



BIOREMEDIATION OF CRUDE OIL & A CASE STUDY



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OUTLINE

- Petroleum Hydrocarbon
- TPH (Total Petroleum Hydrocarbon) Analysis
- Treatment Methods
 - Bioremediation
 - Oil Gator[®]
- A Case Study
- Conclusion

Petroleum Hydrocarbons

Crude oil contains a complex mixture of compounds, mainly hydrocarbons. The major constituents of crude oil are grouped into four major classes:

- the saturated compounds,
- the aromatics,
- the resins, and
- the asphaltenes.

Total petroleum hydrocarbons (TPH)

- Total petroleum hydrocarbons (TPH) is a term used to describe a large family of several hundred chemical compounds that originally come from crude oil.
- There are so many different chemicals in crude oil and in other petroleum products, it is not practical to measure each one separately. However, it is useful to measure the total amount of TPH at a site.
- Some chemicals found in TPH are hexane, jet fuels, mineral oils, benzene, toluene, xylenes, naphthalene, fluorene and etc

TPH ANALYSIS

- EPA Method 4 18.1

- ✓ it does not provide information on the composition
- ✓ depends on the ability of the solvent used to extract the hydrocarbon from the environmental media and the absorption of infrared (IR) light by the hydrocarbons in the solvent extract.
- ✓ is not specific to hydrocarbons and does not always indicate petroleum contamination.

- EPA Method 8015 Modified

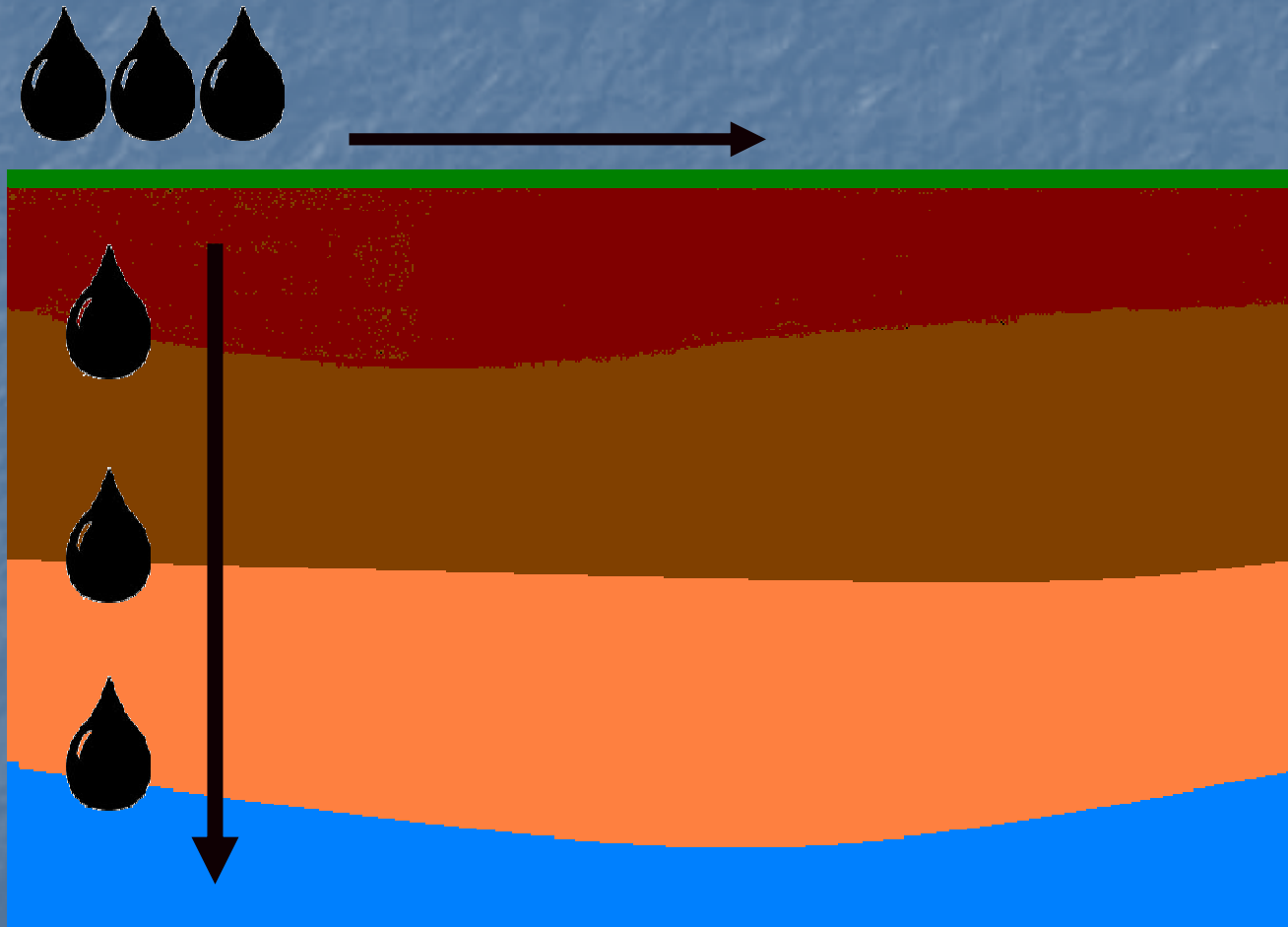
- ✓ reports the concentration of purgeable and extractable hydrocarbons; these are sometimes referred to as gasoline and diesel range organics.

Soil & Petroleum

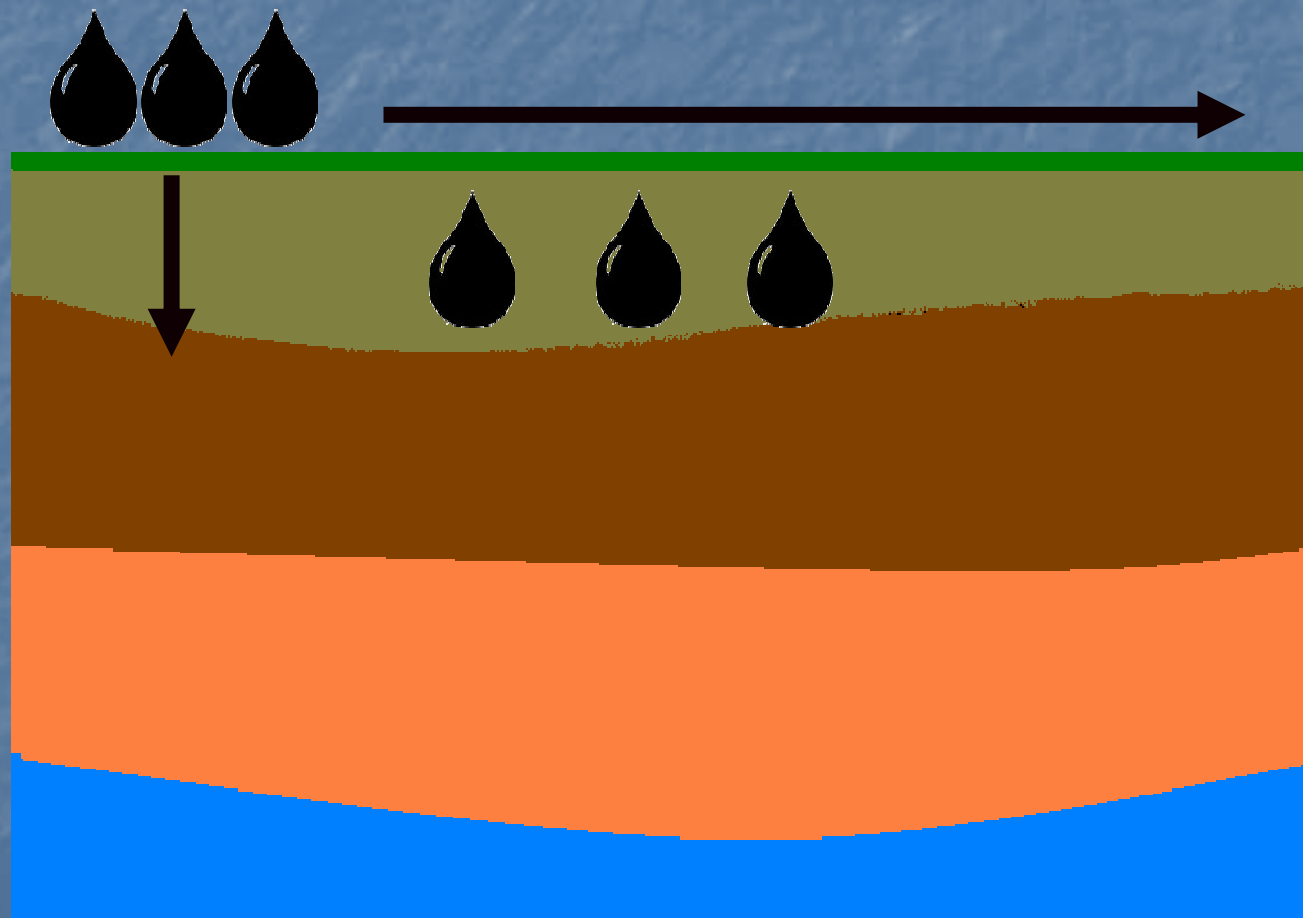
- Destroy plants on the soil
- Groundwater pollution
- Destroy ecological balance



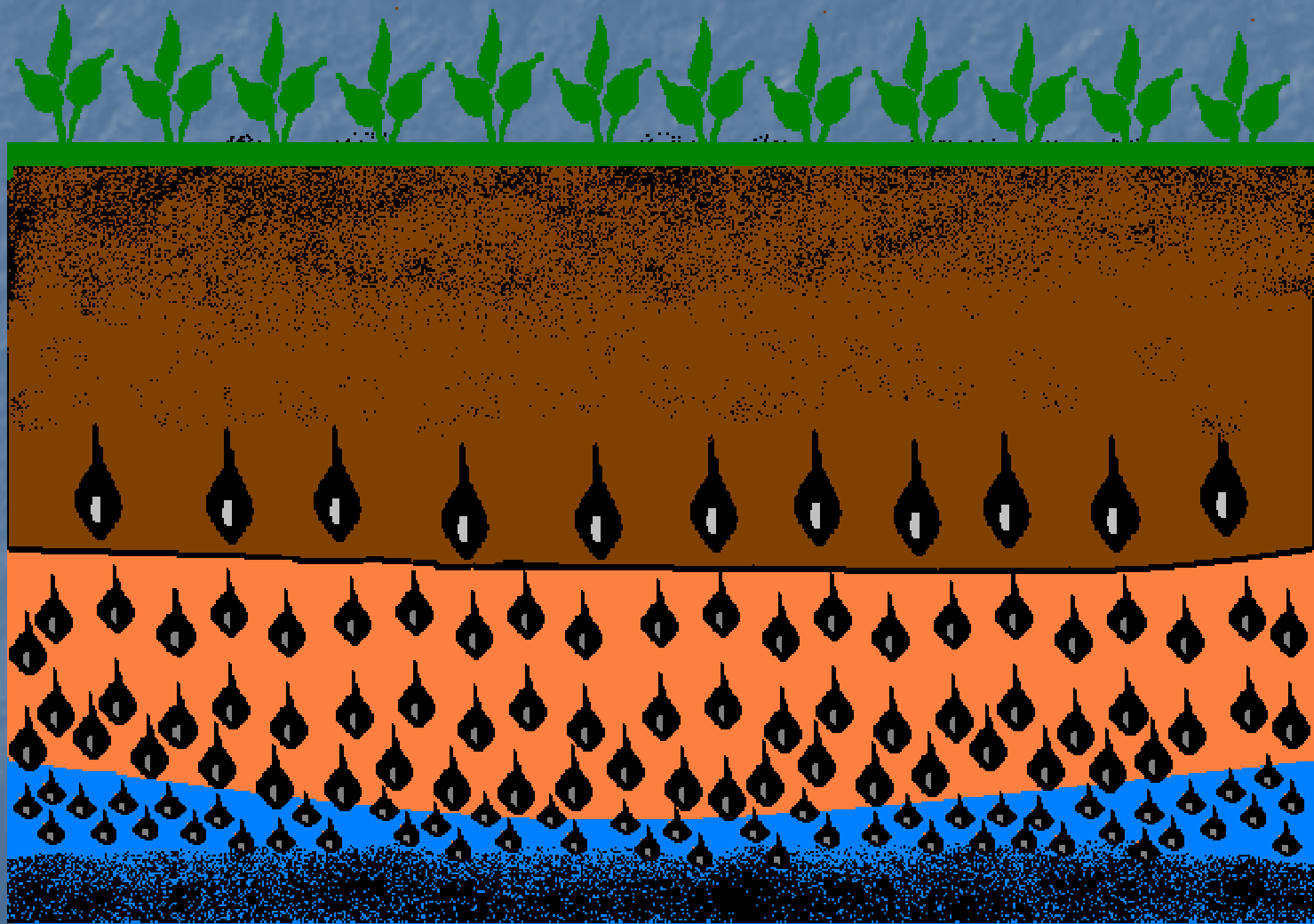
Petroleum spreading in permeable soil



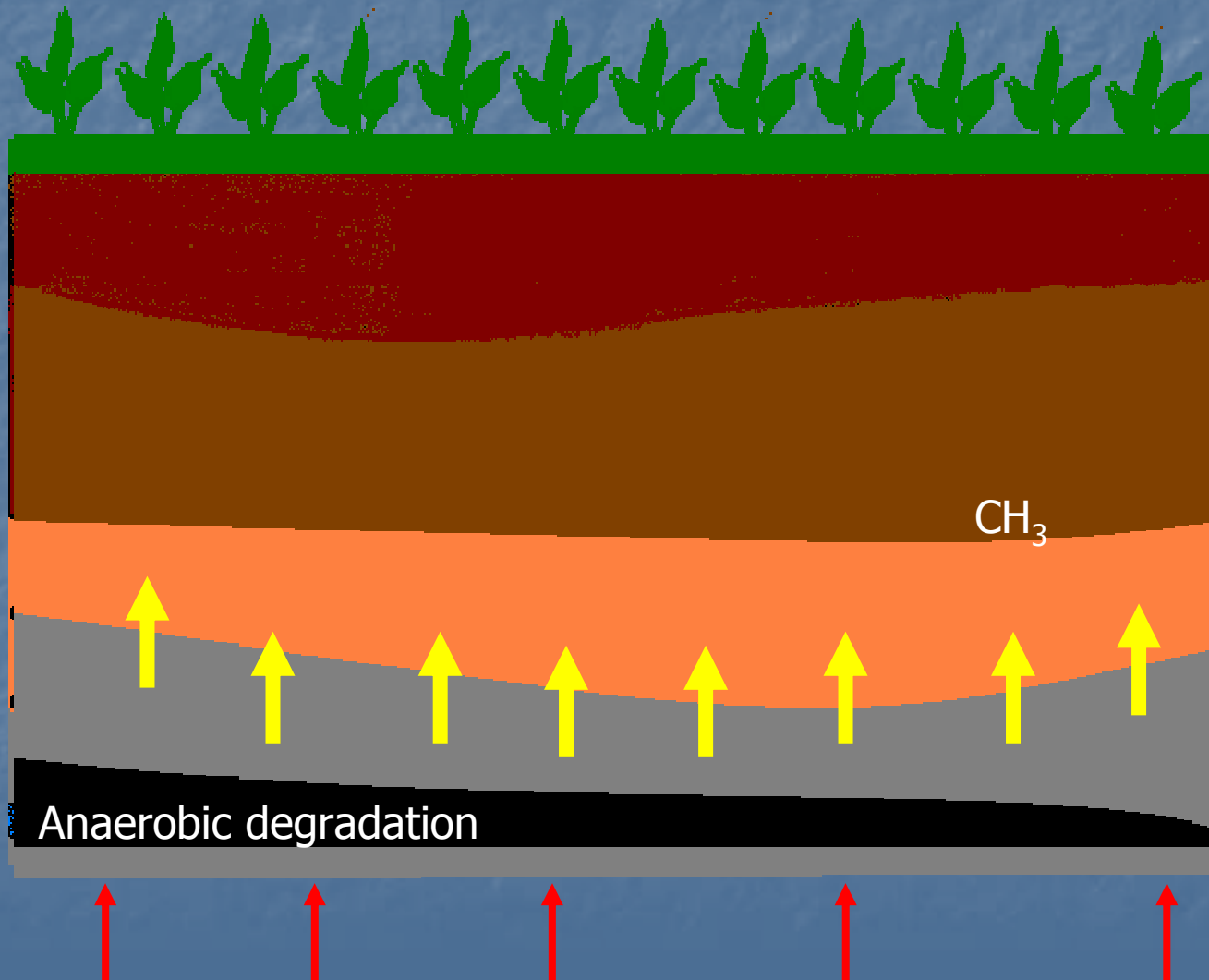
Petroleum spreading in impermeable soil



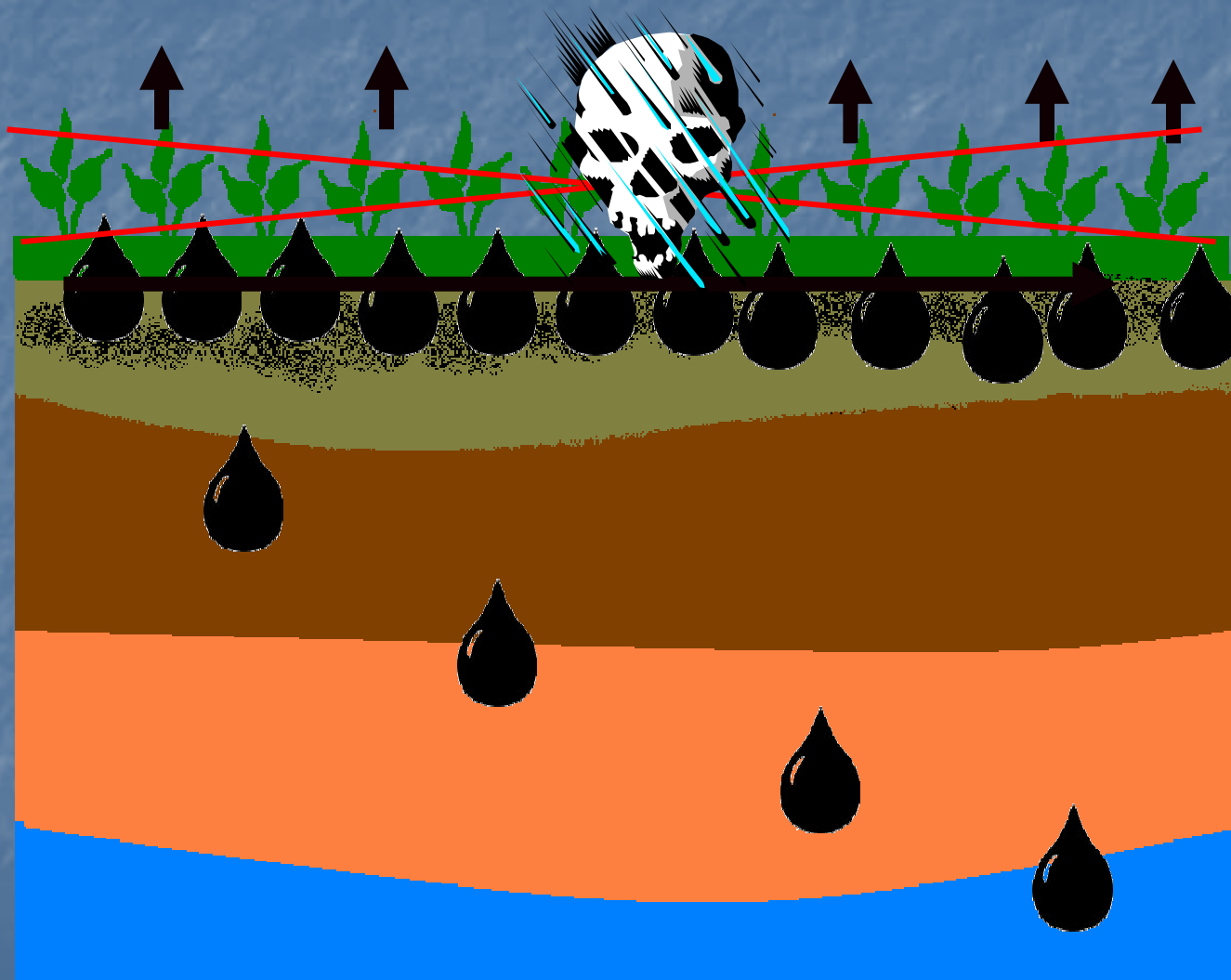
Petroleum spreading in permeable soil



Petroleum spreading in permeable soil



Petroleum spreading in impermeable soil



Health Effects of PH Compounds

- affect central nervous system
 - ✓ nerve disorder called "peripheral neuropathy";
- effects on the blood, immune system, lungs, skin, and eyes;
- reproduction and the developing fetus in animals.

Treatment Methods of TPH

Petroleum-contaminated soil is treated using three processes:

- Physical (landfill, incineration, thermal treatment)
- Chemical (chemical oxidants), and
- Biological (bioremediation, phytoremediation, soil washing with biosurfactants).

Physical Treatment Methods

- disposal in a landfill, and
- incineration
- thermal treatment (thermal desorption)
 - expensive.
 - Incineration is also a source of air pollution
 - Thermal desorption involves heating soil to 250-700°F . Thermal treatment differs from incineration because there is no combustion of the soil.

Chemical Treatment Methods

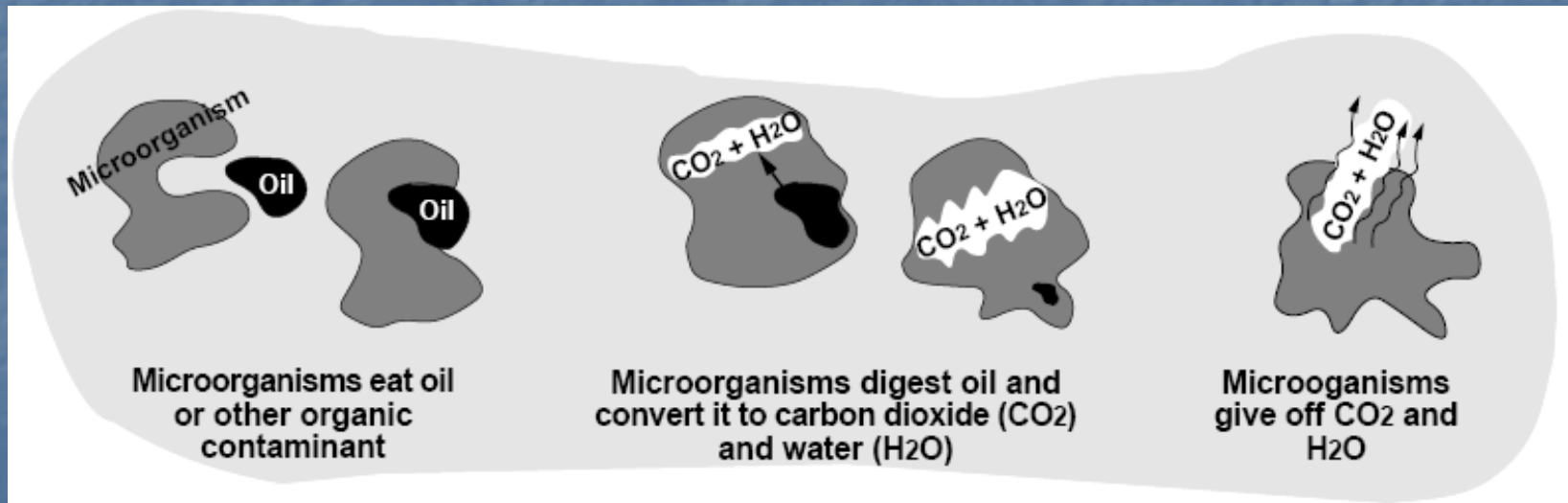
- Chemical treatment includes direct injection of chemical oxidants into contaminated soil and groundwater.
- Altering native chemistry.
 - ✓ Hydrogen peroxide -this process delivers oxygen to stimulate the activity of naturally occurring microorganisms by circulating hydrogen peroxide through contaminated soil to speed the natural biodegradation of organic contaminants.

Biological Treatment Methods

- bioremediation
- phytoremediation,
- soil washing with biosurfactants

BIOREMEDIATION

Bioremediation is a treatment process that uses naturally occurring microorganisms (yeast, fungi, or bacteria) to break down, or degrade, hazardous substances into less toxic or nontoxic substances. The microorganisms break down the organic contaminants into harmless products- mainly carbon dioxide and water.



BIOREMEDIATION^(con't)

The specific bioremediation technology used is determined by

- The type of the microorganisms
- The site conditions
- The quality and the toxicity of the compounds

BIOREMEDIATION^(con't)

Bioremediation applications fall into two broad categories:

- ***in situ***-treats the contaminated soil or groundwater in the location in which it was found.
- ***ex situ*** - require excavation of contaminated soil or pumping of groundwater before they can be treated

BIOREMEDIATION^(con't)

In Situ Bioremediation

- *Bioaugmentation* involves the introduction of microorganisms that have been cultured to degrade various chains of hydrocarbons into a contaminated system.
- *Biostimulation* introduces additional nutrients in the form of organic and/or inorganic fertilizers into a contaminated system, which increases the population of the indigenous microorganisms. Various nutrient sources such as inorganic fertilizer, urea, sawdust, compost, manure, and biosolids have been used in biostimulation
- *Bioventing* systems deliver air from the atmosphere into the soil above the water table through injection wells placed in the ground where the contaminants exist.

BIOREMEDIATION(con't)

Ex Situ Bioremediation

- *Slurry-phase bioremediation*-Contaminated soil is combined with water and other additives in a large tank called a "bioreactor" and mixed to keep the microorganisms in contact with the contaminants in the soil.
- *Solid-phase bioremediation*-is a process that treats soils in above-ground treatment areas equipped with collection systems to prevent any contaminant from escaping the treatment. Solid-phase soil treatment processes include
 - ✓ *Landfarming*- contaminated soils are excavated and spread on a pad with a built-in system to collect any "leachate" or contaminated liquids that seep out of contaminant-soaked soil.
 - ✓ *Biopiles*-Contaminated soil is piled in heaps several meters high over an air distribution system.
 - ✓ *Composting*- Biodegradable waste is mixed with a bulking agent such as straw, hay, or corn cobs to make it easier to deliver the optimum levels of air and water to the microorganisms. Three common designs are *static pile composting*, *mechanically agitated in-vessel composting*, and *windrow composting*.

BIOREMEDIATION^(con't)

The advantages of in-situ bioremediation

- ✓ the contaminated soils do not require excavation and treatment before or sometimes after
- ✓ less expensive
- ✓ the process creates less dust
- ✓ there is less volatilization of contaminants
- ✓ it is possible to treat a large volume of soil at once
- ✓ are most effective at sites with permeable (sandy or uncompacted soil)
- ✓ can be used to considerable depths

BIOREMEDIATION^(con't)

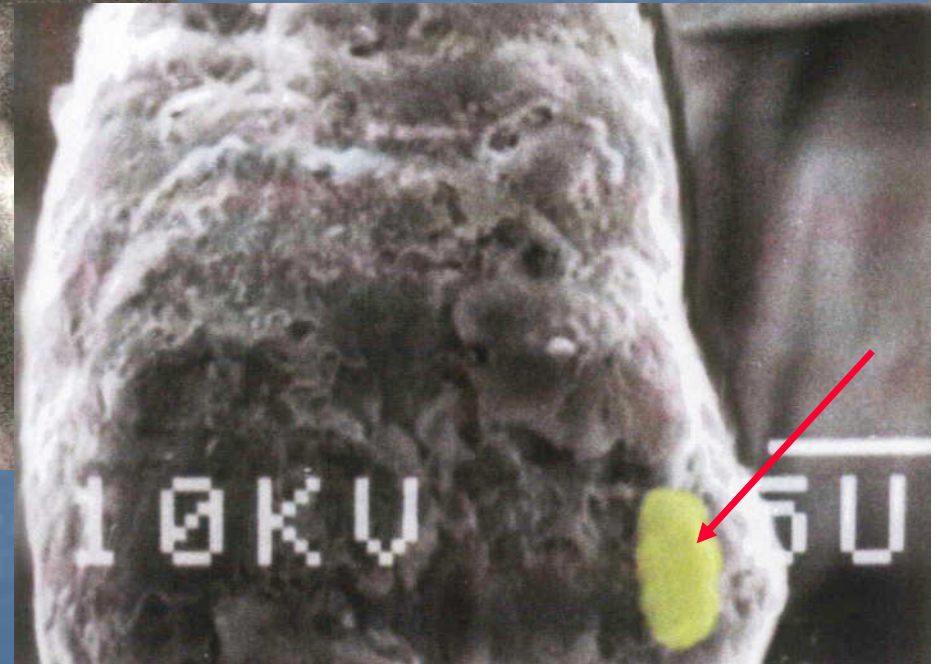
The advantages of ex-situ bioremediation

- ✓ the rate of bioremediation is often significantly faster than in-situ
- ✓ the bioremediation process is easier to control
- ✓ can treat a wider range of contaminants and soil types
- ✓ are most effective at sites where the soil is impermeable (clays, compacted soils) and where there are highly layered subsurface environments (because oxygen can not be evenly distributed in-situ throughout the treatment area)
- ✓ they may be used as an intermediate step to reduce contaminant burden and so reduce landfill costs
- ✓ it is not necessary to know the precise nature and spatial distribution of the contamination
- ✓ contaminant distribution can be made relatively homogenous
- ✓ can more easily prevent the migration of gases and liquids off-site
- ✓ remediation progress can be more easily monitored

OIL GATOR®

- The primary product is based upon a biodegradable by-product of the cotton seed delinting process.
- Cotton seeds are acidified and scrubbed to remove their lint, prior to grading and packaging.
- The product contains 95% cellulose and 5% proprietary compounds – compounds which act as both nutrients and electron acceptors for the indigenous microorganisms.
- When treated, the cellulose lint also becomes an effective sorbent that preferentially absorbs hydrocarbons in the presence of water, and which supports the growth of naturally occurring, hydrocarbon-reducing bacterial forms. These groups of microorganisms rapidly degrade the sorbed hydrocarbons into simpler organic compounds, and eventually into carbon dioxide and water.

Bacteria in the Cellulose Fiber



OIL GATOR®(con't)

The results of the viable cell counts are approximated as follows:

- aerobic heterotrophic bacteria (can use any carbon source) 100,000 count/gram Oil Gator®
- anaerobic heterotrophic bacteria (can use any carbon source) 100 count/gram Oil Gator®
- petrophilic bacteria (petroleum degraders) 1000 count/gram Oil Gator®

OIL GATOR®(con't)

Features & Benefits

- In-situ or ex-situ treatment methods can be used
- Eliminates leachate problems (without the need for site liners), thereby protecting groundwaters and nearby inland and coastal waterways.
- Avoids nutrient overdosing with its associated eutrophication problems.
- Targets a variety of different hydrocarbon contaminants simultaneously.
- Can be used safely in urban settings, reducing the need for transportation of hazardous wastes
- Cost effective in terms of time, labour and financial outlay.
- Eliminates the need to landfill many forms of hydrocarbon contamination

OIL GATOR®(con't)

Bioremediation with Oil Gator®

- Oil Gator® contains the naturally occurring microorganisms and nutrients to degrade the absorbed hydrocarbons into simpler organic compounds, and eventually to carbon dioxide and water.
- To bioremediate, Oil Gator® requires no surfactants- thus problems with the leaching of toxic surfactants are eliminated. Oil Gator also does not require nitrogen or nutrient addition. These nutrients are encapsulated in the fibres of the Oil Gator®
- Oil Gator® contains a wide variety of aerobic and anaerobic micro-organisms which allows the remediation of a wide range of hydrocarbons, including compounds typically difficult to degrade, such as PAH's and PCB's.
- Oil Gator® can remediate the contaminant hydrocarbon in-situ (in-place) thus eliminating the need for digging up and landfilling contaminated soil, and eliminating the use of ex-situ "landfarming" where land space is at a premium.

OIL GATOR®(con't)

The sorption properties of Oil Gator® are based on its ability to draw the target liquid into the inside of its tube-shaped cellulose fibers. It is the capillary action of these fibers, which sorbs and encapsulates the liquid, and prevents leaching. The fibers appear to have a higher affinity for hydrocarbons (oils) than for aqueous solutions, possibly because the fibers originate from an oil-bearing plant. The sorption properties of the Oil Gator® fibers are thus dependent on the physical properties of the liquid being sorbed – particularly its viscosity.



OIL GATOR®(con't)

Acetone	Hexene
Acetonitrile	Isoamyl Acetate
Benzene*	Isobutanol
Bromodichloromethane	Isoprene
Bromoform (Tribromomethane)	Jet Fuels*
Bunker C Fuel Oil*	Kerosene*
Butanol(s)	Lube Oils*
Canola Oil	Methanol
Carbon Disulfide	Methyl Ethyl Ketone
Carbon Tetrachloride	Methylphenol
Chlorobenzene	Mineral Oil (Paraffin Oil)*
Chloroform (Trichloromethane)	Motor Oil*
Chloromethane (Methyl Chloride)	Nitrobenzene
Corn Oil	Oil-based Inks
Cutting Oils*	Oil-based Fluids
Cyclohexane	Oil-based Paints

OIL GATOR®(con't)

Dichlorobenzene(s)	Pentane
Dichloromethane (Methylene Chloride)	PAH's (PolyAromatic Hydrocarbons)*
Diesel Fuels*	PCB's (PolyChlorinated Hydrocarbons)*
Ethanol	Styrene
Ethyl Benzene*	Tetrachloroethane
Ethyl Ether	Tetrachloroethylene (Perchloroethylene)
Ethylene Chloride (1,2-Dichloroethane)	Tetrahydrofuran
Ethylene Glycol	Toluene*
Gasoline/Petrol*	Trichloroethylene
Heptane	Unleaded Petrol*
Hexachlorobenzene	Varsol*
Hexane	Xylenes*

* Denotes specific hydrocarbons that have been bioremediated by Oil Gator

A CASE STUDY: BIOREMEDIATION OF CONTAMINATED SITE WITH OIL GATOR®

- **Contaminated Site:** Approximately 1000 m² agricultural area
- **Amount of used product:** 14 bags (approximately 192 kg) Oil Gator®
- **Required time for Application:** 9 hours



A Case Study^(con't)



At first soil samples were taken from 20 different points of the contaminated site. The samples were homogenized and two different test were applied ; TPH and leached TPH

The first day of application was accomplished on 400 m² of the area. At first Oil Gator[®] was spread and waited two hours in order to absorb the crude oil by Oil Gator[®].



A Case Study^(con't)



- ✓ After the two hours contaminated soil was mixed with Oil Gator[®].
- ✓ The second day of the application was accomplished on 600 m² of the area. The same application procedure done on the first day was applied to the 600 m² of the area.



Before the Oil Gator® Application



During the Oil Gator® Application



After the 35 day



After 51 day

Results

Sample Number	Date	TPH (ppm)	Leached TPH (ppm)
GP 760/05/SS/01	16.03.2005	129 300	78.7
GP 760/05/SS/02-1	08.04.2005	62 300	2.5
GP 760/05/SS/02-2	06.05.2005	26 100	-
GP 760/05/SS/02-3	04.06.2005	7 800	-
GP 760/05/SS/02-4	24.06.2005	1 700	-
GP 760/05/SS/02-5	20.09.2005	216	-

Results(con't)

✓ 1st day-129,300 ppm

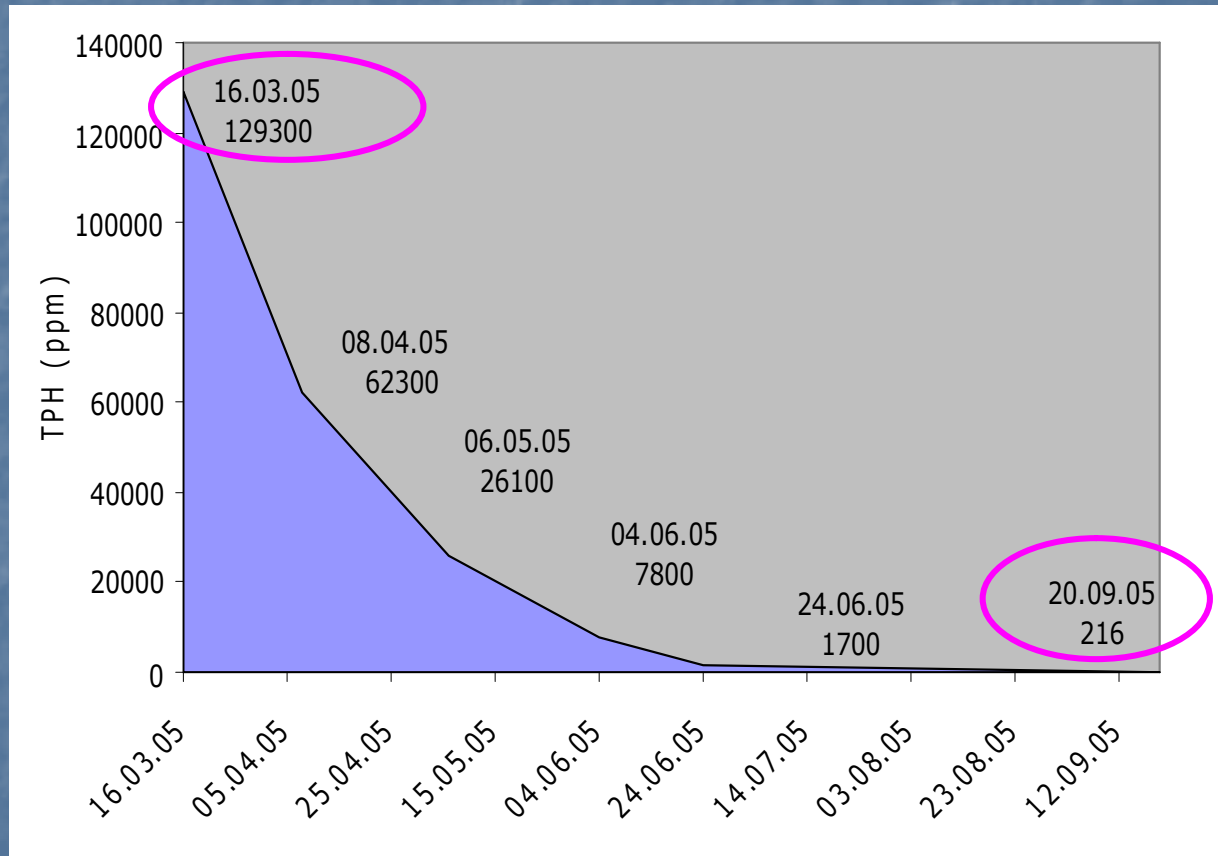
✓ 23th day-62,300 ppm

✓ 51^h day-26,100 ppm

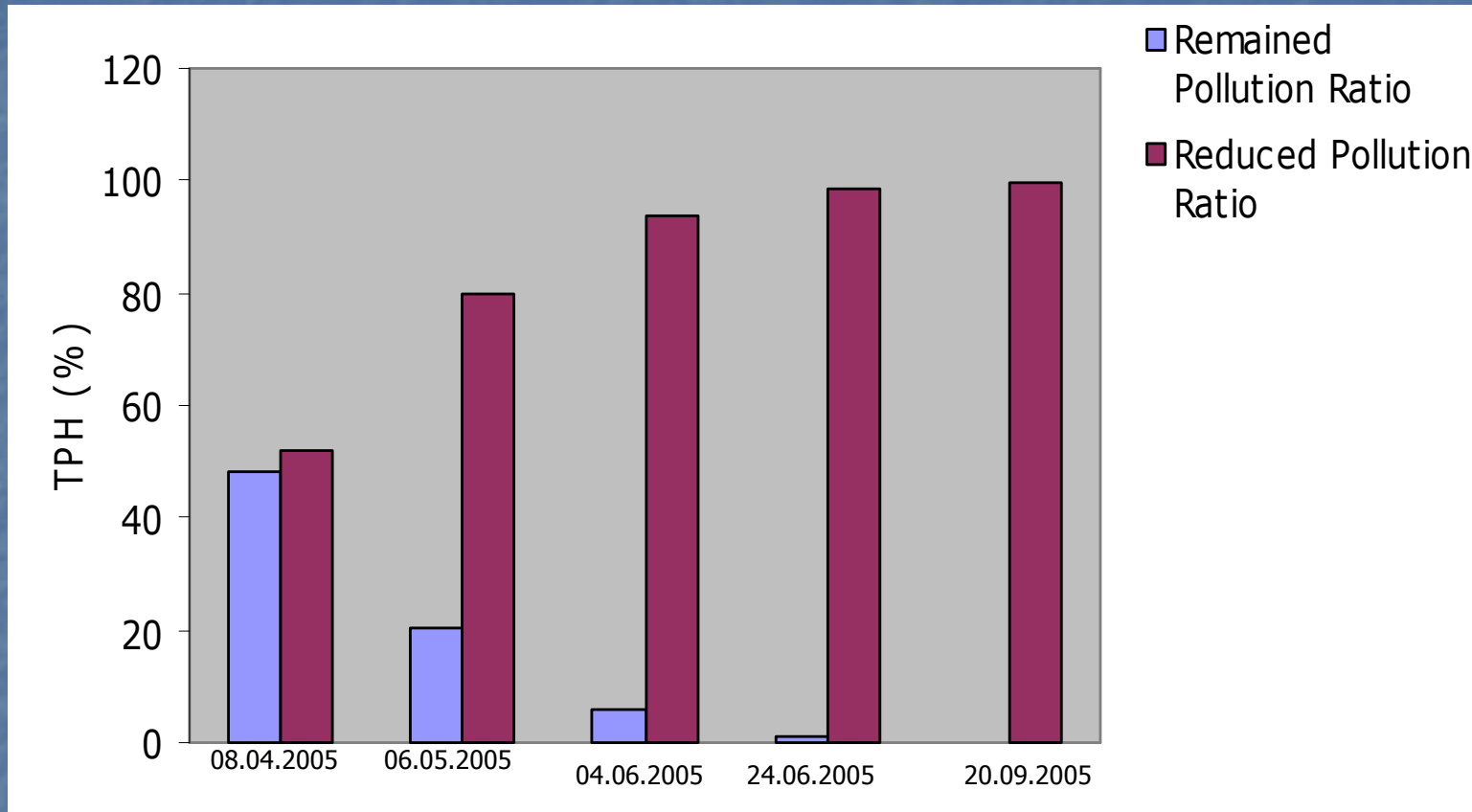
✓ 101th day-7,800 ppm

✓ 121th day-1,700 ppm

✓ 188th day-216 ppm

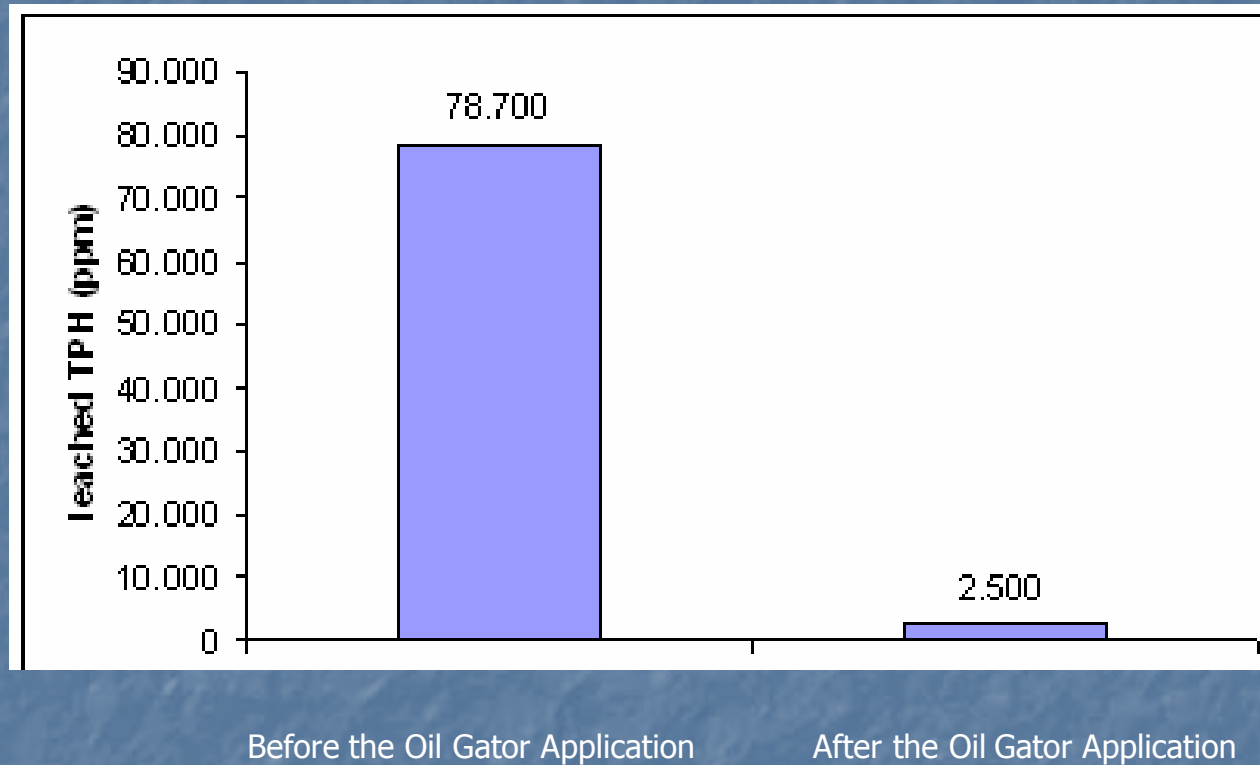


RESULTS(con't)



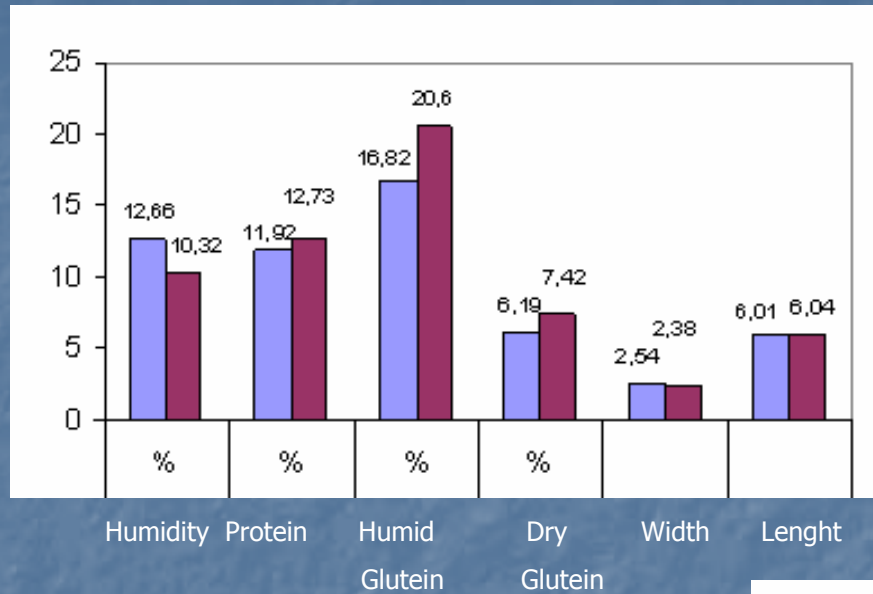
✓ After the 188 day of the Oil Gator application the remained pollution ration was 0.17% and the the reduced pollution ratio was 99.83%

Results(con't)



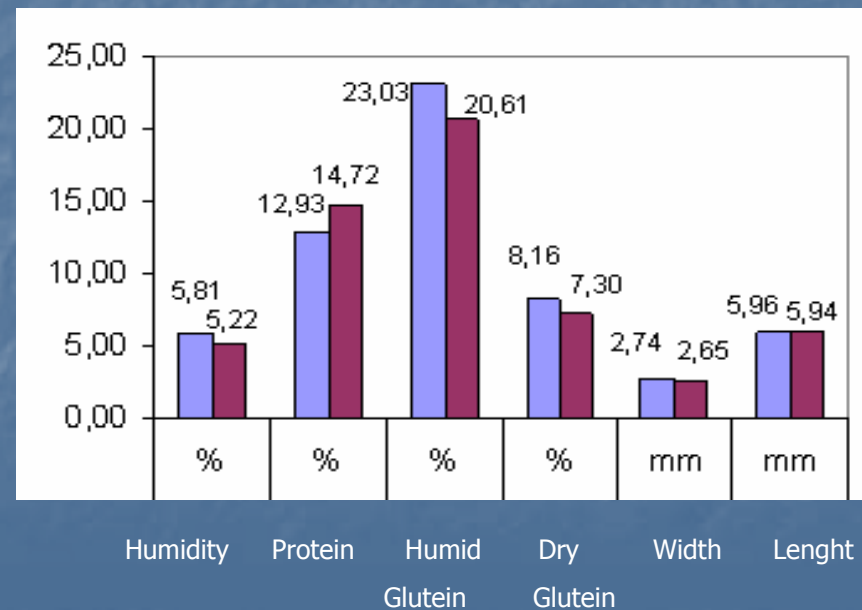
- ✓ Leached TPH was reduced 78.700 ppm to 2.500 ppm and after the 188 days the leached TPH was lower than 1 ppm

Results(con't)



- Wheat grown in nonpolluted area
- Wheat grown in polluted area

✓ There was no difference between grown wheat in impolluted and polluted area



Conclusions

- The analyzes showed that the amount of TPH was reduced from 129,300 to 216 ppm after 188 days.
- Reduction in TPH amount proved that Oil Gator absorb the crude oil.
- Similarly, parallel with reduced TPH analyzes done with grown wheat in the contaminated area proved that result since there was no difference between the wheat grown in contaminated and clean area.
- The results showed that Oil Gator can be used in bioremediation of the contaminated soil with crude oil.
- Also, according to EPA and some European countries legislation soil which has TPH lower than 1000 ppm can be used for general purposes.

thank you for your attention...