IMPROVEMENTS IN THE BIOTREATMENT OF SOIL CONTAMINATED BY HEAVY HYDROCARBONS

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ENVIRONMENTAL SERVICES INC.

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Outlook of the presentation

I. Background

II. Objectives

III. Soils treated

IV. Results, R&D and full-scale

V. Field snapshots

VI. General findings

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Background

- Difficulty for biotreatment in soil to deal with:
  - Heavy weathered petroleum hydrocarbons
  - Fine grained soils (silt and clay)
- Prior work of Sanexen and of others
- Requirements of two site owners in Montreal (FIPM and Imperial Oil)
- Research with the MCEBR (Montreal Center of Excellence for Brownfield Remediation)

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Background

- Desire of the FIPM Trust to deal with the site in a socially and environmentally responsible manner

  (FIPM or *Fiducie des Installations Pétrochimiques de Montréal*, is responsible for the property of the former Gulf/Kemtech refinery)

- Involvement of the MCEBR (Montreal Centre of Excellence for Brownfield Remediation) to develop state of the art environmental solutions.

- Selection of Sanexen as the organization with the best price and best performance warranty to perform the required decontamination

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Objectives

- Improve the performance of biotreatment of soil contaminated with heavy petroleum hydrocarbons
- Reduce soil biotreatment costs by 30%
- Improve knowledge and understanding for this type of treatment
- Better identify constraints and optimal strategies in view of these constraints

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Specific objectives

- Improve the microbial flora (quantity and effectiveness)
- Attain a favorable soil temperature at a low cost
- Identify the best amendments for bulking of soil and increased bio-availability of the contaminants
- Identify optimal mechanical handling of the soil
- Does our frame of thinking make sense?

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Soils treated

- Backfill and native silty-clay soil at the site of the decommissioned fluidized catalytic cracking unit (FCCU) of the Gulf refinery in Montreal-East (new PTT Shell site) (35,000 metric tonnes)
- Backfill and native blue clay soil at the former Texaco refinery in Montreal-East in the area of the visbreaking unit (120,000 metric tonnes)

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Soil at the FIPM (formerly Gulf) site

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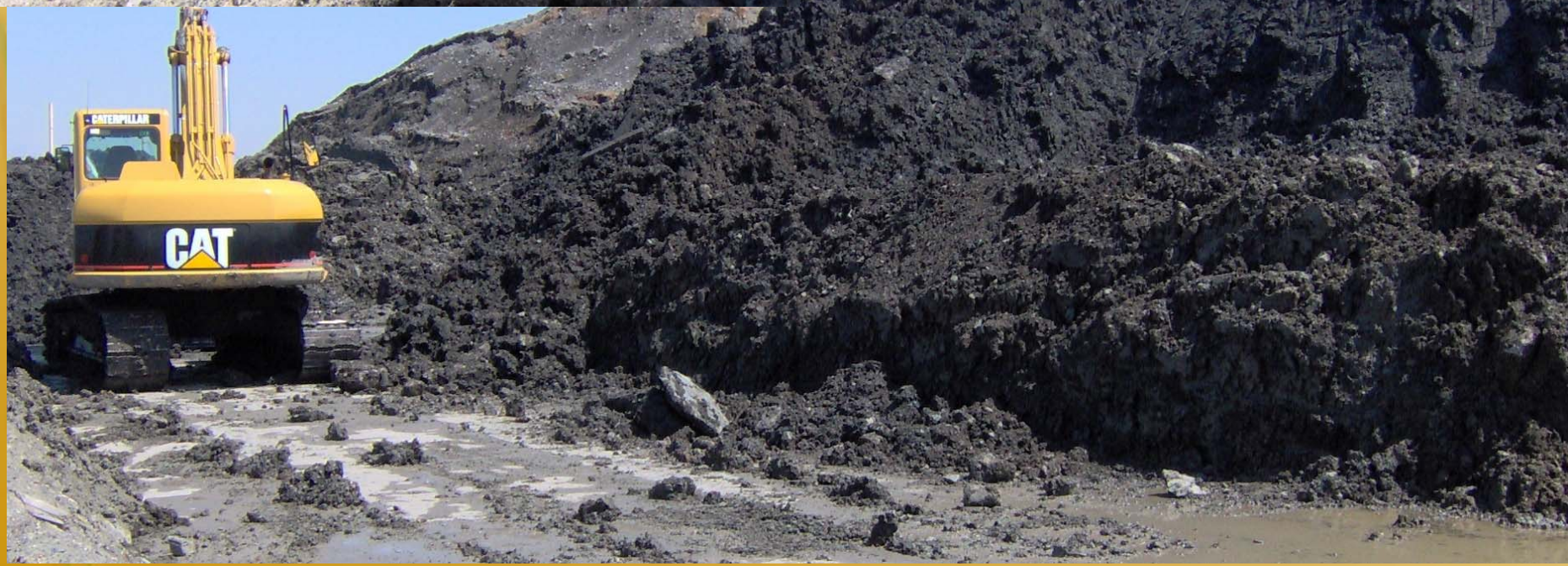

Soil at the Imperial Oil site (formerly Texaco)

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R&D carried out

- Compare alternative/supplemental treatment methods with a standard method of biotreatment (pilot and full-scale)
- Verify respirometry, toxicity and contaminant mineralization in the laboratory
- Monitor respirometry, temperatures and contaminant degradation in the field

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Standard method of biotreatment

- Condition the soil through mechanical mixing with additives to:
  - obtain an optimum water content
  - insure there are enough bio-available N-P-K
  - bulk the soil with a biomass amendment
  - provide heat (10-25 ^{o}C > ambient) through aerobic activity
  - adjust the pH for optimal PAH degradation
- Forced aeration in biopiles with repeated conditioning of the soil as needed

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Alternative/supplemental methods tested

- Closed loop recirculation of oxygen with production of ozone for chemical oxidation
- Bioaugmentation
- Use of surfactants
- Alternative/supplemental biomass amendments
- Addition of easily degradable substrates for population increase and production of heat
- Cycling of aerobic/anaerobic conditions

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Initial investigation by the MCEBR

- Mandate from PIPM to identify the best biotechnologies and proponents to treat contaminated soil removed for construction of the PTT plant.
- Call for proposals and pilot testing by qualified proponents.
- Pilot tests – Autumn and winter of 2003
- Establishment of site specific clean-up criteria based on the best results: - 1300-1500 mg/kg TPH (C_{10}-C_{50})
  - criteria B (residential) for PAH's
- Selection of three proponents/bidders

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Pilot test carried out by Sanexen

- Collection of 10 metric tonnes of soil from the site and testing (MCEBR and Sanexen)
- Conditioning of the soil as per Sanexen's standard method of biotreatment (slide 11)
- Placement of soil into two sealed containers with recirculation of air and oxygen addition as needed
- Reconditioning of soil and continued biotreatment in test A
- Reconditioning of soil and continued treatment with recirculation of O_2 and ozone in test B
- After a total of four months of treatment (2 + 2), sampling and testing of the soil (MCEBR and Sanexen)

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Results of the pilot test

(average concentrations)

- Initial concentrations:

  Petroleum hydrocarbons (C_{10}-C_{50}): 3500 mg/kg

  PAHs (80% methyl,dm and tm naphtalenes) 74 mg/kg

- Concentrations after initial biotreatment

  Petroleum hydrocarbons (C_{10}-C_{50}): 2450 mg/kg

  PAHs 3,1 mg/kg

- Final concentrations

	Test A (bio)	Test B (bio + O_3)
C_{10}-C_{50}	1400	1730
PAHs	2,8	4,4

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Soil treatment at the FIPM site

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Pilot testing of various amendments

- Thirty (30) m^3 of soil was conditioned in the standard method for this site.
- Nine (9) piles of 3 m^3, each with a passive aeration system, were prepared with different amendments.
- Amendments (microbial consortia, surfactants, composts, growth substrates, bulking agents).
- Treatment over a period of one year.
- Concentrations decreased from 2000 to 1100 mg/kg on average.
- No recipe yielded a significant benefit over the control.

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Conditioned soil

Connections to the air treatment system

Biofilters and an adsorption filter for the treatment of air

Blower to circulate air and increase temperature above the dew point

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Sludge box and bioreactor for seeding of soil

Biomass amendment for bulking of soil

Soil after conditioning with amendments and mechanical mixing

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Bulk solution of 11% ethanol

Pumping to well points in the biopile

Monitoring of quantity added

Testing for O_2, CO_2, CH_4 and temperature

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Laboratory biotreatability testing

- As part of the research program with MCEBR, soils that received different amendments were tested at BRI for their ability to degrade added hexadecane and naphtalene
- Tests performed over a period of 28 to 39 days on microcosms with 20 g of soil
- There was an abundant microbial population in all soils (2-7 x 10^7 CFU/g)
- No recipe appeared to provide an advantage at this scale over the untreated soil

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Cycling of air circulation in sections of a biopile to induce occasional anoxic conditions

Automated valve

Well points for gas and T monitoring

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Reconditioning of soil in November 2005

Soil at 25 °C vs ambient T of – 5 °C

Operation throughout the winter of 2005-2006

Monitoring of air drawn from the soil

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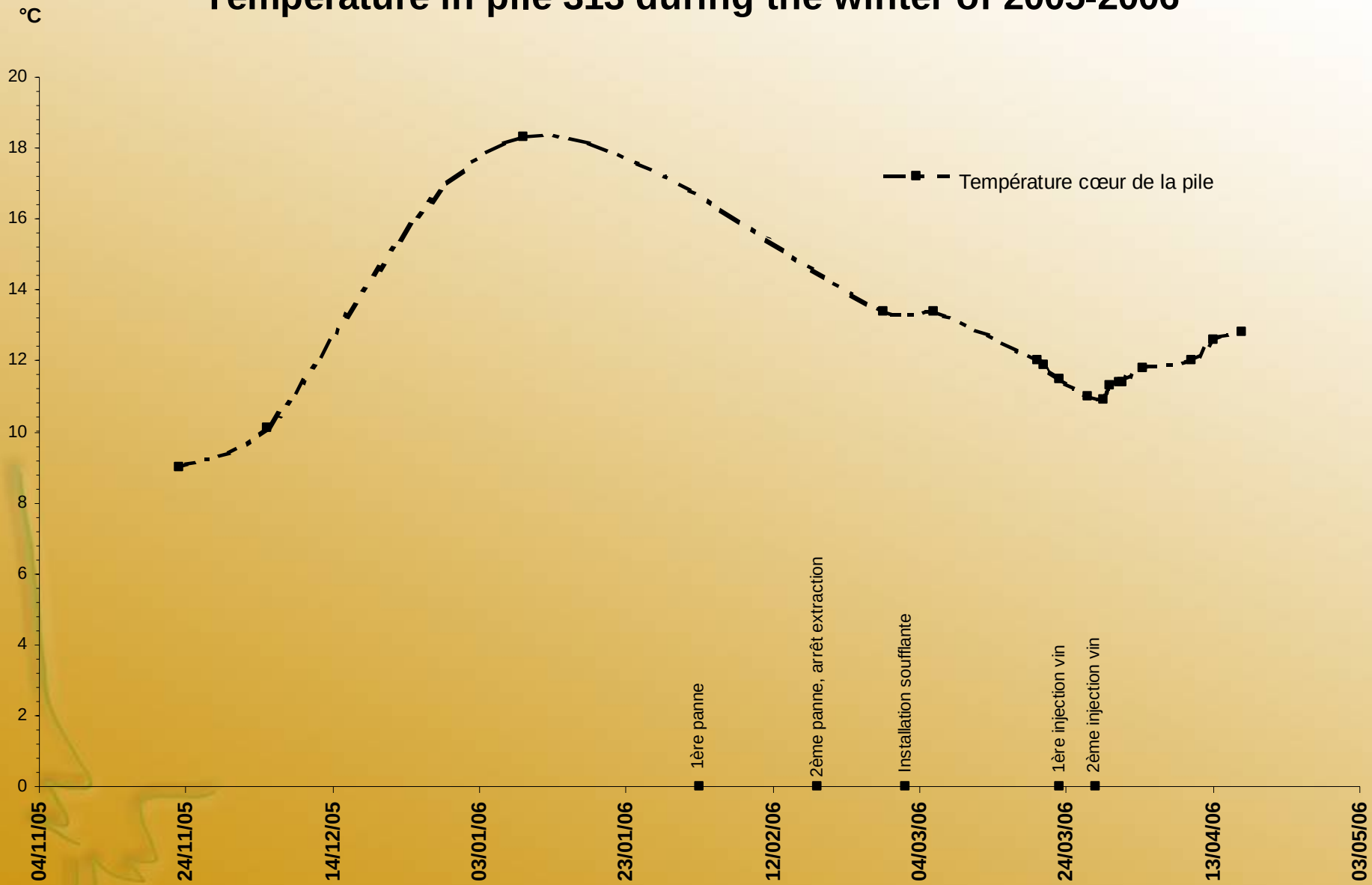
Temperature in pile 313 during the winter of 2005-2006



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Overall results of the treatment of the 20 000 m^3 of soil

Parameter	Initial soils (mg/kg)	Treated soils (mg/kg)	% elimination
PH (C_{10}-C_{50})	**2910**	**1033**	64,5
PAH's	**58,5**	**2,6**	95,6

Note: The concentrations of PH (C_{10}-C_{50}) and of PAH's continued to decrease below these treated soil concentrations after placement of the soils in the K1 and K8 berms

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Loading of treated soil

Delivery of the soil at the K-1 site for construction of a berm for a visual barrier

Profiling of the berm

Addition of a top soil

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Trees for revegetation

K-1 berm along the Metropolitain highway

K-8 berm along a brownfield site

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Toxicity testing

- As part of the research project with MCEBR, soil at various stages of the treatment was sampled and tested by the Biotechnology Research Institute (BRI) of the NRC.
- **Soil sampled and tested**

Untreated soil	314
Soil from piles 311 & 313	311-313
Soil with ethanol addition	313v
Soil with more bulking agent	313f
Treated soil in K1 berm	K1
Treated soil in K8 berm	K8
Background (soil out of site)	316

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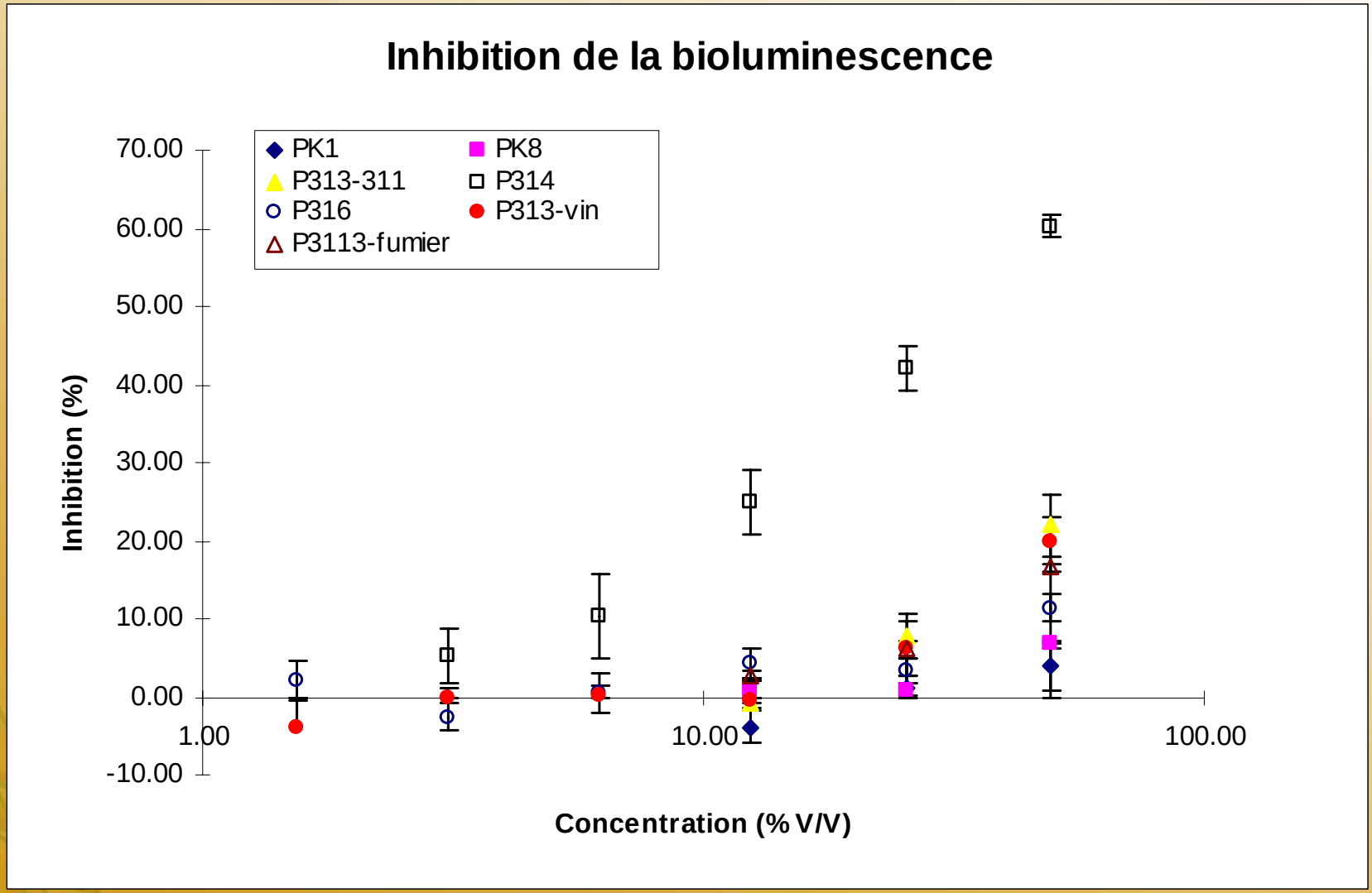
Toxicity of the soils on the bacteria Vibrio fischeri



The percentage of inhibition is calculated in reference to a salt water sample.
The average values with the errors for 3 replicates are presented.

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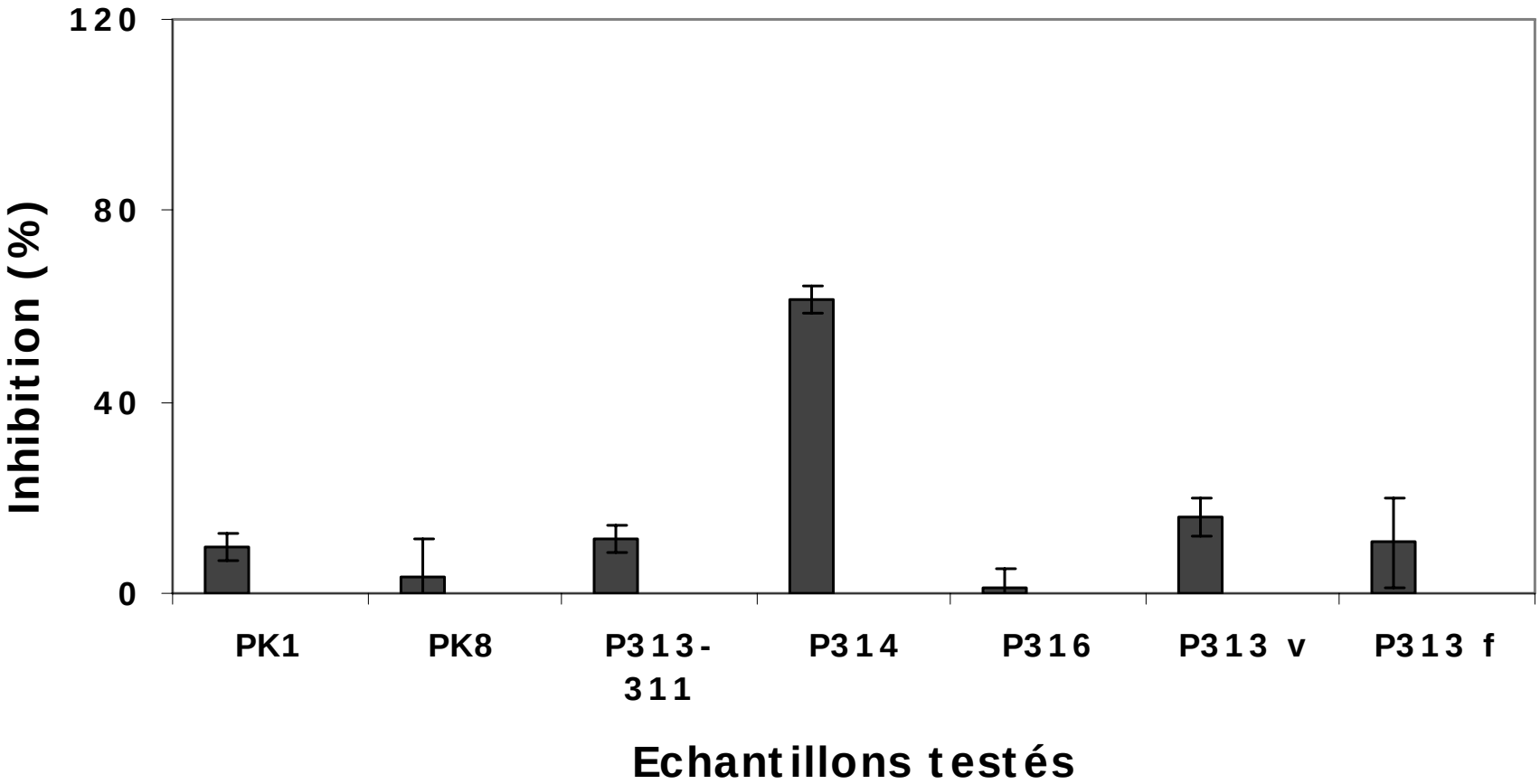
Toxicity of the soils on the germination of lettuce



Percentage of inhibition calculated with respect to a reference (commercial silica)
Average values with typical errors for 3 replicates are presented

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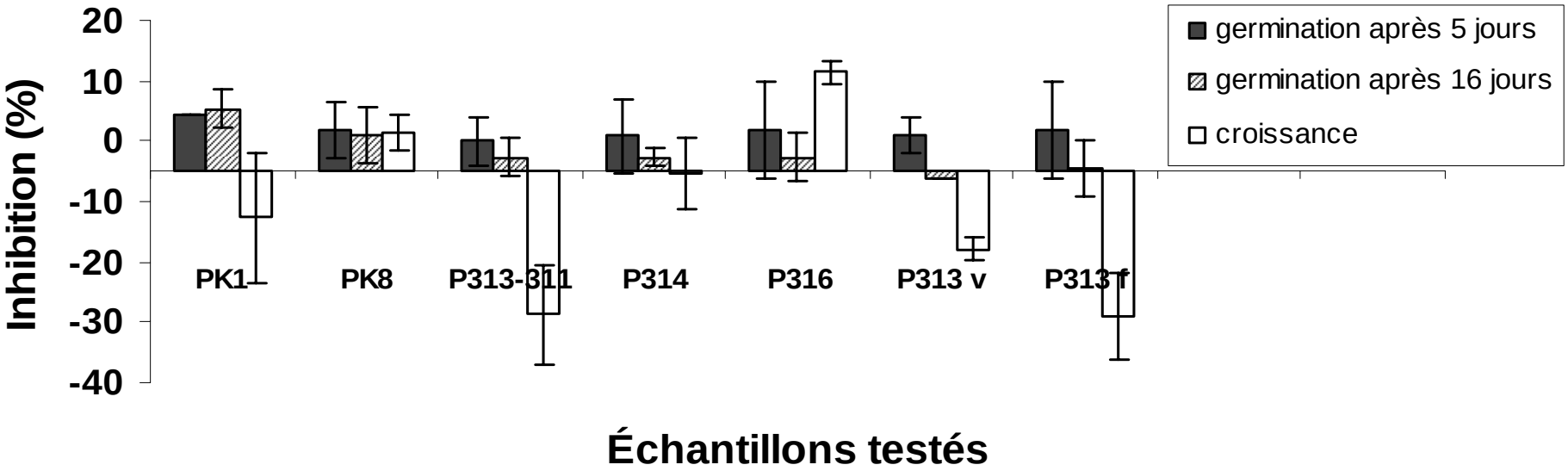
Toxicity of the soils on the germination and growth of barley



Percentage of inhibition calculated with respect to a reference (silica sand)
Average values with typical errors for 3 replicates are presented

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Aerial view of the MFI Imperial Oil site in Montreal

Processing of 120,000 metric tonnes of soil now undergoing at the site

A look at the soil slated for biotreatment

Close-up on the clayey soil

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Visiting Canada geese

A bioreactor is used to grow an indigenous microbial population

Daily bug food

Aeration and mixing

The foam indicates when a batch is ready

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Pumping of the fluid to the soil

Application of the solution to the soil

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Segregation and loading

Transportation to the conditioning pad

Cellulosic amendment to improve the structure of the soil

Treated soil returned to the site

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Results

- Increase of approximately 10 fold on average in microbial population after soil conditioning.
- Average rates of mineralization of 46 mg/kg C_{10}-C_{50} -day at an average C_{10}-C_{50} concentration of 4000 mg/kg and at an average temperature of 25 ^{o}C, based on 80 samples.
- Soil treated and declassified at a lower cost and more quickly with the amendments and the addition of indigenous microorganisms used

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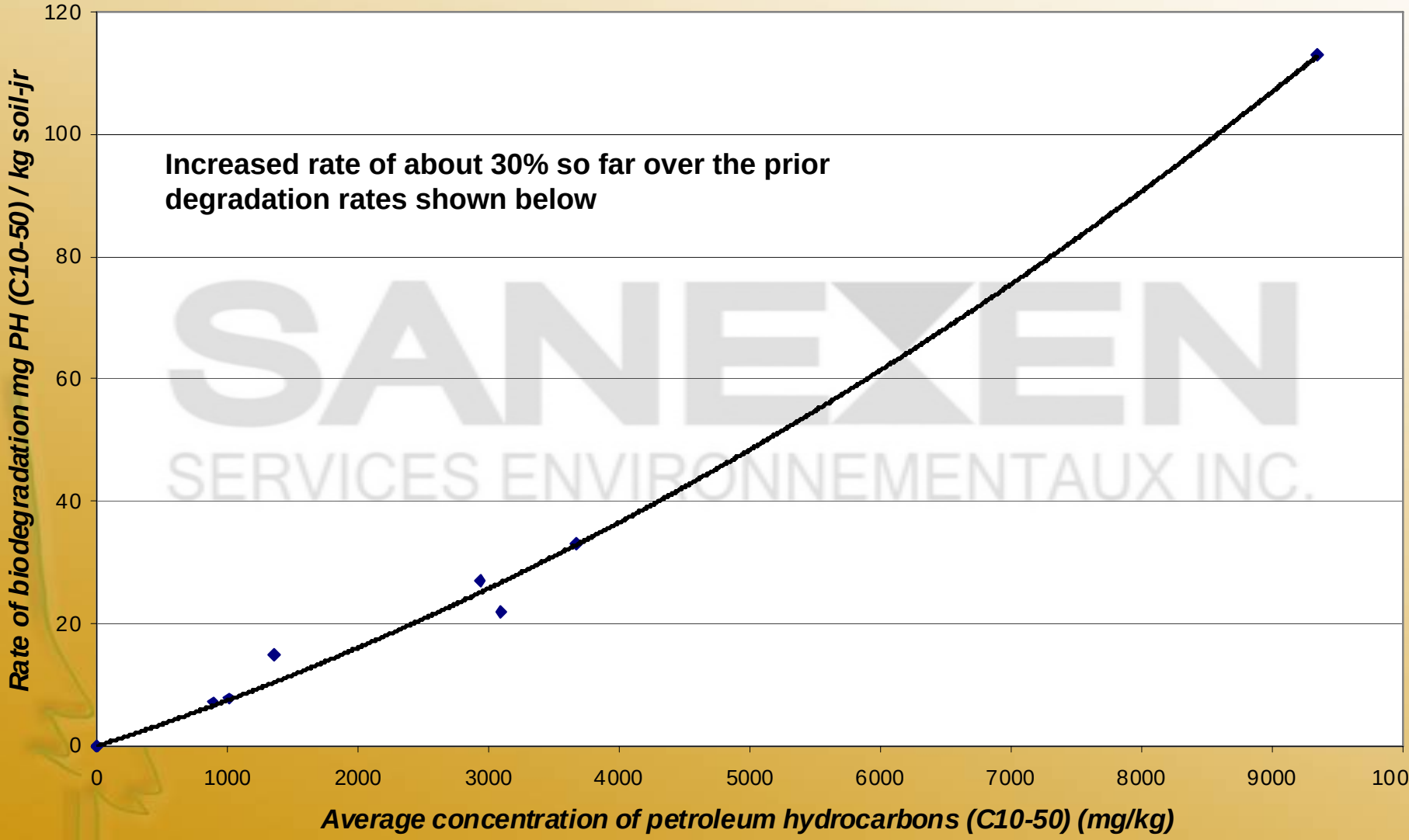
Rate of biodegradation of petroleum hydrocarbons (C10-50) in soils in function of contamination levels for diesel and heavier products



RD04-057 / Biodegradation.xls

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Findings on the methods tested to improve biotreatment results

• Use of ozone	No benefit*
• Exogenous consortia (bio-augmentation)	No benefit
• Surfactants	No benefit*
• Cycling of aerobic/anoxic conditions	No benefit
• Use of a growth substrate	No benefit*
• Use of biomass bulking agents	Beneficial
• Generation of heat	Beneficial
• Bioreactor for population increase	Beneficial

*under the conditions tested

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Conclusions

- The biotreatment of heavy hydrocarbons in fine grained soils is not a lost cause
- The techniques used allowed to reduce biotreatment costs by approximately 25%
- Petroleum hydrocarbon concentrations do not tell the whole story
- Research is continuing to gather more data

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Special thanks to

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CEMRS

(the Montreal Center of Excellence for Brownfield Remediation)

Imperial Oil

The Biotechnology Research Institute
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Questions?

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