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Tailor-made Assessment of Remediation of Oil-contaminated Soil and Groundwater in Kuwaiti Oilfields

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Presentation overview

- **Background information**
  - Environmental damage in the oil fields
  - Environmental claims & UNCC awards

- **Tailor-made approach for monitoring remediation of oil-contamination in**
  - Soil
  - Groundwater

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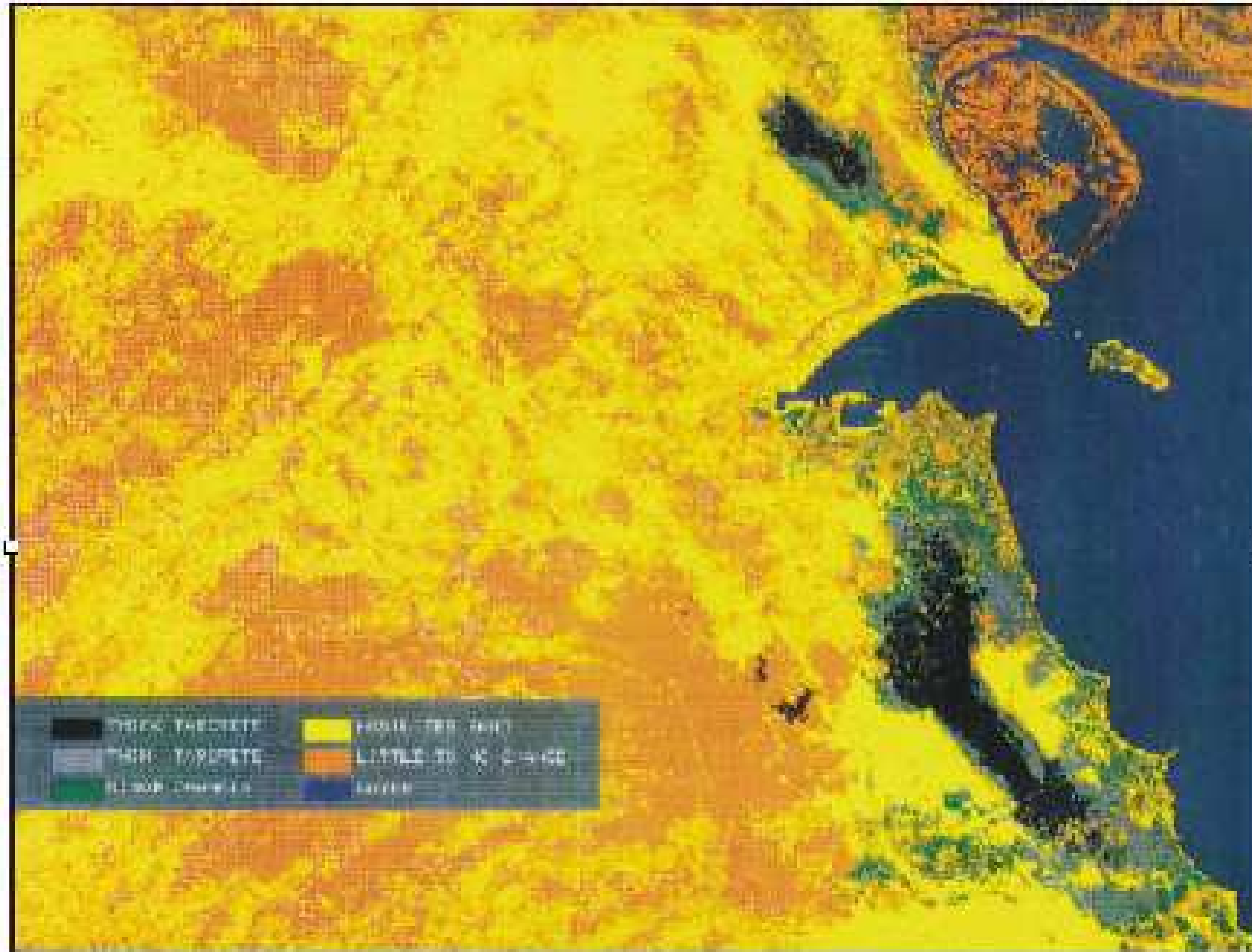

Change detection map showing war-related surface change in Kuwait

Background information

Environmental damage in the oil fields

	Volume (million m^3)	Extent (area km^2)
Wet oil lakes	4.6	7.2
Dry oil lakes	24.5	98.4
Oil-contaminated piles	14.8	8.6
Oil trenches	5.7	1.6
Tarcrete	12.3	267.8
Grand Total	**61.9**	**383.6**

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Wet/Dry Oil Lake


Wet/Dry Oil Lake


Oil-contaminated Pile
Wet Oil Lake


Tarcrete

Background information

Environmental claims & UNCC awards

Environmental "F4" claims	Claimed US Dollar	Awarded US Dollar
M&A study	460,421,114	108,908,412
Groundwater remediation	185,167,546	41,531,463
Terrestrial	5,050,105,158	643,814,034
Wellhead pits, Tarcrete		174,765,767
Coastal damage	33,901560	3,990,152
OB/OD	695,119,160	162,259
Oil lakes (remediation)	5,863,998,176	1,975,985,580
Oil lakes (re-vegetation)	940,312,445	283,300,389
Marine preserve	967,831,391	7,943,030
Soil remediation in the oil fields		2,150,751,347

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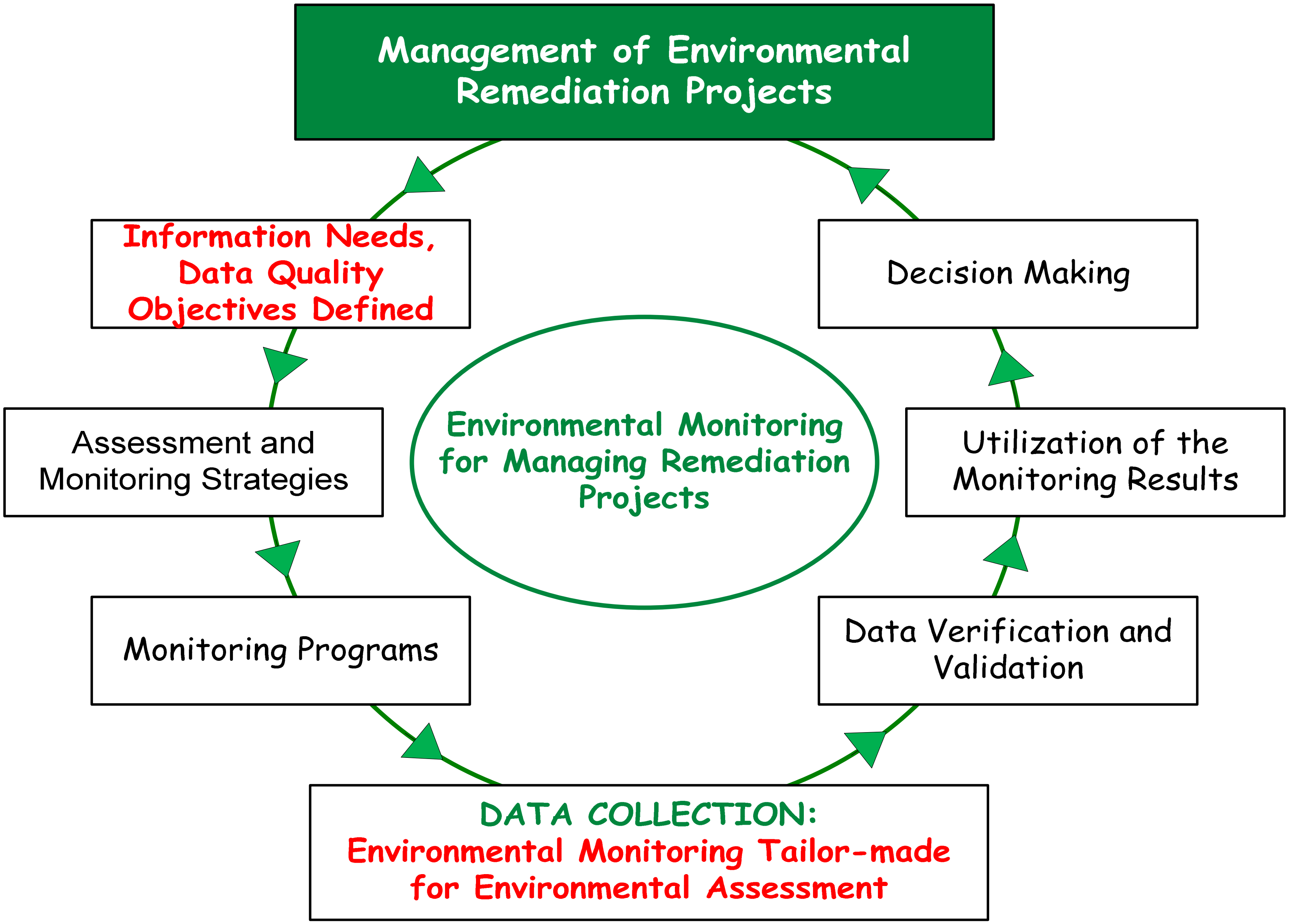
Tailor-made approach for monitoring remediation of oil-contamination in
Soil and Groundwater



Chain of events in the monitoring cycle

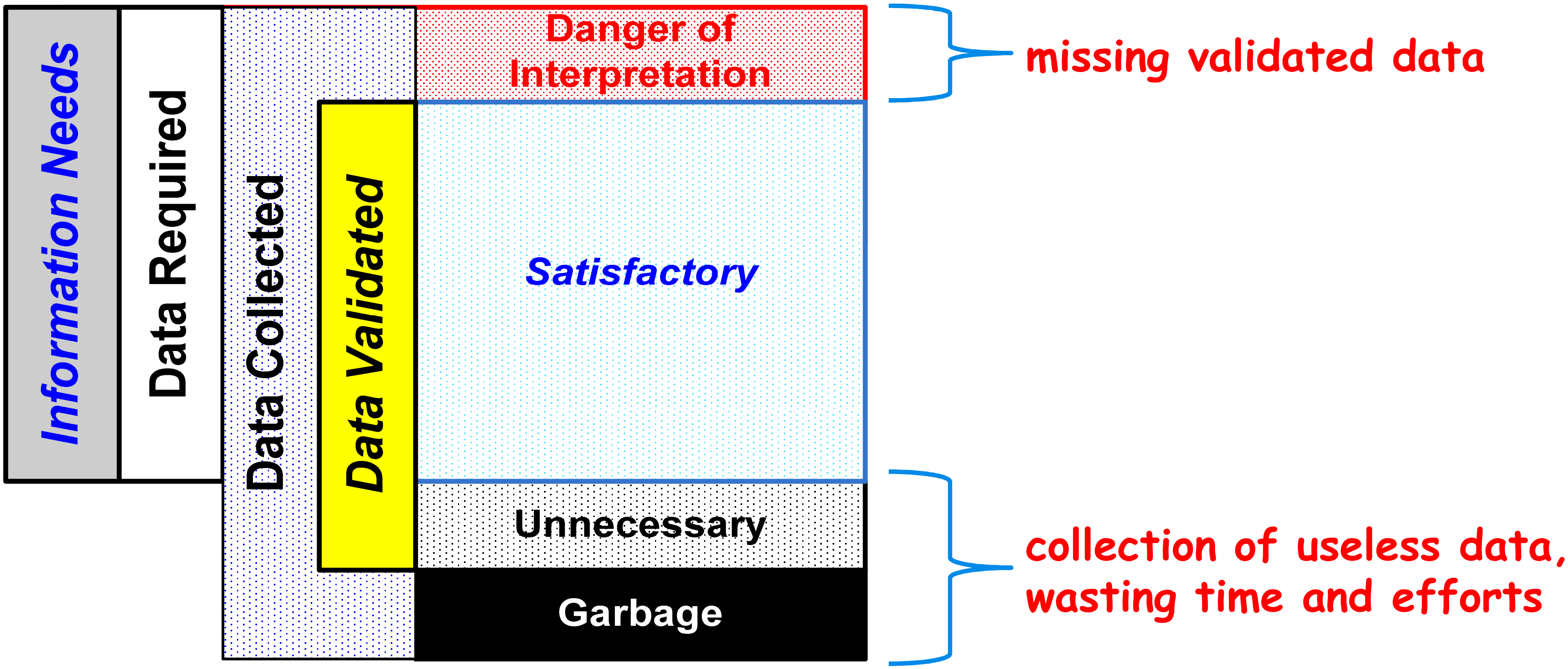
The information needs:

- Selection of parameters/indicators that sufficiently represent a specific information needs, without losing needed data and avoiding collection of unnecessary data, e.g., do not use costly (requiring specific instruments) analysis if a cheap one (simple) satisfy the requirements
- Relevant information margins for each monitoring parameter, that the information user is concerned about
- Specified requirements for reporting the information, such as short response time, e.g., achievement of the cleanup target concentration during excavation

Analytical methods to determine parameters satisfying the data/information needs:

There is no single analytical method to characterize oil-contamination in environmental samples. There are different analytical methods:

- starting from the simplest solvent extraction with gravimetric measurement to the
- identification and quantification of individual substances using the costly chromatographic separation and mass-spectrometric identification



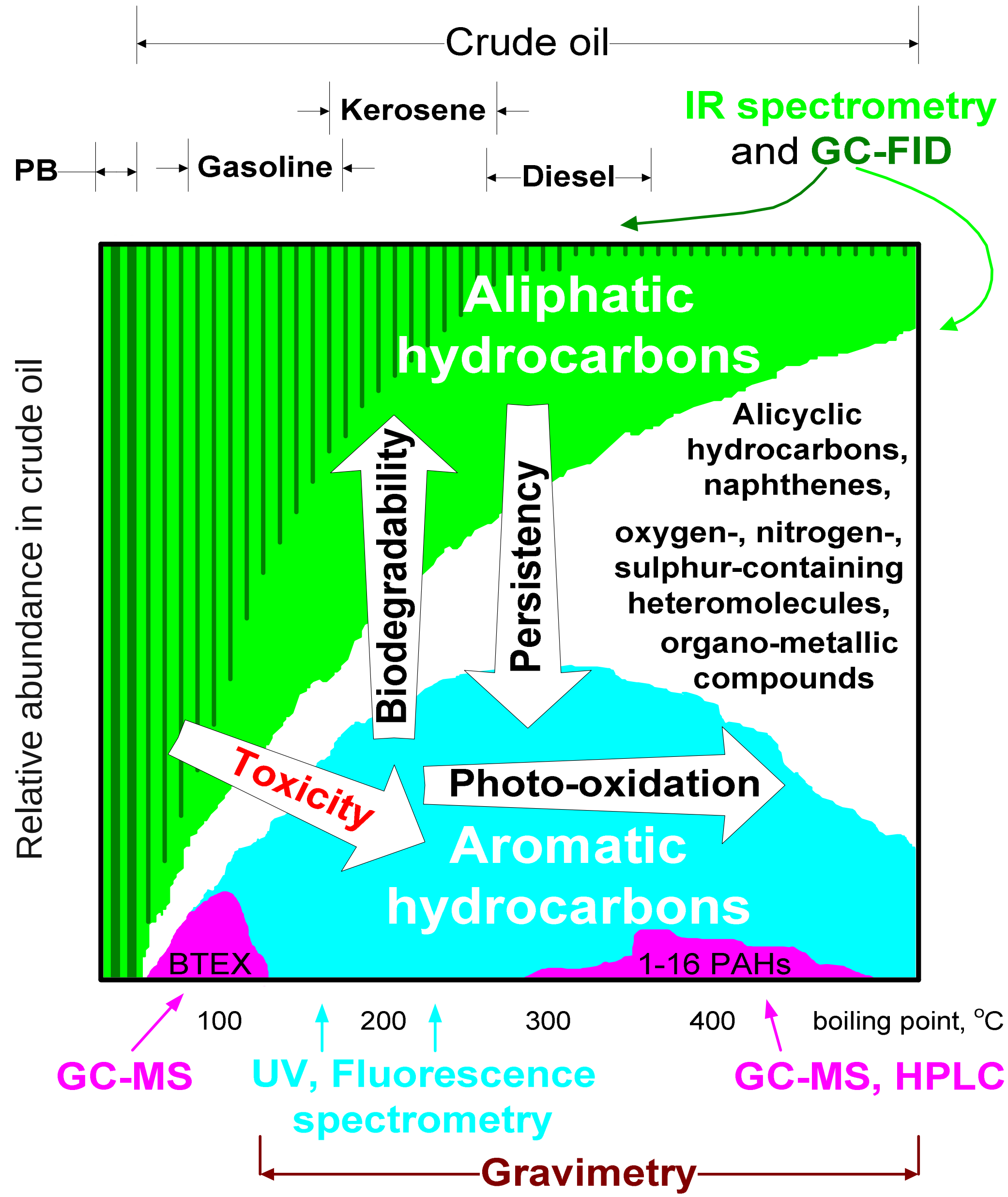
"Data Rich - Information Poor" syndrome

Considerations for selection of the fit-for-the-purpose analytical methods:

Petroleum is a complex mixture of

- aliphatic, aromatic and naphthenic hydrocarbons,
- hetero-molecules containing sulfur, nitrogen, oxygen atoms as well as trace metals in organic complexes

Alteration in the oil composition occurs during refining as well as during the physical, chemical and biological weathering processes in the environment



Overview: methods used to determine different petroleum components

Remediation of oil-contaminated desert soil

UNCC recommended:

(a) Excavation/landfilling (heavily contaminated soil, e.g., oil lakes, contaminated piles, trenches and spills)

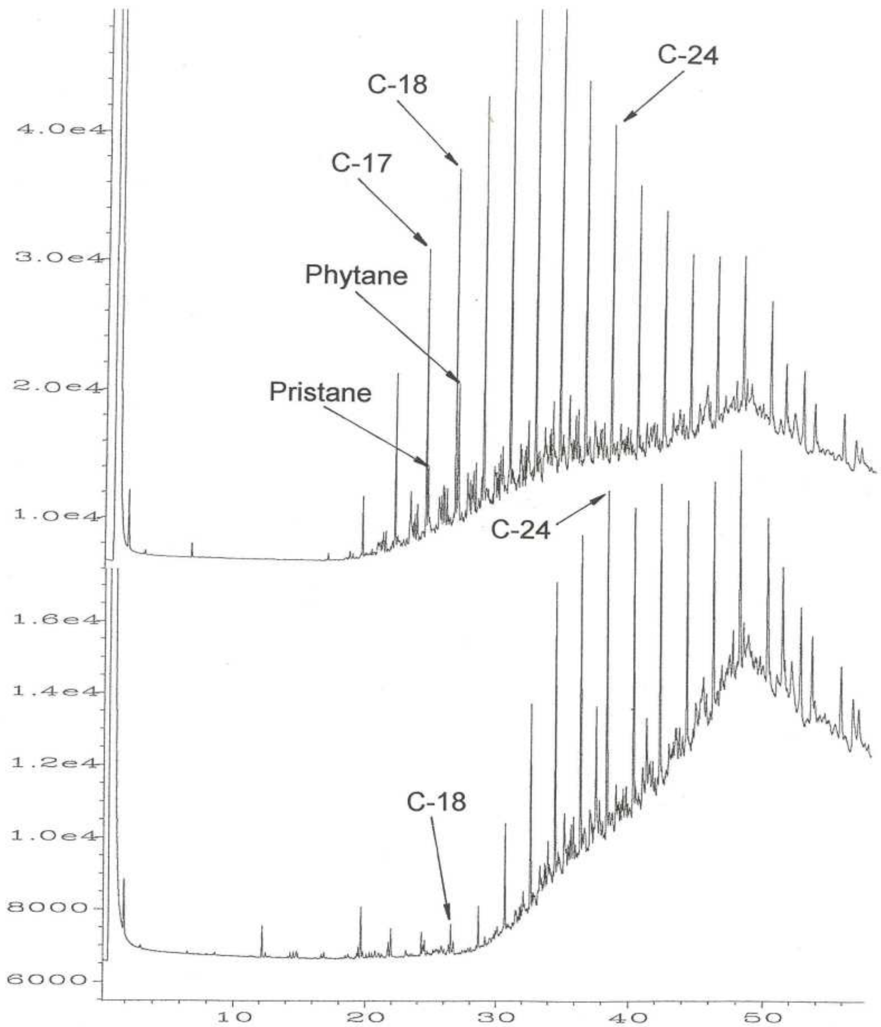
(b) Bioremediation of residual oil-contamination after excavation

Final clean-up target TPH: 5,000 mg/kg

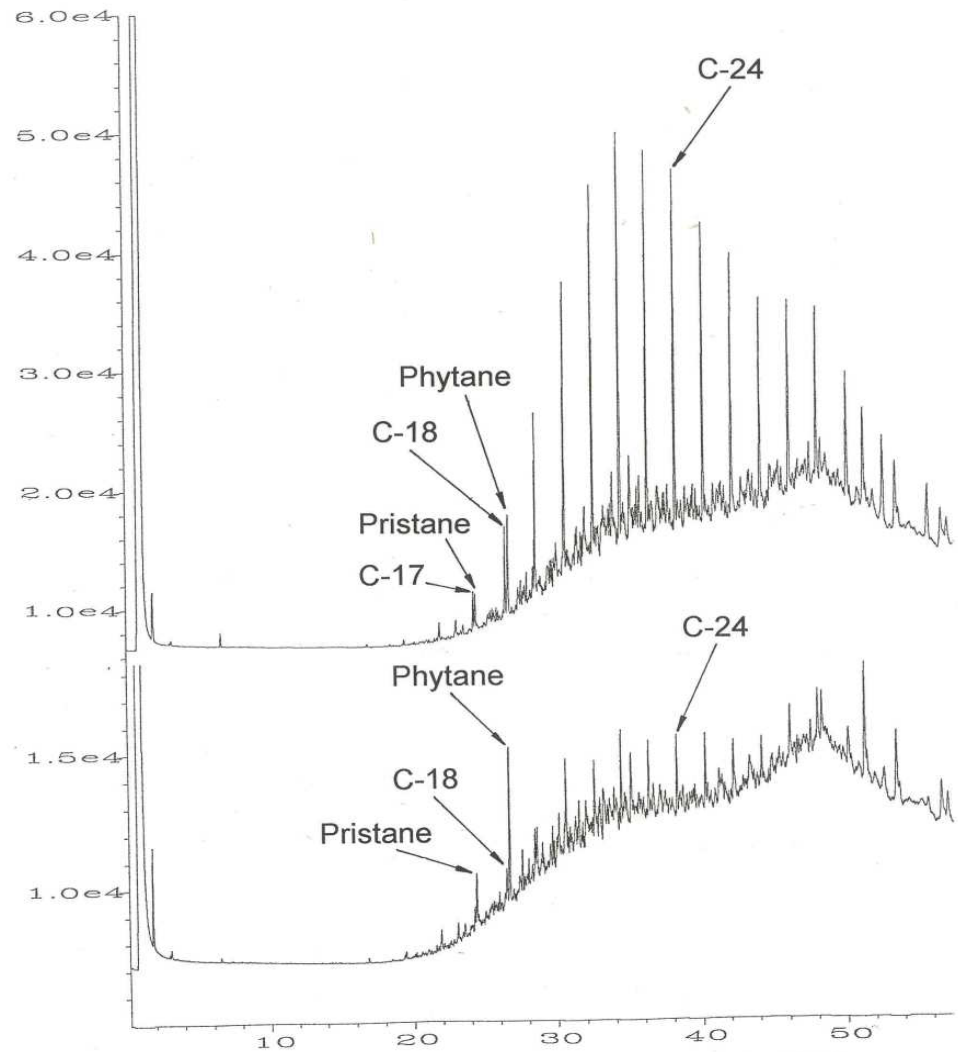
The tailor-made analytical approach for

(a) excavation/landfilling: GRAVIMETRY with the US-EPA Method 9071B, using n-Hexane as solvent, and

(b) bioremediation: GRAVIMETRY and GC/FID, as well as supporting parameters like nutrients, moisture, etc.

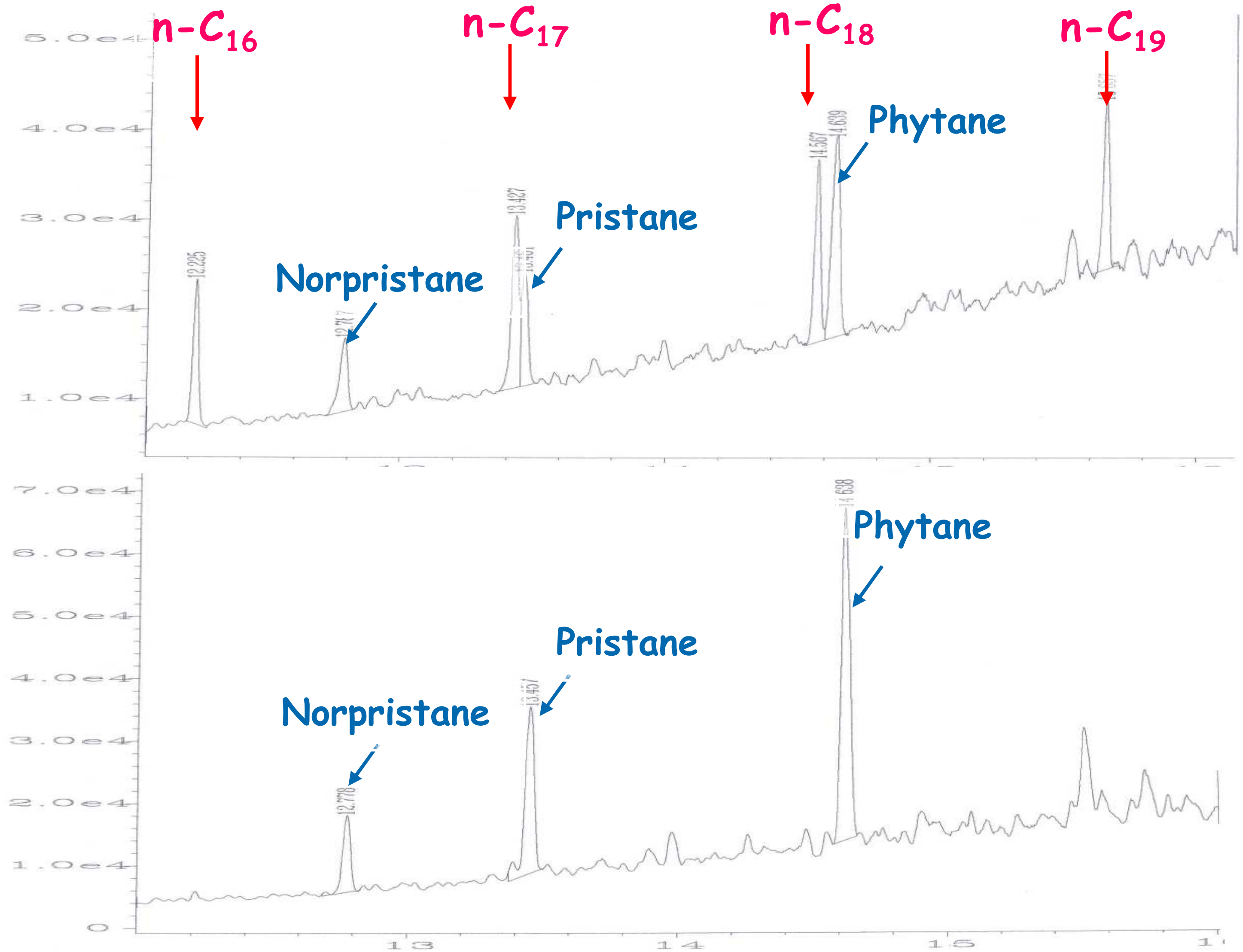


EVAPORATION

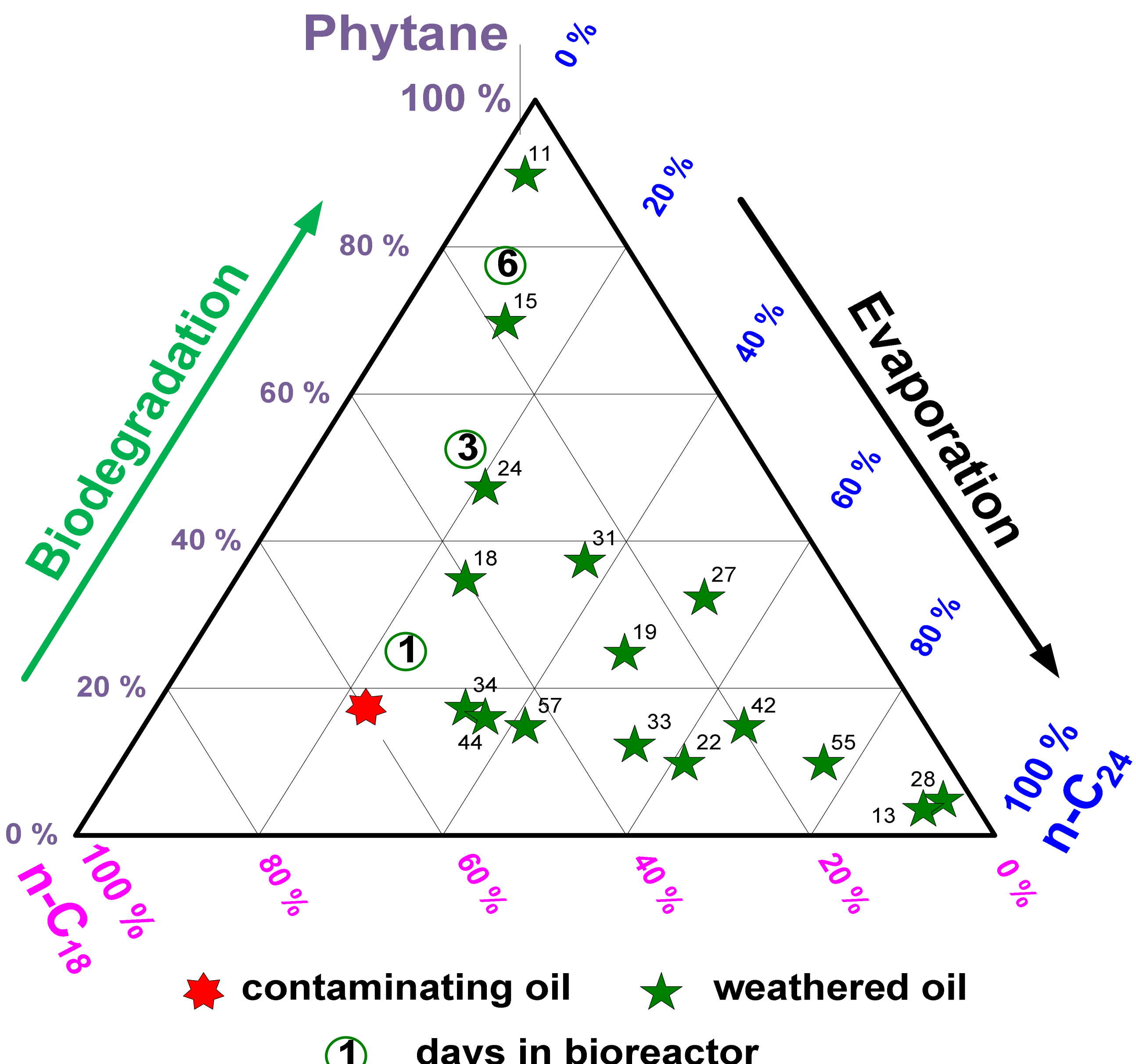


BIODEGRADATION

GC/FID profiles for characterization of evaporation and biodegradation of crude oil in the environment



Biodegradation of n-Alkanes versus Isoprenoid-alkanes



Variation in the composition of selected saturated hydrocarbons during physical/biological weathering of oil

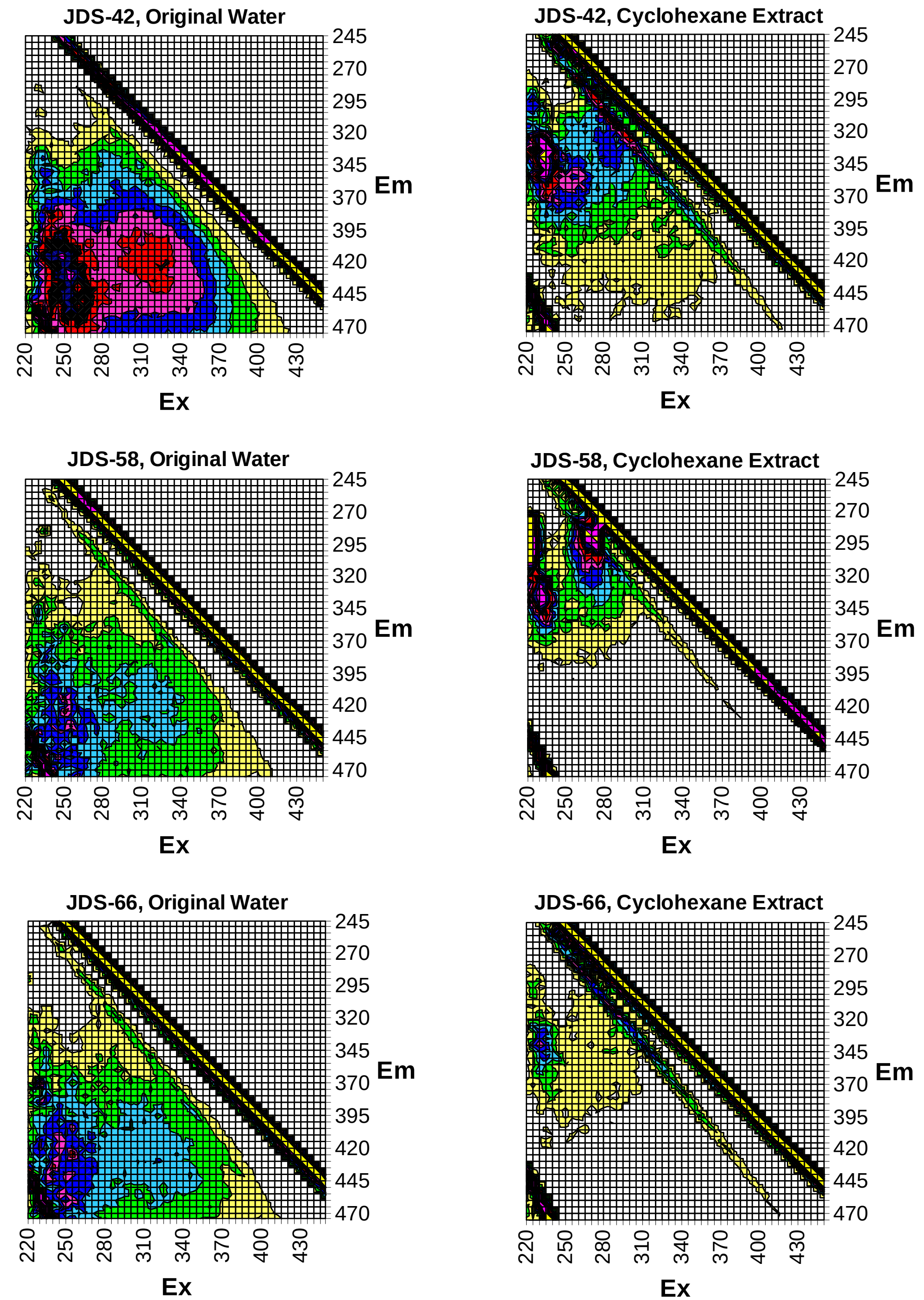
Remediation of contaminated groundwater

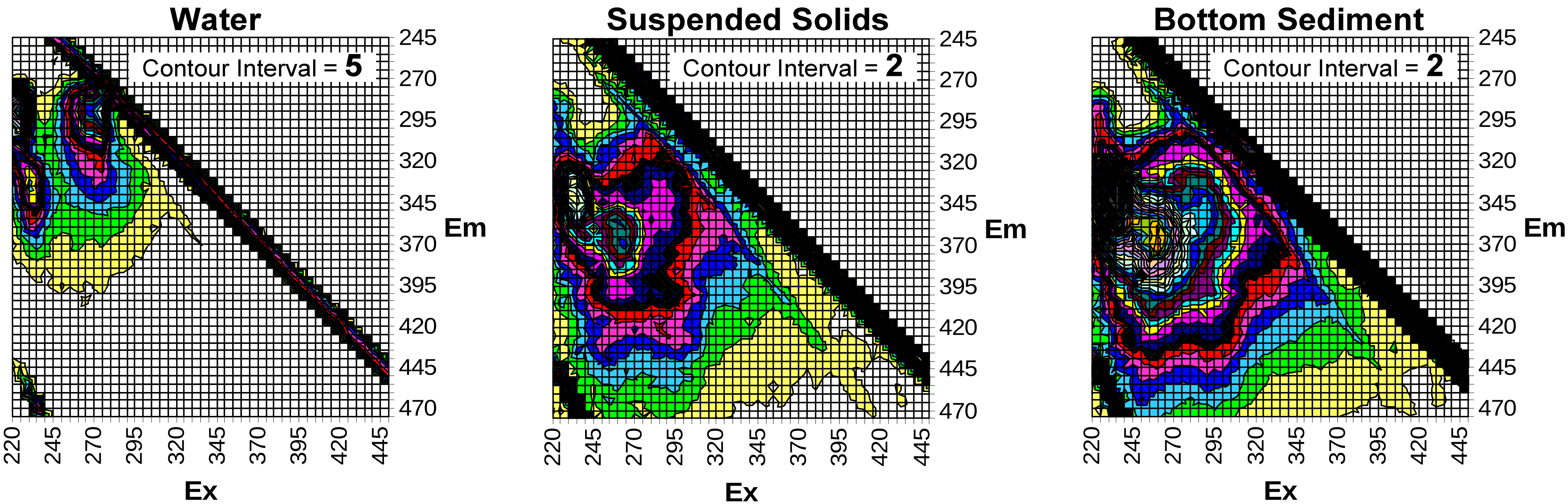
UNCC Independent Reviewers recommended to use the concentrations of oil-related parameters, i.e., Benzene and Benzo[a]pyrene in the WHO Drinking Water Guidelines, as remediation targets during remediation of contaminated fresh groundwater in the Northern oilfields in Kuwait: Raudhatain and Umm Al-Aish

Since neither Benzene nor Benzo[a]pyrene were present in detectable concentration in groundwater samples, KISR adapted a fluorescence "fingerprinting" method, which has been successfully used for tracing the migration of the oil-related contamination from the surface, e.g., from oil lakes, to the sub-surface (groundwater) aquifer

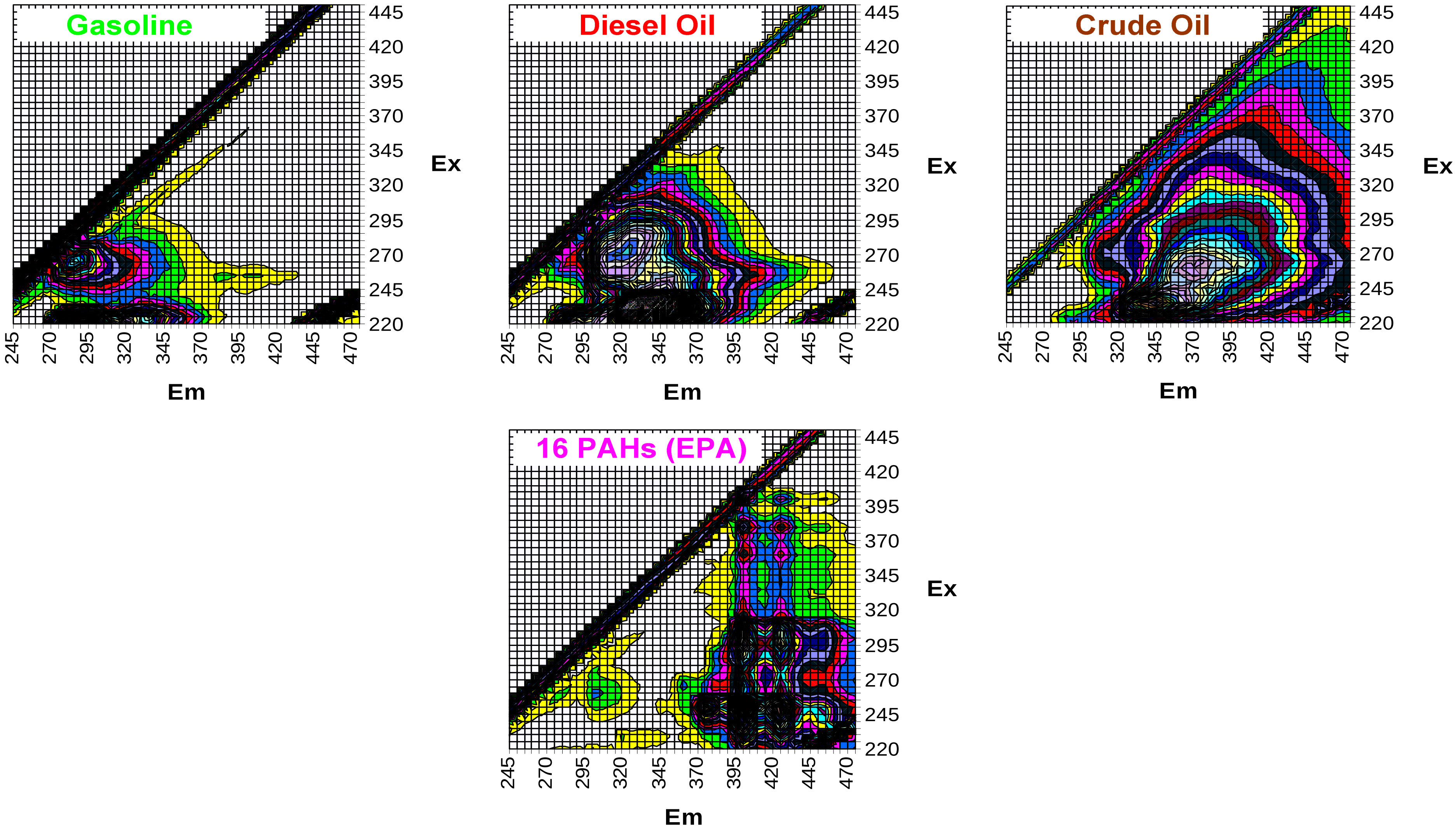
Earlier studies in the Danube river basin:

Fluorescence contour diagram of river water samples and their cyclohexane extracts showing gasoline/diesel oil contamination and presence of humic substances





Fluorescence contour diagram of cyclohexane extracts of water, suspended solids and bottom sediment samples in surface water (Danube river)

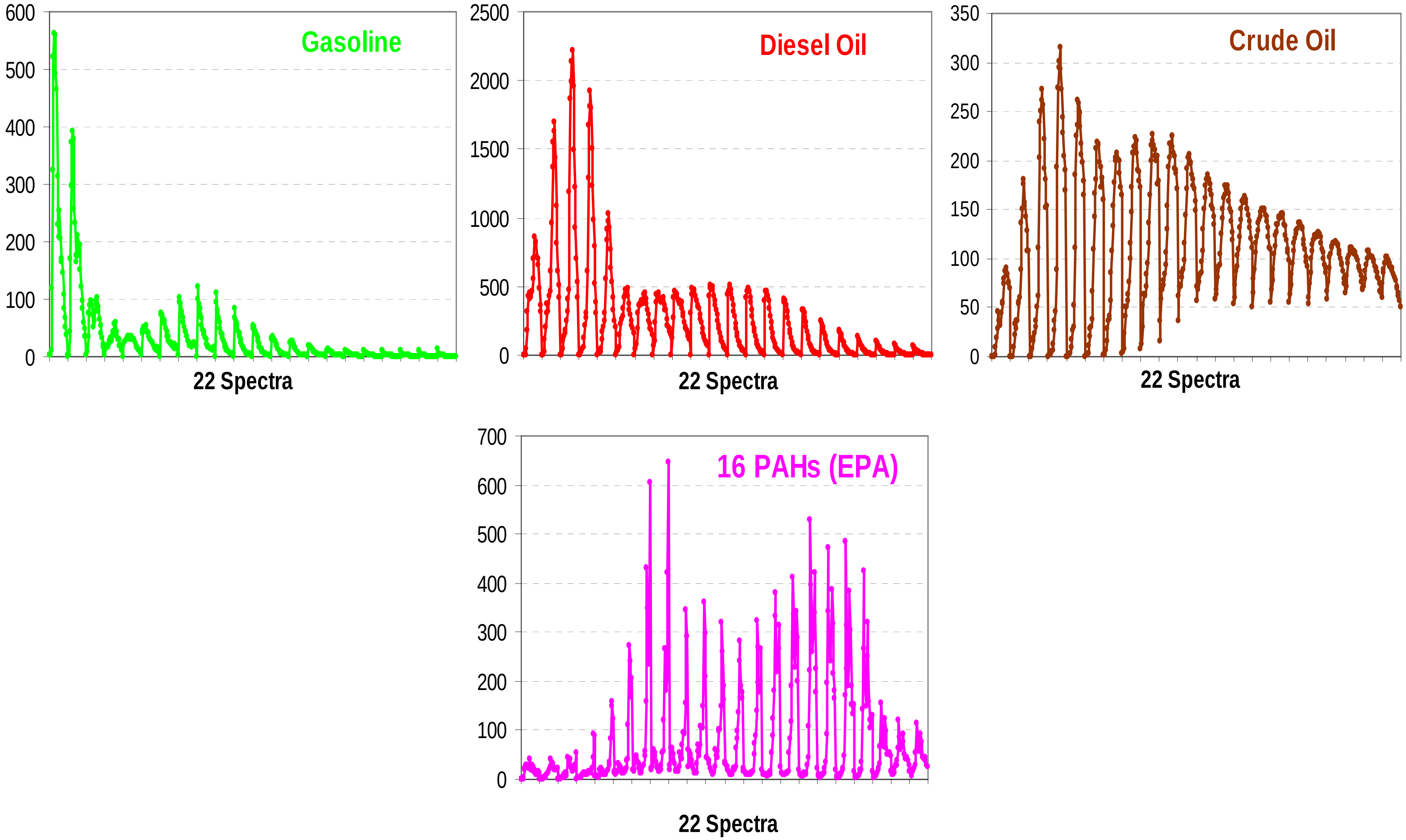


Fluorescence fingerprints (contour diagrams) of selected calibration standards

(Gasoline, 1 µg/ml; Diesel Oil, 1 µg/ml; Crude Oil, 1 µg/ml; and 16 PAHs (US-EPA), each 3 ng/ml; in cyclohexane).

Spectrum Number	Excitation Wavelength	Emission Range	
Spectrum 1	220 nm	250 nm	365 nm
Spectrum 2	225 nm	255 nm	370 nm
Spectrum 3	230 nm	260 nm	375 nm
Spectrum 4	235 nm	265 nm	380 nm
Spectrum 5	240 nm	270 nm	385 nm
Spectrum 6	245 nm	275 nm	390 nm
Spectrum 7	250 nm	280 nm	395 nm
Spectrum 8	255 nm	285 nm	400 nm
Spectrum 9	260 nm	290 nm	405 nm
Spectrum 10	265 nm	295 nm	410 nm
Spectrum 11	270 nm	300 nm	415 nm
Spectrum 12	275 nm	305 nm	420 nm
Spectrum 13	280 nm	310 nm	425 nm
Spectrum 14	285 nm	315 nm	430 nm
Spectrum 15	290 nm	320 nm	435 nm
Spectrum 16	295 nm	325 nm	440 nm
Spectrum 17	300 nm	330 nm	445 nm
Spectrum 18	305 nm	335 nm	450 nm
Spectrum 19	310 nm	340 nm	455 nm
Spectrum 20	315 nm	345 nm	460 nm
Spectrum 21	320 nm	350 nm	465 nm
Spectrum 22	325 nm	355 nm	470 nm

Decomposed concatenated spectra



Concatenated fluorescence spectra of the calibration standards

(Gasoline, 1 µg/ml; Diesel Oil, 1 µg/ml; Crude Oil, 1 µg/ml; and 16 PAHs (EPA), each 3 ng/ml; in cyclohexane).

Application of fluorescence fingerprinting in characterization of oil-contamination in groundwater in the Northern oilfield in Kuwait

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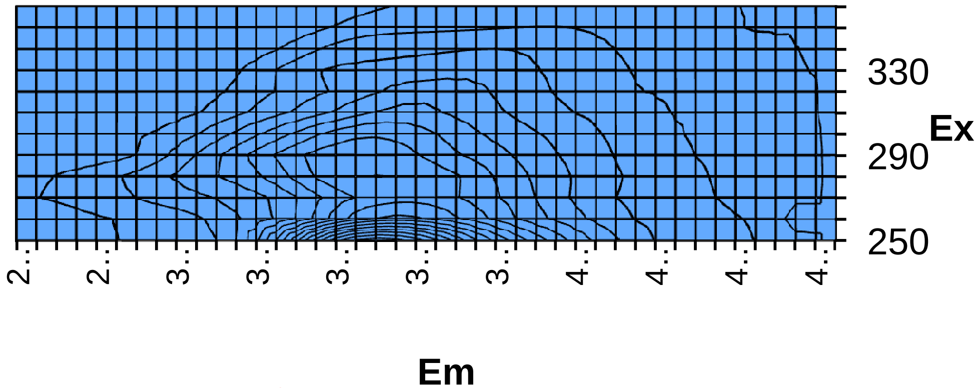
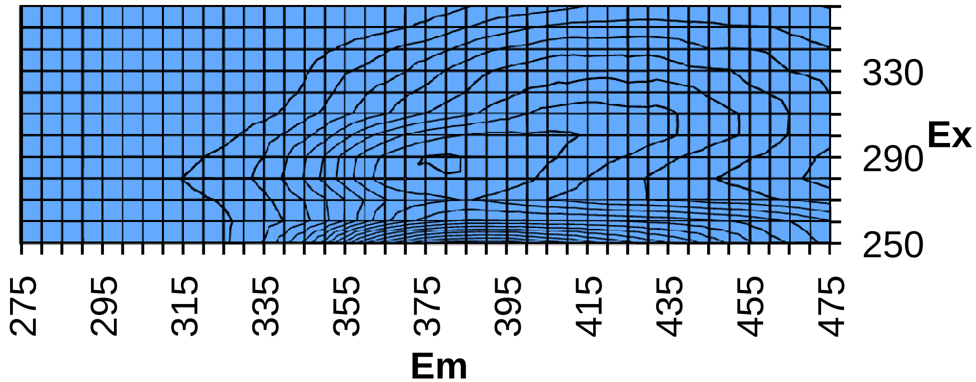
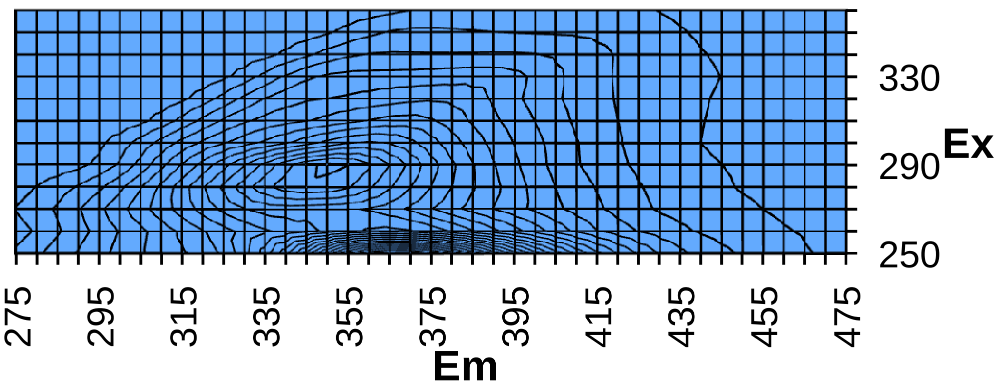
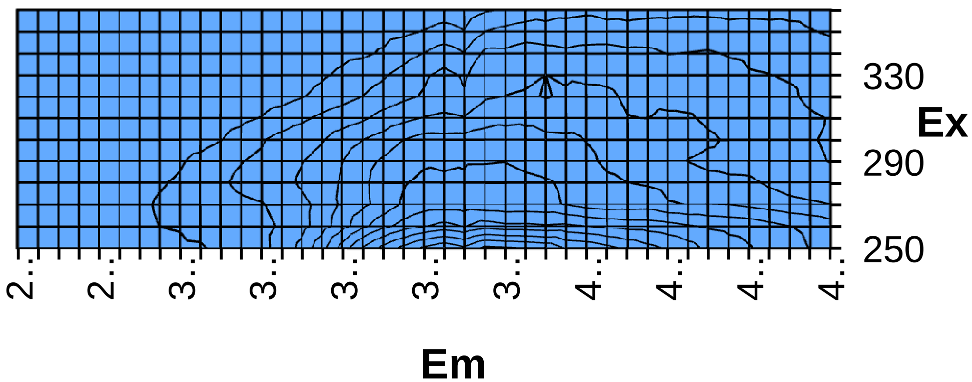




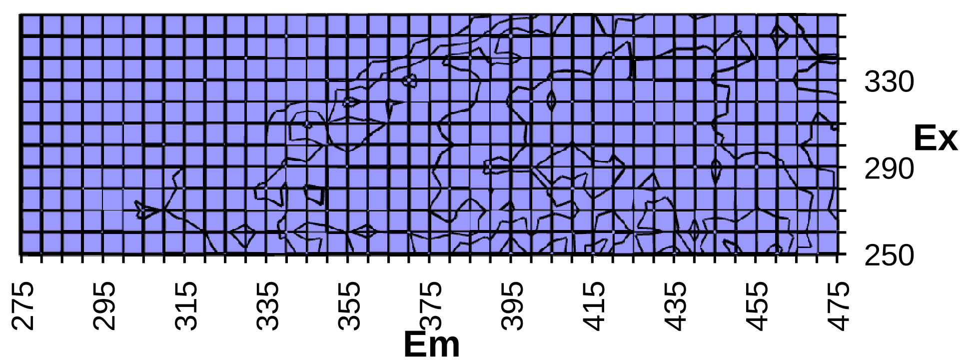
Cyclohexane extract and Water leachate
of oil-contaminated surface soil in the Northern oilfield



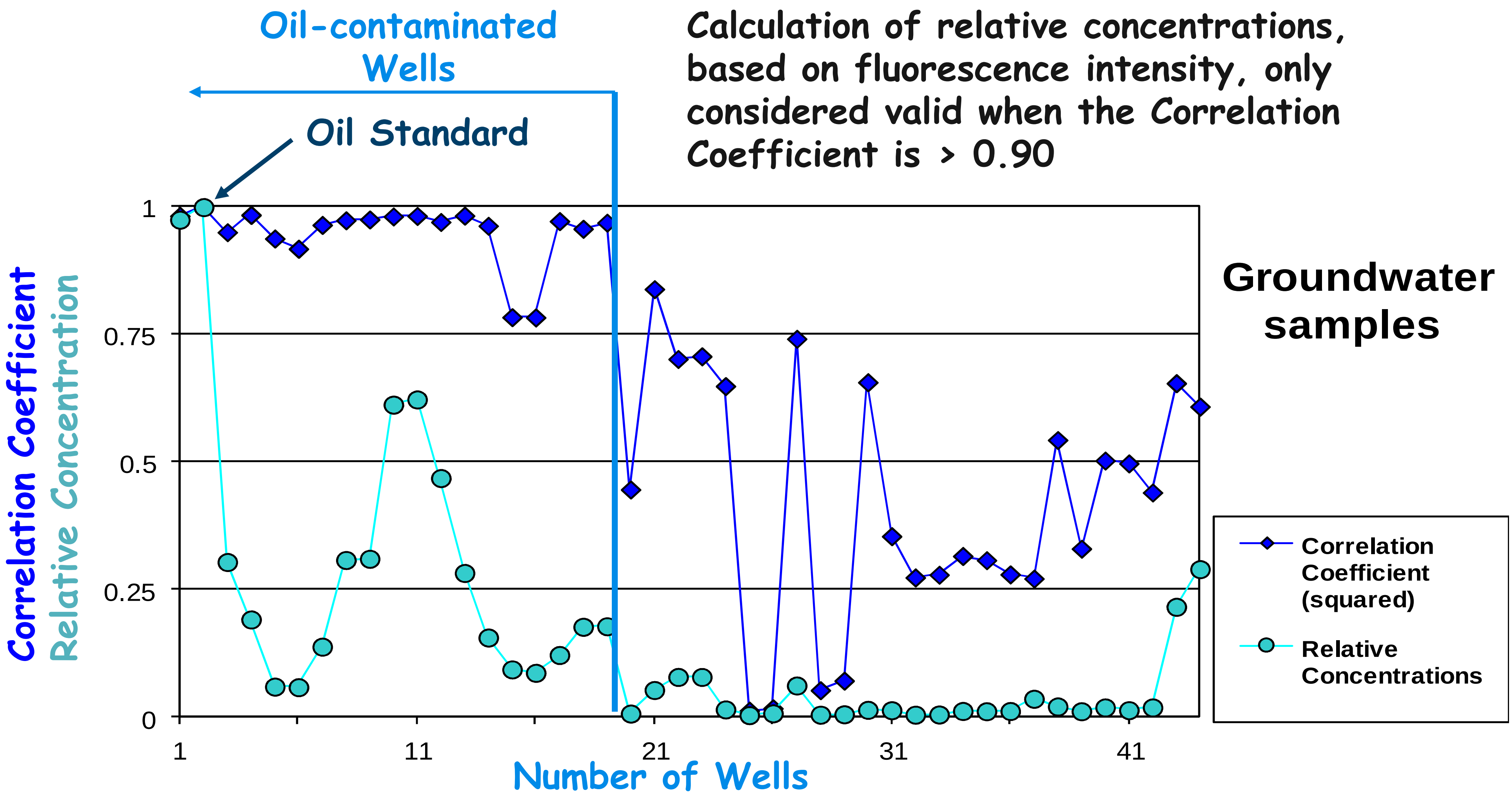


Cyclohexane extract and Water
of well (P18) water from the Northern oilfield

Humic substances in water



Calculation of relative concentrations, based on fluorescence intensity, only considered valid when the Correlation Coefficient is > 0.90



Groundwater samples collected from North Kuwait (Umm Al-Aish) underneath oil-contaminated surface soil

Concatenated fluorescence spectra of water samples correlated against "Oil Standard" (water leachate from oil-contaminated soil)

In-situ detection of petroleum contamination

Laser induced fluorescence (LIF) technique has been used to remotely screen oil contamination in the environment.

The technique has been extended to oil-contaminated soils; this has led to the development of LIF systems that can be used as screening tools for characterizing oil-contamination.

The accuracy of the technique has been improved through the introduction of appropriate calibration procedures and by combining LIF measurements with diffuse reflectance (DR) measurements to take into consideration the variability in the optical properties of different soil types.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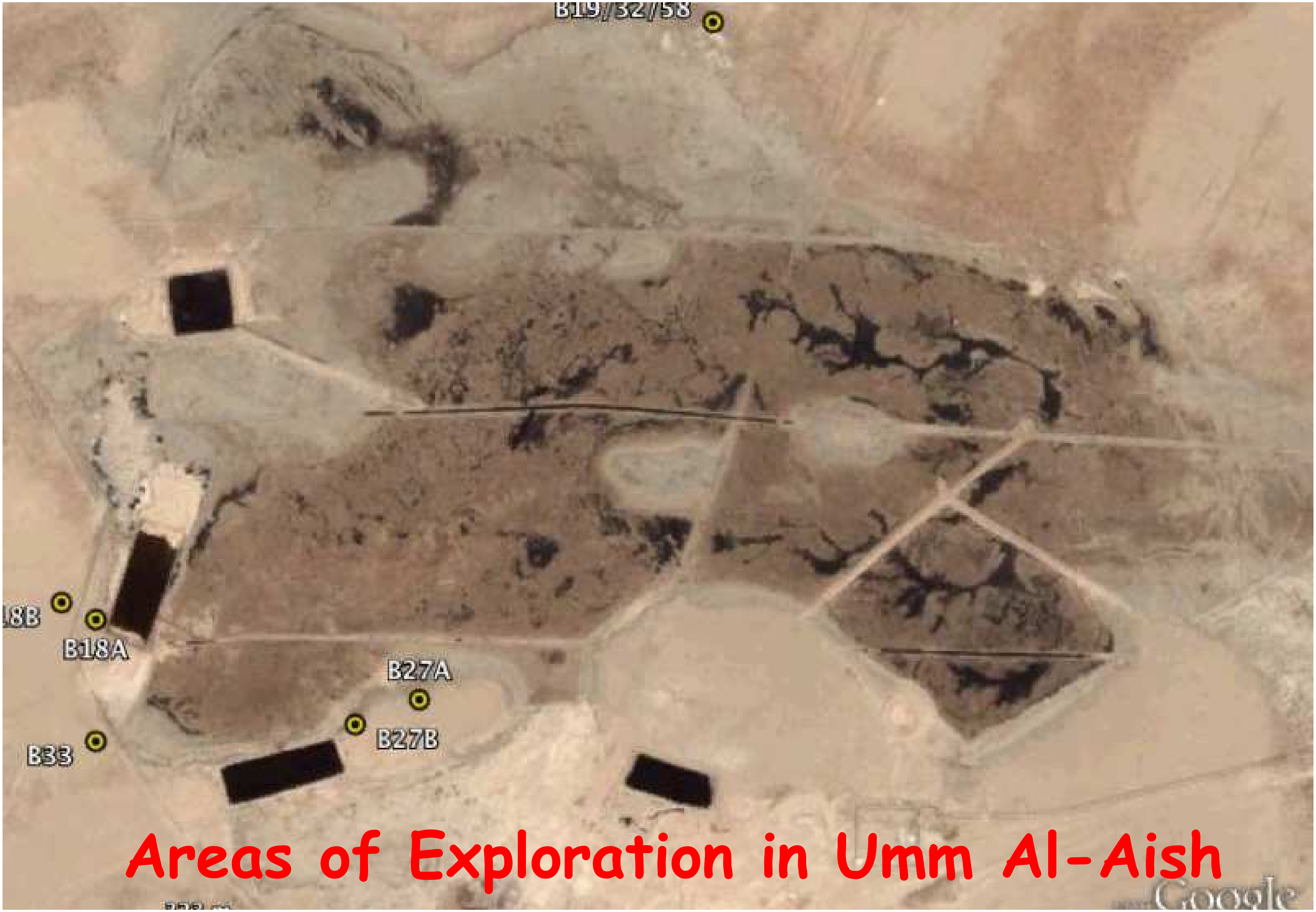
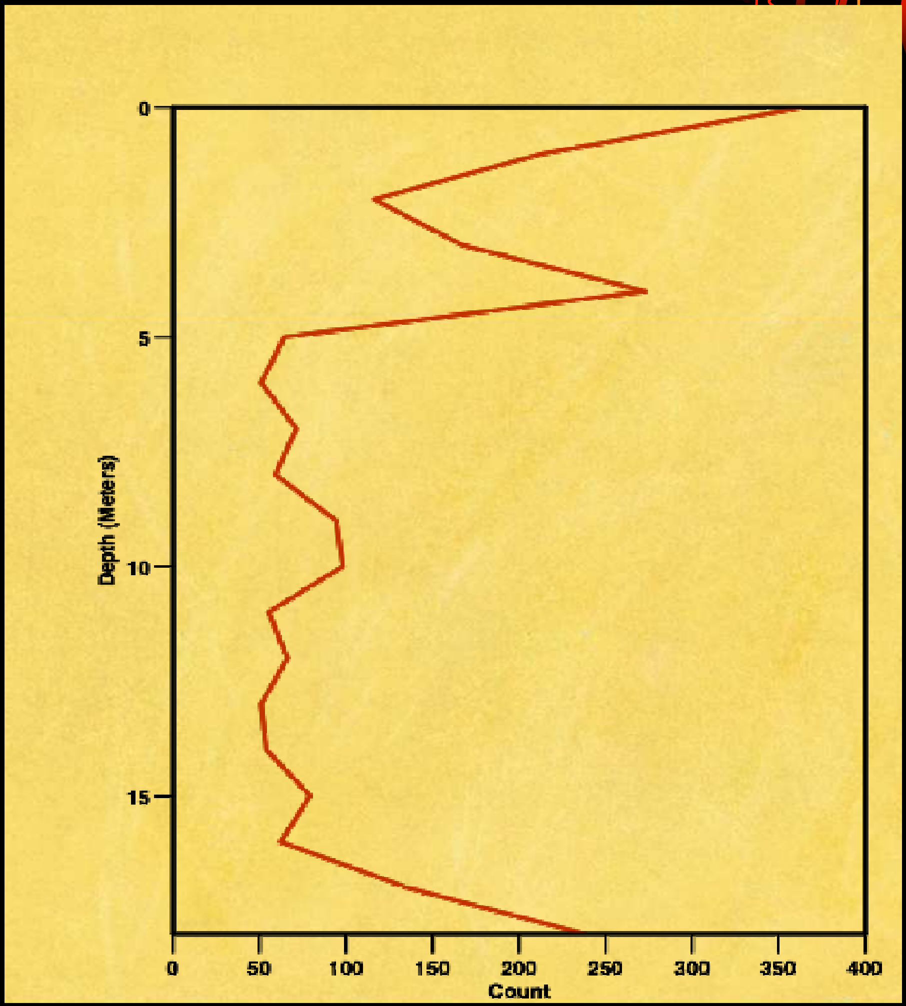
The LIF Probe

Operating the LIF Probe


B18A
B27A
B27B
B33
Areas of Exploration in Umm Al-Aish

Taking Depth Measurements
Example: Borehole 18A

Depth, m	Count
0	364
1 2 3 4 5 6	214
2	116
3	167
4	273
5	64
6	51
7	71
8	59
9	94
10	98
11	55
12	66
13	51
14	54
15	79
16	62
17	136
18	238



Conclusions (1)

Measuring the total extractable matter with gravimetric method can be acceptable for monitoring the effectiveness of excavation and landfilling of highly oil-contaminated soil, as well as the achievement of the 5,000 ppm (TPH) remediation target during bioremediation of the residual oil-contamination after excavation

GC/FID chromatogram can be effectively used for characterizing the effectiveness of bioremediation of the oil contamination, as well as differentiation between progressing biodegradation and evaporation of the petroleum components in the environment

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Conclusions (2)

After long-time environmental weathering of the crude oil, the mono- and poly-aromatic parent hydrocarbons are likely evaporated or degraded, into polar conversion products, that infiltrate into the subsurface aquifer. The total fluorescence spectra of the water and its cyclohexane extract can be effectively used for monitoring the oil-related contamination and its natural attenuation in the groundwater

The *in-situ* measurement of the fluorescence with the LIF probe to map the level of oil-contamination in the soil in the affected areas was proved to be cost-effective for fast screening, characterizing and mapping of the oil-contaminated soil in the oilfields


THANK YOU