



UNIDO Green Chemistry Serbia
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"BIOREMEDIATION BELONGS TO GREEN CHEMISTRY - YES OR NO?"

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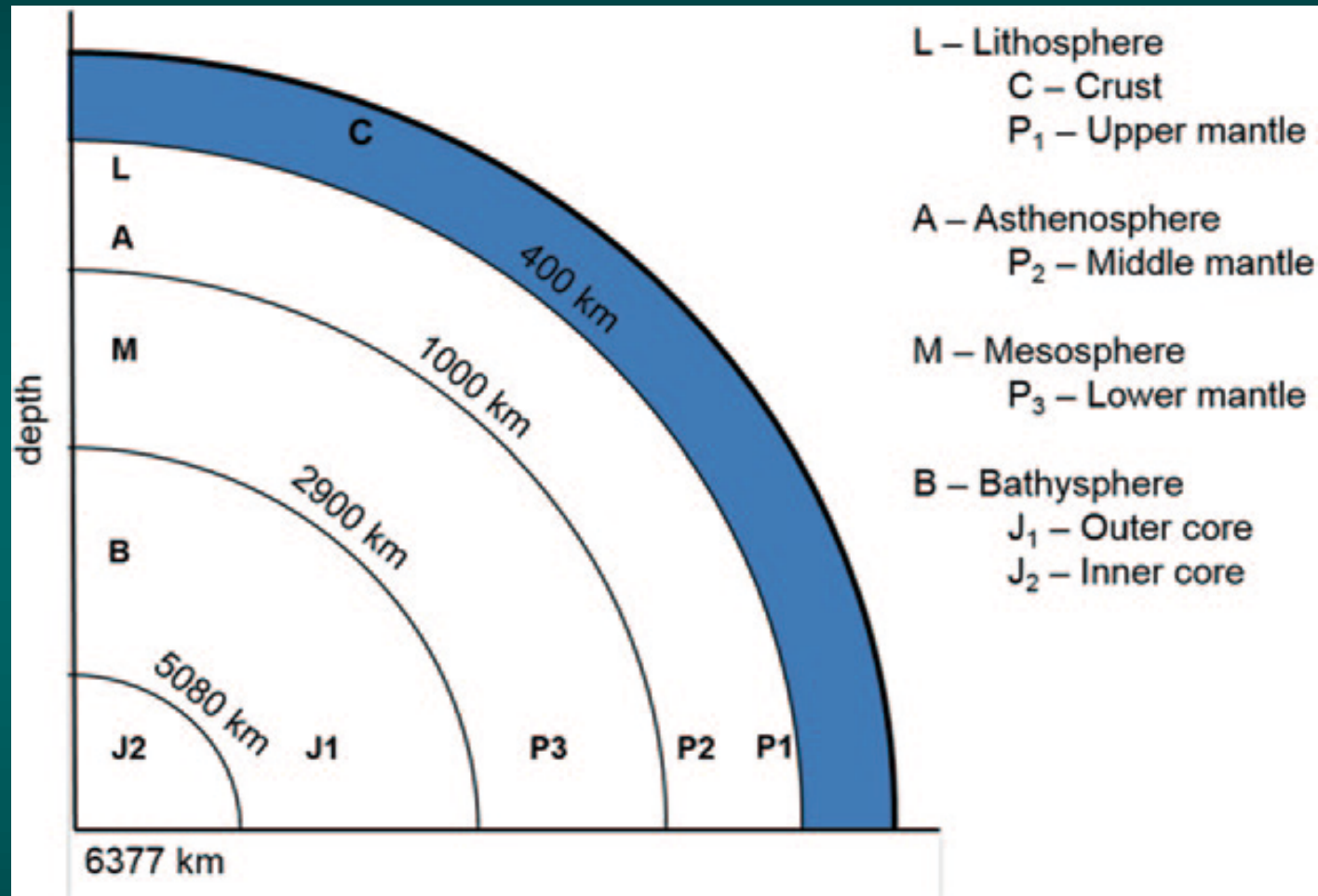
Petroleum

Crude oil

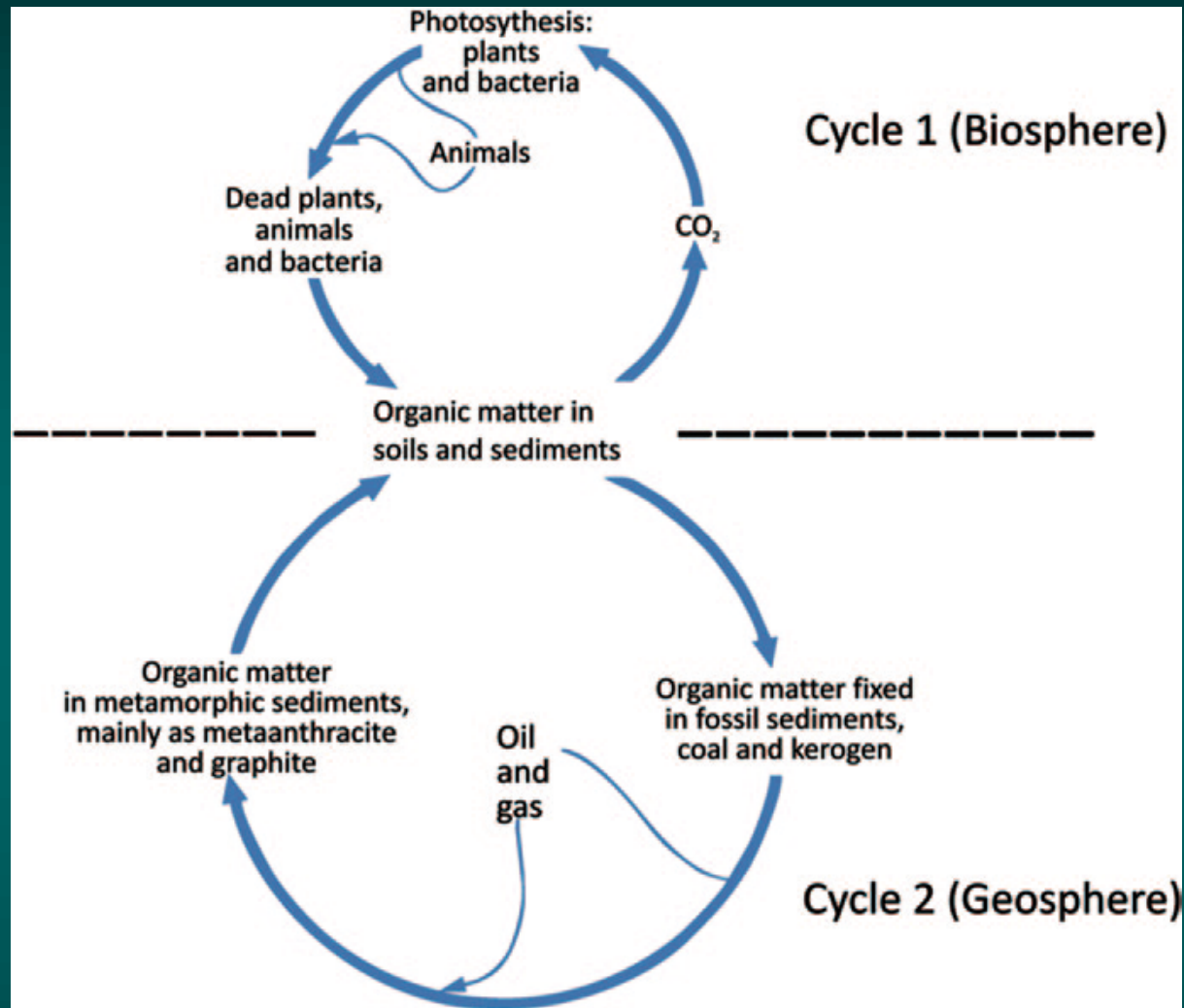
Nafta

In spite of remarkable advancement of petroleum exploration, transport and refining technologies, petroleum and its refining products continue to be one of the most abundant environmental pollutants.

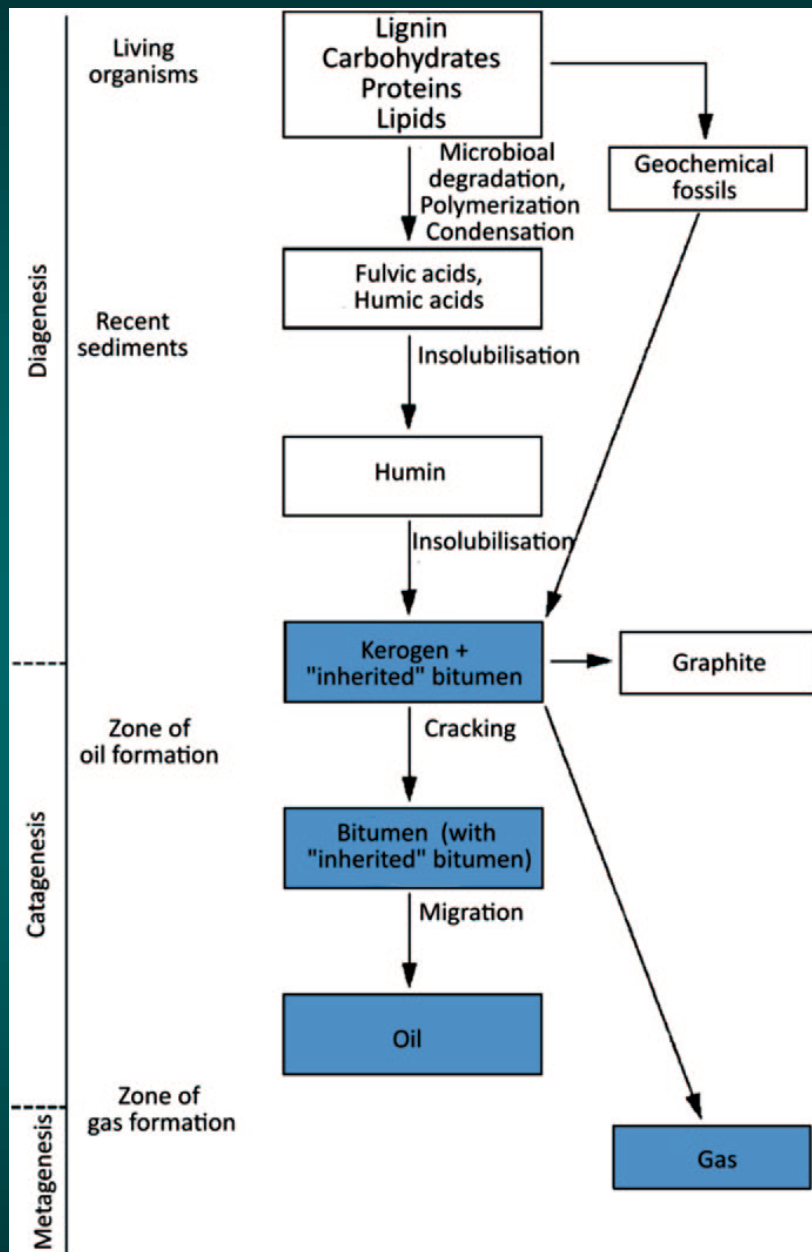
Consequently, studies on the environmental fate of petroleum-type pollutants remain to be an actual scientific interdisciplinary problem.



The general structure of Earth.



Cycling of carbon in nature.



A simplified scheme of the transformation of organic matter in the Earth's crust.

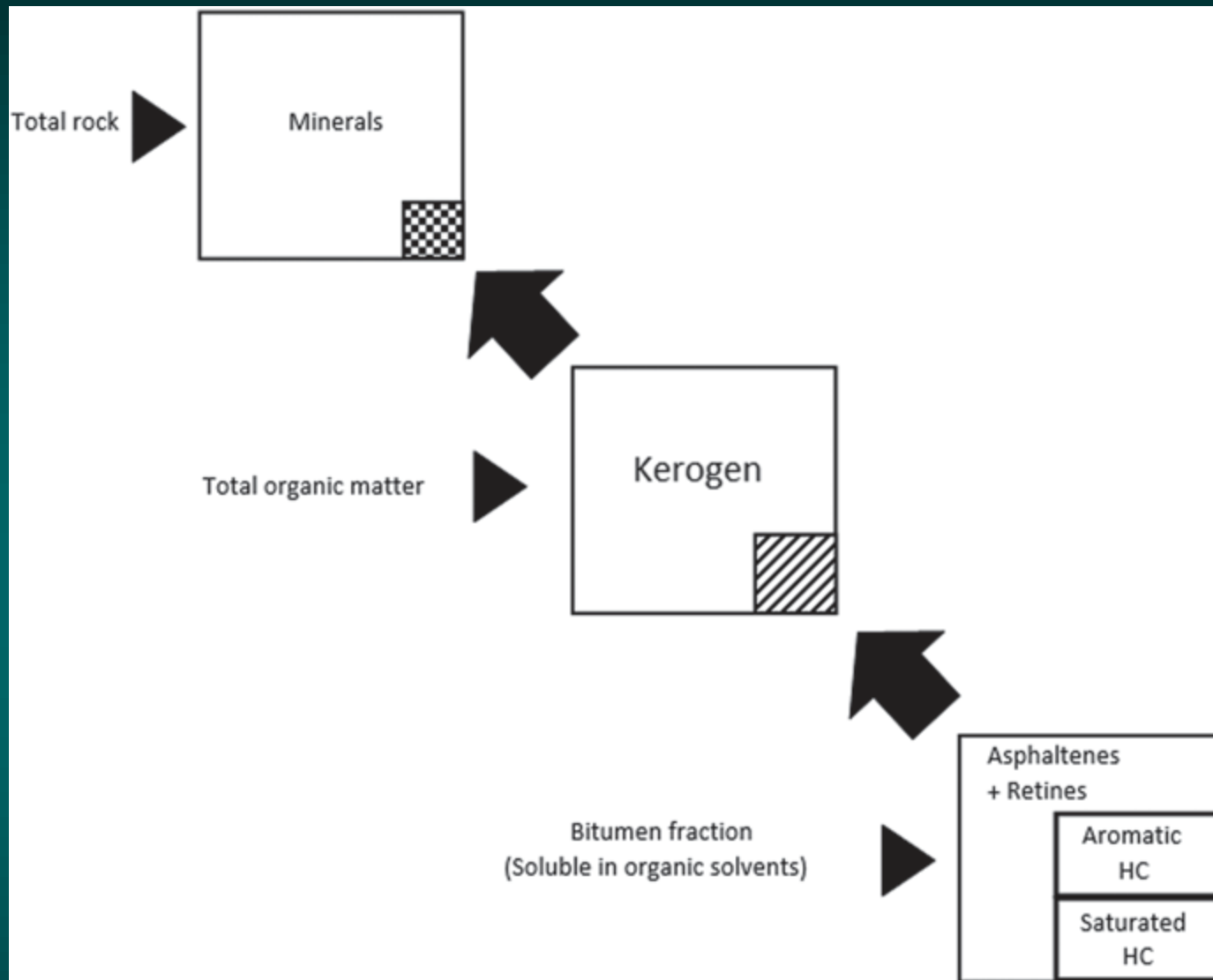
fulvic acids, humic acids, humin
diagenesis



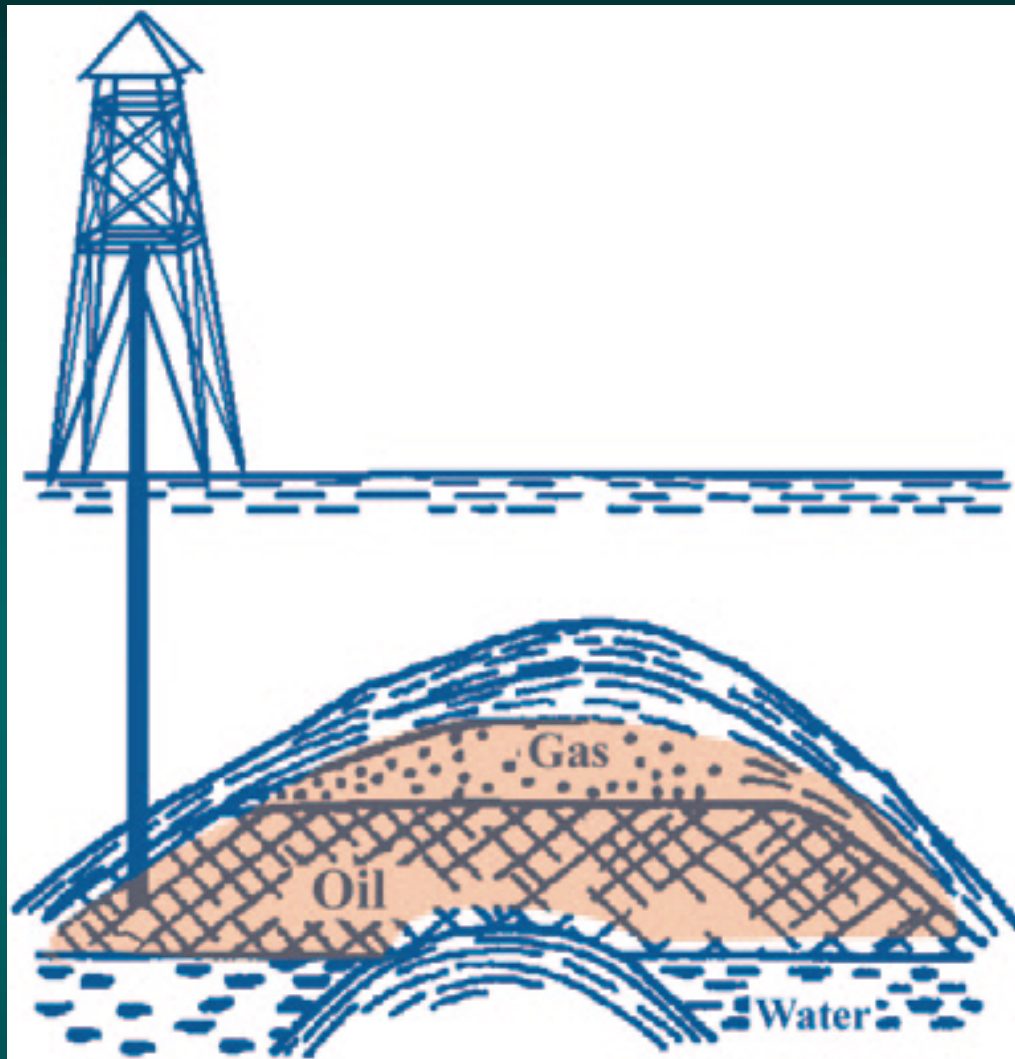
kerogen



bitumen, oil, gas, graphite
*catagenesis, metagenesis,
metamorphosis*



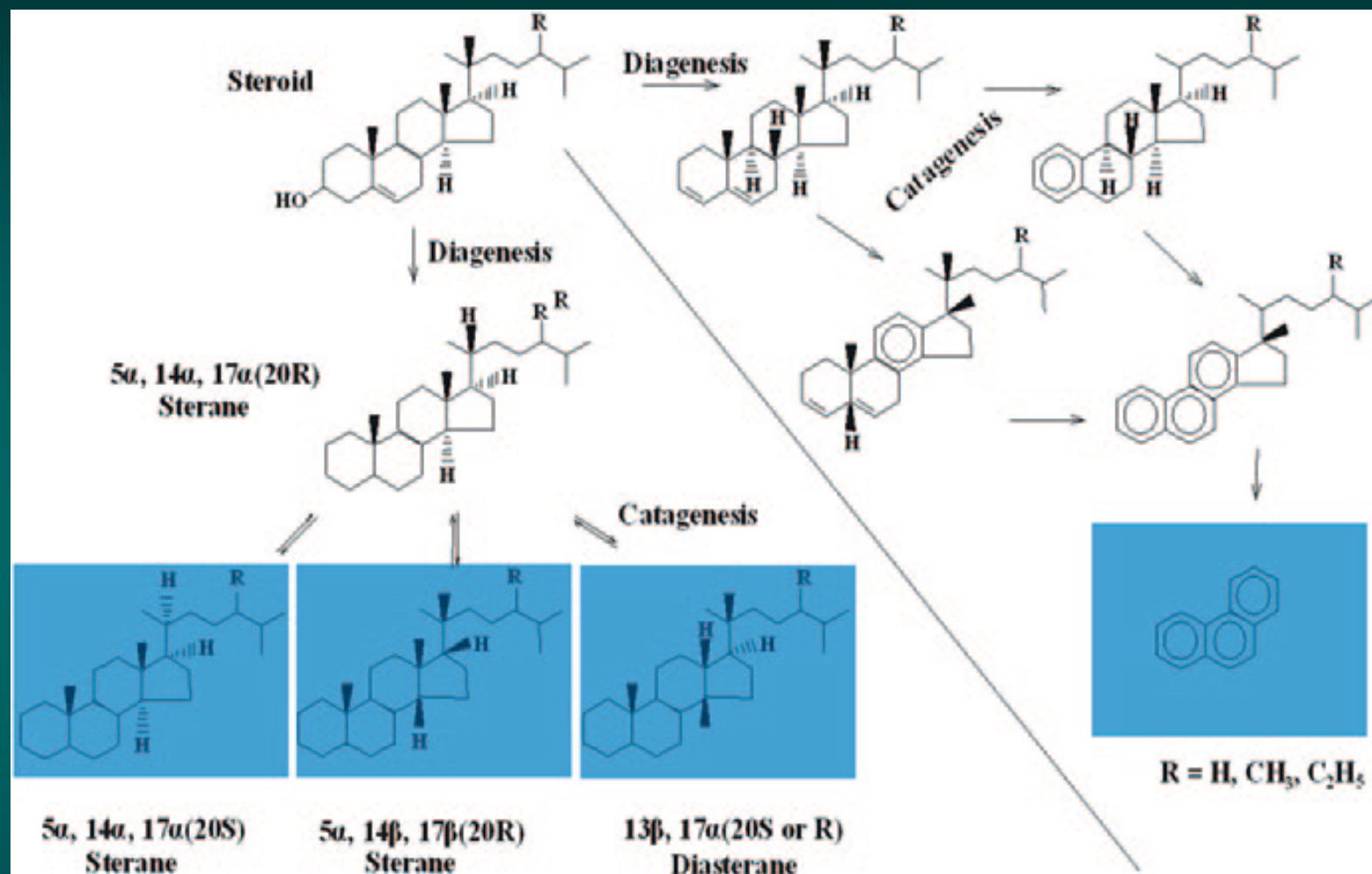
Quantitative kerogen position within the inorganic and the organic part of the sediments.



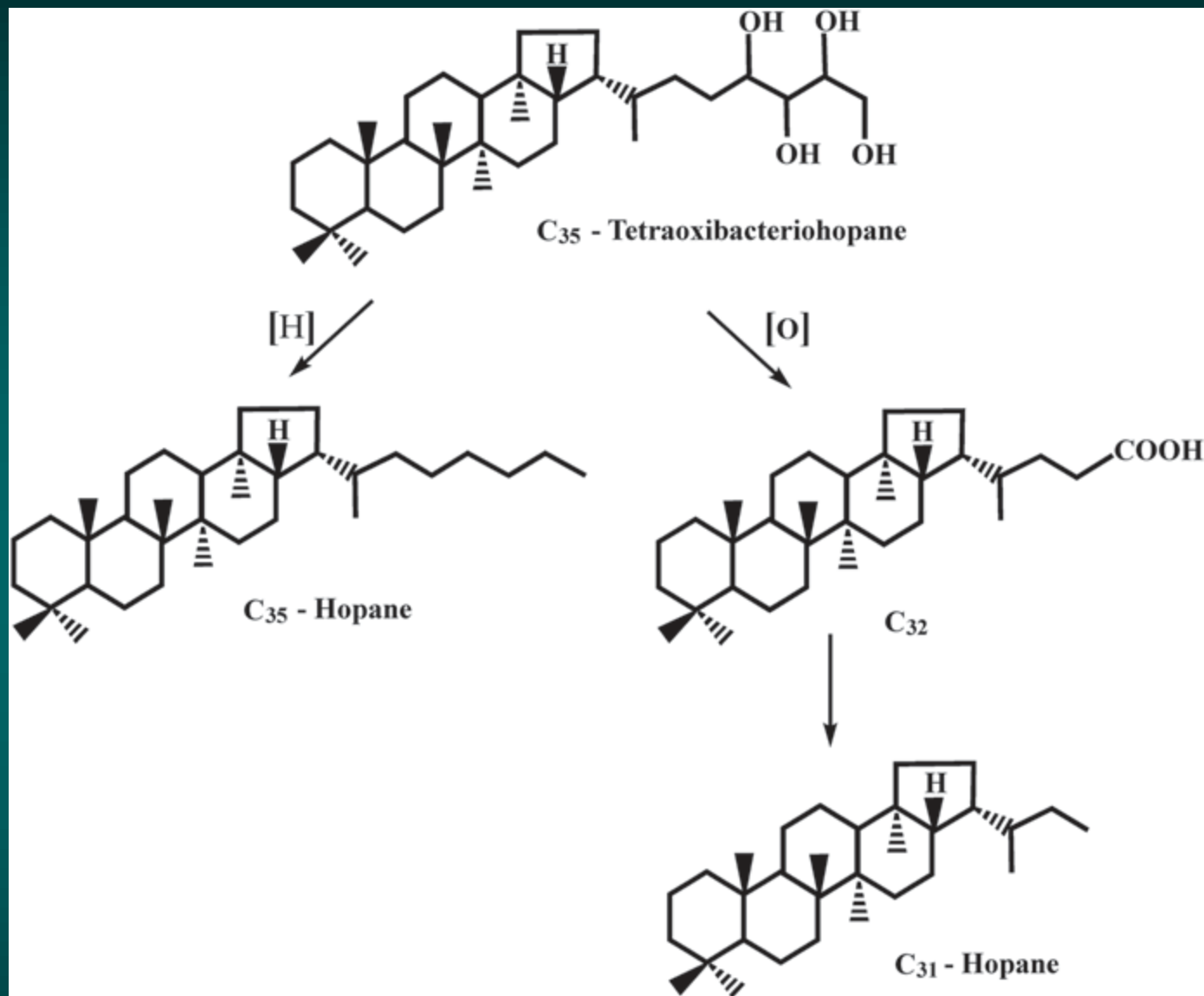
A simplified illustration of the oil
reservoir rock.

Petroleum (oil) fractions and its main components

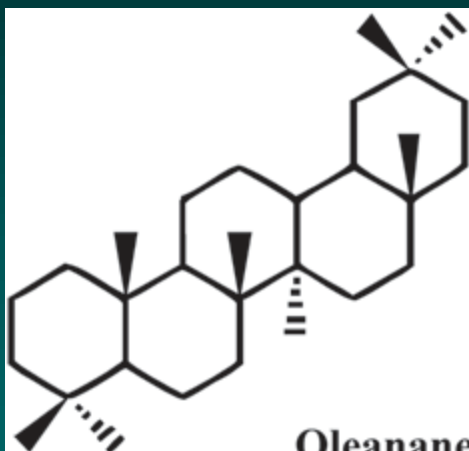
Fraction	Components
Saturated hydrocarbons	<i>n</i> -Alkanes Isoprenoids and branched hydrocarbons Alicyclic alkanes, including steranes, diterpanes and triterpanes
Aromatic hydrocarbons	Aromatic hydrocarbons Naphthenoaromatic hydrocarbons Small molecules with sulfur
Resins (polar NSO-fraction)	Porphyrins Fatty acids and alcohols Aliphatic and cyclic ketones Sulfuric aliphatic and aromatic compounds
Asphaltenes	Condensed aromatic compounds with a large number of heteroatoms



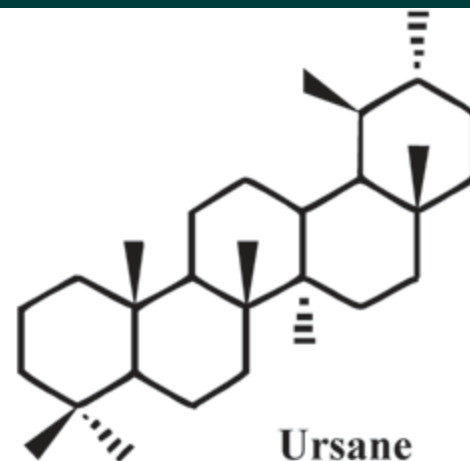
Structural and stereochemical transformations
of steroids in the geosphere.



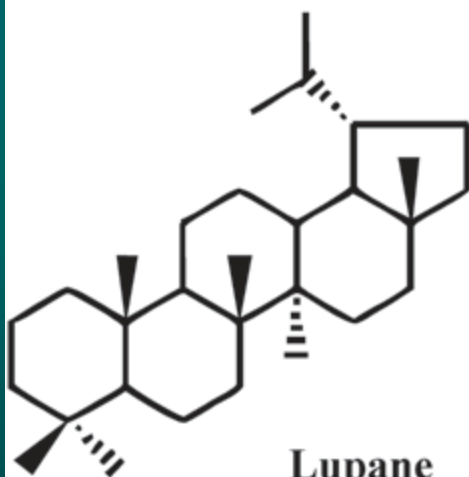
The possible mechanism of genesis of hopanes from tetraoxibacteriohopane.



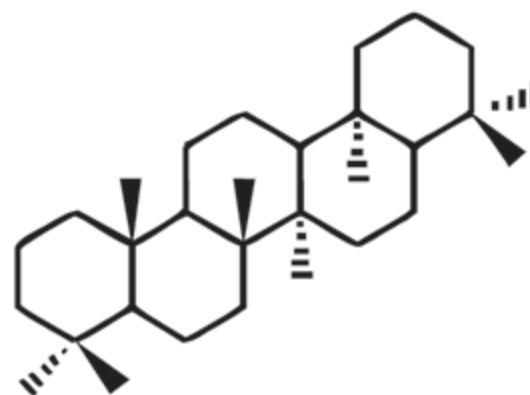
Oleanane



Ursane

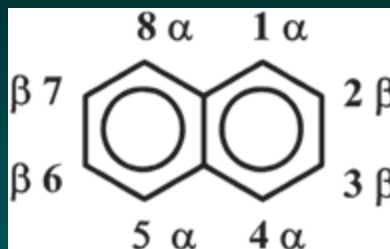


Lupane

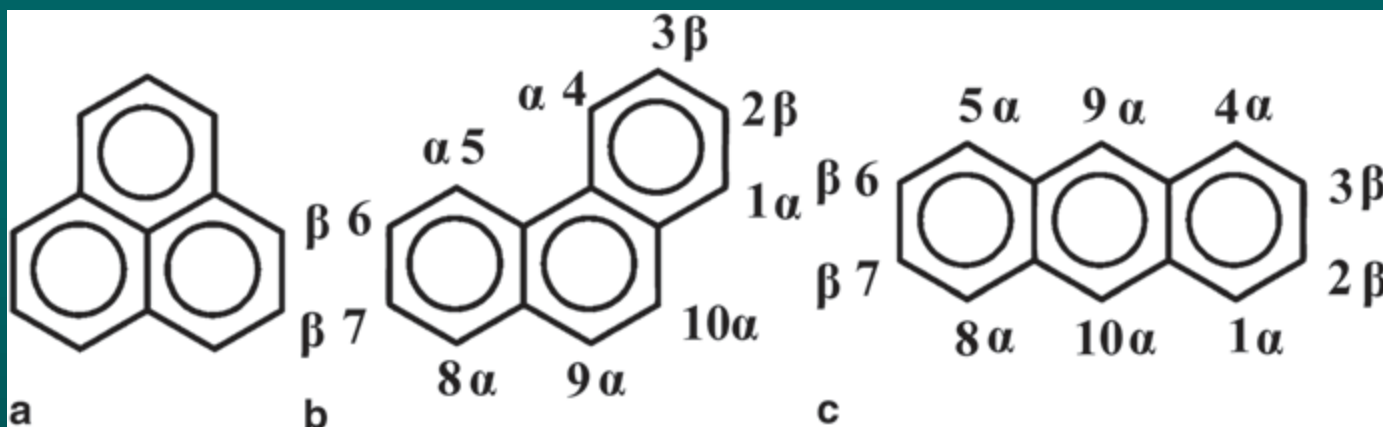


Gammacerane

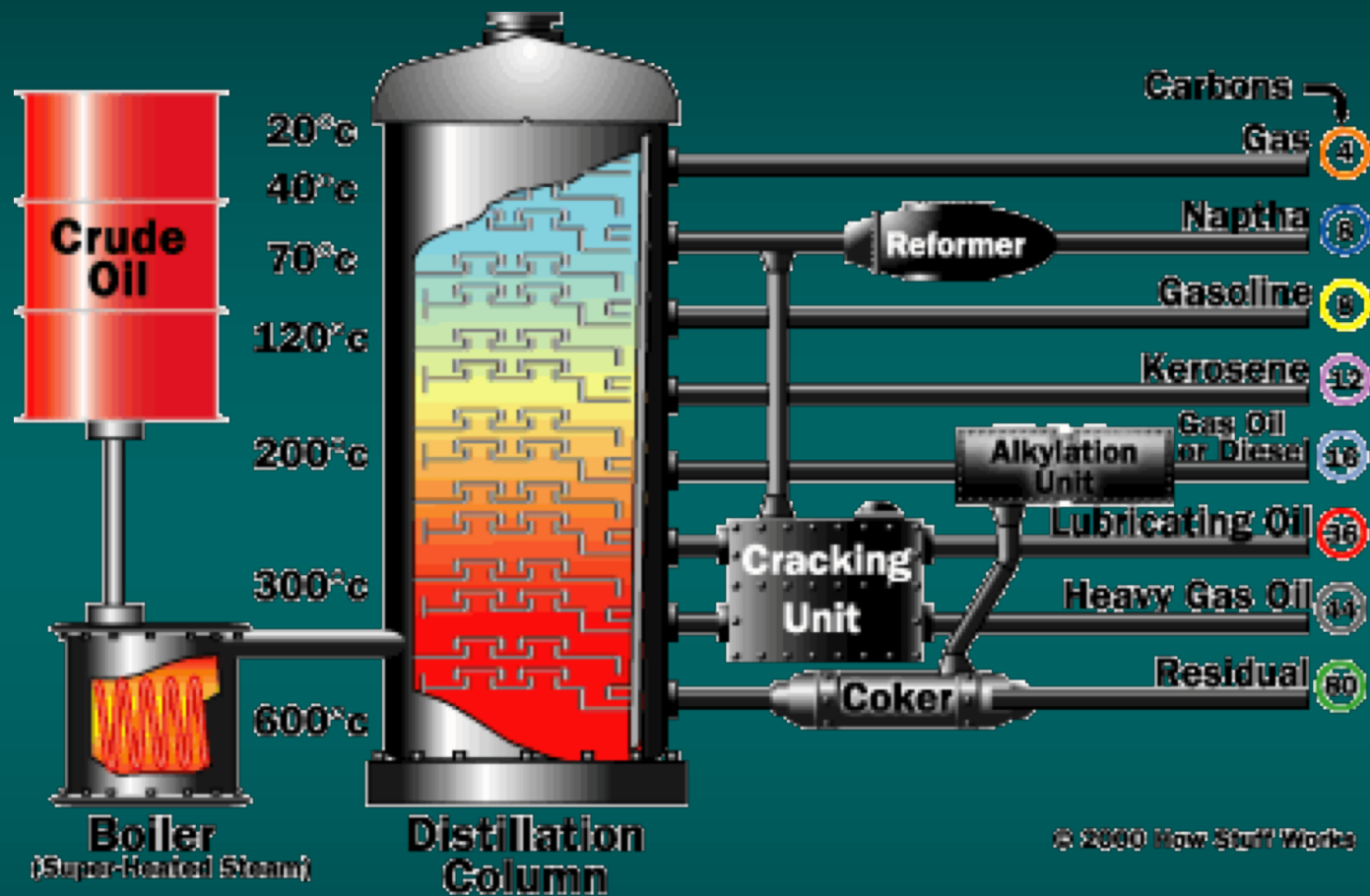
Some types of pentacyclic terpanes identified in sediment bitumens and oils.



Molecular structure of naphthalene



Molecular structures of perinaphthene (a),
phenanthrene (b), and anthracene (c)



Oil refinery processing.

The main products of oil refining in the refinery:

Liquid fuels:

- 1) gasoline, 50-200°C ("gasoline"), fuel for internal combustion engines, solvent
- 2) Petroleum, 200-280°C ("kerosene") fuel for jet engines, previously "gas for lighting"
- 3) gas oil, 280-350°C ("gas oil") fuel for diesel engines, fuel oil

Lubricant:

- 1) Lubricating oils and fats, > 350°C ("lubricating oil")
- 2) fuel oil, for fueling

Asphalt residue, bitumen

Gases

- 1) the accompanying gas (C₁-C₄)
- 2) cracking gases (many olefins)
- 3) reforming gases (hydrocarbons, 60-80% hydrogen)

Solid products

- 1) petrol-coke, 2) chad, 3) paraffin

Petrochemical products

- 1) acetylene, 2) olefins C₂-C₄, 3) aromatic hydrocarbons

Possible pollution sites:

- 1) Exploitation on boreholes.
- 2) Collection in collecting stations on oil fields.
- 3) Transport (car tanks, tanks, tankers, oil pipelines).
- 4) Processing in refineries.
- 5) Transport of finished products.
- 6) Storage of finished products.
- 7) The use of.

1) Identification - differentiation of petroleum-type pollutants

2) *n*-Alkanes

$\delta^{13}\text{C}_{\text{PDB}}$ Values

Steranes and triterpanes

2) Fate in the environment

Biodegradation

Migration

3) Bioremediation

Biodegradation of the oil pollutant in the laboratory

ex situ Bioremediation

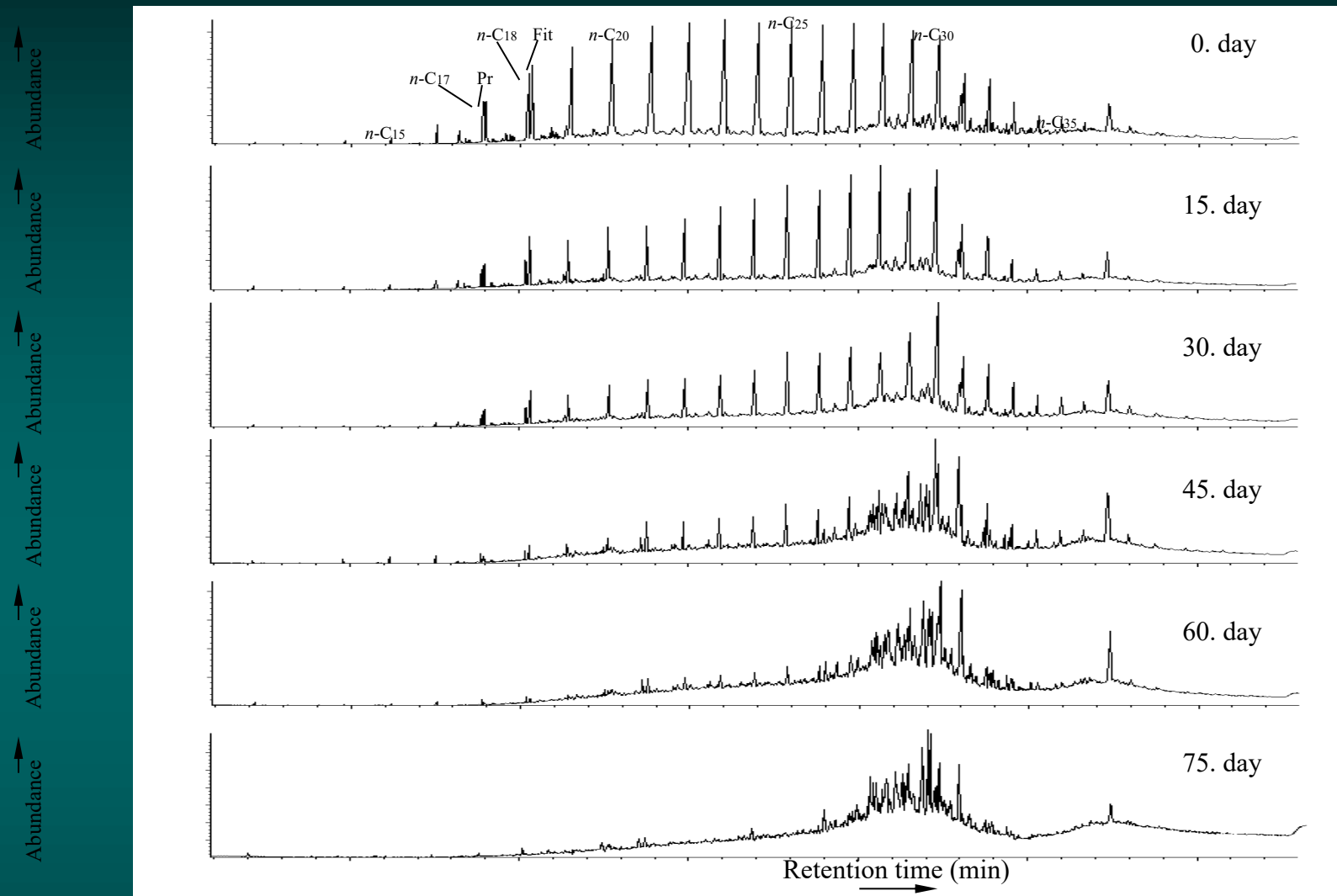
in situ Bioremediation

Bioremediation

1. Biodegradation of the oil pollutant in the laboratory
2. *ex situ* Bioremediation
3. *in situ* Bioremediation

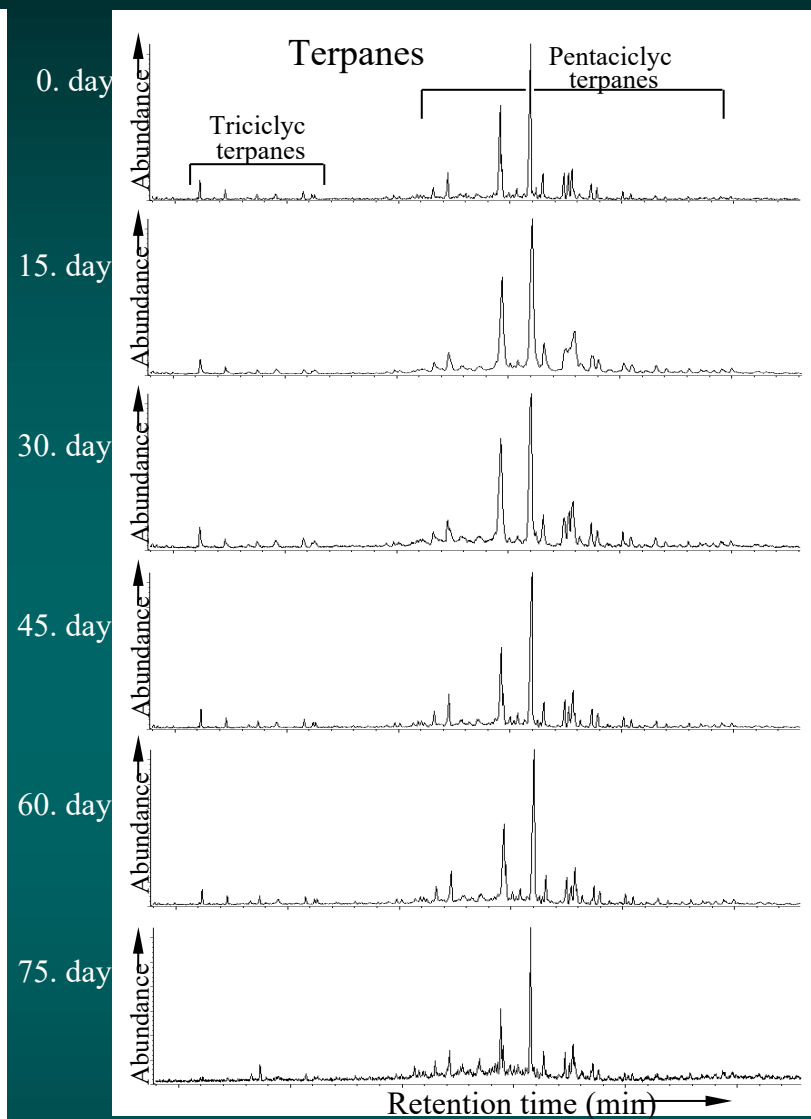
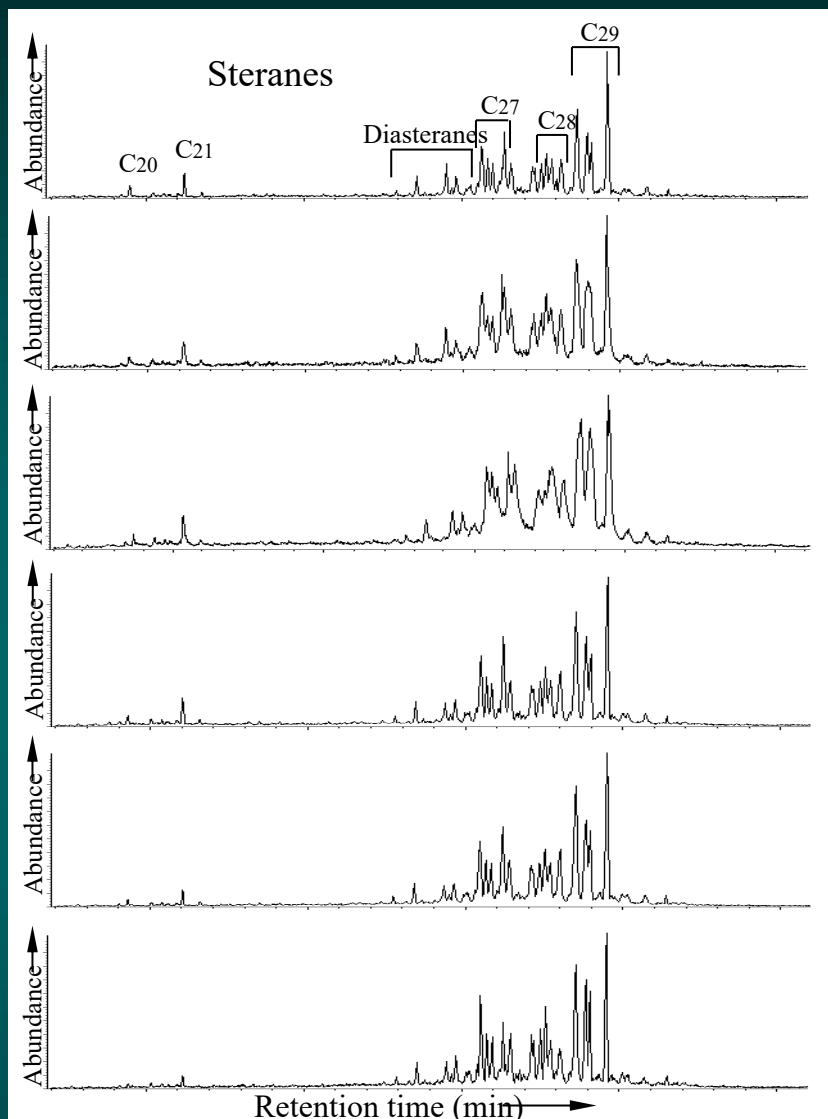
1. Biodegradation of the oil pollutant in the laboratory

The fate of a petroleum-type pollutant in environment was foreseen on the basis of laboratory simulation experiments of microbiological degradation of petroleum using microorganism consortiums similar to those typical for the natural environment.

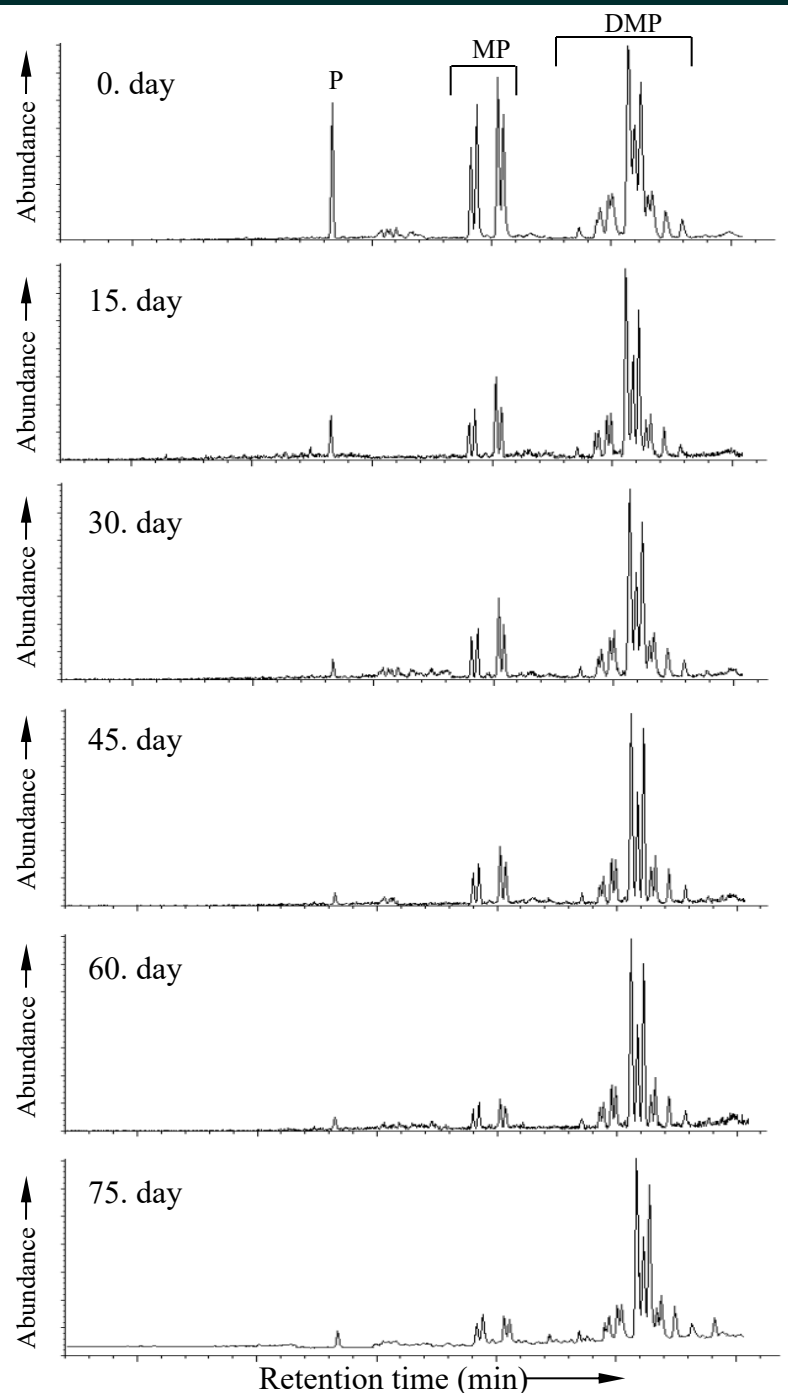


Total ion chromatograms (TIC) of saturated fractions after the experiment of simulated biodegradation with consortium of bacteria and fungi.

Jovančičević et al., 2009 ; Šolević et al., 2011



GC-MS ion fragmentograms of steranes ($m/z = 217$) and terpanes ($m/z = 191$) after the experiment of simulated biodegradation with consortium of bacteria and fungi.



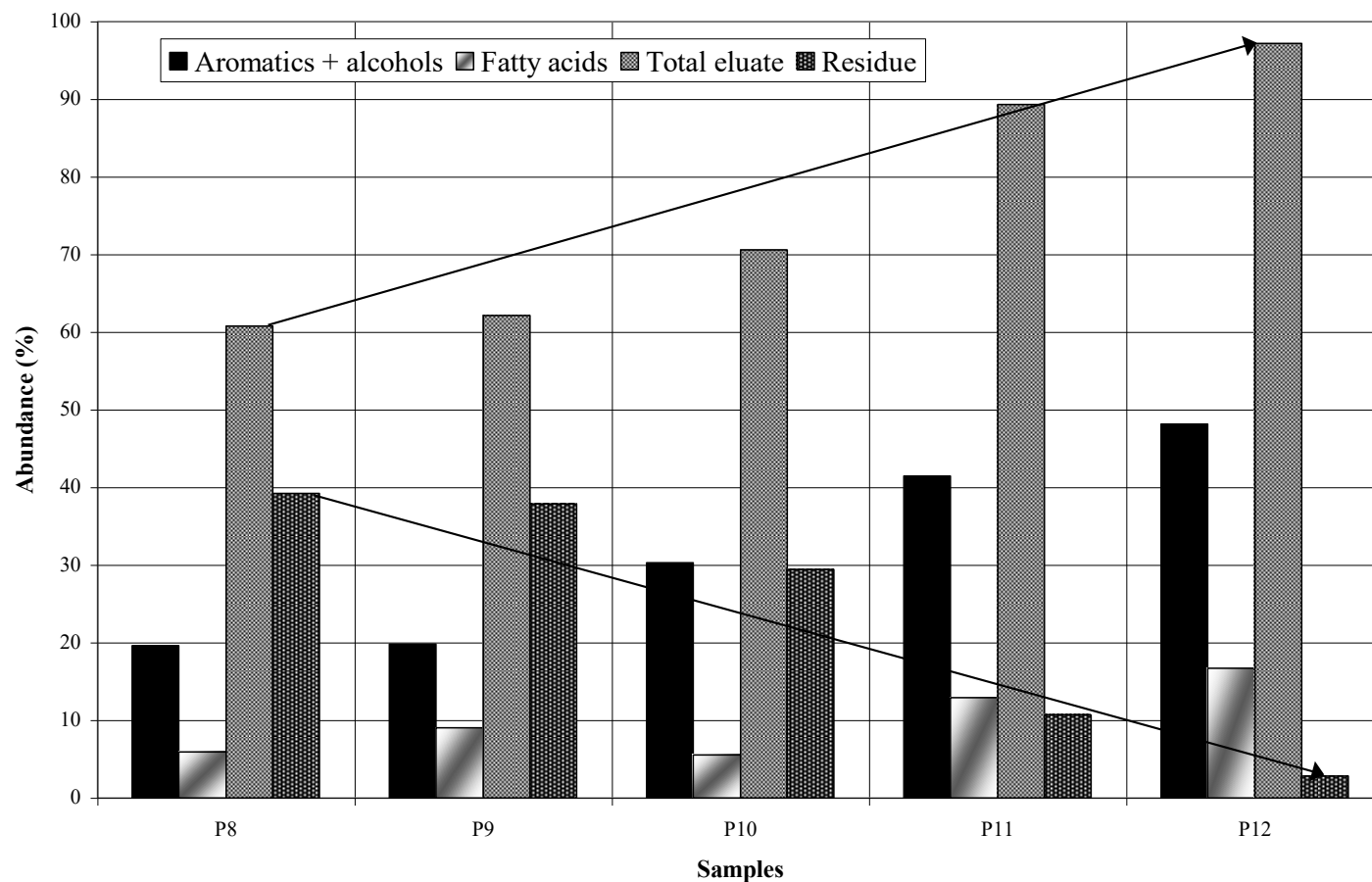
GC-MS ion fragmentograms of phenanthrene (P), methylphenanthrenes (MP) and dimethylphenanthrenes (DMP) after the experiment of simulated biodegradation with consortium of bacteria and fungi.

Jovančičević et al., 2009 ; Šolević et al., 2011

2. *ex situ* Bioremediation in designed biopile

- Homogenization of soil and sawdust
- Biostimulation - organic fertilizer as a source of nitrogen and phosphorus
- Aeration - system of perforated pipes, mixing
- Bioaugmentation





Contents of total aromatics and alcohols, fatty acids, total eluate and the column residue for samples P₈-P₁₂.

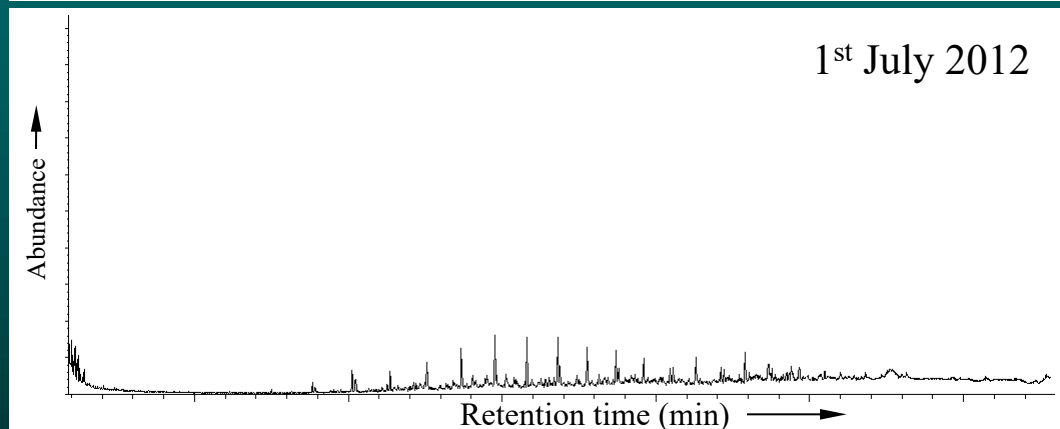
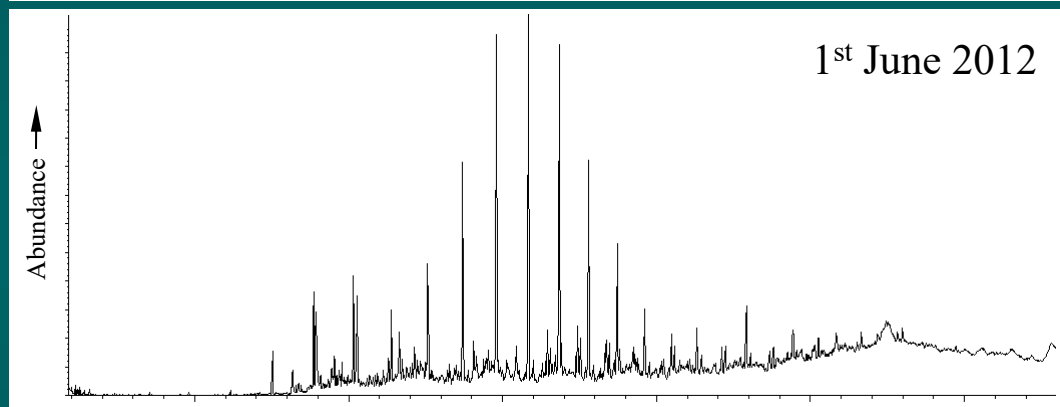
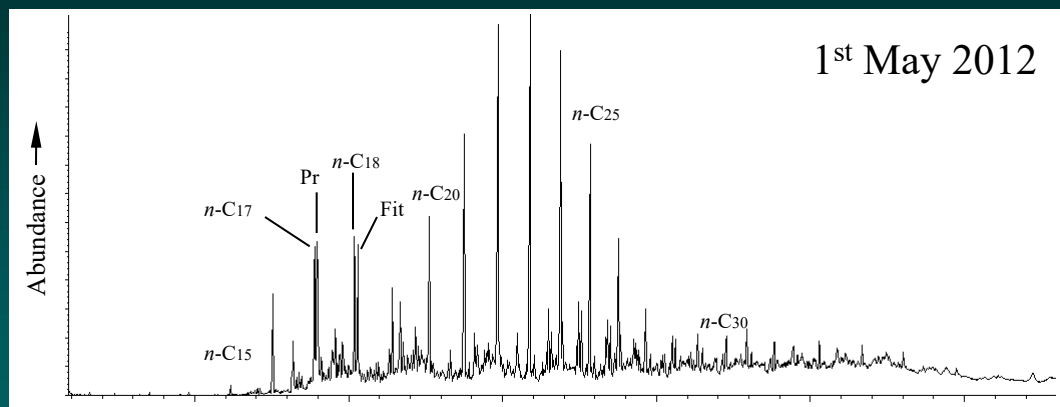
Results of *ex situ* bioremediation:

- Removal of all *n*-alkanes.
- Removal of all isoprenoids.
- Polycyclic alkanes unchanged.
- Phenanthrene partially degraded.

3. Bioremediation – - *in situ* bioremediation

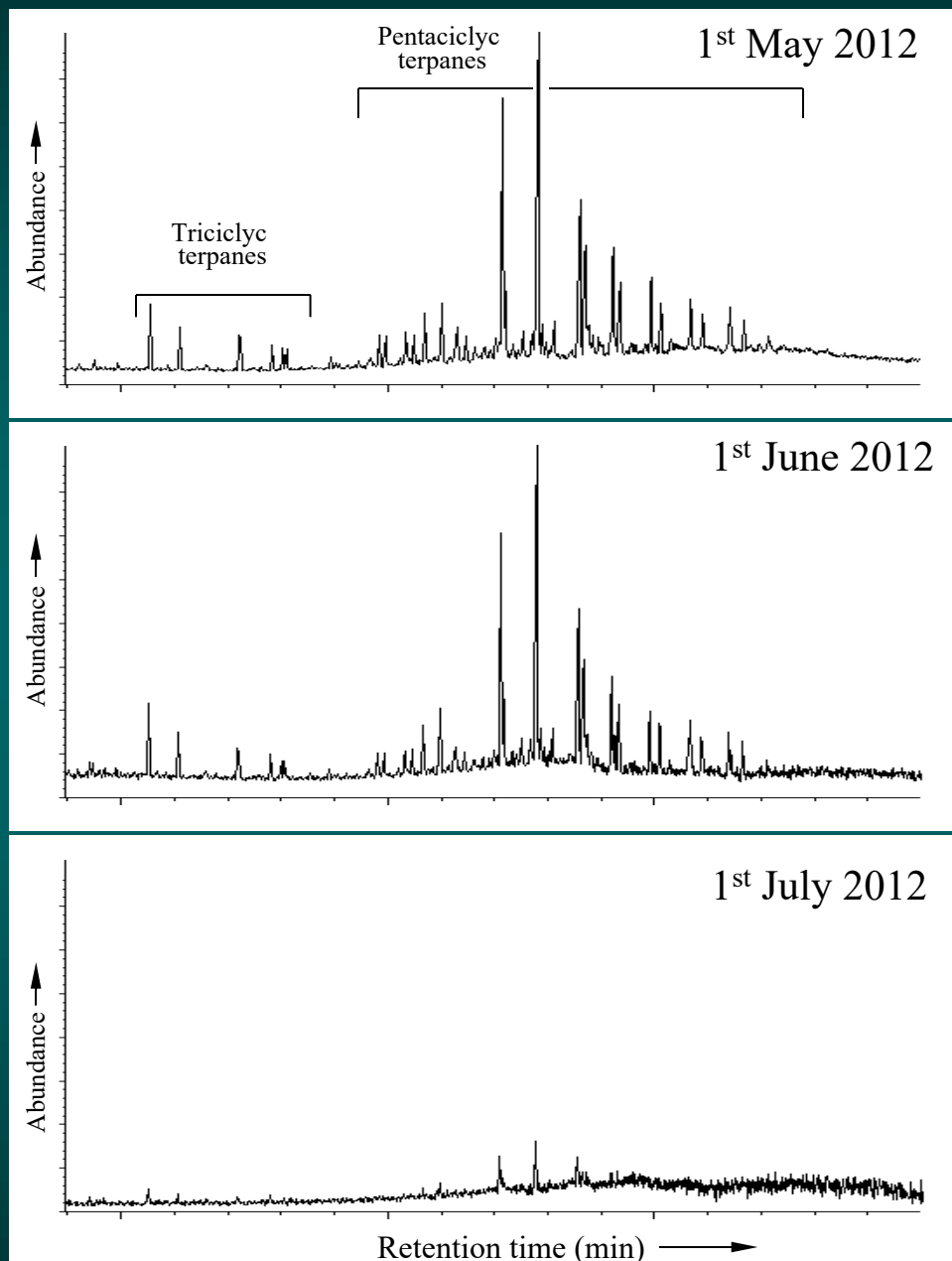


The locality of the company Niteks-Benetton in Niš (Serbia) was contaminated over several years with petroleum products due to the continuous pollution from leaking tanks.



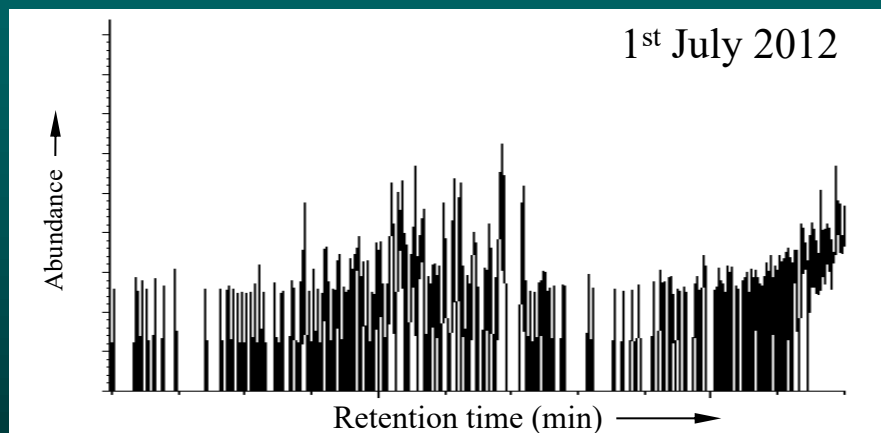
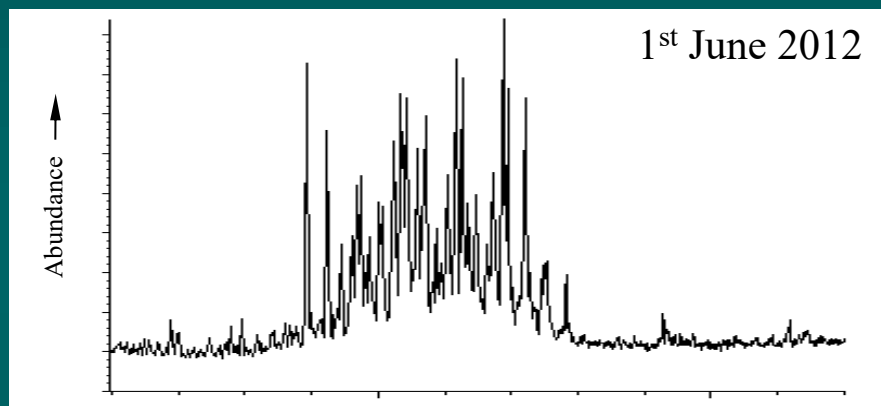
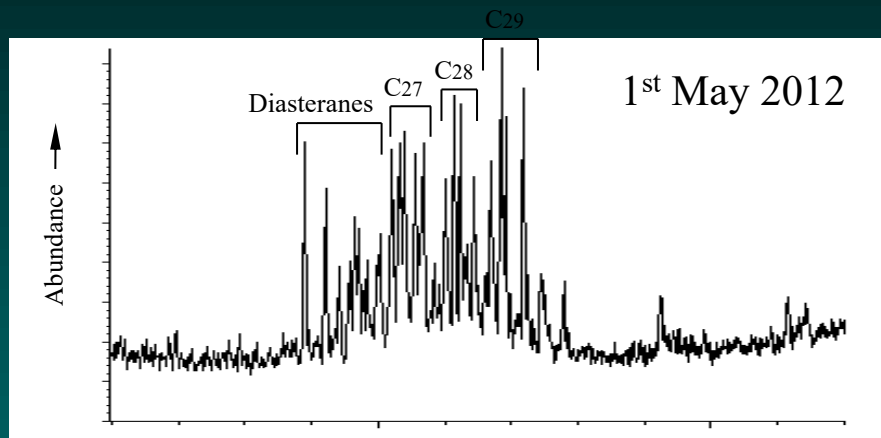
Fragmentograms of n -alkanes and isoprenoids ($m/z = 71$) obtained by GC-MS analysis of the extracts isolated from the samples at the beginning of the experiment, after 30 days and after 60 days.

Jovančičević et al., 2012



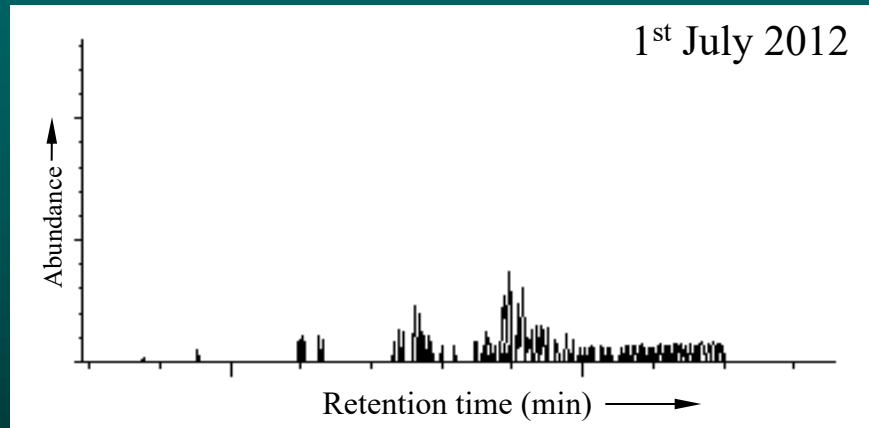
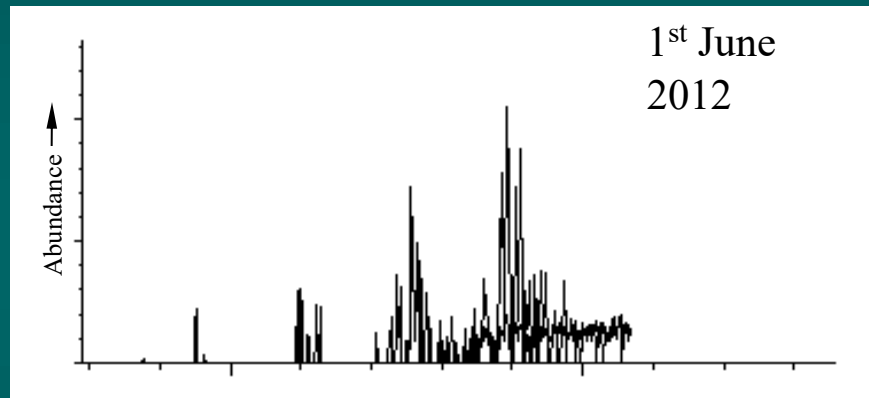
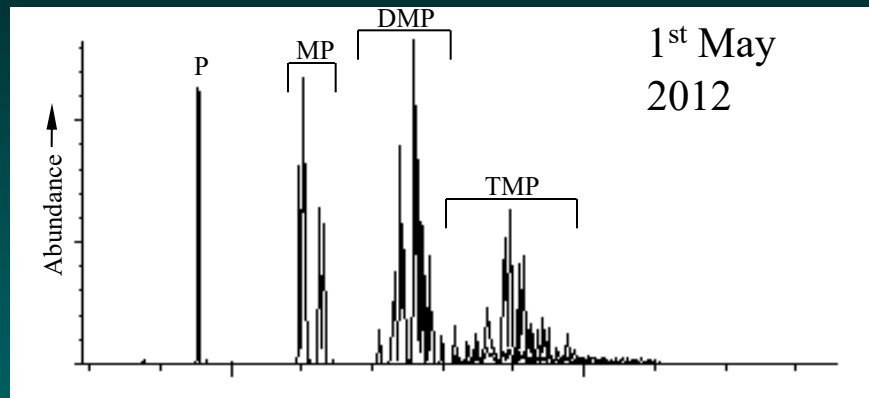
Fragmentograms of terpanes ($m/z = 191$) obtained by GC-MS analysis of the extracts isolated from the samples at the beginning of the experiment, after 30 days and after 60 days.

Jovančičević et al., 2012



Fragmentograms of steranes ($m/z = 217$) obtained by GC-MS analysis of the extracts isolated from the samples at the beginning of the experiment, after 30 days and after 60 days.

Jovančičević et al., 2012



Fragmentograms of phenanthrene (P; $m/z = 178$), methylphenanthrenes (MP; $m/z = 192$), dimethylphenanthrenes (DMP; $m/z = 206$) and trimethylphenanthrenes (TMP; $m/z = 220$) obtained by GC-MS analysis of the extracts isolated from the samples at the beginning of the experiment, after 30 days and after 60 days.

Jovančičević et al., 2012

Results of *in situ* bioremediation:

- Removal of all *n*-alkanes.
- Removal of all isoprenoids.
- Removal of all polycyclic alkanes.
- Removal of all phenanthrene.

**"BIOREMEDIATION
BELONGS TO GREEN
CHEMISTRY:**

YES OR NO?"



Hvala na pažnji!

Thank you for your attention!

