percent on only one occasion near Day 21, but did not remain there for long. The indigenous microorganisms showed a very close response to the oxygen concentrations.

d. VOC CONCENTRATIONS.

Like most other windrows, and as portrayed in **Figure 4.26 - Mean VOCs, MOG, Oxygen, Temperature versus Time**, VOC concentrations rapidly fell from 1947 mg/kg by approximately three-fold in the first week to 627 mg/kg and slowly declined to 167 mg/kg by the end of the project. As with the other windrows, it can be assumed that this was as a result of initial concentrations of light petroleum hydrocarbons in the soil which were quickly mineralized. Since light and medium hydrocarbons were not tested at the end of the project, no quantitative data are available to prove that the intermediate breakdown products of the heavy hydrocarbons were consumed. However, the reducing concentrations of VOCs in the soil-gas suggested that such was the case. There is no apparent relationship between VOCs and oxygen, temperature or bioactivity.

e. NUTRIENT CONCENTRATIONS.

As portrayed in **Figure 4.27 - Nutrients, Microbial Activity, Oxygen, Temperature versus Time**, the nutrient concentration of ammonia was comparable to the other two windrows with fertilizer. Like the other fertilized windrows, the ammonia concentrations of 470 $\mu\text{g/g}$ dropped significantly by approximately 400 mg/kg by Day 27. Since there was a relatively neutral pH (starting at 8 and dropping to 7.5 by Day 6), it is unlikely that significant amounts of ammonium were transferred to ammonia and lost as a gas. Therefore the ammonia was consumed in response to the microbial requirements for organic nitrogen. As a result of the ample supply of ammonia, the slow release nitrate in the fertilizer was not consumed in significant amounts and it accumulated over the four week period. It appears that for the low level of microbial activity, the initial concentration of ammonia was sufficient for the microorganisms without consuming the nitrates too. The

Figure 4.26 - Mean VOCs, MOG, Oxygen, Temperature vs Time
 Windrow 3B - Fertilizer, No turning

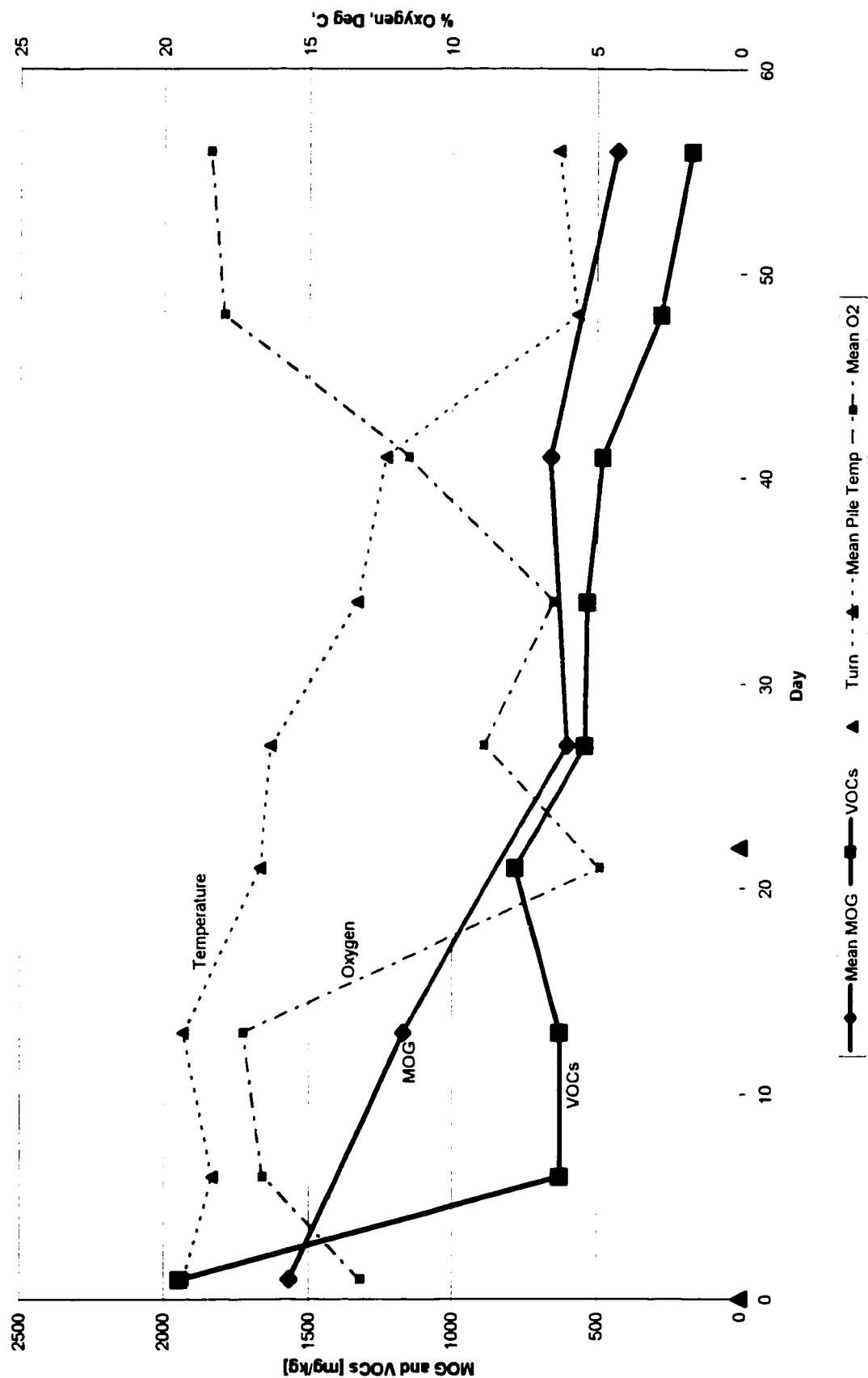
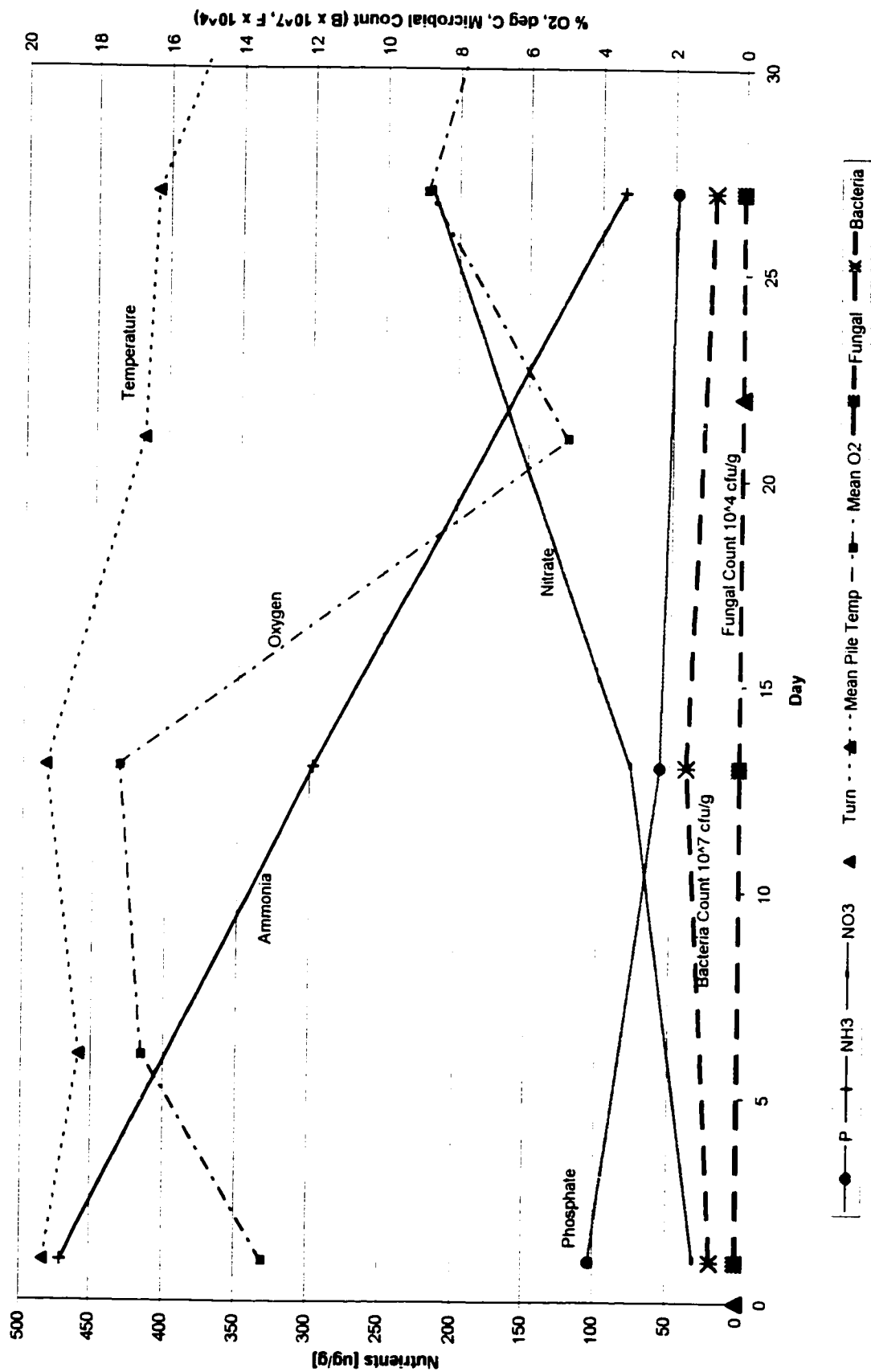


Figure 4.27 - Nutrients, Microbial Activity, Oxygen, Temperature vs Time
Windrow 3B - Fertilizer, No turning



low initial available phosphate concentrations declined by half to 48 mg/kg, indicating that there was microbial utilization of the soluble phosphate but that there were sufficient concentrations that the soluble phosphate was not depleted. Fertilizer provided an ample supply of the major nutrients for stimulating the microbial populations.

f. STATISTICAL SIGNIFICANCE AND REGRESSION ANALYSIS.

Figure 4.28 - MOG True Mean Range (90% Confidence). plots Student's 90 percent confidence intervals for the MOG true mean and a regression analysis of the mean MOG. The exponential trend line is a good fit since all points are well within the confidence intervals. Whereas the mean MOG crossed the 1000 mg/kg criteria concentration on Day 17, the regression line, which started at a low initial concentration, indicates that the reduction to criteria concentration nominally occurred on Day 8.

4.7 COLLECTIVE RESULTS

4.7.1 *MOG*

Figure 4.29 - Comparative Mean MOG relates the mean MOG data for all windrows to time. The 'Y' axis is logarithmic since biological degradation usually follows exponential decay trends. The starting MOG concentrations are relatively the same for windrows 2A and 2B, and for 3A and 3B, however, windrows 2A and 2B started with an initial MOG concentration of approximately 6000 mg/kg, whereas windrows 3A and 3B were at only one quarter of this concentration - approximately 1500 mg/kg. Windrow 1's starting concentration was 2400 mg/kg. This disparity in starting concentrations creates a situation whereby the data on one windrow are hard to compare to another. Nonetheless, it can be seen that all windrows reached their asymptotic points by Day 27. Although the data points are connected by straight lines, it is unlikely that these portray the actual concentrations at other than the sampling dates. Therefore it is possible that some windrows could have reached their asymptotic point before Day 28. Moreover, the problem of attempting to take representative samples of such a heterogeneous soil/compost mixture is well illustrated by windrow 2A's data on Day 41. It is unlikely that the MOG concentration increased from Day 28. This underscores the inherent inaccuracy of sampling soil and illustrates that such data must be considered with an allowance for error.

Figure 4.28 - MOG True Mean (90% Confidence)
 Windrow 3B - Fertilizer, No turning

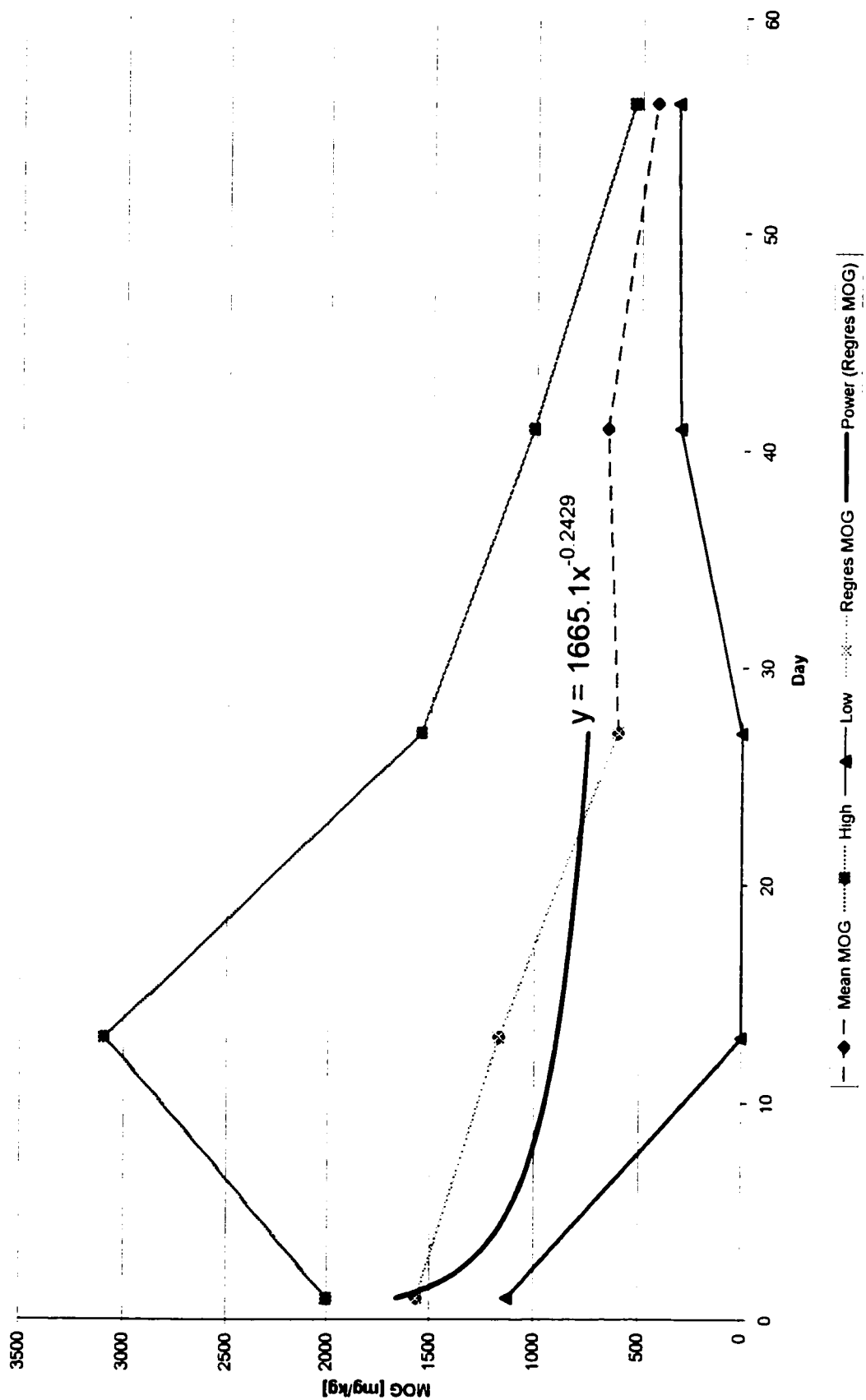
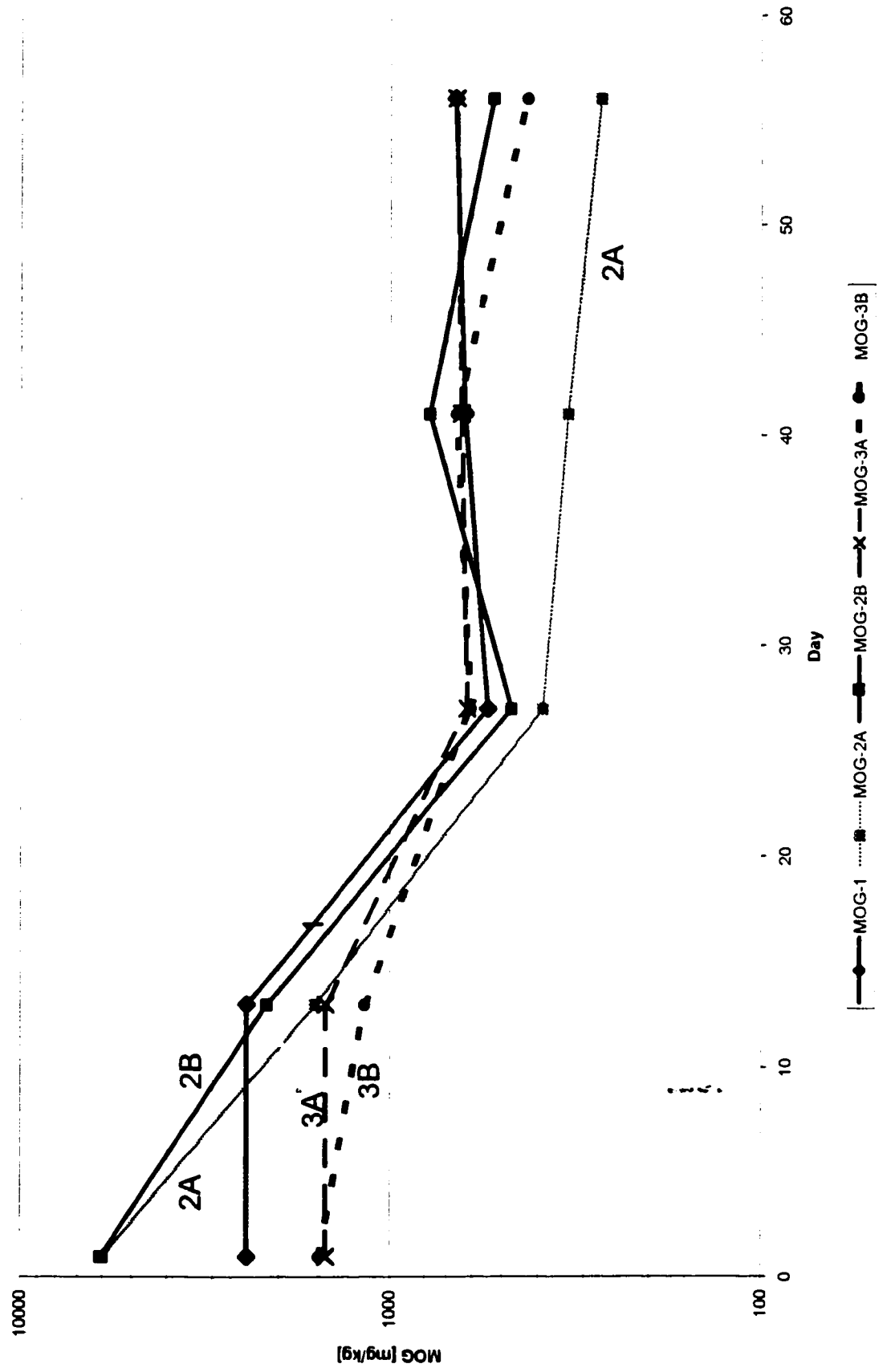


Figure 4.29 - Comparative Mean MOG



4.7.2 PAH

Although the PAH concentrations were not high, they were detectable in the initial samples from each windrow. Only total PAHs were reported for the initial concentrations. **Table 4.8 - Final PAHs** indicates the types and mean concentrations of PAHs found in the windrows on Day 56. The second row indicates the carbon number and the third row indicates the MOEE (1997) remediation criteria for each compound.

Table 4.8 - Mean Final PAHs ($\mu\text{g/g}$)

R O W	Total Start	Final Concentrations										
		NPH	ACE	APH	FLU	PHE	ANT	FLN	PYR	CHR	BEF	BEP
		C10	C12	C12	C13	C14	C14	C16	C16	C18	C20	C20
		4.6	130	15	340	40	28	40	1.3	17	18	1.9
1	24	nd	1	nd	nd	nd	nd	1	1	nd	nd	nd
2A	21	nd	1	nd	nd	nd	nd	nd	nd	nd	nd	nd
2B	16	nd	1	nd	nd	nd	nd	1	1	nd	nd	nd
3A	44	nd	1	nd	nd	nd	nd	nd	nd	nd	nd	nd
3B	16	nd	1	nd	nd	nd	nd	nd	nd	nd	nd	nd

NPH Naphthalene

ACE Acenaphthylene

APH Acenaphthene

FLU Fluorene

PHE Phenanthrene

ANT Anthracene

FLN Floroanthene

PYR Pyrene

CHR Chrysene

BEF Benzo(k)fluoranthene

BEP Benxo(a)pyrene

Although no breakout of PAHs was available for the starting concentrations, the final concentrations showed low levels of ACE, FLN, PYR, and trace levels of PHE and CHR. All windrows, including 3B with just indigenous bacteria, degraded the PAHs. The higher the carbon number or larger the molecule, the harder it is to bioremediate. Without the breakout of initial concentrations, it is impossible to determine whether the different treatments had any distinctive abilities to remediate one group of PAHs over others. However, assuming that the final compounds represent the presence of the initial compounds, it is apparent that this soil which came from the same excavation had a mix of lower and higher molecular weight PAHs and it is speculated that had the ratios remained relatively the same from starting to final concentrations, all treatments were effective in degrading the range of PAHs.

4.7.3 **TEMPERATURE.**

Temperatures showed a direct response to the level of bioactivity. The relative windrow temperatures are shown in **Figure 4.2 - Comparative Air/Windrow Temperatures**. As seen in this figure, windrow 2A had the highest temperatures, indicating that it had the highest rate of bioactivity. For the last 3 weeks of the project, it can be seen that windrow 1 was sustaining an elevated temperature when the other windrows were subsiding. This indicated that bioactivity was continuing in windrow 1 and was one of the reasons the windrows were resampled the following spring, on Day 255. The MOG analysis from Day 255 indicated that the mean MOG had dropped by one third to approximately 400 mg/kg which indicates that the windrow was still significantly bioactive after Day 56.

Peak temperatures and rates of temperature rise are summarized in **Table 4.9 - Peak Temperatures and Rates of Rise**. Windrow 2A had the highest temperature and rate of rise. On Day 6 when Windrow 2B reached its peak of 27°C, Windrow 2A was at 29°C, to carry on to a peak of 36°C on Day 13, so in effect Windrow 2A also reached its peak the soonest of all windrows. Although Windrow 3A showed the second highest peak temperature, by **Table 4.9**, one can see that its overall rate of remediation was relatively poor. The maximum rate of temperature increase 6°C in Windrow 3A occurred when its mean temperature was 28°C for the week whereas Windrow 2B's 5°C rise occurred at a mean temperature of 24°C. Therefore although both windrows were similar, except for turning, it is inconclusive whether the better rate of temperature rise of Windrow 3A was as a result of the natural white rot fungus mycelium not being disturbed or the higher mean temperature having a beneficial effect on the bioactivity.

Table 4.9 - Peak Temperatures and Rates of Rise [°C]

	1	2A	2B	3A	3B
	WRF, limited turning	Compost, manure, turning	Compost, fertilizer, turning	Compost, fertilizer, no turning	Fertilizer, no turning
Peak temperature	29	36	27	31	19
Day of peak	Day 27	Day 13	Day 6	Day 13	Day 1
Maximum rate of rise (°C/week)	4	6	5	6	1

Temperature was very easy and inexpensive to measure. It provided a good indication of bioactivity inside the windrow. It is concluded that soil bioremediation projects should monitor the temperature on a regular basis and that if windrow temperatures approach 20°C, then the remediation is either nearing completion or corrective action should be taken to spur on the bioremediation process.

4.7.4 **OXYGEN.**

Figure 4.30 - Comparative Oxygen, shows the measured oxygen concentrations in the windrows relative to each other. Data from Day 56 has been deleted since it was in error. Ticks on each curve indicate when that windrow was turned. As discussed earlier, such turning would have caused the soil-gas to be restored to near atmospheric concentrations. Apart from the obvious increase in oxygen concentrations when the windrows were turned, the concentration of oxygen showed a direct response to the degree of bioactivity and increased infiltration due to high winds. It appears that for all windrows, oxygen concentrations below five percent tended to have a negative effect on the bioactivity, particularly with respect to fungal activity.

Turning was an effective means of thoroughly raising the oxygen concentrations in the soil-gas. In comparison to other traditional methods of forcing air through the windrows by pipes, adding oxidants, or putting the soil in a rotating drum, this seemed to be a simple method and one which could be rapidly implemented when soil-gas oxygen concentrations were detected to be low. Unlike the forced ventilation methods, turning had secondary benefits of providing a means to easily mix amendments into the soil and of reducing pockets of high contamination so that remediation criteria concentrations would be reached sooner. As seen by the varying initial mean MOG concentrations for the different windrows and the wide range of each of the samples, the soil was not as well mixed as desired during the construction of the windrows. Therefore, as the windrows were further turned during the project, there was a better mixing which likely contributed to bringing the range of each sample closer to its mean. Turning seemed to have a disruptive effect on the mycelium of the commercial white rot fungus, however, it did not appear to have as much, if any, effect on the mycelium of the natural fungi on the compost.

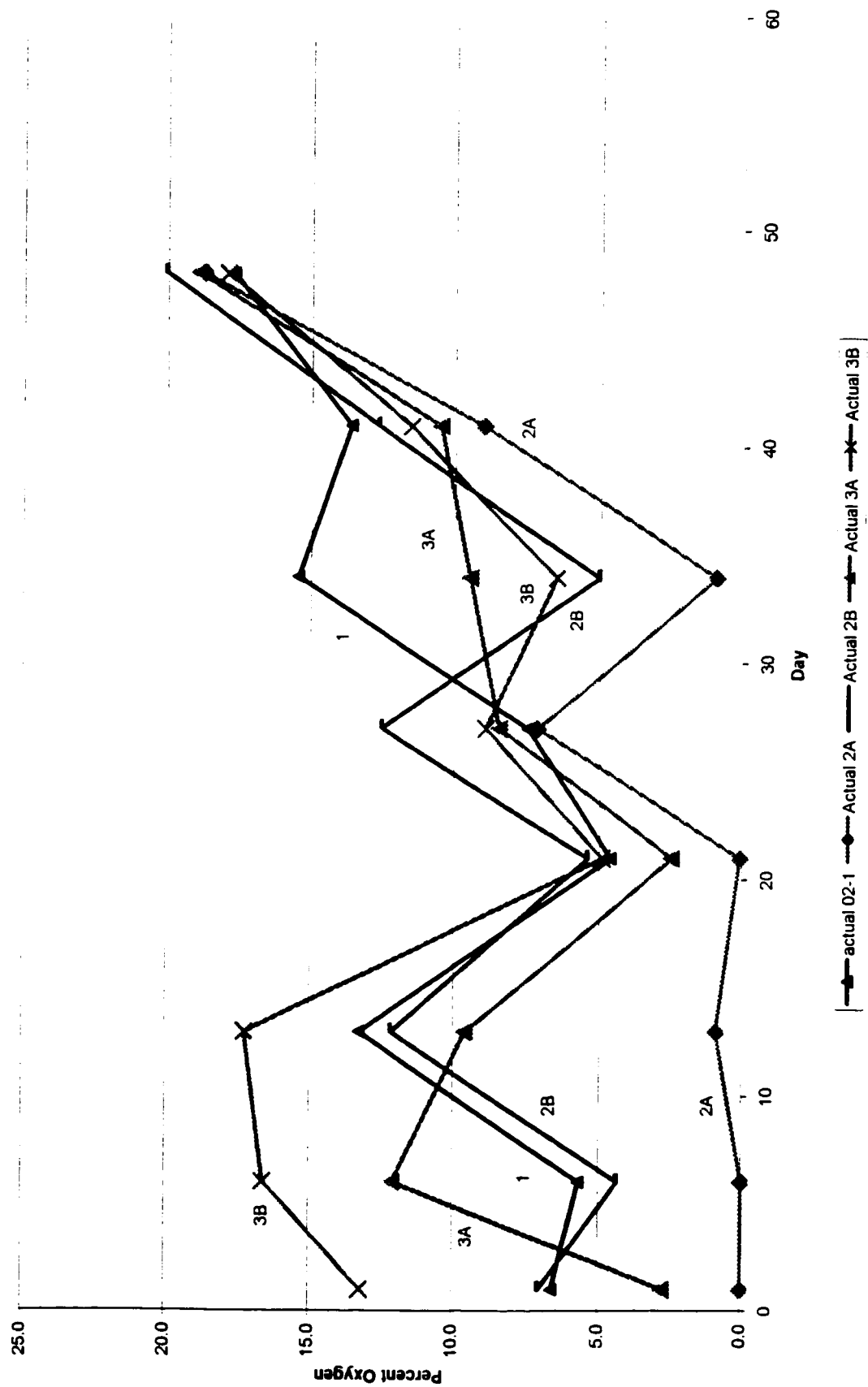
Oxygen concentrations are easy to measure and are reliable when carried out with a dedicated soil probe and portable oxygen monitor. The soil-gas oxygen concentrations can not be measured reliably if the probe hole is created first, then monitor probe inserted into the hole.

4.7.5 **WINDROW SURFACE EFFECTS**

An analysis of temperature, VOCs and oxygen at the exterior end-of-windrow to in-windrow conditions indicates that there was no consistently significant trend in the data (i.e. greater than 10 percent difference if ranges do not overlap) for the end-of-windrow versus the other monitoring locations. Refer **Table 4.10 - Comparison of End to Inner Windrow Conditions** for a representative analysis of Windrow 2A.

The MOG composite soil sample analyses from the ends of the half windrows were compared to the composite sample data for the inner windrow locations for each sampling event. No consistently

Figure 4.30 - Comparative Oxygen
(Measured Weekly)



significant trend (i.e. greater than 10 percent difference if ranges do not overlap) was detected. Refer to **Table 4.11 - Comparison of End to Inner Windrow MOG Concentrations** for a representative analysis of Windrow 2A.

Table 4.10 - Comparison of End to Inner Windrow Conditions (Windrow 2A)

Day	Temperature (°C)			VOCs (mg/kg)			Oxygen (mg/kg)		
	End	Inner	Apparent trend	End	Inner	Apparent trend	End	Inner	Apparent trend
1	21	26. 27	Higher	3500	3660. 4160	Nil	0	0.0	Nil
6	30	32. 32	Nil	4700	4160. 4240	Lower	0	0.0	Nil
13	35	36. 36	Nil	4540	3200. 14000	Nil	0.6	0.3. 1.8	Nil
21	30	30. 33	Nil	3200	2000. 3200	Nil	0.0	0.1. 0.1	Nil
27	34	24. 28	Lower	7000	1400. 1740	Lower	0.3	9.8. 11.3	Higher
34	25	21. 21	Lower	>10000	7780. >10000	Nil	0.4	1.0. 1.3	Nil
41	19	17. 18	Nil	2100	1100. 1600	Lower	8.0	7.5. 11.5	Nil
48	10	8.8	Lower	500	300. 420	Lower	17.3	19.4. 19.6	Higher

Table 4.11 - Comparison of End to Inner Windrow MOG Concentrations (mg/kg) (Windrow 2A)

Day	End of Windrow			Inner Windrow				Apparent trend
1	1531	5330		3207	8423	8597	8940	Nil
13	108	754	1150	628	5350			Nil
27	169			485	506			Higher
41	520			238	238			Lower
56	158			119	534			Nil

4.7.6 FERTILIZERS

The main nutrient concentrations in this project are summarized in **Table 4.12 - Start & Finish Mean Nutrient Concentrations**. As evidenced by Windrow 2A temperatures peaking at 35°C it was demonstrated that poultry manure is better than synthetic fertilizer for initiating very high bioactivity rates under the conditions of the project. The compost-manure-turned windrow showed that overall it was the most biologically active windrow in the project.

Table 4.12 - Start & Finish Mean Nutrient Concentrations [mg/kg]

Nutrient	Day	1	2A	2B	3A	3B
			manure	fertilizer	fertilizer	fertilizer
Ammonia	0	36	1007	514	376	470
	27	13	561	96	54	84
Nitrate	0	6	19	12	16	31
	27	4	48	185	39	218
Phosphate	0	52	329	149	63	103
	27	25	515	139	36	48

This information is further illustrated by **Figure 4.31 - Comparative Ammonia**, **Figure 4.32 - Comparative Nitrate**, and **Figure 4.33 - Comparative Orthophosphate**. As can be seen in each, the poultry manure provided the highest levels of ammonia, nitrate and orthophosphate. Windrow 1 was at the other extreme with very low levels of nutrients.

Synthetic fertilizers are a common method of providing the major nutrients to bioremediation processes. This project demonstrated that these fertilizers are readily used by the microbial populations. All windrows showed a decline in ammonia concentrations. Ammonia, due to its higher energy level, was used by the microbial population in preference to the nitrates. As discussed earlier, without total nitrogen analysis being carried out, it is impossible to verify what, if any, nutrients were lost to volatilization and leaching. Turning did not appear to cause any appreciable loss of ammonia since ammonia decreases were similar in windrows being turned to those not being turned. In addition, ammonium (at pH of 7 or less) does not leach easily since with its positive charge it is attracted to the negatively charged clay and organic matter (O'Leary et al., 1997). Although ammonium and especially nitrates are very soluble, the precipitation event around Days 17 and 18 did not appear to leach the nitrates. This could be due to the higher water-holding potential of the fine-textured soil in this project and the fact that the soil moisture was less than its apparent field capacity so that there was no net leaching of water from the windrows. Nitrates showed a tendency to accumulate. It is speculated that this is due to the effect of slow growing nitrifying bacteria converting organic nitrogen into nitrates without a corresponding consumption of the nitrates by other organisms.

An application rate of 1.5 kg/m³ of synthetic fertilizer and 5 kg/m³ of poultry manure were adequate based on a ratio of 1 part nitrogen to 10 parts hydrocarbon contamination.

The phosphorous levels appeared to be adequate and support the rule of thumb that only one part phosphorous is required for 100 parts of petroleum hydrocarbon contamination. Since the laboratory

Figure 4.32 - Comparative Nitrate

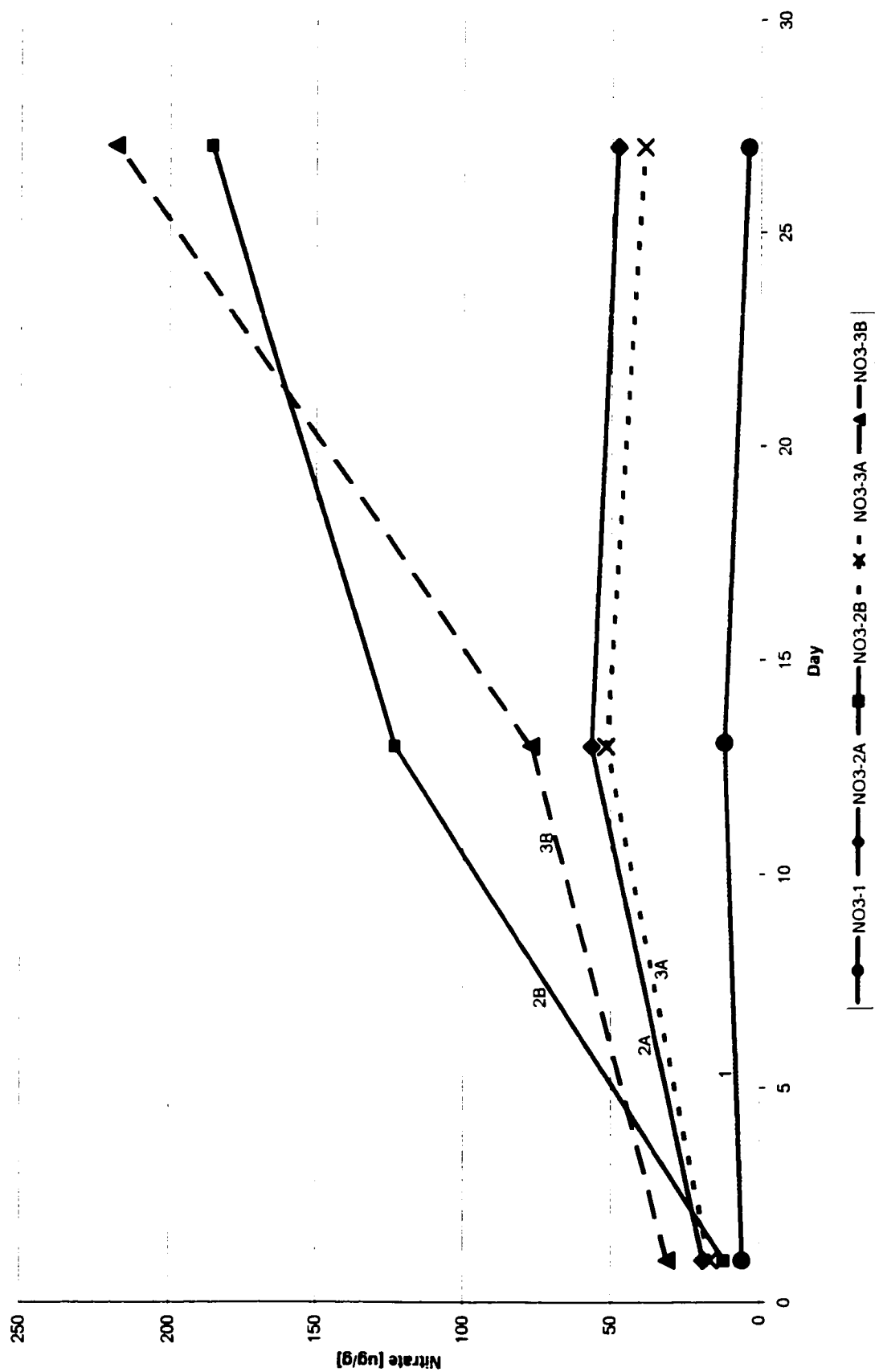
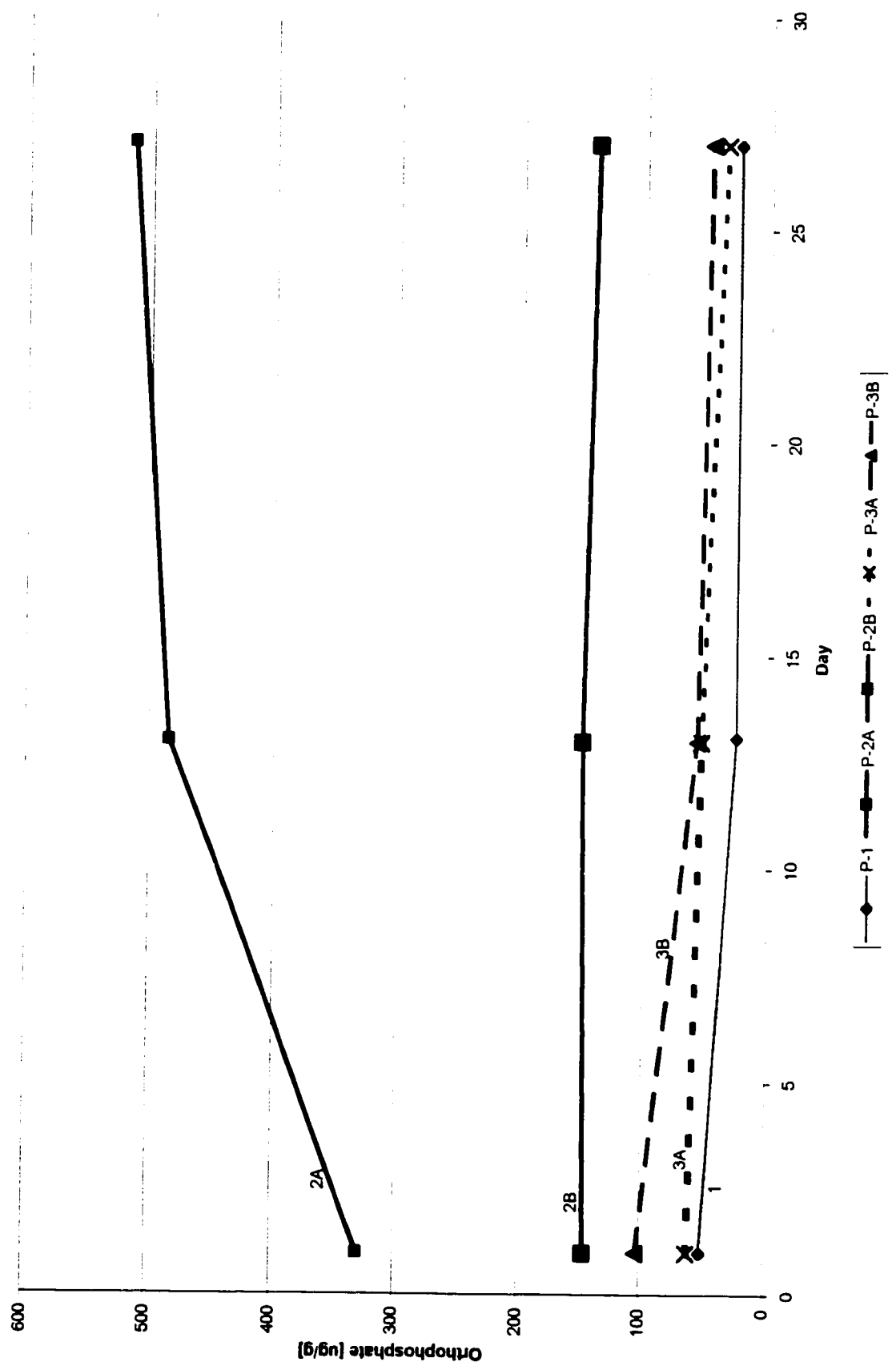


Figure 4.33 - Comparative Orthophosphate



analysis was for available phosphorous, only the soluble forms of the total phosphorous were determined and therefore, progress sampling showed varying concentrations of phosphorous.

4.7.7 **MOISTURE.**

Measurement of moisture was difficult due to the varying porosity of the windrow matrices. There was poor correlation among the field tensiometer, field dielectric tests and the laboratory gravimetric methods. Refer to **Appendix D - Field Monitoring Equipment** for a discussion of difficulties with calibrating the equipments and correlating the results to each other.

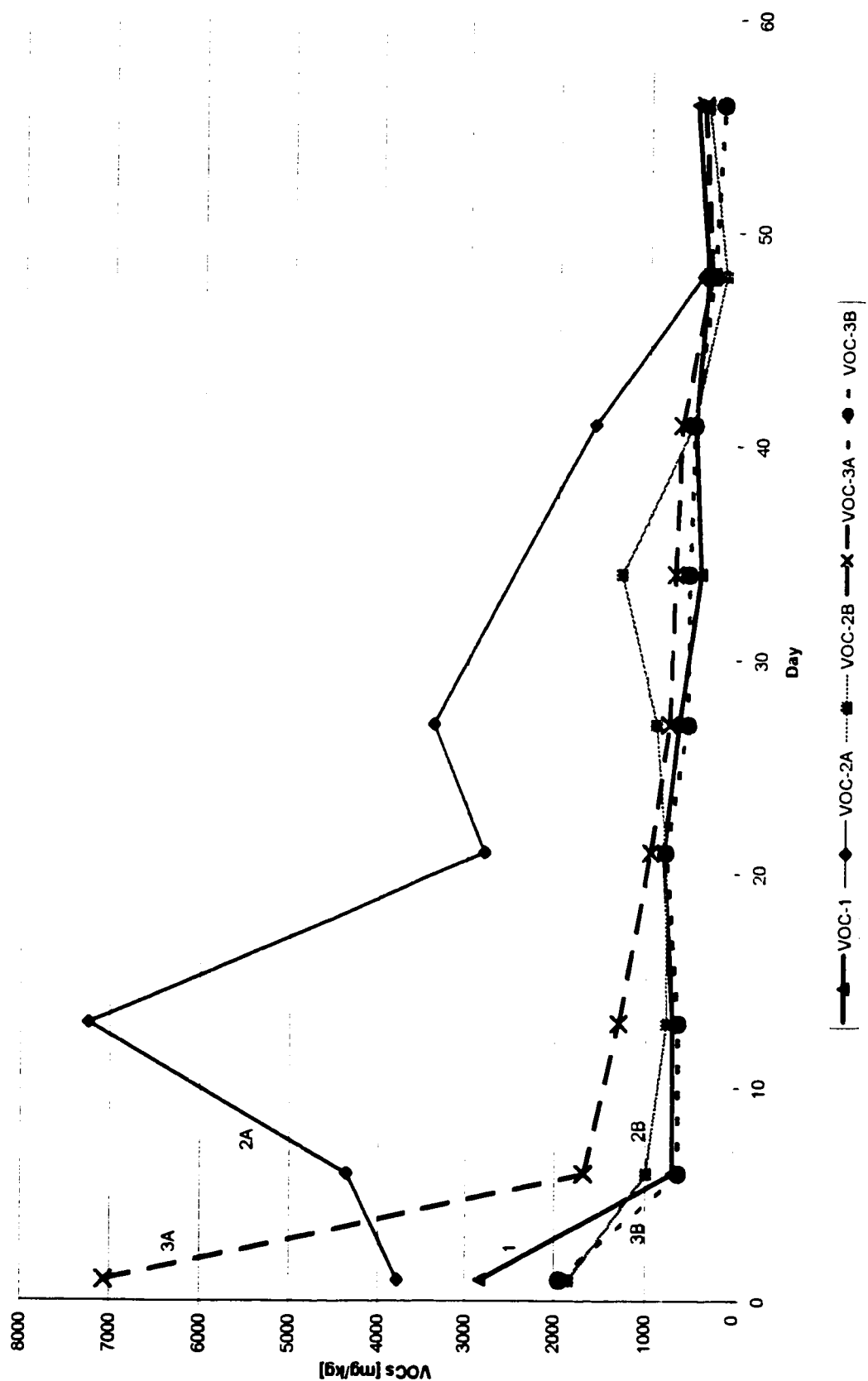
It does not appear that the windrows dried out to a point where microbial activity was negatively affected. At times the windrows seemed to be getting too wet which would have reduced their soil-gas content. However, they were not so wet as to appear to be leaching. At these times, the windrows were covered with a plastic tarp to let them dry somewhat.

4.7.8 **VOCs.**

Figure 4.34 - Comparative VOCs indicate the mean VOC data for all windrows. The field soil-gas measurements of VOCs is an indicator of the general presence of light to medium hydrocarbons. It should be remembered that these devices each have their own range of organic vapours which they can detect, that these devices respond in varying sensitivities to the different petroleum hydrocarbons, and the vapour concentrations do not represent the actual concentrations of liquid compounds in the soil but only their respective vapour pressures. Although the readouts are in ppm (mg/kg), the different readings by the three instruments for the same headspace indicate that the readouts are only relative to each instrument. The field soil-gas screening methods used in this project are widely employed by the environmental community, however it is recognized that data produced by these methods are erratic. There is little detection of the low vapour pressure heavy petroleum hydrocarbons by these devices. Except for windrow 2A, the VOCs for all windrows declined rapidly in the first week. It is assumed that the initial reading for windrow 3A is in error since the VOC reading on this windrow the day before was 3800 mg/kg. As discussed earlier, the rise in VOCs in windrow 2A would likely have been due to the elevated temperatures of the windrow liberating some SVOCs from the soil and poultry manure.

After the required sample jars were filled for laboratory analysis, each composite sample bag was closed with its remaining soil, labelled, and set aside for a head space analysis to be carried out at the end of the sample preparation work. This holding period allowed the vapour concentration in the bag's air space to reach equilibrium with the compounds in the soil and all samples to reach a uniform temperature. The head space was tested by inserting the detector's probe into the neck of the bag while making sure no

Figure 4.34 - Comparative VOCs



air escaped or entered. (Refer to **Appendix C - Project Quality Control and Standard Operating Procedures**)

The headspace readings of the bagged soil composites of the three hand held monitoring devices (PID, FID and GT408), were compared to each other (Refer to **Figure 4.35 - VOC Measurement (PID:GT408)**, and **Figure 4.36 - VOC Measurement (FID:GT408)**). The three detectors did not respond with the same relative sensitivity to the headspace vapours. The inconsistency of their readings to each other indicates the approximation of this monitoring concept and reinforces the environmental community's recommendation that these devices should only be used for very rough indications of the presence of organic vapours and not be used for quantitative indications of the actual degree of contamination. Their detection of organic vapours in this project is a rough indication of the potential presence of the lighter intermediate breakdown products of MOG and methane - a product of anaerobic decomposition. As expected, data produced during this project by headspace analysis were useful indicators of the presence of contamination but were very much a function of sample handling, operator skill and care, environmental conditions and soil conditions.

Figure 4.37 - GT408 VOC Measurement: Headspace to Direct Soil-Gas Measurements. shows that there was not a good correlation between these two detection methods.

4.7.9 **COMPOST**

Compost proved to be an inexpensive yet effective bulking agent and inoculant of natural fungi. Coarse wood chips should be aged for a year and allowed to be rained on or kept damp to foster the growth of natural fungi.

4.7.10 **MICROBIAL POPULATIONS**

4.7.10.1 **WHITE ROT FUNGI**

Figure 4.38 - Comparative Fungal Counts indicates the effect of inoculating windrow 1 with the commercially grown white rot fungus by its population growing almost four-fold. Moreover, since this windrow was the same in composition and turning as windrow 2B on Day 13, there should have been a similar fungal count for both. However, Windrow 1 was double that of windrow 2B. This may indicate that the fertilizer in windrow 2B was having a negative impact on the growth of the fungi as the US EPA predicted, or the rate of compost application was significantly different. It appears that the poultry manure had a negative effect on the indigenous fungus on the compost since the fungal counts dropped off immediately. Windrow 3B obviously had negligible fungi. The white rot fungus, *pleurotus ostreatus*,

Figure 4.36 - Volatile Organic Compound Measurement
 FID Headspace versus GT 408 Direct Soil-Gas

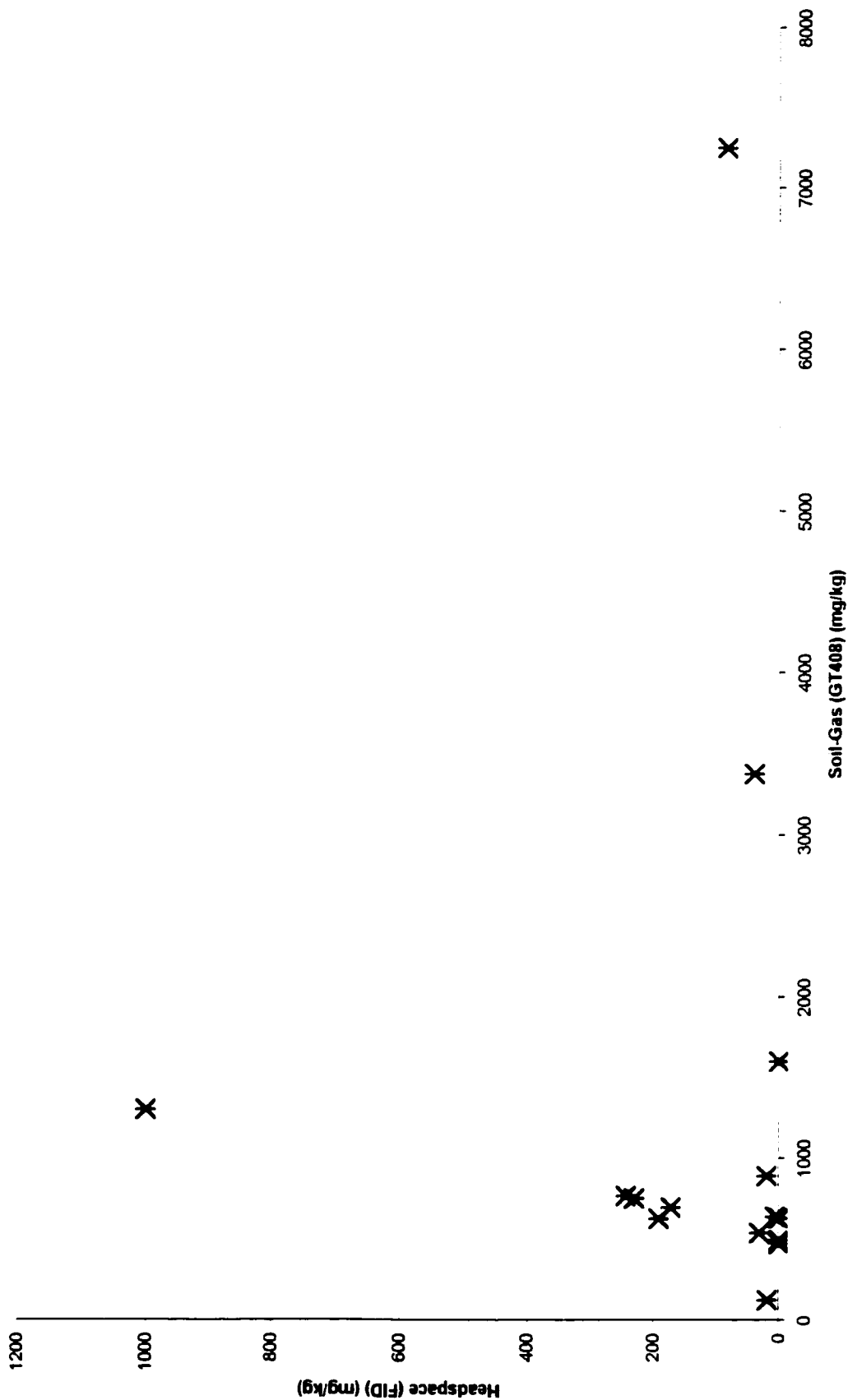


Figure 4.37 - Volatile Organic Compound Measurement
GT408 Headspace vs Direct Soil-Gas Measurement

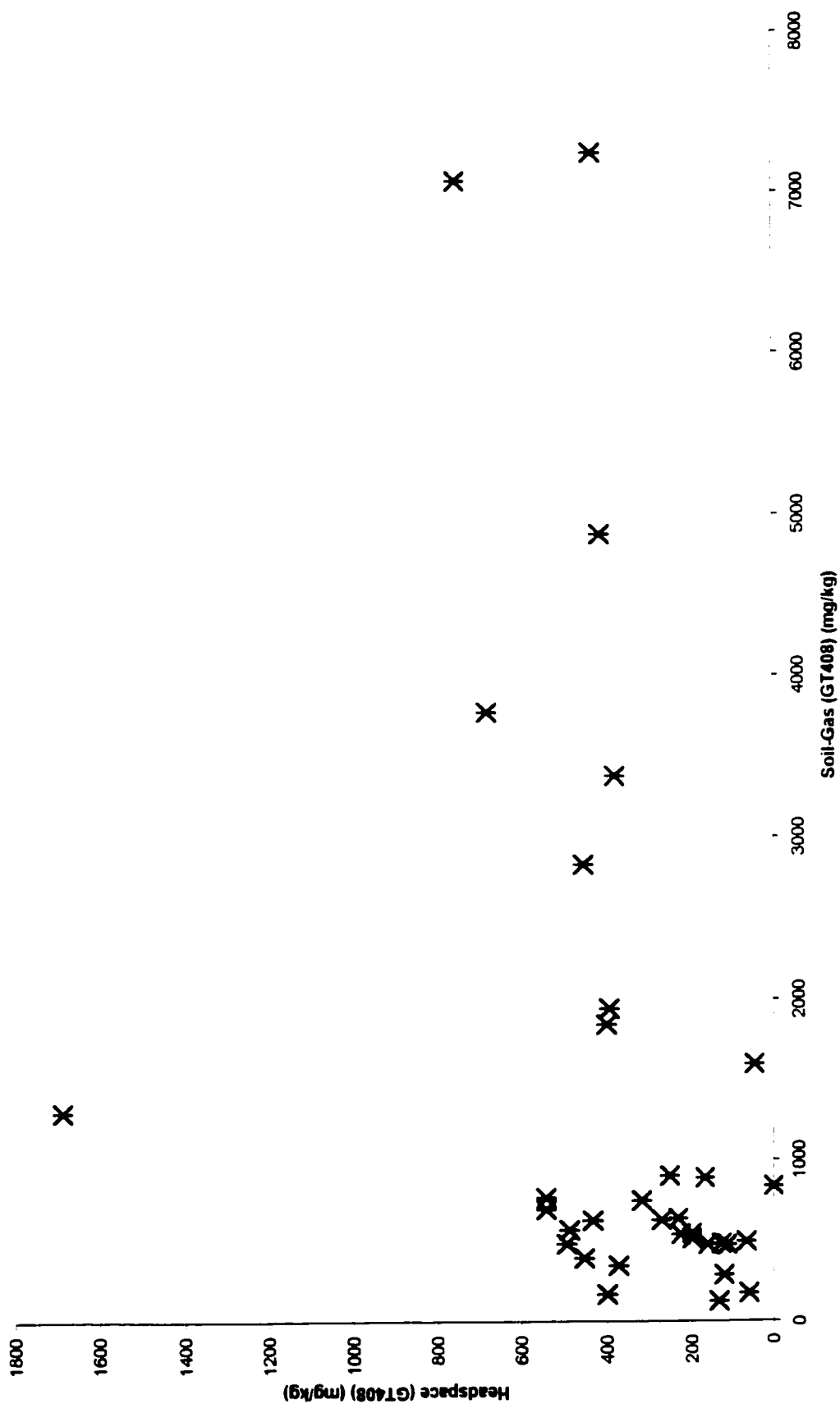
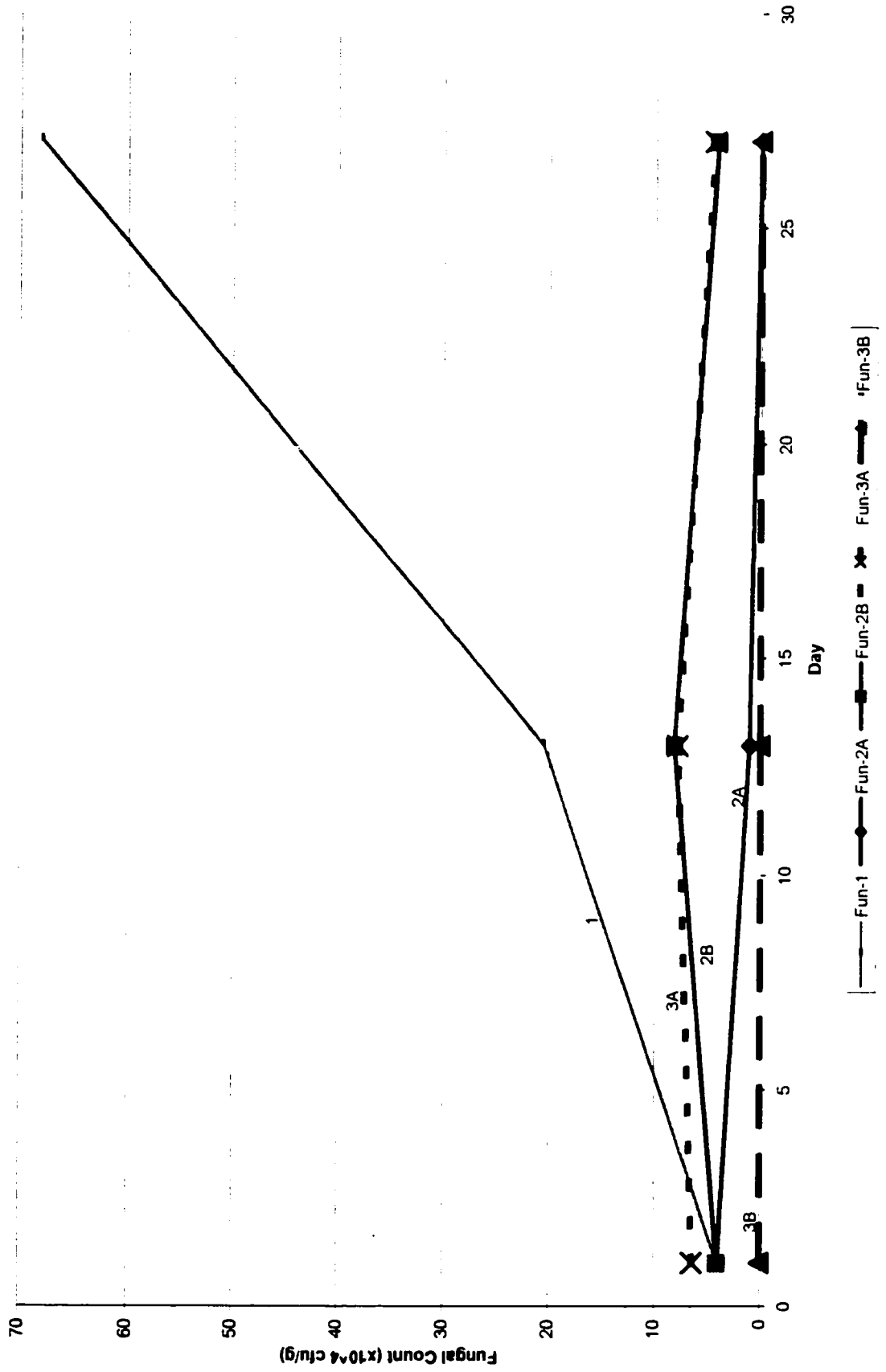


Figure 4.38 - Comparative Fungal Counts



proved to be very fragile during its breeding on the hay-sawdust substrate. As a result, any consideration for its use in a soil remediation project must include not only its purchase cost (\$47 per equivalent tonne of contaminated soil - Refer to **Appendix B - Calculations**) but also the cost of close supervision during its breeding. It appears that this variety of white rot fungus is very susceptible to disruption of enzyme production rate by having its mycelium disturbed by soil turning. The main purpose of turning was to reintroduce oxygen into the windrow. Therefore, the soil should be turned as infrequently as possible, by only turning when soil-gas oxygen levels decline to less than five percent. Another means of achieving this restoration of oxygen concentrations without turning would be to construct the windrow with ventilation piping.

4.7.10.2 **BACTERIA**

Figure 4.39 - Comparative Bacteria Counts, illustrates the relative bacterial populations of the windrows. The poultry manure in windrow 2A had a considerable bacterial population which initially dropped by half and then started to grow again as they became adapted to the soil/compost/contaminant environment. The bacteria in windrows 1, 2A and 2B started from similar levels and grew at similar rates for the first 13 days. Although windrow 3B had ample oxygen and fertilizer, the lack of compost prevented its bacteria from growing at the same rates as the others. This may be due to the reduced pore space which was causing the biologically active areas in the microcosm to go anoxic quickly. Since windrow 3B did remediate the MOG and PAHs over the course of 56 days, it must be assumed that the indigenous soil bacteria in this windrow (and the others) were adapted to the contaminants in the fire fighter training area from years of exposure and were able to solubilize and absorb the contaminants when then came into contact with the bacteria.

4.7.11 ***TREATMENT COSTS***

Based on calculations in **Appendix B, Table 4.13 - Estimated Commercial-Scale Project Costs**, estimates the nominal remediation cost per tonne of contaminated soil for the different processes in this project, applied on a commercial scale. Since the amount and cost of labour in a project is highly variable, the cost of labour as projected for commercial projects is not included. Moreover, excavation and treatment area preparation costs can vary considerably due to the depth of contamination, type of soil/aggregate to be excavated, distance the soil must be transported from the excavation to the treatment area, and type of area selected for the treatment site. Therefore these work costs are not estimated for commercial-scale projects. The options are arranged in order of preference, based on remediation rate, final remediation objective and cost.

Figure 4.39 - Comparative Bacteria Counts

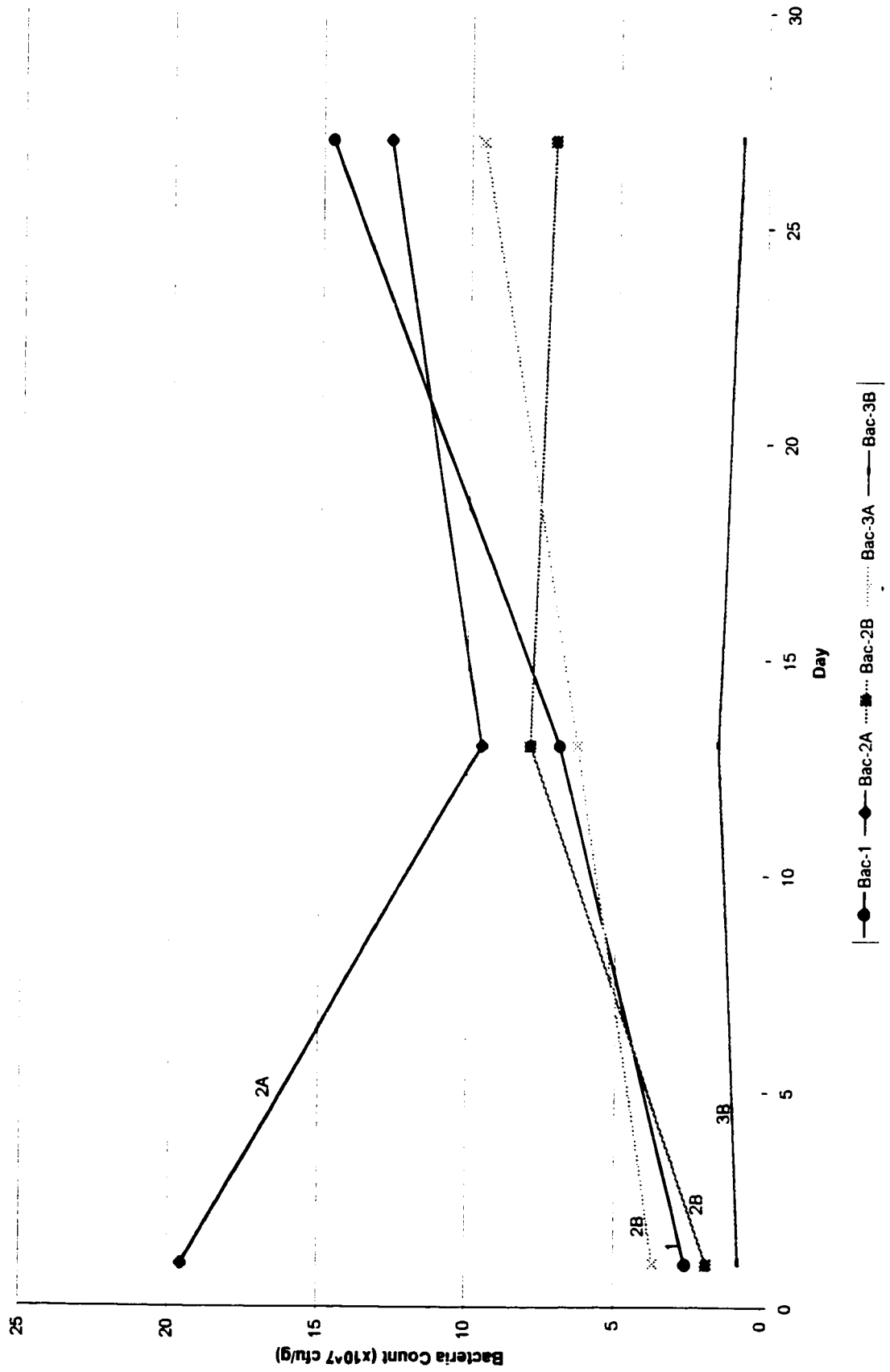


Table 4.13 - Estimated Commercial-Scale Project Costs (Per tonne of Contaminated Soil)

Treatment Option	Estimated Rate of Remediation (mg/kg/d)	Final MOG (mg/kg)	Quantity (tonnes)	Cost per Tonne	Remarks
Compost, manure, turning	100	300	660	\$18 to 29	Low cost and end point, but cost sensitive to cost of manure.
Compost, fertilizer, turning	100	500	660	\$19	Low cost but end point not as low as compost/manure.
Static Biopile (fertilizer)	20	300	850	\$10	Low cost and labour involvement, but slow rate of remediation.
WRF, compost, limited turning	30	400	660	\$63	High cost relative to other methods.
Compost, fertilizer, no turning	15	700	660	\$13	Low cost and labour involvement, but slow rate of remediation.

Note: The cost estimates exclude labour (engineering, project management, turning and monitoring), excavation, and site preparation.

CHAPTER 5

CONCLUSIONS

This project set out to demonstrate a technique to remediate soil contaminated with heavy petroleum hydrocarbons which would be robust, and have a broad applicability and low cost. This project demonstrated that this fire fighter training area soil had an indigenous bacterial population and despite no prior characterization of the soil or microbial populations, productive remediation rates were achieved by aerating the soil. The blending of compost and fertilizer with the contaminated soil introduced additional bacteria and fungi into the soil and increased the pore space. When aerobic conditions were maintained, the bioremediation rates increased by up to five fold.

The following conclusions are made from this project:

- a. Soil contaminated with heavy petroleum hydrocarbons can be effectively and inexpensively remediated by placing the soil in windrows, adding amendments consisting of 20 percent (v/v) compost, and five percent (v/v) poultry manure, or synthetic N:P:K fertilizer in the ratio of 100 parts petroleum contamination, 10 parts nitrogen and 1 part phosphorous, and aerating by turning on an as-required basis. The compost should be coarse wood chips that have been left fallow for a year under suitable conditions to permit the development of a good fungal population. The ratio of compost of 20 percent (v/v) compost to soil appeared to be satisfactory for a moderately heavy soil.
- b. Commercially produced white rot fungus is too expensive for simple remediation projects involving heavy petroleum hydrocarbons.
- c. The elevated face compost turner is a simple and effective means of mixing amendments into the soil and aerating it. Turning of windrows with a compost turner, for those processes using white rot fungus inoculum, is disruptive to the mycelium of the fungi and should be done only when soil-gas oxygen concentrations are approaching five percent.
- d. Soil-gas oxygen concentrations under five percent are indicative of in-pile conditions becoming anaerobic and the soil should be aerated. Fungal populations are more sensitive to bulk oxygen levels approaching five percent than bacterial populations.
- e. Bioremediation conditions in windrows can be easily monitored with simple temperature, oxygen and moisture measurements, with the frequency being relative to the apparent rate of bioactivity. Temperatures of 35°C can be expected for windrows undergoing peak bioactivity with oxygen concentrations declining from 20 percent to almost zero in a week, or less.

- f. When bulk temperatures are approaching ambient temperatures, soil-gas oxygen is above 15 percent and moisture concentrations appear adequate, it is an indication that the asymptotic levels of remediation have been reached and confirmatory sampling should be undertaken for site closure.
- g. Measurement of carbon dioxide, VOCs and microbial populations is unnecessary.
- h. Monitoring of VOC vapours is quantitatively unreliable. Monitoring of VOCs is only useful as a coarse indication of their presence and an indication where potentially high concentrations of organics should be sampled for laboratory analysis.

CHAPTER 6

RECOMMENDATIONS FOR FUTURE RESEARCH

The application of soil composting for remediation of hazardous, large molecular weight organic compounds holds a promise of being able to remediate contaminated soils at low cost in comparison to conventional remediation technologies. Based on the results of this project, the following are recommended for future study:

- a. Further projects should be carried out to determine the effect of the compost, poultry manure/fertilizer and turning process in other soils and weather conditions, especially in heavy clay soils and in cold weather.
- b. Although this project used petroleum hydrocarbons due to their rather nonhazardous nature, the successes of this project indicate that natural fungi grown on wood chips or commercially produced white rot fungus in combination with indigenous soil bacteria can be used successfully with other large molecular weight contaminants such as PAHs, PCBs and pesticides. Similar field scale projects should be carried out with other heavy molecular weight organic contaminants to prove and gain regulatory approval for the technology.
- c. Aeration of the windrows by turning appeared to have a negative effect on the bioactivity of the fungus. A field scale project should be carried out to determine the effect and cost of this method of aeration in comparison to simple forced air systems based on perforated pipes being laid in the windrows and hooked up to a blower.
- d. Further research is required into the phenomena of organic substances binding to soil organic matter (SOM) to determine the binding forces, the amount of substance which becomes bound to the SOM and the degree to which these substances remain bound to the SOM especially during bioremediation.

APPENDIX A

RAW DATA

1. Temperature, Precipitation, Winds and Field Observations.
2. Individual Windrow and Background Data.

Temperature, Precipitation, Winds and Field Observations.

Date	Day	Observed Windrow Temperatures in Field										Meteorological Data			
		1		2A		2B		3A		3B		Air	ea	Mean	Mean
		deg C	Obsn	deg C	Obsn	deg C	Obsn	deg C	Obsn	deg C	Obsn			Temp	Rain
18-Sep	-3			18		18		18		18		20		12.9	10
17-Sep	-2													14.2	6
18-Sep	-1													9.7	0.1
19-Sep	0													9.7	5
20-Sep	1	22		25		22		21		19		17 cloudy		12.2	7 ppt 3.7mm
21-Sep	2													15.7	7 ppt 0.2mm
22-Sep	3													12.2	7 ppt 2.4mm
23-Sep	4													7.7	5
24-Sep	5													7.3	4
25-Sep	6	26		31		27		25		18		18		10.1	3 ppt 2.4mm
26-Sep	7													12.9	8 ppt 2.4mm
27-Sep	8													14.3	11
28-Sep	9													8.3	5
29-Sep	10													10.3	6
30-Sep	11													13.8	5
1-Oct	12													14.1	5
2-Oct	13	27		36		27		31		19		20 Sunny		14.2	5
3-Oct	14													9.7	5 ppt 5.2mm
4-Oct	15													11.4	4 ppt 0.5mm
5-Oct	16													11.2	10 ppt 36.2mm
6-Oct	17													12.8	-3 6 ppt 44.6mm
7-Oct	18													15.2	-3 6 ppt 5.8mm
8-Oct	19													11.9	13
9-Oct	20													9	5
10-Oct	21	26		31		23		22		17		15 Sun w		10.7	6
11-Oct	22													13.6	4
12-Oct	23													16.8	10
13-Oct	24													15.8	10
14-Oct	25													12.6	7 ppt 12.1mm
15-Oct	26													8.3	22 ppt 3.4mm
16-Oct	27	29		29		24		25 uc		16 uc		14 Windy		7	4 ppt 0.8mm
17-Oct	28													5.9	18
18-Oct	29													13	8
19-Oct	30													9.3	23
20-Oct	31													13.5	-3 2 ppt 15.0mm
21-Oct	32													8.9	-3 15 ppt 50.8mm
22-Oct	33													7.5	-3 4 ppt 7.0mm
23-Oct	34	23 vw		22 vw		19 vw		20 vw		13 vw		16 Soils v		11.1	10
24-Oct	35													12.4	11 ppt 4.8mm
25-Oct	36													5.3	12
26-Oct	37													6.1	23
27-Oct	38													10.5	14 ppt 11.6mm
28-Oct	39													10	15 ppt 2.4mm
29-Oct	40													2.8	5
30-Oct	41	26		18		16		17		12		3 Overc		3.4	5 ppt 1.0mm
31-Oct	42													3.2	6 ppt 0.2mm
1-Nov	43													3.3	-3 12 ppt 4.0mm
2-Nov	44													10.7	-3 15 ppt 20.0mm
3-Nov	45													7.8	24
4-Nov	46													0.9	10 snow 0.6mm
5-Nov	47													1.9	17
6-Nov	48	19		9		8		10		6		8 Cold.		2.6	13
7-Nov	49													4	7 ppt 8.4mm
8-Nov	50													-0.5	17 snow 0.2mm
9-Nov	51													-3.8	12
10-Nov	52													4.3	6 ppt 1.6mm, snow 2mm
11-Nov	53													6.9	-3 3 ppt 47.6mm
12-Nov	54													-1.3	26
13-Nov	55													-1	4 snow 3.1mm
14-Nov	56	23 vw		8		8		8		6		5		1.1	6 snow 6.4mm

ppt = precipitation

vw = very wet

uc = windrow uncovered

All temperatures in degrees Celcius and mean daily values where applicable

Windrow 1: WRF and compost, limited turning

Windrow Monitoring														ENVIRONMENT CANADA																					
Date	Day	Loc	Pile	WRF	Turn	Add	Temp		Moisture		VOCs		O2		CO2		PID		- Headspace bags -		DND	EC	pH	Moist	P&T		CE	HC	MOG						
							mean	C	mean	Temp	mean	Temp	mean	%	mean	%	mean	%	mean	ppm					mean	ppm				mean	ppm	mean	ppm	mean	ppm
Criteria																																			
18-Sep	0				5		22	22	26	27	3080	2833	6.0	6.6	>5	>5	14	6.8			11	44	7.5	18	18	65	40	53	30	2469	781	2438			
20-Sep	1	1c					21		30			2980	5.4	>5	>5	4				30	42	7.4	16	16	84		91	1	2715	1233					
20-Sep	1c																																		
20-Sep	1e						24	N/A				2180	6.3	>5	>5	12				34	52	7.4	18	4			1	1805	1555						
20-Sep	1e																																		
20-Sep	1e						23	N/A				1960	5.6	>5	>5	7				28	46	7.4	20	62			3	5677	2001						
20-Sep	1w						21	20				3440	11.6	>5	>5	2				73	40	7.1	18	10			48	2764	2715						
20-Sep	1w						21	30				3360	4.6	>5	>5	2				6	38	7.4	20	15			47	1555	3109						
20-Sep	1w																																		
25-Sep	6	1c					25	26	24	28	660	700	8.2	5.7	-0.5	F																			
25-Sep	1c						27	27	28			680	3.9	-0.5	F																				
25-Sep	1e						25	27				800	5.3	-0.5	F																				
25-Sep	1e						27	22				640	7.9	-0.5	F																				
25-Sep	1w						25	26				740	4.3	-0.5	F																				
25-Sep	1w						27	28				680	4.5	-0.5	F																				
02-Oct	13	1c			5		27	27	24	28	5	6	660	693	15.0	13.3	>5	>5	4	3.8	65	172	500	540											
02-Oct	1c						28	28				700	13.3	>5	>5	10				1029	14	7.6	16	17											
02-Oct	1e						25	25				680	12.0	>5	>5	2				1001	1	7.1	16												
02-Oct	1e						28	28				700	12.9	>5	>5	2				1037	19	7.4	16												
02-Oct	1w						30	30				720	12.0	>5	>5	5				1034	18	7.3	22												
02-Oct	1w						25	27				700	14.5	>5	>5	0				1010	5	7.5	17												
03-Oct	14						26	26	17	13	8	7	600	607	8.7	4.6	>5	>5			1020	10	7.5	15											
10-Oct	21	1c					25	18				640	5.9	-0.5	F																				
10-Oct	1c						25	6				1540	0.5	-0.5	F																				
10-Oct	1e						26	10				660	5.6	-0.5	F																				
10-Oct	1w						26	10				680	4.5	-0.5	F																				
10-Oct	1w						25	19				720	2.5	-0.5	F																				
11-Oct	22				5	2																													
16-Oct	27	1c					28	29				680	640	4.6	7.5	-0.5	>5	0	0.3	5	6	220	233												
16-Oct	1w						28					32	660	6.3	-0.5	F				2015	7	7.5	28	25											
16-Oct	1w						32					580	11.5	>5	>5	1				2011	5	7.5	28												
16-Oct	1w																			2010	4	7.5	14												
16-Oct	1w																			2020	11	7.5	28												
17-Oct	28				5															2030	16	7.5	29												
23-Oct	34	1c					23	23				400	400	15.0	15.4	>5	>5																		
23-Oct	1e						26					500	12.6	>5	>5																				
23-Oct	1w						19					300	18.7	4.7																					
30-Oct	41	1c					22	26				380	473	16.9	13.6	4.8	5	0	0																
30-Oct	1c						22					340	18.1	4.8						3025	24	7.5	35	29											
30-Oct	1e						31					31	760	4.0	>5	>5																			
30-Oct	1e						30					680	4.0	>5	>5																				
30-Oct	1w						27					300	19.9	2.3	0					3006	5	7.4	27												
30-Oct	1w						25					380	18.9	4.5	0					3019	18	7.5	24												
31-Oct	42				5																														
06-Nov	48	1sc					21	19	20	19	8	7	460	337	14.1	17.7	>5	3.7																	
06-Nov	1sc						19					300	18.9	3.2																					
06-Nov	1sw						17					300	18.9	3.2																					
06-Nov	1sw						15					400	16.5	>5	>5																				
06-Nov	1sw						18					200	19.8	1.5																					
06-Nov	1sw						25					360	18.1	4.1																					
07-Nov	49																																		
14-Nov	58	1sc					21	23	6	5	10	8	660	479	5.9	7.1	>5	>5																	
14-Nov	1sc						23					58	10.9	>5	>5					4034	19	7.5	24	33											
14-Nov	1sw						24					720	4.5	>5	>5					4019	11	7.3	34												
14-Nov	1sw																			4030	17	7.5	32												
14-Nov	1sw																			4025	14	7.5	40												
14-Nov	1sw																	</																	

[illegible]

INTEGRATED EXPLORATIONS

SD	MOG confid interval (2*05)		PAH		PCB		DND IE		pH		Moist		F count		F enzyme		B Count		PO4		NO3		NH3		Date	Day	Remarks		
	deg F	t-stat	(-)	(+)	mg/kg	Seq	mean	mg/kg	mean	mg/kg	mean	mg/kg	10*4	mean	laccase	mean	10*7	mean	µg/g	mean	µg/g	mean	µg/g	Criteria					
2523	5	2015	3020	8080	8	5	21	0.13	0.10	19	25		6.4	4.1	0	4.7	40	19.6	15	329	10.40	18.7	1080	1007	19-Sep	0	Lab moisture error - ignored		
						7	7	0.16		27	19		3.1		0		5.7		373		34.01		821	20-Sep	1	only screened, PID rdgs 21/8/95			
						43	8	0.045																20-Sep					
						11	11	0.13		50	24		2.7	14	14	13	599			11.81		1120	20-Sep						
						53	43	0.08																20-Sep					
						5	53	0.07																20-Sep	6				
																								25-Sep					
																								25-Sep					
2130	4	2132	-433	3628						1004	18		0.44	1.1			10	9.5	443	483	87.81	56.5	738	863	28-Sep	7			
										1041	21		2.7				16	312			61.21		762		02-Oct	13			
										1013	23		0.02			2.6	695			20.40		1390		02-Oct				VOC-28%LEL	
																								02-Oct					
																								02-Oct					
																								02-Oct					
																								03-Oct	14				
																								10-Oct	21				
																								10-Oct					
188	2	202	68	705						2007	10			0.033	0.1		13	12.7	481	515	44.01	47.9	578	561	11-Oct	22			
										2016	3		6.2	22	169										18-Oct	27			IE triplicate
										2053	9		6.3	23	96	0.052									18-Oct				IE triplicate
										2034	2		5.9	24	170										18-Oct				IE triplicate
										2023	6				0.065		10	464			51.41		557		18-Oct				
																								17-Oct	28				
																								23-Oct	34				
																								23-Oct					
183	2	282	58	608																					30-Oct	41			FID not operating correctly
																								30-Oct					
																								30-Oct					
																								31-Oct	42				
																								08-Nov	48				
																								08-Nov					
																								08-Nov					
228	2	282	-116	657	1	1	1																		07-Nov	49			
																									14-Nov	56			
																									14-Nov				too wet for soil gas
89	3	2353	185	395																					14-Nov				
																									31-May	255			Interior very wet, poor readings
																									31-May				Follow-up sampling

Windrow 2b: Compost and fertilizer, turning weekly.

Windrow MONITORING													ENVIRONMENT CANADA												
Date	Day	Loc	Pile	WRF	Turn	Add	Moisture			VOCs			CO2			- Headspace bags -			GT408						
							Temp	mean	Tens	mean	diel	mean	ppm	mean	%	mean	%	mean		%	PID	mean	FID	mean	ppm
Criteria																									
20-Sep	1	2bc					23	22	N/A	1460	1847	8.5	7.0	>5	>5	3	18			340	400				
20-Sep	2	2bc					20		N/A			8.4	>5			6				380					
20-Sep	3	2bc					22		N/A			4.2	>5			45				480					
20-Sep	4	2bc					26	27	28	28	880	993	5.9	4.4	-0.5 F	>5									
20-Sep	5	2bc					25	28	28	820	5.4	-0.5 F													
20-Sep	6	2bc					29	28	28	1280	1.8	-0.5 F													
20-Sep	7	2bc																							
02-Oct	13	2bc					23	27		10	10	620	767	15.9	12.2	>5	>5	15	28	100	243	540			
02-Oct	14	2bc					24			9		640	14.5	>5			15	180	540						
02-Oct	15	2bc					35			10		1040	6.1	>5			47	450	540						
03-Oct	16	2bc																							
10-Oct	21	2bc					23	23	10	20	7	9	680	780	7.5	5.4	-0.5 F	>5							
10-Oct	22	2bc					18	19.5		9		660	8.5	>5											
10-Oct	23	2bc					27	30	>10			1000	0.2	-0.5 F											
11-Oct	24	2bc																							
18-Oct	27	2bc					23	24	>10	10	480	893	16.0	12.5	>5	>5	4	6	12	19	100	167			
18-Oct	28	2bc					22			9		580	12.0	>5			2	8		180					
18-Oct	29	2bc					27		>10		1620	9.6	>5			11	38			220					
17-Oct	30	2bc																							
23-Oct	34	2bc					17	19	>10	10	740	1284	1.1	5.0	-0.5 F	>5									
23-Oct	35	2bc					20		10		840	4.3	-0.5 F												
23-Oct	36	2bc					21		>10		2302	9.7	>5												
30-Oct	41	2bc					18		10		240	493	12.7	>5		0				67					
30-Oct	42	2bc					16		10		240	19.0	1.2	>5		0				20					
30-Oct	43	2bc					14		10		500	11.8	>5			0				0					
30-Oct	44	2bc					17		9		740	7.2	>5			0				180					
31-Oct	45	2bc																							
06-Nov	48	2bc					9	8	8	15	>10	10	100	133	20	20.1	0.8	1.0							
06-Nov	49	2bc					6	20	10		100	20.1	1.1												
06-Nov	50	2bc					8	18	>10		200	20.1	1.0												
07-Nov	51	2bc																							
14-Nov	56	2bc					7	8	0	1	>10	10	360	347	14.1	14.3	3.9	3.5							
14-Nov	57	2bc					8	4	>10		500	10	>5							360	373				
14-Nov	58	2bc					8	0	>10		180	18.7	1.5							400					
31-May	255	2bc					17	17			640	907	7.6	7.5	>5	>5				220	253				
31-May	256	2bc					18				600	12.1	>5							300					
31-May	257	2bc					15				1480	2.8	>5							240					

W - 2B

INTEGRATED EXPLORATIONS																									
SD	MOG confid interval (2* 05)		PAH		PCB		DND IE Ser # Lab #	pH	Moist %wM	MOG mg/kg	F count		F enzyme		B Count		PO4		NO3		NH3		Date	Day	
	deg F	t-stat	(-)	(+)	mg/kg	seq					mean	mg/kg	mean	130	10*4	mean	laccase	mean	10*7	mean	ug/g	mean			ug/g
3069	5	2 015	3548	8598	8	8	16	0.06	0.07	17	32		5.4	4.0	0	0.7	0.3	18	97	146	6.81	11.7	407	514	Criteria
					19	12	0.07			40	27		4.2		2.1		0.53						20-Sep	1	
					22	15	0.1																20-Sep		
					15	17	0.1																20-Sep		
					12	19	0.05			80	17		2.5		0	4.7	308	18.01			5.73	20-Sep			
					17	22	0.06															20-Sep			
2871	2	2 92	2680	7000																			25-Sep	6	
																						25-Sep			
																						25-Sep			
																						28-Sep	7		
										1002	18		6.1	8.2		8.4	7.9	107	149	87.20	123.7	399	466		
										1035	12		1.2			7	72		173.81		287			02-Oct	13
										1036	15		17.2			8.3	268		110.01		713			02-Oct	
																						03-Oct	14		
																						10-Oct	21		
																						10-Oct			
320	2	2 92	68	1009																			11-Oct	22	
										2028	15		2.2	4.1		6.6	7.2	124	139	248.01	185.4	180	98		
										2056	12		8.7			5	59		108.20		12			18-Oct	27
										2029	14		1.5			9.9	235		204.01		96			18-Oct	
																						17-Oct	28		
																						23-Oct	34		
681	4	2 132	149	1409																			23-Oct		
																						30-Oct	41		
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																						30-Oct			
																						31-Oct	42		
																						06-Nov	48		
																						06-Nov			
																						06-Nov			
269	2	2 92	75	881	6	6	3																07-Nov	49	
																							14-Nov	56	
																							14-Nov		
172	2	2 92	237	818																			31-May	255	
																							31-May		
																							31-May		

Windrow 3a: Compost and fertilizer, no turning.

Date	Day	Loc	Pile	WRF	Windrow Monitoring										- Headspace bags										ENVIRONMENT CANADA																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																				
					Temp		Moisture		VOC's		O2		CO2		PID		FID		GT408		DND	EC	pH	Moist	P&T HC		CE HC	MOG																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																	
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W - 3B

INTEGRATED EXPLORATIONS																										
SD	MOG confid Interval (2* 05)				PAH		PCB		DND IE Ser# Lab #	pH	Moist %w/w	MOG mp/kg	F count		F enzyme		B Count		PO4		NO3		NH3		Date	Day
	deg F	t-stat	t		mp/kg	Seq	mean	mp/kg					mean	mp/kg	mean	laccase	mean	10*4	mean	10*7	mean	µg/g	mean	µg/g		
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18-Sep 0																										
20-Sep 1																										
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Backgrounds, temperatures and controls.

Windrow Monitoring										ENVIRONMENT CANADA																				
Date		Day	Loc	Pile	WRF	Temp		Moisture		VOCs		O2		CO2		PID		FID		GT408		DND	EC	pH	Moist	P&T HC	CE HC	MOG		
C	mean	Tens	mean	dielec	mean	Grav	mean	ppm	mean	%	mean	%	mean	ppm	mean	ppm	mean	ppm	mean	ppm	mean	Ser #	Lab#	%	mean	mg/kg	mean	mg/kg	seq	mean
Criteria																														
16-Sep	19		air																											
20-Sep	19	1	air					60		20.9		0.5																		
25-Sep	18	6	air					0		20.9		0.1																		
02-Oct	19		13	air				0		20.7		0.0																		
10-Oct	19		21	air				0		20.5		0.0																		
16-Oct	12		27	air				0		20.7		0.0																		
23-Oct	18		34	air				40		20.8		0.1																		
30-Oct	3		41	air				0		20.8		0.0																		
06-Nov	8		48	air				0		20.6		0.0																		
14-Nov	2		56	air				0		20.9		0.0																		
31-May	19		255	air				0		20.9		0																		
20-Sep			1	bigrid																										
02-Oct			13	bigrid																										
16-Oct			27	bigrid																										
30-Oct			41	bigrid																										
14-Nov			56	bigrid																										
31-May			255	bigrid																										
20-Sep			1	lub spk																										
02-Oct			13	lub spk																										
16-Oct			27	lub spk																										
30-Oct			41	lub spk																										
14-Nov			56	lub spk																										
20-Sep			1	mix spk																										
02-Oct			13	mix spk																										
16-Oct			27	mix spk																										
30-Oct			41	mix spk																										
14-Nov			56	mix spk																										
30-Oct			41	ballast																										
30-Oct				ballast																										
31-May			255	ballast																										
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Legend

1. Units of measure are mg/kg unless indicated for each column
2. Combustibles readings in %LEL converted @ 20%LEL to 10,000 mg/kg
3. Non-detect indicated by zero for graphing purposes
4. CO2 readings greater than 5 (off scale) shown as 5 for graphing purposes
5. Dielectric moisture readings (Kmart) greater than 10 (off scale) counted as 10 for graphing purposes
6. Although data is rounded off in the spreadsheet, plotting of data used actual values. Therefore, two values of '27' may show to be a different concentrations
7. If confidence level less than zero, minimum contamination level of zero assumed

APPENDIX B

SAMPLE CALCULATIONS

FUEL CONSUMPTION OF LTDD

The LTDD unit heats the soil to 330°C to volatilize organic contaminants (and water). The off-gas is then combusted in a catalytic oxidizer at 650°C or in a secondary combustion chamber at 950°C. Processing 20 tonnes per hour the fuel consumption is approximately 500 litres of diesel fuel. If the contamination of the 20 tonnes is assumed to be 15 litres of diesel fuel, 33 litres are used to remediate 1 litre of contamination.

VOLUME AND WEIGHT OF WINDROWS. (Sample calculation regarding Windrow 1)

Measured Field Density:

- a. soil = 1400 kg/m³.
- b. compost = 557 kg/m³.
- c. white rot fungus substrate = 366 kg/m³.
- d. poultry manure = 156 kg/m³

Volume of Windrow 1 measured on Day 68:

$$29\text{m} \times 4\text{m} \times 1.6\text{m} \times 0.5 = 95\text{m}^3.$$

Net weight of Windrow 1 at nominally 20% compost, 20% white rot fungus substrate:

$$\begin{aligned} & (0.2 \times 557\text{kg/m}^3 \times 95\text{m}^3) + (0.2 \times 366\text{kg/m}^3 \times 95\text{m}^3) + (0.6 \times 1400\text{kg/m}^3 \times 95\text{m}^3) \\ &= 10.6 \text{ t} + 6.9 \text{ t} + 79.8 \text{ t} \\ &= 97 \text{ tonnes.} \end{aligned}$$

Net density of windrow 1 with amendments:

$$97 \text{ tonnes} / 95 \text{ m}^3 = 1025 \text{ kg/m}^3, \text{ say, } 1000 \text{ kg/m}^3$$

COST OF WHITE ROT FUNGUS

Inputs:

Cost of white rot fungus:	\$3,400 for 1800 kg spawn, or \$1.90 per kg spawn.
Cost of hay and sawdust substrate:	\$1,000 for 20 tonnes

Amount of soil treated: 80 tonnes (windrow 1)

(Note, transportation cost of white rot fungus to site, mixing costs and supervision not included)

Unit cost of white rot fungus:

\$4,400 / 80 tonnes = \$55 per tonne of contaminated soil.

SYNTHETIC NITROGEN FERTILIZER APPLICATION RATE

At a nominal application of 10 parts of nitrogen fertilizer to 100 parts of contamination, for a biopile of 100 tonnes contaminated to 2,500 mg/kg with a density of 1,400 kg/m³ :

Hydrocarbon Contamination:

$(2500 \text{ kg of HC} / 1 \times 10^6 \text{ kg soil}) \times 100,000 \text{ kg soil} = 250 \text{ kg of hydrocarbons}$

At 1 part nitrogen per 10 parts hydrocarbons:

$(250 \text{ kg hydrocarbons} / 10 \text{ parts hydrocarbon/nitrogen}) = 25 \text{ kg nitrogen}$

For a 48-8-2 fertilizer, there are 48 kg of nitrogen per 100kg of fertilizer. For 250 kg of nitrogen the amount of 48-8-2 fertilizer required will be:

$25 \text{ kg} \times (100 \text{ kg fertilizer} / 48 \text{ kg nitrogen}) = 52 \text{ kg fertilizer.}$

The application rate per m³ of soil:

$52 \text{ kg fertilizer} / (100,000 \text{ kg soil} / 1,400 \text{ kg/m}^3)$

$= 0.7 \text{ kg/m}^3$ (for soil contaminated at a nominal 2500 mg/kg).

Assume safety factor of 2 for poor mixing, variations in actual to estimated bulk contaminant concentration and local contaminant concentrations above the nominal value. Therefore apply 1.5 kg/m³.

POULTRY MANURE APPLICATION RATE

At a nominal application of 10 parts of nitrogen fertilizer to 100 parts of contamination, and assuming 6 percent nitrogen, for a biopile of 100 tonnes contaminated to 2,500 mg/kg with a density of 1,400 kg/m³ :

As per the above calculation, hydrocarbon contamination = 250 kg / 100 tonnes

Requiring 25 kg nitrogen.

For the 6 % nitrogen poultry manure:

$$25 \text{ kg} / (0.06 \text{ N/ kg manure}) = 417 \text{ kg manure for 100 tonnes contaminated soil}$$

For the 80 tonnes of contaminated soil in windrow 1 (95 m³), require:

$$417 \text{ kg} \times 80/100 = 333 \text{ kg, or } 3.5 \text{ kg/m}^3.$$

Since the greater volume of manure will be easier to distribute throughout the windrow than the synthetic fertilizer, assume a safety factor of 1.5 for poor mixing, variations in actual to estimated contaminant concentration and local contaminant concentrations above the nominal value. Therefore apply 5 kg/m³.

TREATMENT COSTS OF COMMERCIAL-SCALE PROJECTS

Since a focus of the project was to evaluate potentially low-cost remediation technologies, the designs, materials and services used in the project were aimed at providing the minimum cost approach.

For example:

- since most bioremediation studies have found that the soil matrix in their projects was suitable for bioremediation, biotreatability testing is not required.
- since there was sufficient evidence in other projects to demonstrate that large numbers of indigenous bacteria normally exist in the soil and since it could be assumed that the bacteria present in a site are well adapted to the climate, soil conditions, and contamination, identification of species and populations of bacteria is not necessary.
- since this project was providing only macro-nutrients at the standard ratio of 100 parts hydrocarbon contamination to 10 parts nitrogen and 1 part phosphorous, bench scale testing of nutrients on the indigenous bacteria was deemed unnecessary.

Summary of Project Costs:

preliminary characterization	\$ 1,400
geomembrane, laminated two ply 12 mil polyethylene film with reinforcing scrim.	
• mixing pad 35m x 45m:	\$ 3,996
• treatment pad 53m x 55m:	\$ 6,668
ballast sand:	\$ 2,500
poultry manure, 500kg:	\$ 500
fertilizer, 48-8-2, with 40% slow release nitrogen, 250 kg:	\$ 100
sawdust and straw:	\$ 1,000
white rot fungus:	\$ 3,400

excavator rental:	\$ 3,400
6 inch shaker screen rental:	\$ 6,200
SCAT 481 rental (\$1,250/week):	\$ 7,500
Towing tractor (front end loader):	Supplied by Base
Monitoring equipment:	
• GT408 four gas monitor (combustible/oxygen/CO/CO ₂):	\$ 5,658
• Reotemp 0.9 m stem temperature probe:	\$ 114
• Quickdraw Moisture Probe, 24 inch long:	\$ 581
• AMS soil probe (3 ft with retract-a-tip, pvc tubing)	\$ 680
• Hand auger (3 1/4 inch dia head, 3 ft with handle)	\$ 250
Sample jars:	Supplied by laboratory
Bio laboratory testing	\$ 7,867
Chemical laboratory testing	\$26,148

(Equipment transportation, personnel and travel costs not included)

Commercial-scale projects would not incur costs such as much of the soil preparation and rigorous progress testing used in this project. Moreover, spacing of the windrows would be sufficient only for the passage of equipment (2.5 m versus the 4 m in this project). It is assumed that the remediation will take three weeks for the turned compost and nutrients, and six weeks for the white rot fungus and static biopile.

Inputs: The 53 x 55 m treatment pad would contain: 9 windrows (each of 3 m x 30 m x 1.5 m), or 67 m³ total soil.

Total amount of contaminated soil in 9 windrows:

Soil only windrows @ 1.4 tonnes/m³:

$$(9 \times 67 \text{ m}^3 \times 1.4 \text{ t/m}^3) = 850 \text{ tonnes, or } (850/1.4) = 600 \text{ m}^3$$

Soil with 20% compost windrows @ 1.1 tonnes/m³:

$$(9 \times 67 \text{ m}^3 \times 1.1 \text{ t/m}^3) = 660 \text{ tonnes, or } (660/1.1) = 600 \text{ m}^3 \text{ contaminated soil}$$

$$\text{Since soil is only 80 \% of windrow, } (600 \times 0.8) = 480 \text{ m}^3 \text{ contaminated soil.}$$

Treatment pad with sand ballast: \$6.5K

White rot fungus @ \$47/tonne: \$31K

Compost @ \$2/tonne: \$0.3K

Nutrients:

Synthetic fertilizer @ 1.5 kg/m³:

$(\$100/250 \text{ kg} \times 1.5 \text{ m}^3 \times 600 \text{ m}^3) = \0.4 K for soil only windrows. or

$(\$100/250 \text{ kg} \times 1.5 \text{ kg/m}^3 \times 480 \text{ m}^3) = \0.3 K for soil/compost windrows.

Poultry manure @ 16 kg/m³:

$(\$500/500 \text{ kg} \times 16 \text{ kg/m}^3 \times 480 \text{ m}^3) = \7.6 K for soil/compost

Monitoring: Flat fee for rental/depreciation of GT408 and probe, temperature gauge: \$100/wk.

Compost turner:

Rental of SCAT turner @ \$1,200 per day per week:

For turned compost and nutrients, 3 weeks: \$3.6K

For WRF, assume 2 weeks: \$2.4K

Lab Analysis @ 5 composites for >1,000 m² contaminated soil, testing for purgeables, cold extractables, and MOG in the initial and completion tests @ \$90 per composite: \$1K

Table B.1 - Total and Unit Costs of Treatments.

Treatment	Time (wk)	Soil on Pad (t)	Cost for Pad Filled with Contaminated Soil							Unit cost \$/t
			Pad \$K	WRF \$K	Compost \$K	Nutrient \$K	Turning \$K	Monitor \$K	Lab \$K	
WRF	6	660	6.5	31.0	0.3		2.4	0.6	1.0	63
Turned compost, manure	3	660	6.5		0.3	7.6	3.6	0.3	1.0	29 (18 if manure contributed)
Turned compost, fertilizer	3	660	6.5		0.3	0.3	3.6	0.3	1.0	19
Static compost, fertilizer	6	660	6.5		0.3	0.3		0.3	1.0	13
Static Biopile	6	850	6.5			0.4		0.6	1.0	10

Note: - all total costs are reported in \$K and unit costs in \$/tonne.
 - the cost estimates exclude labour (engineering, project management, turning and monitoring), excavation, and site preparation.

GRAIN SIZE ANALYSIS OF CONTAMINATED SOIL

(Refer to attached analysis)

Trenton Soil Characterization - Grain Size Analysis & Hydrometer Method

Report date: 3 Mar 96
 Test by: JG Critchley
 Test date: 15/16 Feb 96

Particle Distribution:

Dia (mm)	% Finer	Grading 5% gravel
6.3500	95.5	60% sand
3.1750	90.5	
1.2700	78.5	
0.6350	66.8	
0.2540	35.8	
0.1270	26.6	36% silt & clay
0.0774	18.6	
0.0565	16.8	
0.0421	14.1	
0.0309	11.8	
0.0225	10.0	
0.0164	7.7	
0.0123	5.9	
0.0088	5.0	
0.0063	3.6	
0.0045	2.8	
0.0033	2.4	
0.0014	1.5	

Soil description: fine grained, light grey
 Sampling location: South side middle Windrow 3
 Sampling date:
 Sample preservation Freeze/Refrigeration

Soil Preparation:

Weight @ EC: 447.43 g (soil + 250 mL jar)
 Weight after drying: 399.57 g (soil + jar, kitchen dried)
 Moisture loss: 47.86 g

Crucible tare weight: 136.53 g (crucible #5)
 Crucible + soil: 365.44 g
 Wt of soil (calculated) 228.91 g Moisture loss wrt EC wt: 20.91%
 Wt of empty jar: 170.75 g
 Total wt after furnace 356.46 g (furnace temp 600°C at ± 2 hr)
 Soil wt after furnace: 219.93 g
 Organic weight: 8.98 g Ratio organics (w/w): 4.08%

Sieve Analysis

Sieve size (mesh/in)	Sieve size (mm)	Sieve ser #	Clean Weight g	Wt with Soil g	Soil Weight g	Ratio by sieve g	% Retained	% Finer
4	6.350	158	549.44	559.29	9.85	4.48%	4.5	95.5
8	3.175	695	489.71	500.81	11.1	5.05%	9.5	90.5
20	1.270	-	432.88	459.26	26.38	11.99%	21.5	78.5
40	0.635	-	404.84	430.52	25.68	11.68%	33.2	66.8
100	0.254	589	359.59	427.7	68.11	30.97%	64.2	35.8
200	0.127	-	341.55	361.79	20.24	9.20%	73.4	26.6
Under tray					0.4	0.18%	73.6	26.4
Total retained on sieves:					161.76	73.55%		
Passing 200 sieve (silt&clay):					58.17	26.45%		
Totals by sieves:					219.93	100.00%		
Original starting weight:					219.93			

Hydrometer Analysis (ASTM D422)

Hydrometer # 152H
 Specific gravity of solids, G: 2.65 (assumed) Weight of solids, W: 58.17 g
 Dispersing agent/neutralizer: sodium metaphosphate-Calgon Amount: 20 g in 500 mL distilled water
 Zero correction: 5 Meniscus correction: 1

Date	Time	Elapsed time (min)	Temp °C	Temp Correction	Act hydro Reading Ra	Corrected Reading Rc	% Finer	Meniscus Correction R	Eff depth L (cm)	L/t	Constant (table 3) K	Particle Dia (mm)
16/2/95	1150	0.25	23.8	0.94	45	40.94	70.4	46	8.8	35.2000	0.01304	0.0774
	1150	0.5	23.8	0.94	41	36.94	63.5	42	9.4	18.8000	0.01304	0.0565
	1151	1	23.8	0.94	35	30.94	53.2	36	10.4	10.4000	0.01304	0.0421
	1152	2	23.8	0.94	30	25.94	44.6	31	11.2	5.6000	0.01304	0.0309
	1154	4	23.8	0.94	26	21.94	37.7	27	11.9	2.9750	0.01304	0.0225
	1158	8	23.8	0.94	21	16.94	29.1	22	12.7	1.5875	0.01304	0.0164
	1205	15	23.8	0.94	17	12.94	22.2	18	13.3	0.8867	0.01304	0.0123
	1220	30	23.8	0.94	15	10.94	18.8	16	13.7	0.4567	0.01304	0.0088
	1250	60	23.8	0.94	12	7.94	13.6	13	14.2	0.2367	0.01304	0.0063
	1350	120	24.3	1.09	10	6.09	10.5	11	14.5	0.1208	0.01296	0.0045
	1550	240	21.1	0.22	10	5.22	9.0	11	14.5	0.0604	0.01346	0.0033
17/2/96	1150	1440	21.1	0.22	8	3.22	5.5	9	14.8	0.0103	0.01346	0.0014

Corrected reading, Rc: @sum(Ra - zero correction + Temp correction)

% Finer: @sum(Rc * 100 * G * 1.65 / ((G - 1) * 2.65 * W))

Meniscus correction, R: @sum(Ra + Meniscus correction)

L/t: @sum(L/elapsed time)

Particle dia, D: @sum(K * ((L/t) ^ 0.5))

APPENDIX C

PROJECT QUALITY CONTROL AND STANDARD OPERATING PROCEDURES

1. PROJECT QUALITY CONTROL.

The following observations were made as a result of the quality control program:

- a. The quality control program repeatedly demonstrated the heterogeneous nature of soil and the varying concentrations of contamination in a soil matrix. The range of each windrow's MOG data in each sampling event were clear indications of this heterogeneity. Field prepared replicates showed a difference of up to three- to four-fold or generally up to a difference of 1300 mg/kg MOG (Refer to **Appendix A** for actual replicate data: Windrows 1, 14 Nov; Windrow 2bc, 30 Oct; Windrow 3ae, 2 Oct; Windrow 3be, 30 Oct).
- b. The MOG MDL reported by the Environment Canada laboratory was 500 mg/kg.
- c. The recovery of surrogates was 97 percent for MOG. It was found to be based on the use of acid-cleaned sand rather than the site's soil. Subsequently the laboratory was directed to use specified background soil samples on hand at the laboratory and surrogate recoveries were reported as 90 percent. However, the laboratory data indicated that the background soil MOG concentrations prior to spiking showed non-detect. Since these samples of background soil had previously shown some MOG contamination, the Environment Canada report does not correlate with their earlier analysis of these soils. Therefore the correction for surrogate recovery may not have adequately measured the matrix effects. However, it was deemed that even though the Environment Canada laboratory results may not have been accurate for site cleanup certification purposes, they still would have been relative to each other and therefore suitable for trend analysis.
- d. Inter-laboratory duplicates revealed that there was not good correlation between the MOG results. (Reference **Table C.1 - Inter-Laboratory Blind Duplicate Results**) The Environment Canada laboratory was using the Ontario MISA dichloromethane protocol for MOG extraction versus the Integrated Explorations laboratory analysis for MOG using EPA standard methods employing Freon 113. Although the dichloromethane behaved as predicted in literature by demonstrating a stronger solubilization of greases (Thomson, 1994), the variance was not uniform. This can be explained by the methodologies or recovery corrections of one or both laboratories were not being applied consistently, or the scatter is the result of the heterogeneity of the soil.

Table C.1 - Inter-Laboratory Blind Duplicate Results [mg/kg MOG]

Envir Cda Lab		Int Expl Lab		Mean Difference	Ratio to Envir Cda
MOG	mean	MOG	mean		
506	506	169 96 170	145	361	71%
1436 556	996	284	284	712	71%
591 463	527	489	489	38	7%

Note: Integrated Explorations Laboratory uses Freon 113 for extraction
Environment Canada laboratory uses dichloromethane for extraction

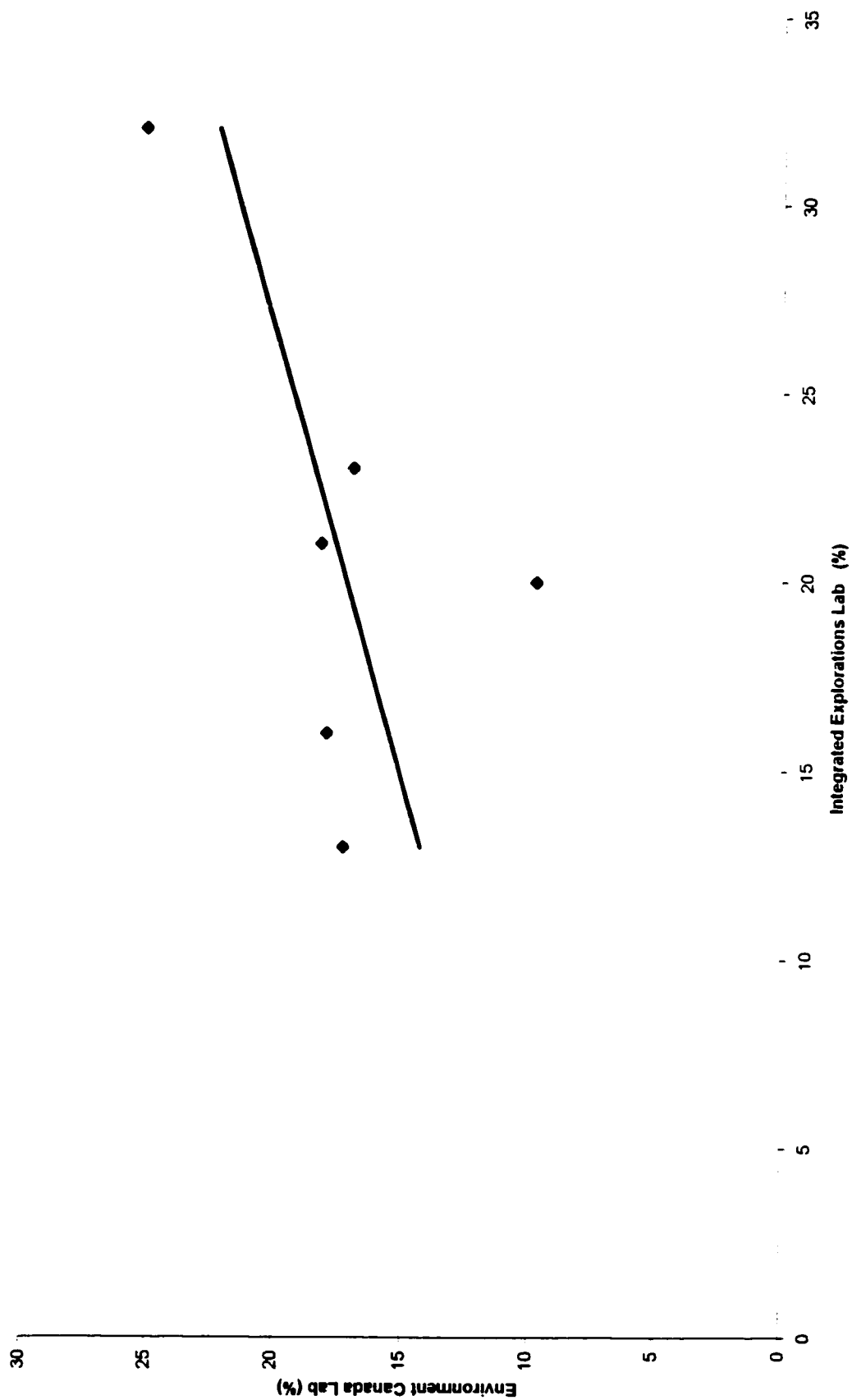
- e. Inter-laboratory duplicate analysis of moisture determination by the gravimetric method did not correlate which, for this rather simple method, should have shown a reasonable correlation. On a scatter plot, the results which should have been closely clustered around a straight line starting from 0.0 and up to 35.35. The scatter plot in

Figure C.1 - Inter-Lab QC Moisture Determination shows that there was wide scatter and bias. This would affect the accuracy of the moisture correction applied to the purgeable hydrocarbons analyses.

Summary. The importance of a thorough quality control program that covers all aspects of a project can not be minimized. A significant amount of time must be allocated to quality control. Standard field and laboratory quality control protocols should be followed. These include:

- use of composite samples to represent soil parameters.
- use of a statistically significant amount of samples per sampling event.
- selection of sampling locations so that data are representative of the whole site.
- use of standard laboratory procedures which are selected on the required levels of accuracy and precision, and the potential matrix/contaminant interferences.
- randomly numbered samples.
- blind replicates.
- blind field spikes.
- blind background samples.
- proper sample handling, storage and chain-of-custody procedures.

Figure C.1 - Inter-Lab QC Moisture Determination
Gravimetric



- laboratory reporting procedures that include MDL results, moisture and surrogate recovery corrections, date of analysis, and data assessment by the laboratory quality control personnel, and
- inter-laboratory duplicates.

2. **STANDARD OPERATING PROCEDURES**

The SOPs were a useful guide, both in ensuring that all phases of the were planned well and in managing the monitoring, sampling and data management. The value of the SOP as a checklist ensured that all steps were taken and in the same sequence. The SOPs did not require revision during the project.

2.1 **MONITORING SOPs**

- Turn on GT408 and hold down "adjust" to zero equipment. Select "ppm" for combustibles. (Note that the CO cell has been deactivated, and although the alarms can not be turned off, they are set at 10,000 ppm combustibles, 0% Oxy and 5% CO₂.)
- Inspect two moisture probes, temperature probe and gas probe (including its hose for kinks or cracks where fresh air could be drawn in). Connect GT408 and open gas sampling port screen. Log settings in fresh air for the 4 gases, moisture and temperature. Disconnect GT408.
- Turn QuickDraw moisture metre knob fully clockwise, then while tapping dial, back to a reading of approximately 30 centibars. Use the coring tool to establish a hole for the probe. Remove moisture probe from case. Vertically insert probe slowly and carefully into soil. While tapping dial gently, adjust knob in direction of pointer movement to find stable reading.
- Insert the "K Mart" moisture probe, and the temperature probe (by holding onto the shaft and NOT the dial) near the QuickDraw moisture probe.
- Insert the gas probe near the moisture probe to a depth of 2 to 3 feet. Pull gas probe back approximately 3 to 4 inches to open sampling screen. Tamp soil at soil surface of gas probe to prevent fresh air from entering around probe.
- Connect GT408 after it has zeroed itself on fresh air (in soils with high combustibles, a return to approx 100 ppm OK. When moisture, temperature and combustibles stabilized (after approx 1 min, readings should be the same for 10 to 15 sec), log readings for moisture, temperature and each gas along with sampling location and depth. (If combustibles are > 10,000 ppm, switch to LEL and annotate log entry with 'LEL". Return GT408 to ppm for next reading.) If GT408 pump shuts down for lack of air flow, disconnect it from the probe, press RESET, and try again.
- Disconnect GT408 to let instrument zero itself. Keep sampling hose clear of any soil.
- Remove probes. Clean dirt off gas sampling port with fingers. Dip moisture probe tip in water and wipe it with tissue to remove sod particles, trying not to rub soil into porous tip, and rewet tip.
- Continue to sample other soil locations by repeating steps c. to h.
- At completion of monitoring, again take fresh air readings with all probes and log.
- Disconnect GT408, clean and store. (Recharge battery for 8 hours before next use).

- l. Disassemble gas probe tip and clean in water. (Start by unscrewing round nut with 2 flats off the cylindrical body, then removing the nut holding the screen onto the hollow core) Dry and reassemble, tightening connections with an 18mm or 11/16 inch wrench.
- m. Wipe off temperature probe and replace in its protective case.
- n. Remove moisture probe from its case, fill probe side of case with water and invert case to flush out accumulated soil particles and to replenish moisture in the case's sponge. Replace probe in case and store upright.

2.2

SOIL SAMPLING SOPs

- a. Soil Sampling. Determine which location will be selected for preparing the Environment Canada triplicate, Integrated Explorations triplicate and comparative MOG analysis duplicate and identify on log sheet for multiple jar preparation.
- b. Remove 5 grab soil samples (ideally from each location where the monitoring was performed) and place grab samples in a clean plastic bag, marked with the sample location by a felt nib pen. Samples should be taken as follows: 6" in from side surface, 6" in from top, two samples from different mid depths with the 3" auger and one sample from near the bottom centre of the windrow again taken with the 3" auger.
- c. Clean sampling equipment between each windrow (remove soil, wash off with water and paper towel, and dry. If still discoloured, wash with naphtha and let air dry).
- d. Sample Preparation. Remove stones, wood, etc, greater than 1/2". From outside bag, mix soil well.
- e. Place composited soil in sample jars and seal as required by the chart below. Label jar with randomly selected labels and indentify which label corresponds with which location in the log. The three columns provided for each lab are so that for the location where triplicates are taken, the 3 label numbers can be shown.
- f. Select soil from the background soil area (marked off with stakes East of the treatment cell, beside the woodline), place in the appropriate sample jars. Then close, randomly label and bag the jars in the appropriate fashion.
- g. Place jars in their respective shipping coolers and ensure ice/ice packs present. If ice to be used, ensure jars are placed in bags to prevent labels from soaking off and being mixed up.
- h. Complete Chain of Custody form.
- i. Clean the sampling equipment and return it to the sewage treatment plant.
- j. Head Space Analysis. Keeping an air space in the bag, close off bag with a rubber band and place at the end of the windrow.
- k. Assemble and turn on the HNu photoionization detector (PID), Century flame ionization detector (FID) and Gastech GT408. The PID and FID must be fully assembled before they can be turned on. (For the Century FID, turn on INSTR for 5 min, move CALIBRATE to X10 and ADJUST dial to zero, turn PUMP on, open H₂ Tank Valve one turn and H₂ Supply Valve one half turn (only when pump is on). Depress red button igniter (for not greater than 6 sec) until pointer starts to move up. If no ignition, let unit run for 3 minutes before attempting ignition. ADJUST calibration to 1 ppm on X1 range. (Note that FID designed to cut flame if LEL is approached.)
- l. Log fresh air readings with each instrument.

- m. At least 15 min after sealing the bags, and without allowing headspace air to escape, open each plastic bag sufficiently to insert probe of each the PID, FID and GT408 in turn to read VOC concentration. Ensure probe does not touch the dirt. Log readings.
- n. At completion of monitoring, again take fresh air readings with each instrument and log.
- o. Turn off PID, FID and GT408. Close H₂ Supply and Tank Valves, turn off INSTR, after 5 min, turn off PUMP. (Batteries have to be recharged before next use and H₂ tank refilled if it had less than 150 psi.) Wipe off instruments.

2.3 **EXAMPLE OF SAMPLE PREPARATION SCHEDULE (Week 0: 20 Sep)**

Windrow	Envir Cda	Analysis	Integrated	Analysis	Remarks
1a	1 each: w, c, e	a,b	1 each: w, c, e	d	Select one of these 18 locations to prepare the QA/QC triplicates, randomly labelled and sent to Envir Cda.
1b	1 each: w, c, e	a,b	1 each: w, c, e	d	
2a	1 each: w, c, e	a,b	1 each: w, c, e	d	
2b	1 each: w, c, e	a,b	1 each: w, c, e	d	
3a	1 each: w, c, e	a,b	1 each: w, c, e	d	
3b	1 each: w, c, e	a,b	1 each: w, c, e	d	
4	1 each: w, c, e	a	1 each: w, c, e	e	Another location for duplicates - in a glass jar for Envir Cda and a plastic jar for Integrated. Have analysis a and e done on them respectively.
5	1 each: w, c, e	a	1 each: w, c, e	e	
6	1 each: w, c, e	a	1 each: w, c, e	e	
7	1 each: w, c, e	a	1 each: w, c, e	e	
8	1 each: w, c, e	a	1 each: w, c, e	e	
Prep	Glass jars, alum foil, tape lids and bag. Cool to 4°C		Plastic jars. Cool to 4°C		

Note: Soil taken from each location, eg. 2be, should be a composite of 5 grab samples and placed in one plastic bag from which sample jars for both labs are filled.

Analysis Legend:

- a: 7 tests on screened sample (pH, moisture, purgeables, cold extractables, MOG, PAH, PCB)
- b: 7 tests on total matrix (pH, moisture, purgeables, cold extractables, MOG, PAH, PCB)
- c: 3 tests on screened sample (pH, moisture, MOG)
- d: 6 tests (fungal enzyme & plate counts, bacterial plate count, avail phosphate, std nitrate, std ammonia)
- e: 5 tests (fungal & bacterial plate counts, avail phosphate, std nitrate, std ammonia)

APPENDIX D

FIELD MONITORING EQUIPMENT

1. HAND HELD VOC DETECTORS.

The project employed Century and Heath FIDs, an HNu PID and a GasTech GT408 for detection of VOCs or combustibles. All provide real-time information on the presence of many organics which traditionally have been used to make field decisions regarding indications of site contamination and selection of samples for higher quality analysis. However, the use and interferences affecting each are different.

1.1 *FLAME IONIZATION DETECTORS (FID).*

The FID is a non-specific total vapour detector. An internal vacuum pump provides the sample stream which is filtered and directed to the detector chamber. Here, the gas stream is exposed to a hydrogen flame which ionizes organic vapours. The resulting positively charged particles are collected, measured and displayed as a concentration level. Tables are available which provide the responses of different organic compounds relative to the calibration gas (Century, 1975). Its sensitivity is greater for hydrocarbons than for any other class of organic compounds. It is resistant to the effects of humidity but can be affected by naturally occurring compounds such as methane and pine tree terpenes [which can be present in yard waste composts such as those used in this project] and will stop functioning in oxygen deficient atmospheres (<15%) [as could be found in aerobic bioremediation situations] because the hydrogen flame will be extinguished (DOEP, 1994). The hydrogen supply is nominally sufficient for an 8 hour operation and since it was used in the project only for headspace analysis at the end of each sampling day for about an hour, recharging of the hydrogen tank was unnecessary. Due to the pressurized tank, it can not be carried on an airplane. The Century FID was difficult to light when cold and resulted in it not being used some days.

1.2 *PHOTOIONIZATION DETECTOR (PID)*

Like the FID, the PID is a non-specific total vapour detector which can not identify unknown substances. An internal vacuum pump extracts a gas sample stream and passes it through a filter before exposing it to the detector chamber. In the chamber, the organic vapours are exposed to a specific wave length of energy to excite the molecules with ionization potentials below the energy of the lamp. The excitation energy levels are detected and displayed as an organic vapour concentration. Compounds with

energies equal to, or slightly above those of the lamp, may also be detected. Tables are available which list the ionization potentials of compounds (HNU User Guide). It's sensitivity is greater for VOCs such as the aromatics (BTEX compounds) rather than semi-volatile compounds. The PID does not respond to certain low molecular weight hydrocarbons such as methane and ethane. It cannot detect certain high energy bond compounds such as carbon tetrachloride and hydrogen cyanide. The internal ionizing lamp voltage can be changed from the normal one of 10.2 eV to 11.5 eV or 9.5 eV to increase or decrease the sensitivity of the PID to various organic compounds as desired for specific site screening applications. It is affected by humidity especially above 85% and can be affected by naturally occurring compounds such as pine tree terpenes [which can be present in composts such as those used in this project]. Oxygen deficient atmospheres (<15%) [as could be found in aerobic bioremediation situations] can bias readings high. Cold temperatures can affect the readings and shorten the life of the battery which would normally be adequate for an 8 hour day (DOEP, 1994). A felt nib pen can be held near the inlet to confirm instrument response to organic vapours on startup.

1.3 ***GASTECH GT408 FOUR GAS DETECTOR.***

The GT408 is a prototype developed for other than environmental screening uses. It combines oxygen, carbon dioxide, carbon monoxide and combustible sensing cells in one hand held instrument. It's setup is primarily for detection of toxic and flammable vapours and to give warning as harmful concentrations are being approached. This could be used in roles such as confined space entry. The CO and O₂ sensors are electrochemical, the CO₂ is non-dispersive infrared and the combustibles is a platinum bead catalytic. The O₂ range is 0 to 30%, CO: 0 to 300 ppm, combustibles: 0 to 10,000 ppm at which it can be switched to LEL (Lower Explosive Level) for up to 100%, and the CO₂ is 0 to 5%. The combustibles transition is 10,000 ppm equals 20% LEL (methane). This transition is approximately 0.3 that of hexane which would be used for gasoline, jet fuel and diesel vapour environments. The combustibles cell does not have a methane elimination switch as did an earlier version of the GasTech series. Since the instrument zeros itself on ambient air on startup, the startup should be done in a "clean air" location. The operator can check the combustibles response by holding a felt nib pen near the intake, and the CO₂ and O₂ response by breathing across the intake. The internal pump has an automatic shut down feature if insufficient gas is being pumped. It has a number of alarms aimed at alerting personnel of unsafe working conditions. Chlorine and fluorine compounds can damage the combustibles sensor, if O₂ concentrations are below 10% the LEL readings may bias low, combustible concentrations above LEL will display "over" and a number of gases may cause the CO sensor to respond (hydrogen, ethylene, acetylene, heavy olefines and aromatic hydrocarbons) (GasTech, 1994). Tables are available that list the instrument's response to various gases

and vapours. Unlike the FID and the PID, the instrument can be operated in damp environments, a feature which will permit work in rainy conditions.

A number of problems were experienced with the GasTech GT408 four gas detector. This monitor was a new design and was only coming on the market. This monitor used a more energy efficient pump than the previous models. However, it did not have sufficient power to draw in soil-gas samples when the soil was wet. This caused a low-flow alarm condition and the monitor would shut down. Secondly, the gas-train in the monitor included a Gore-Tex® filter. This became quickly clogged by the very fine dust particles and again caused the monitor to shut down due to low flow conditions. Monitoring of carbon dioxide failed to be useful since the detector cell had a span of 0 to 5 percent and soil-gas carbon dioxide concentrations quickly rose above this level. Hence soil-gas concentrations of this gas were not reported in this project. This detector was used to detect oxygen and VOCs. Field observations of its operation on VOCs indicated a reasonable confidence in the data, except for when the windrows were wet or the ambient conditions were near freezing.

1.4 ***HEADSPACE ANALYSIS.***

Despite the effort to allow the headspace vapour concentrations to equalize in the air space of the bags of composite samples, variations were noted when the FID and PID probes were moved to different locations in the headspace. At lower organic vapour concentrations the GT408 demonstrated greater sensitivity than FID and the FID greater than the PID. At higher vapour concentrations, the FID was more sensitive than the PID and the GT408. The PID generally demonstrated lower sensitivity than the FID and GT408. At times, considerable difficulty was experienced with lighting the FID. As a result, the FID was unable to be used some days. Moreover, the configuration of the sampling head on the Century FID was more for ground surface detection of leaking underground petroleum pipelines (Century, 1975) and was difficult to use in a plastic bag headspace analysis mode without allowing ambient air to dilute the headspace during the probe's insertion. The PID was easy to set up and use and the sampling probe was easy to use in the plastic bag vapour headspace analysis mode. The instrument is sensitive to moisture since the internal lamp can become clouded easily. It was noted that care had to be taken to prevent even condensation on the inside of the plastic bag from being pulled into the instrument by its internal sampling pump. The GT 408 was of a clean design and easily could be cleaned of mud. It proved to be a robust detector and was still working after the PID and FID were no longer able to function due to startup and/or weather problems. The CO detector was deactivated for the project. The ranges of the O₂ and combustibles detectors were adequate for monitoring bioremediation conditions, however the CO₂ detector with its 0 to 5 percent range was often off-scale. Although CO₂ concentrations should not exceed five

percent for maximum effectiveness of bioremediation processes, a range of 0 to 10% would be much better to manage the processes. Since the instrument was designed for hazardous environment warning, the alarms were continually sounding when monitoring the bioremediation conditions since the combustibles, O₂ and especially the CO₂ alarm conditions were frequently being exceeded. This became very annoying. A recommendation has been made to the manufacturer to have the instrument configured for two default setups: a hazardous environment monitoring mode and a remediation monitoring mode. The latter would deactivate the alarms and startup the instrument in the combustibles ppm range instead of the LEL range. Additional problems were encountered with the CO₂ cell giving false negative/fail readings, the instrument probe being somewhat awkward to use and clogging with dust, and the unit not functioning reliably below 5°C.

2. **SOIL-GAS PROBE.**

An AMS probe with retractable tip was used to draw soil-gas from the interior of the windrows for sampling by the GasTech 408. (Refer to **Appendix E -Figures** for an illustration of the probe). The probe had a diameter of 19 mm and consisted of a number of 0.9 m extensions, a driver adaptor and a retractable tip with 6 mm Teflon tubing connecting the tip with the GasTech detector through the interior of the probe. The probe permitted the dedicated sampling of soil-gas without contamination by atmospheric air. No drivers were required since the probe could be inserted by hand to depths of approximately 0.5 to 0.9 m in all windrows. It was robust, and the tip did not become fouled with mud as had been experienced earlier on the site with another rigid probe which had holes drilled on the side of the tip for collecting soil-gas.

3. **TEMPERATURE PROBE.**

A simple 0.9 m stem Reotemp dial thermometer was used to determine the interior windrow temperatures. Temperature sensing was only at the tip. It was robust, had a rapid response time and functioned well.

4. **MOISTURE PROBE.**

A Quick Draw model 2900F soil moisture probe by SoilMoisture Equipment Corp was initially used to determine real-time in-windrow moisture conditions. In that non-saturated soil will tend to suck up water, the probe offers water to the soil through a porous ceramic tip and measures the suction directly in a dial vacuum gauge, reading centibars/kilopascals. A zero soil suction indicates that the soil is saturated, that is, field capacity equals 100 percent. Although the principle sounded fine, in practice, there was no

confidence in the readings since the probe was difficult to calibrate on-site, the required dial adjustments could skew readings to almost anything desired, and moisture concentrations measurements took too long to carry out. Since the readings did not correlate with observed soil wetness, it was apparent that the probe was not working well in the type of open soil matrices of the windrows since full contact with the sensing tip was not being achieved.

Shortly into the project, an inexpensive household plant (dielectric) moisture probe was obtained and used. The dielectric probe (0.2 m) was too short to reach in beyond the surface effects of the windrows, but seemed to have a better correlation with field visual observations than the other methods, especially when the probe was read for its peak readings during insertion. However, the dielectric properties of the soil are related to not only the amount of moisture which would govern the flow of electricity, but the amount of salts dissolved in the water. In both of the above, the readings given by the instruments were site specific and would have to be calibrated to each site. The laboratory gravimetric analysis was required to adjust results of lab analyses to their equivalent dry mass. From the field visual observations and field monitoring, it appeared that the laboratory gravimetric method was a poor indication of bulk windrow moisture conditions. The readings were not calibrated to field capacity or to total moisture capacity since there was no correlation in the data.

In this project, there was no consistent correlation of the field instrument readings to each other or to the apparent moisture conditions as observed. By **Figure D.1 - Field Moisture Measurements**, **Figure D.2 - Field - Lab Moisture Measurements (Tensiometer)**, and **Figure D.3 - Field - Lab Moisture Measurements (Dielectric)**, it can be seen that the scatter plots show that there was poor correlation among the field tensiometer, field dielectric tests and the laboratory gravimetric methods. It is concluded that measuring moisture is more an art than a science. Field moisture determination in future bioremediation projects should continue to use the simple dielectric probe, but with a longer shaft and should consider its peak readings along with the observed moisture state of the soil.

5. **SOIL AUGERS.**

A 90 mm diameter auger on a 0.9 m extension with T-bar handle by Arts Manufacturing was used to extract soil samples from the interior of the windrows. Although the soil samples from deep in the windrow could be collected and withdrawn without contamination by the surface soils, the removal of the soil from the cylindrical auger was difficult. Refer to photograph of soil removal in **Appendix E - Figures**.

Figure D.1 - Field Moisture Measurements

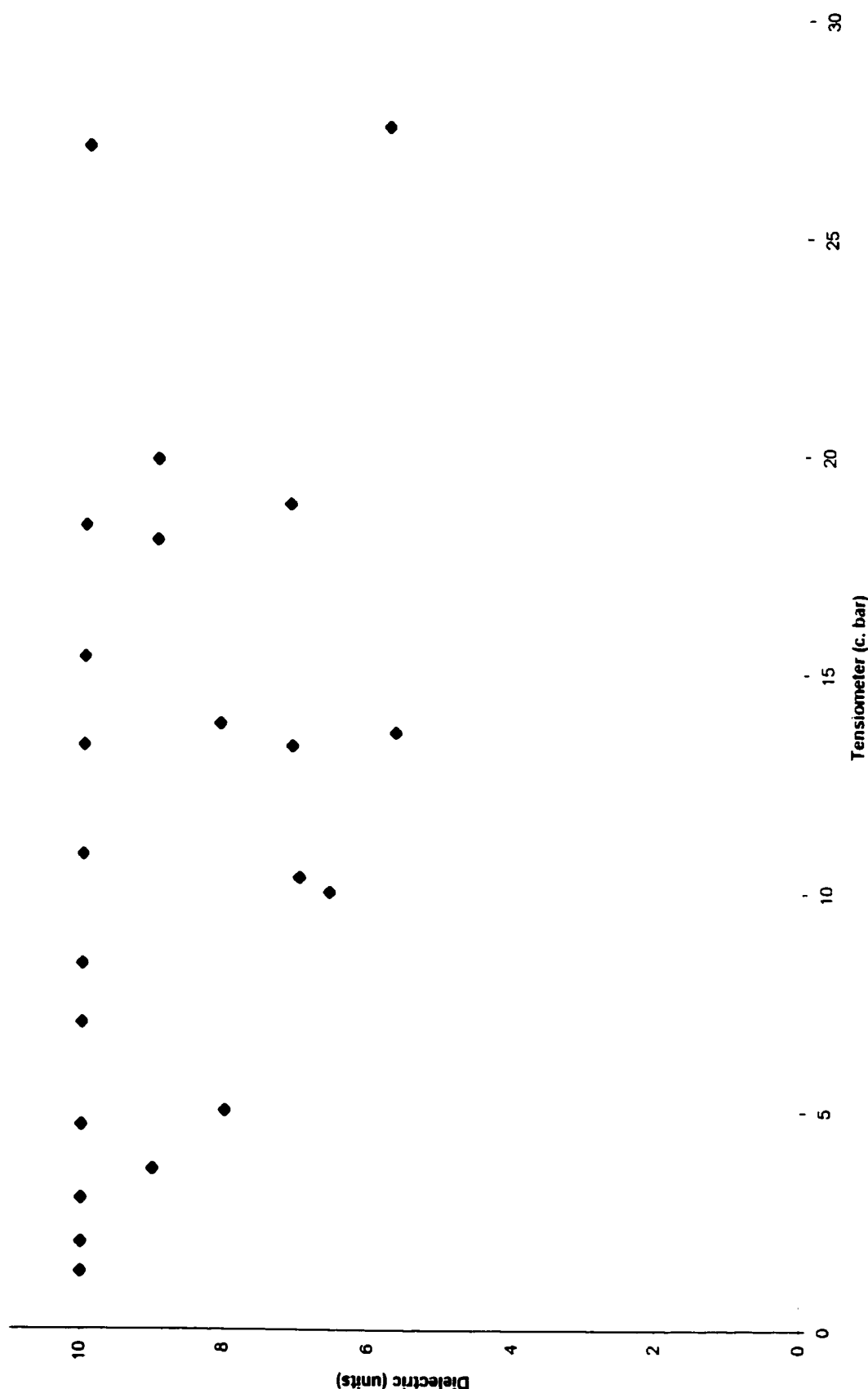


Figure D.2 - Field - Lab Moisture Measurements (Tensiometer)

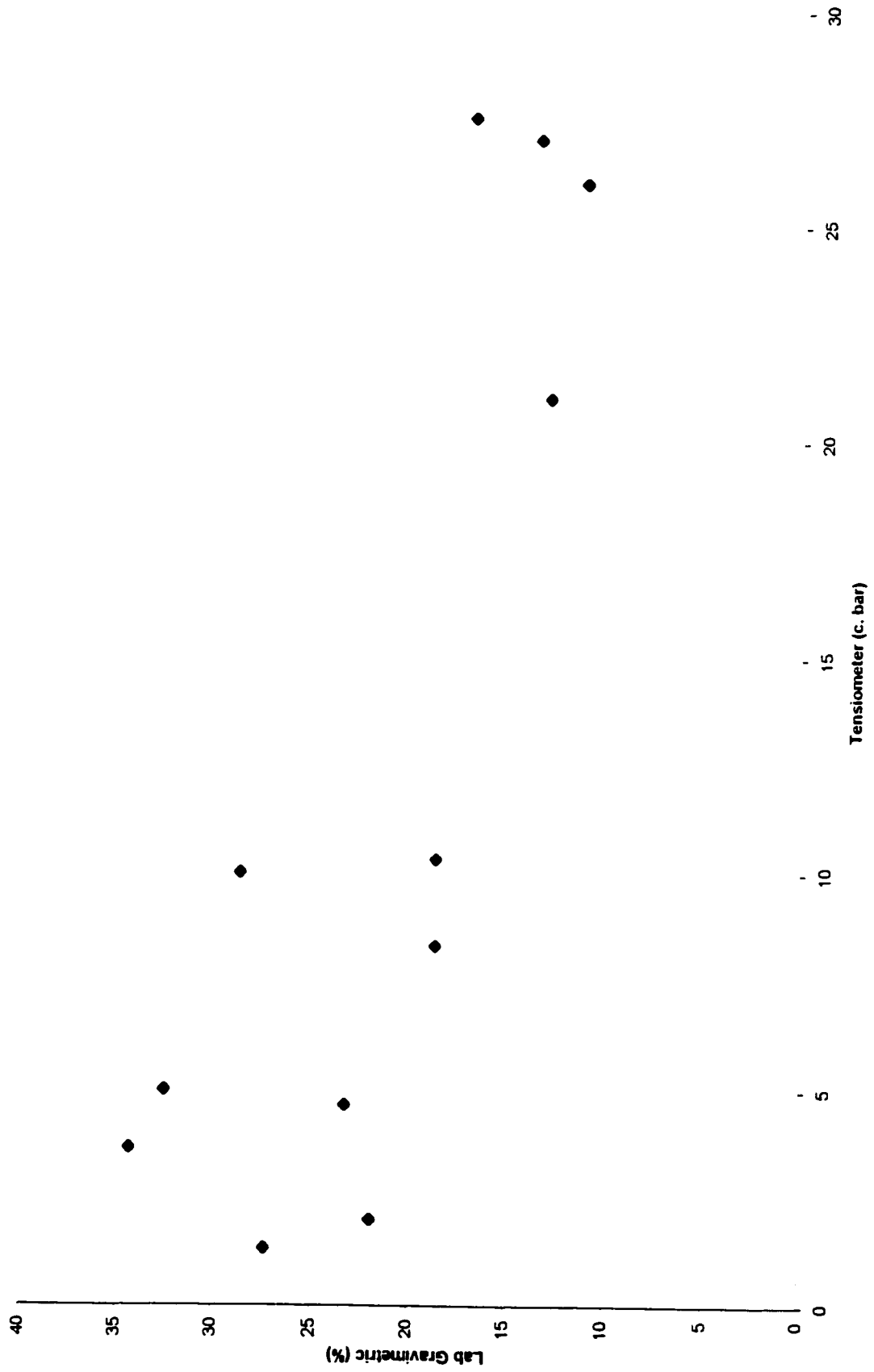
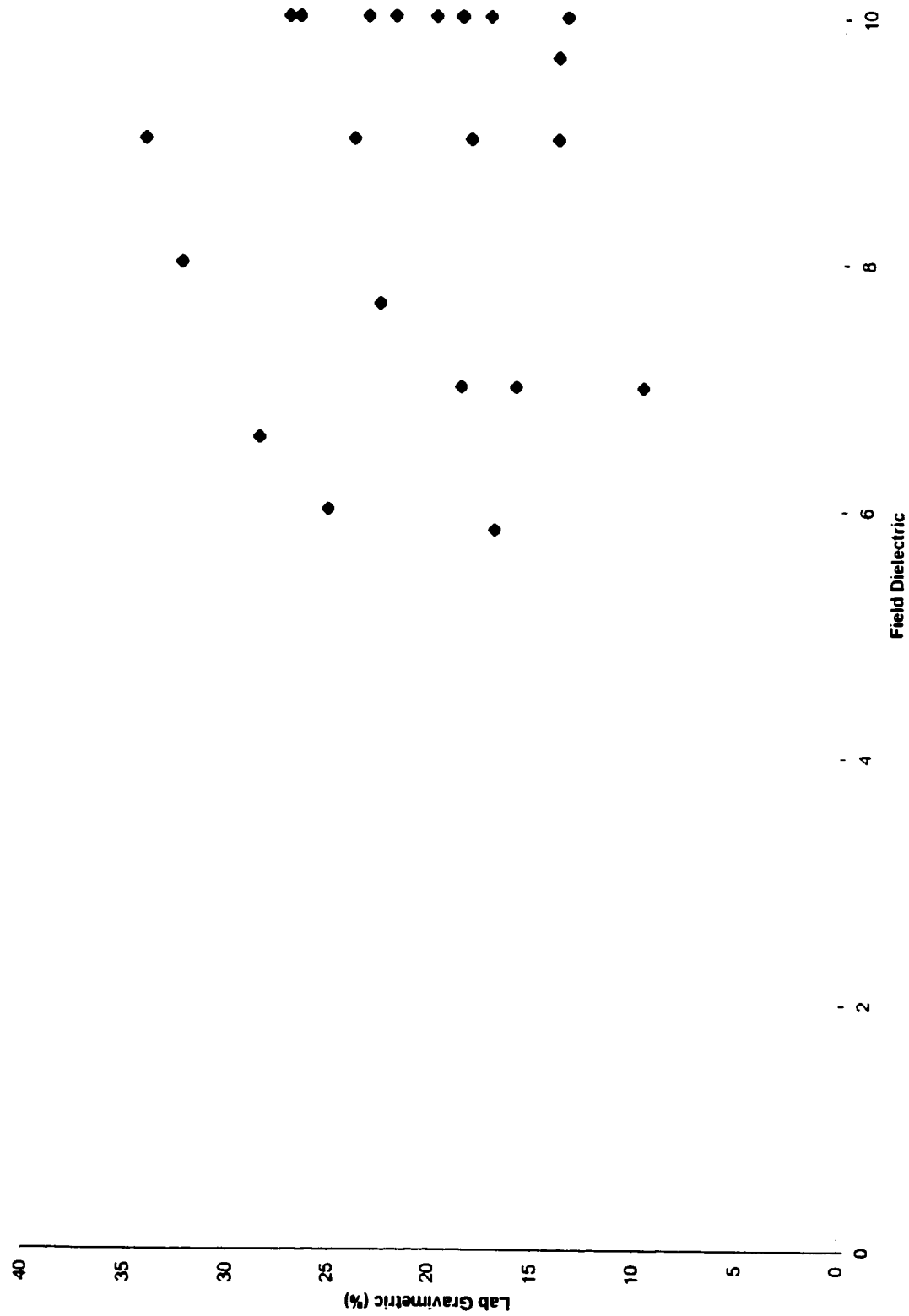


Figure D.3 - Field - Lab Moisture Measurements (Dielectric)



APPENDIX E

FIGURES

- Figure E.1 Mixing White Rot Fungus Spawn into Straw and Sawdust.
- Figure E.2 Excavation of Contaminated Soil (Looking NW).
- Figure E.3 Screening Contaminated Soil.
- Figure E.4 Construction of a Windrow On Ballast and Membrane.
- Figure E.5 Completed Windrow 1 with Compost and WRF With Substrate.
- Figure E.6 Windrow Turning with SCAT Compost Turner.
- Figure E.7 Monitoring Windrow VOC, O₂, CO₂, Temperature and Moisture Conditions.
- Figure E.8 Removing Soil from Auger into Composite Bag.
- Figure E.9 AMS Soil Probe with Retractable Tip.



Figure E.1 - Mixing White Rot Fungus Spawn Into Straw and Sawdust.



Figure E.2 - Excavation of Contaminated Soil (Looking NW).



Figure E.3 - Screening Contaminated Soil.



Figure E.4 - Construction of a Windrow On Ballast and Membrane.



Figure E.5 - Completed Windrow 1 with Compost and WRF With Substrate.



Figure E.6 - Windrow Turning with SCAT Compost Turner.



Figure E.7 - Monitoring Windrow VOC, O₂, CO₂, Temperature and Moisture Conditions.



Figure E.8 - Removing Soil from Auger into Composite Sample Bag.

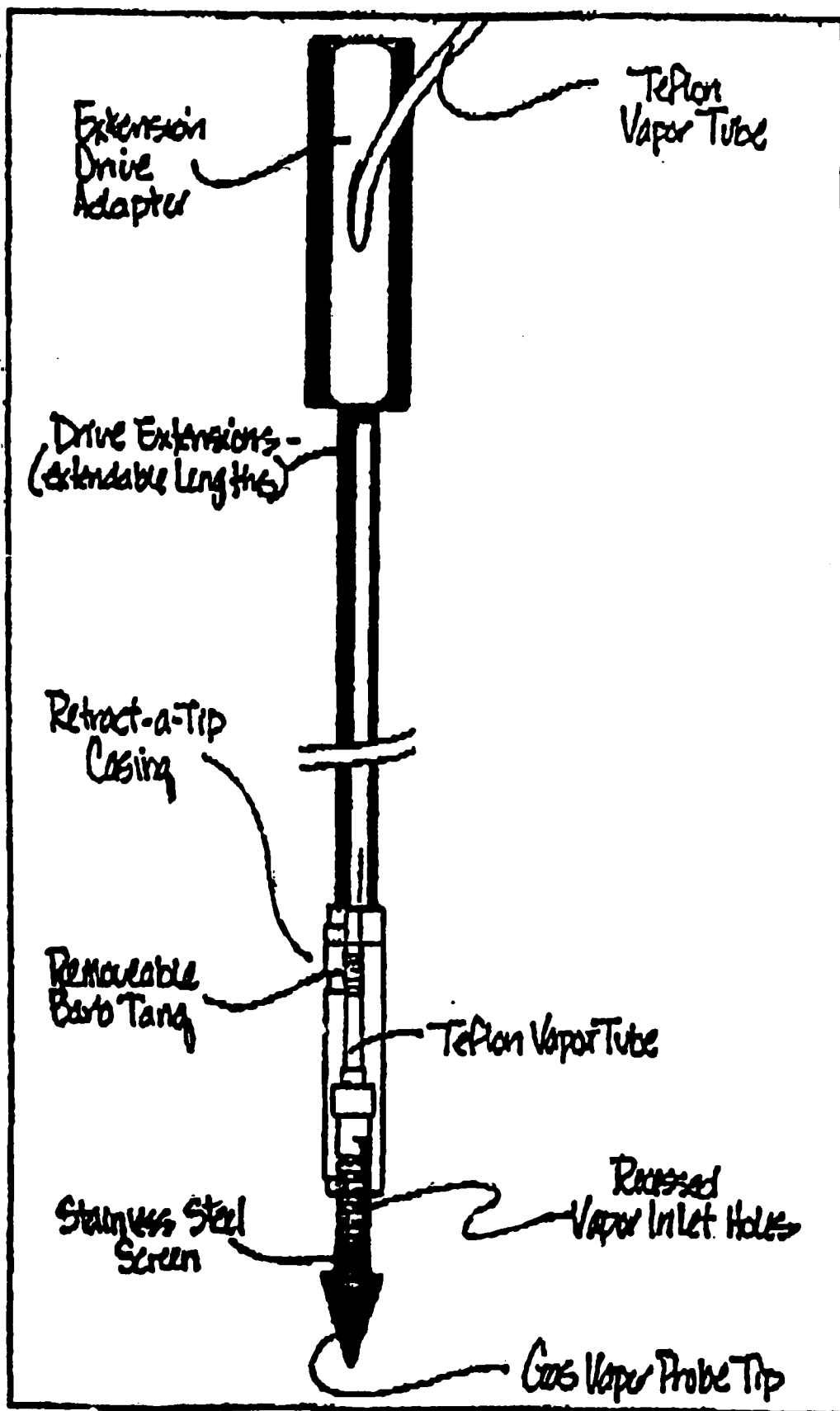


Figure E.9 - AMS Soil Probe with Retractable Tip.

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