# Hazard and Risk Assessment of Heavy Hydrocarbons Undergoing Remediation


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## When is a soil remediated? Comparison of biopiled and windrowed soils contaminated with bunker-fuel in a full-scale trial

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*Windrows outperform biopiles in the bioremediation of bunker oil contaminated soils.*

# Abstract


The focus of my thesis was the investigation of the bioremediation processes on oil spill and evaluation of the rate of the reactions on the impacted sites .

The biodegradation of petroleum and other hydrocarbons in the environment is a complex process and it's rate dependent on:

- The nature of the hydrocarbons present,
- Environmental conditions
- The composition of the indigenous microbial community.

In general, there are two approaches for bioremediating impacted sites,

- *In situ*
- *Ex situ*


# Thesis Aims of My Thesis:

- To understand the factors that determine successful remediation of crude and heavy oils.
- To assess relative changes in hazard and risk as remediation progresses
- To evaluate the performance of a range of appropriate ecological assays
- To assess the key measured parameters to enable effective remediation
- To integrate the findings, where possible, to predict assessment of remediation in a target defined context
- To develop the optimised approaches to genuine environmental samples

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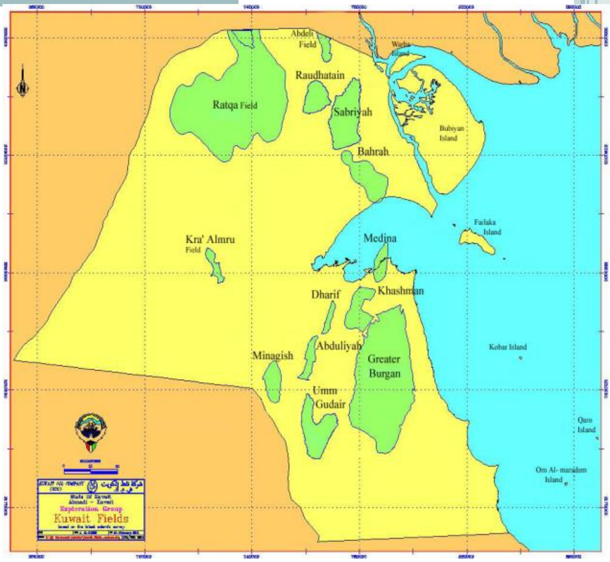
# Introduction

- Petroleum Hydrocarbon
  - Various Composition of HC & Non HC
  - Main groups within it
- Kuwait Oil Production
  - Producing oil since 1938
  - Reservoirs ( around 10% of world oil reserve)
  - Crude oil in the range of (30 – 36 API) , around 2.8 m bbl/day
- Medium to light Crude oil
  - Heavy Oil API ( 10 – 20 ) underdevelopment- Strategic plan for 2020, around 450,000 bbl/day
  - Newly discovered Gas and Gas Condensate Underdevelopment



# Major Contamination

- First Gulf War, 1991
  - Loss of 1.1 billion barrels of crude oil
    - 23 million barrel spilled in the desert
      - Soil contamination in the range of 40 – 50 metric tones
      - Also Area of 1000 $km^2$ of desert soil contaminated due to airborne oily material
- Bioremediation
  - Bioavailability of chemical of interest
  - *In situ* (table 1)
  - *Ex situ* (table 1)
  - Biological assays (table 2)

# Table 1: Common Soil Remediation Techniques for HC

| Strategies | Principle | Advantages | Disadvantages | Application |
|---|---|---|---|---|
| **In Situ** | | | | |
| Natural attenuation | Breakdown of contaminants by indigenous microbial community | Low cost | Long time period | Hydrocarbons |
| Engineered intervention | Breakdown of contaminants by indigenous microbial community with human help | Low cost | Employ technology to control environmental | Hydrocarbons |
| | | Shorter time period | factors | |
| Phytoremediation | Uptake of the contaminant by the plant | Low cost | Shallow Surface | Hydrocarbons |
| | Biodegradation by microorganisms colonising the | Low intensive management | Leaching | |
| | roots or the soil immediately next to the root | requirement | Oxygen demand | |
| **Ex Situ** | | | | |
| Land Farming | Solid phase treatment system | Low in cost | Large area | Surface application |
| | | Large volumes treated | Evaporation | Aerobic process |
| | | Simple to design | Climatic factors | |
| | | | Leaching | |
| Biopiles | Excavation and stacking | Low in cost | Space requirement | Petroleum hydrocarb |
| | | Simple to design | Volatilisation | Pesticides |
| | | Less area | | PAH |
| | | Closed system | | Sewage sludge |
| Bioreactors | Contaminated material maintained in suspension | Rapid degradation | Excavation and transport | Non-halogenated VO |
| | Filtration method | Effective for most hydrocarbons | Cost | Pesticides |

# Comparative toxicity methods used for ecological assessments of contaminated soil

| Toxicity methods | Background | Advantages | Disadvantages |
|---|---|---|---|
| Microbial Assays | Several microbial assays such as bacteria, fungi, algae and protozoa have been developed for soil toxicity assessments. Measurements of respiration, growth inhibition, cell viability, $CO_2$ production, enzyme biosynthesis and the inhibition of bioluminescence are the common. Among these wide varieties of end-points, the most extensive test used is the inhibition of bioluminescence. Vibrio fischeri, Escherichia coli and Pseudomonas putida are the most microbial species used for toxicity tests approaches. | 1. Simple, sensitive, rapid and cost-effective.<br>2. Large number of independent organisms can be tested in a short period.<br>3. Bacterial toxicity tests can measure a wide range of endpoints (e.g. population growth and $CO_2$ production).<br>4. Gene-based bacterial assay have been developed for specific detection of a range of pollutants.<br>5. Only a small amount of sample is required. | 1. Using the Microtox (Vibrio fischeri) toxicity test for terrestrial environment samples is not always successful (sensitive to both pH and somatic conditions).<br>2. Only a small amount of the test sample can be assessed (microbial data obtained from this test will be significantly affected by the heterogeneous distribution of contaminants).<br>3. The laboratory conditions are different from the field conditions which may affect their sensitivity to contaminants. |
| Soil fauna assay | A large range of toxicity assays using soil invertebrates (e.g. protozoa, collembola, nematodes, arthropods and earthworms) has been used in soil toxicity assays. Most of these methods are poorly described. The only existing standard techniques are for Collembola and earthworms. The most common earthworms species used for toxicity assay are Eisenia fetida and Eisenia andrei. | 1. Simple method<br>2. Their size and mobility in soil reduces problems associated with the spatial heterogeneity.<br>3. Field surveys of invertebrate community structure can be utilised as a rapid method to map pollutant effects.<br>4. Soil fauna exposed to soil contaminants by different intake routes (dermal contact, direct ingestion of soil and through food chain transfers, which contribute to an overall exposure.<br>5. Some soil animal species (e.g. isopods) are easily cultured in laboratories. | 1. The sensitivity of soil fauna to contaminants differs from one species to another.<br>2. Many soil physiochemical parameters can influence the soil faunal community composition and interpretation is therefore complex.<br>3. The long life cycle (1-3 years) of some species such as isopod can be a constraint in using them in toxicity assay.<br>4. The laboratory conditions are different from the field conditions which may affect their sensitivity to contaminants |
| Plant assay | The common areas of interest in studies on plant toxicity assays are the seed germination, root elongation and plant growth. Plant respiration, enzyme activities and photosynthesis can be also used in studies on phytotoxicity | 1. The root system usually extends though representative volumes of test soil (providing a degree of integration in terms of the inherent spatial heterogeneity.<br>2. Plant tests are cost-effective.<br>3. Plant assays are relatively easy to perform. | 1. The plant assay requires a large sample volume.<br>2. More experience and a good knowledge are needed when using plant bioindicators for assessments of contaminants.<br>3. Many soil physiochemical factors can limit the use of field surveys of vegetation communities.<br>4. The laboratory conditions are different from the field conditions which may affect their sensitivity to contaminants.<br>5. Time consuming. |

# Chapter Two

# Chapter Three

# Chapter Three Findings

- Routine chemical and biological parameters were measured throughout the twelve week study.
- Findings:
  - Consider spatial variation
  - Crude oil best predicted at T=0
  - Prediction becomes poorer with time
  - Yeast biosensor in not good
  - Mean values need to be interpreted in the context

# Chapter Four

# Chapter Four: Findings

- A similar integrated approach (Ch.3) to assess the bioremediation potential of historically contaminated soils from Kuwait
- Removing physical constraints optimised microbial performance
- HC used were heavy and unrefined
  - Recalcitrant to bioremediation
- Crude oil is hard to analyse and quantify
- Both extractions used were removing the same pool of semi liable HC

# Chapter Four Findings (CONT)

- Respiration is a key indicator of likely HC degradation
  - Also a measure of biomass
  - Not useful here, as experimental design and wide range of samples selected
- Heavy HC breaks down to more bioavailable fractions
- Predictive equation also became less fit with time

# Chapter Five

# Chapter Five: Findings

- Solvents recovery deemed to be poor (hexane, and DCM / acetone)
- Lighter fractions reduced with time, while heavier fractions had lower extractability with time
- Rate of degradation is misleading
- Assays gave different responses
  - Earthworms were too sensitive as an indicator of soil ecotoxicity, whilst seed germination and microbial biosensors revealed that toxicity declined with biodegradation
- Long time points
- Degradation was happening
- Crude oil is a real problem for chemical analysis
- Heavy HC = more toxic

# Chapter Six

<u>6.0 When is a Soil Remediated? Comparison of Biopiled and Windrowed Soils Contaminated With Bunker-Fuel in a Full-Scale Trial</u>

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- 6.3.9 Risk Assessment Derived Remedial Targets

6.5 Discussion

6.6 Conclusion

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# Chapter Six Findings

- End-point clean-up targets were defined by human risk assessment and ecotoxicological hazard assessment approaches
- Findings
  - Active management enhances bioremediation
  - Nutrient additions and inocula accelerated the degradation
  - Microbial and chemical measurements increase the understanding of field bioremediation
  - End points need to be receptor defined
  - More comparative studies

# Chapter Seven

# Chapter Seven Final Discussion

- The aims of the thesis were:
  - To understand the factors that determines successful remediation of crude and heavy oils.
  - To assess relative change in hazard and toxicity as remediation progresses
  - To assess the key measured parameters to enable effective remediation
  - To integrate the findings, where possible, to predictive assessment of remediation in a target defined context
- All of these aims were to be developed in the context of Kuwait
  - The aspects of hydrocarbon bioavailability especially in a climate such as Kuwait
  - The microbial communities and their activity and performance in the relatively carbon starved soils of the Gulf States

# Recommendation for Future Work

- To evaluate the concentration and toxicity of aged crude oils in desert
- To study the spatial variability of hydrocarbon concentrations across a zone
- To evaluate the susceptibility of different hydrocarbon distillates to biodegradation in soils.
- To monitor the relative ecotoxicity of these distillates during the remediation campaign and to evaluate if a suitable end-points
- To appraise the relative merits and shortcomings of selected ecotoxicity assays in their application to soils contaminated with crude oils.
- To develop a field-scale trial of onsite ex situ bioremediation and to monitor changes in ecotoxicity and hydrocarbon concentrations as a function of remediation timescale.
- To relate the degradation and changes in ecotoxicological measurements associated with heavily weathered refined oils to crude oils.
- To consider the relative merits of risk and hazard assessment in the adoption of remediation campaigns

# Any Questions ?