OP KŽP

European Union
Cohesion Fund

MINISTRY
OF ENVIRONMENT
OF THE SLOVAK REPUBLIC

SLOVAK
ENVIRONMENT
AGENCY

SLOVAK ENVIRONMENT AGENCY
is implementing an activity

INTERNATIONAL CONFERENCE
CONTAMINATED SITES
ZNEČISTENÉ ÚZEMIA
MEDZINÁRODNÁ KONFERENCIA

INTERNATIONAL CONFERENCE

CONTAMINATED SITES 2018

BANSKÁ BYSTRICA, SLOVAK REPUBLIC, 8 – 10 OCTOBER 2018

The activity has been implemented within the framework of national project
Information and providing advice on improving the quality of environment in Slovakia.
The project is cofinanced by Cohesion Fund of the EU under Operational programme Quality of Environment.

www.op.kzp.sk *www.minzp.sk* *www.sazp.sk*

Chemical And Biological Remediation Of Kuwait Groundwater After The Gulf War: Laboratory Testing

Karel Waska

EPS biotechnology, s.r.o.; EPS Slovensko, s.r.o.

karel.waska@epsbiotechnology.cz

The activity has been implemented within the framework of national project ***Information and providing advice on improving the quality of environment in Slovakia****.*
The project is cofinanced by Cohesion Fund of the EU under Operational programme Quality of Environment.

OP KŽP

European Union
Cohesion Fund

MINISTRY OF ENVIRONMENT OF THE SLOVAK REPUBLIC

SLOVAK ENVIRONMENT AGENCY

CHEMICAL AND BIOLOGICAL REMEDIATION OF KUWAIT GROUNDWATER AFTER THE GULF WAR

LABORATORY TESTING

Karel Waska[1,2], Boris Bodacz[2], Petr Beneš[1,2], Martina Siglová[1],
Robert Hovorič[2], Miroslav Minařík[1,2]

[1] EPS biotechnology, s.r.o.
[2] EPS Slovensko, s.r.o.

Conclusion:

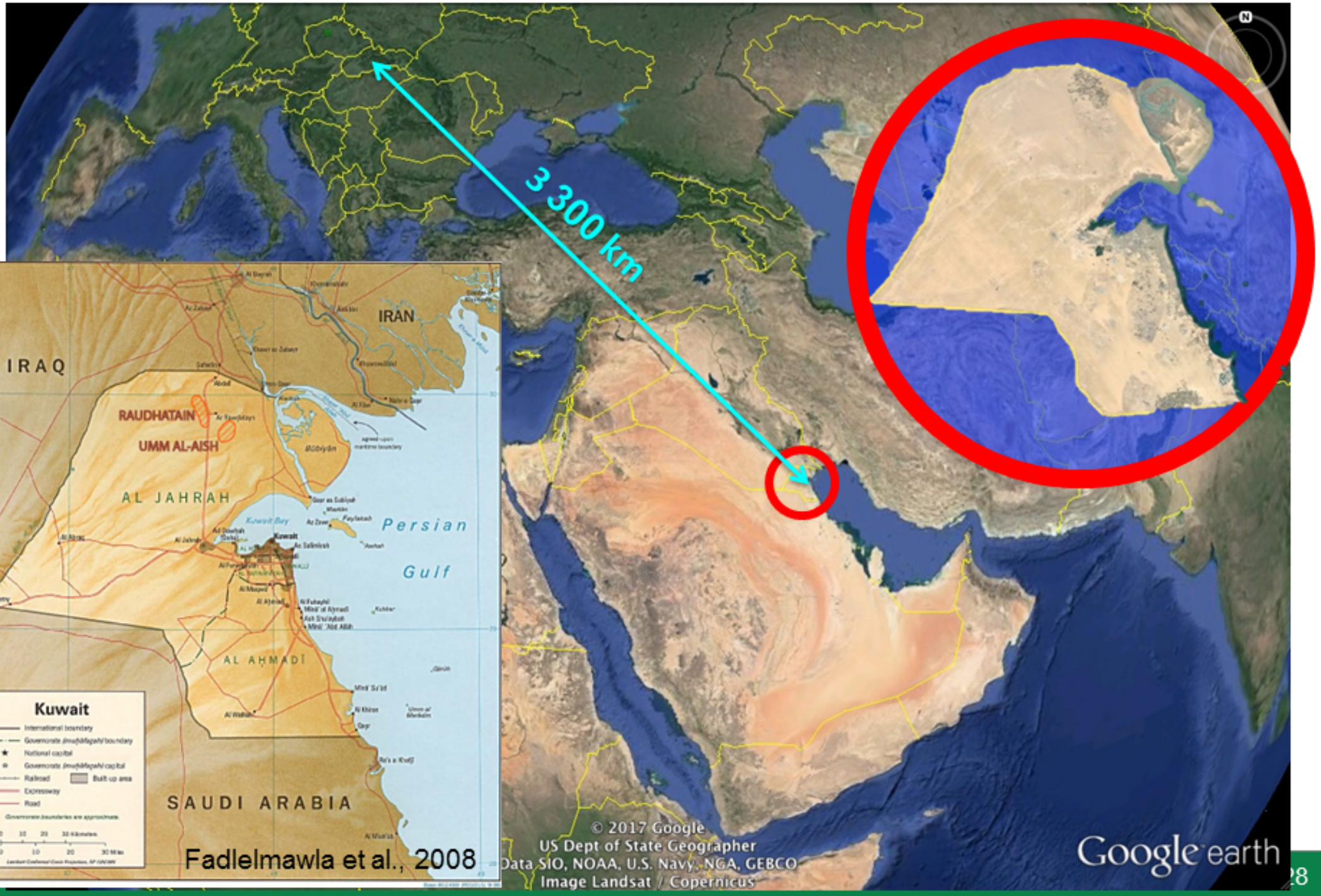
1. Geochemical character of the gw. samples does not allow bioremediation without pre-processing.

2. *In-situ* chemical oxidation of TPH is feasible without pre-processing.

3. Desalination technology of sufficient capacity is available (= a way of pre-processing?).

Take-home message

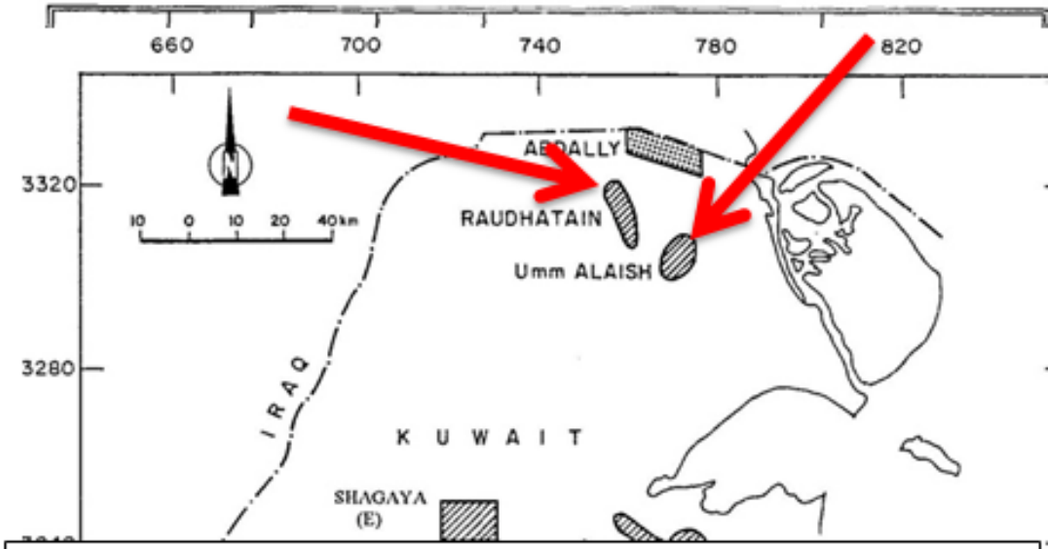
Geography


3 300 km
IRAN
IRAQ
RAUDHATAIN
UMM AL-AISH
AL JAHRAH
Persian
Gulf
Kuwait
AL AHMADI
SAUDI ARABIA
Kuwait
Fadlelmawla et al., 2008
© 2017 Google
US Dept of State Geographer
Data SIO, NOAA, U.S. Navy, NGA, GEBCO
Image Landsat / Copernicus
Google earth

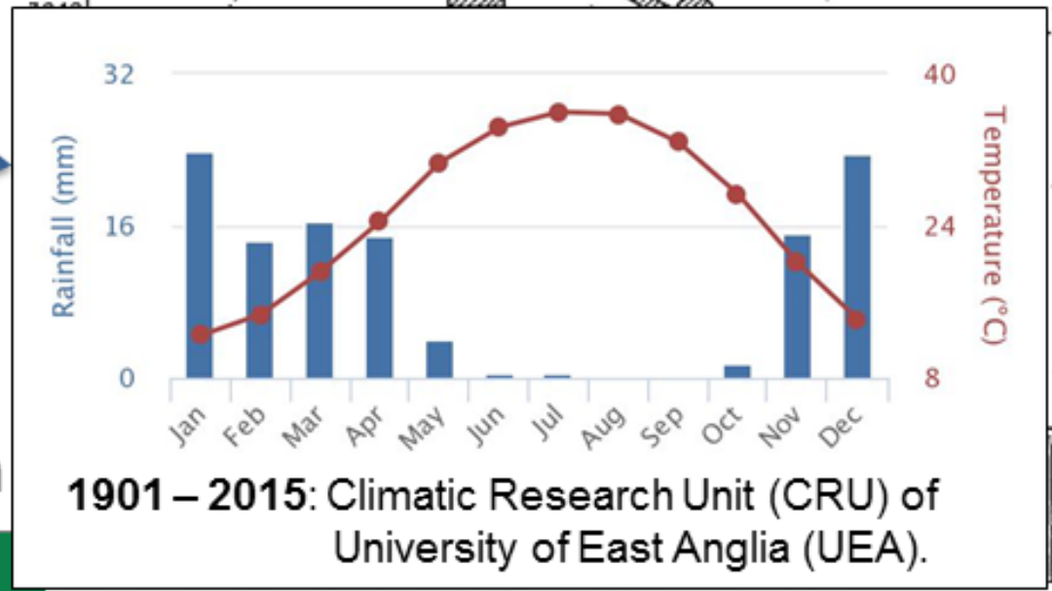
Geology, hydrogeology, hydrology

- 2 major water-bearing formations:
  - Kuwait group (conglomeratic sand/gravel) and
  - Damman formation (limestone, dolomite)

- 2 major drainage basins:
  - **Raudhatain**
  - **Umm Al-Aish**
    - Isolated lenses of freshwater
    - morf.: accumulation basins with large watersheds (wadis, creeks)



- Annual precipitation:
  - 121 mm/yr
  - Occasional rain infiltration (forming "playa" lakes)
  - Max. precipitation 40 mm/15-30 min



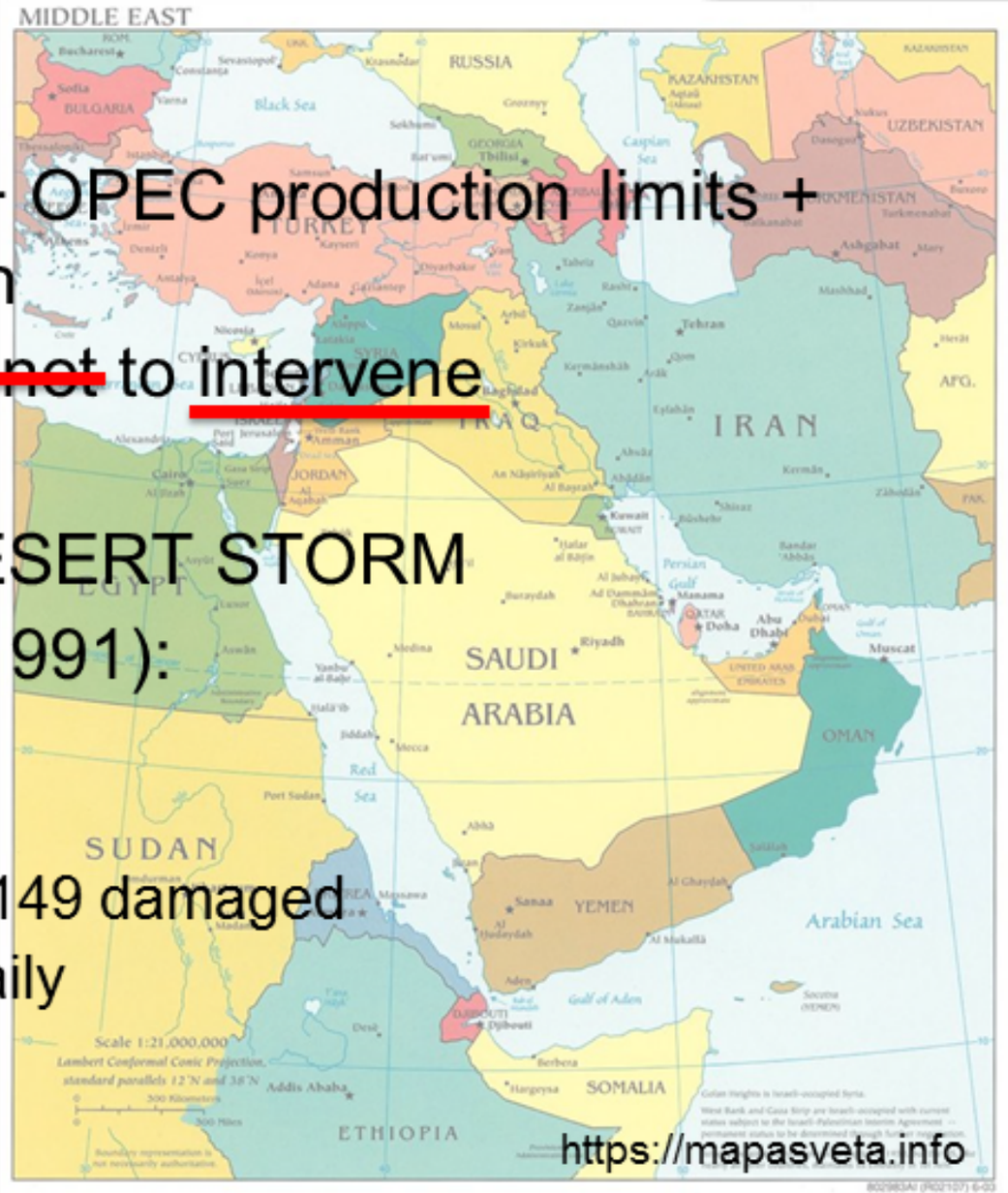
1901 – 2015: Climatic Research Unit (CRU) of University of East Anglia (UEA).

Water resources

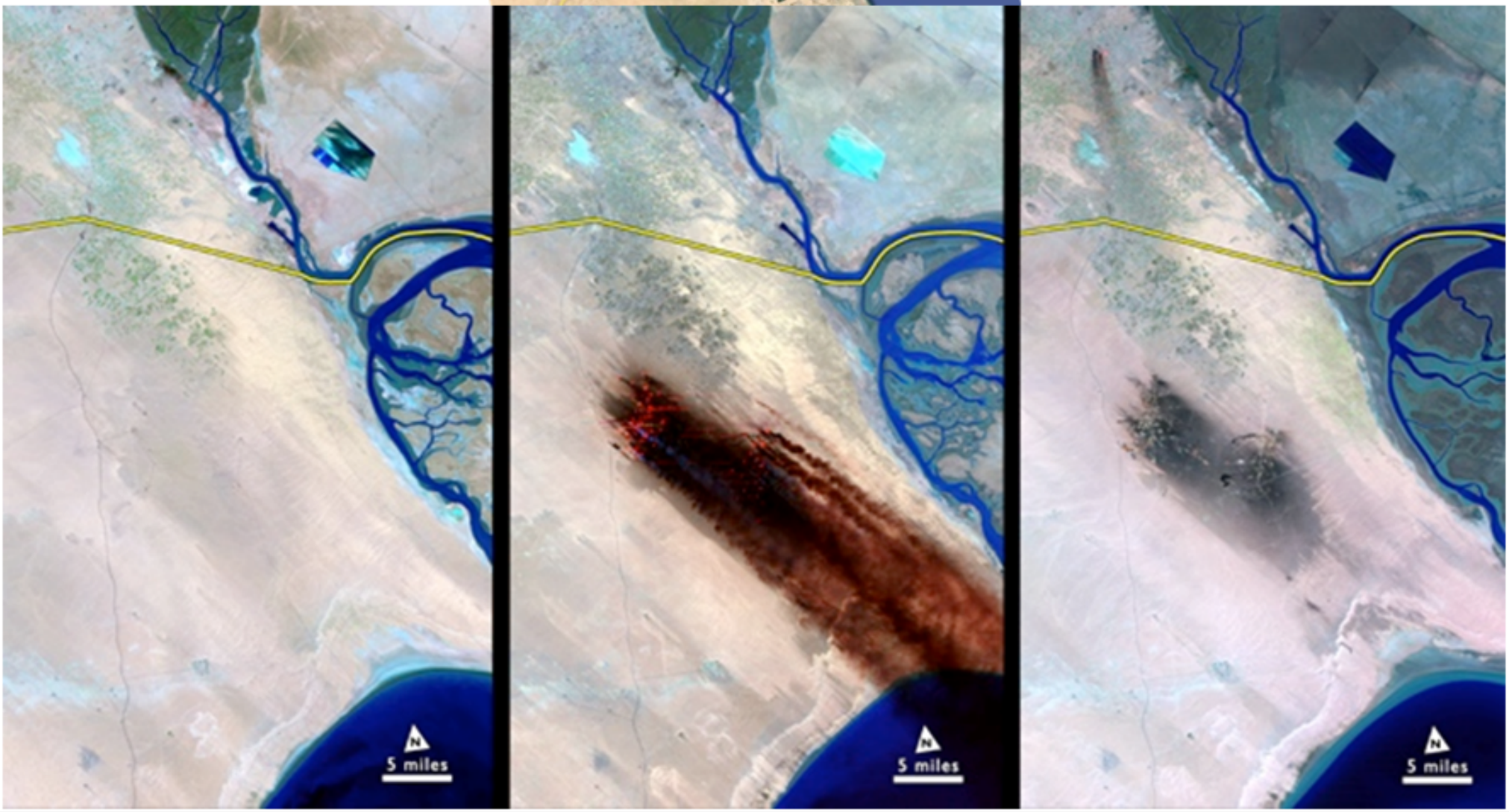
- By 2040, Kuwait will be one of the 9 most draught-threatened countries (World Resource Institute; August 2015).
- Groundwater usage: extraction rate = 12x recharge rate
- Tap water *per capita* usage = 442 L/day in 2014 (Mukhopadhyay and Akber, 2018)
  - (CZE = 87 L/day in 2014; CSO, May-2015)
  - Public use with no taxes/fees (governmental subsidies)
- Sea water desalination = main source of fresh water = 95%
- Gw. pumping = 5% of fresh water usage

The Gulf War

- Aug-2-1990 – Feb-28-1991
- Iraqi debts after war with Iran + OPEC production limits + Kuwait crude-oil overproduction
- USA ensured Saddam Husain ~~not~~ to intervene
- => Iraqi invasion of Kuwait…
- Jan-17-1991: OPERATION DESERT STORM
- "Scorched earth" tactics (Mar/1991):
- Out of 914 operational oil wells
- 798 blasted & undermined =>
- 604 on fire, 45 spouting oil and gas, 149 damaged
- Up to 6 M crude oil barrels burned daily
- Fire-fighting until Nov-6-1991
- TOTAL of 240 M m^3 crude oil burned
- TOTAL of 3,5 M m^3 crude oil leaked
- Combustion products (soot & ash) cover ca. 1772 km^2 (10% of Kuwait)



The Gulf War



The largest crude-oil leak in history

- Ca 2M m^3 of crude oil leaked into Arabian Gulf
- 300 crude oil lakes (h = 2m, A = 49 km^2)

Environmental impact

- Crude oil = complex mixture of multi-carbon chains and VOCs:
- saturated alkanes, or aromatic hydrocarbons, nitrous compounds (e.g., pyrrole, pyridine), or sulphuric compounds (e.g., thiophenol, benzo-thiophene)
- Molecular Sulfur = 2,25 hm.% => atmospheric imissions => acid rain
- **!! Natural and combustion PAH (eg. benzo[a]pyrene)!!**
- Contamination risk-potential (for gw. resources):

1. Direct infiltration from crude oil lakes:
   - Not very likely <= crude oil weathering and "asphalting"=> vadose zone retardation (numerical & empirical models: >100 yrs to reach the aquifer)
2. Combustion products deposited on land and leached by precipitation,
   - Most serious threat identified so far (<20 days to rech the aquifer)
3. Infiltration of the fire extinguishing-seawater => gw. salinization
4. Undetected (underground) leaks from damaged oil infrastructure

- Despite the removal of 95% of the leaked crude oil, sites with highly contaminated soils persist.

Environmental remedy

- Many projects in progress – under the auspices of the UNEP
  - Soil cleaning: among others studied by Dr. Al Mutairi
  - Groundwater remediation:
    - Source areas &
    - Recipient areas **=> EPS =>**
- Laboratory testing of Umm Al-Aish gw. remediation:
  - Bioremediation
  - ISCO
  - Desalination

Remediation target values

Groundwater Quality Parameter	*In situ* conditions	Remediation unit output requirement
TDS	Before contamination: 1 500 mg × L^{-1}	600 mg × L^{-1}
	After contamination: > 3 000 mg × L^{-1}	
TPH	0.01 mg × L^{-1}	(0.01 mg × L^{-1})
Odor	≤ 3 TON[1]	≤ 2 TON[1]
Discoloration	≤ 15 TCU[2]	≤ 10 TCU[2]
PTR[3] Remediation Discharge	Up to 20 L × s^{-1}	
Sizing	Small footprint, relocatable	
Design Life	Temporary (2 years)	

Note: [1] = Threshold Odor Number, [2] = True Color Unit, [3] = Pump-Treat-Reinject

Umm Al-Aish groundwater samples

- Grwoundwater: (NP10, NP10, NP11, NP11, P20, P20, P20, P27U, P28UA, P28UB, P33UA, P33UB, P33UB, P33UB) = TOTAL of 14 L
- Soil: bucket 1, bucket 2
- No crude oil (cultivation C-source)

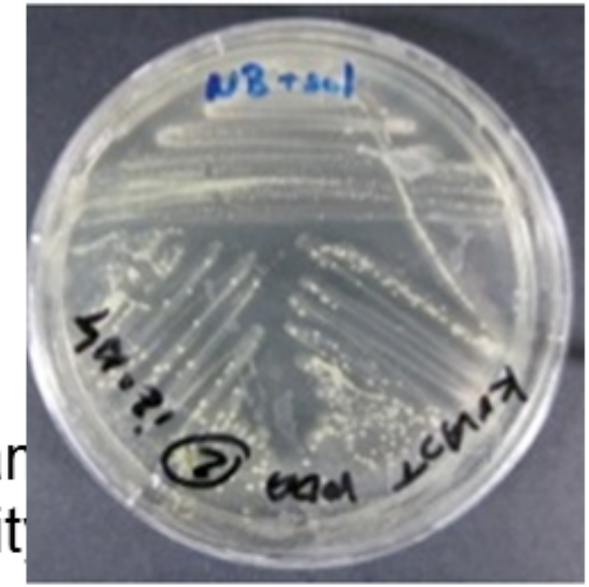
Sample label	pH ( )	ORP (mV)	Salinity ( )	EC (mS/cm)	u'' (%)	TPH (mg/kg)
Mixed water medium	7.48	270.05	1.55	3.04	-	0.35
SOIL1	8.21	-	-	-	0.697	26 600
SOIL2	8.14	-	-	-	0.663	23 200

Note.: FTIR LOQ = 0,1 mg/L (mg/kg) !!

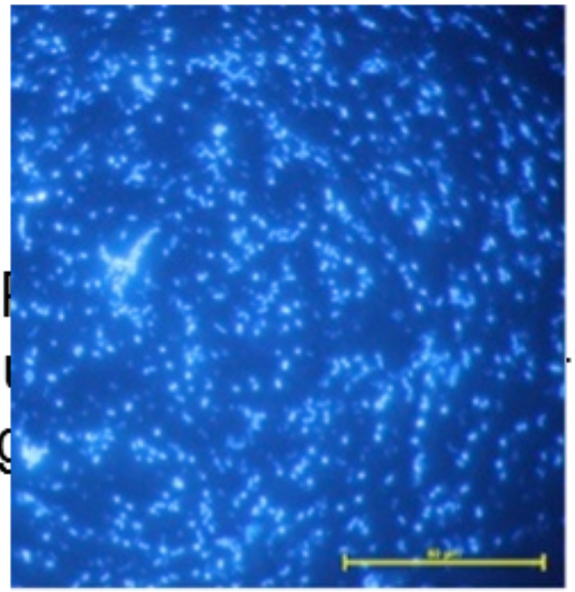
- Crude oil amendment => TPH content increase (BIO & ISCO)
- Mixed Water Medium = geochemical matrix for testing BIO
- Model sea water = geochemical matrix for testing ISCO

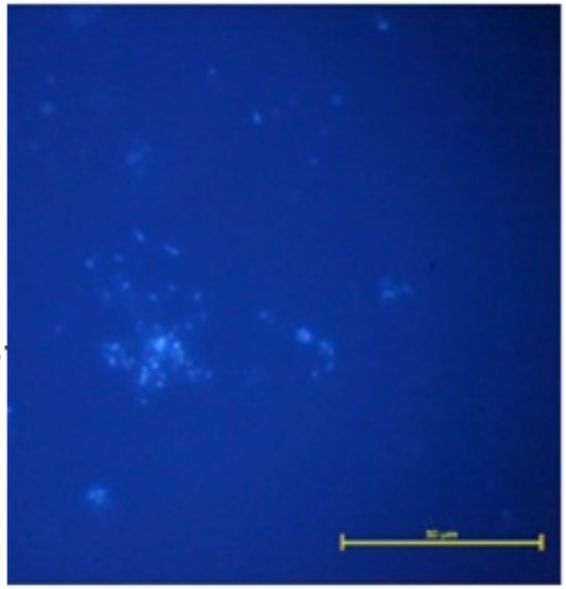
BIO – methodology

- Samples: soil & groundwater



- Remediation:
  - Natural attenuation
  - Biostimulation (nutrient amendment)
  - Bioaugmentation (adding isolates cultivated from sar
  - Surfactant addition (increasing the TPH bioavailabilit
  - Combination of the above said





- Analytics:
  - Agar cultivation
  - Epifluorescent microscopy (DA
  - Respiration capacity (CO_2 produ
  - Plate counts (CFU×g^{-1} (dry weig
  - TPH degradation (%)

BIO – results

Batch	Setup	Initial data (CFU/g, mg/kg)		CO_2 produced [mg/kg/day]	Degrading microbes (CFU/g)	TPH (mg/kg)
19	• ca. 200 g of SOIL1 (dry weight) • sodium azide • N,P nutrients: 0.9 g/L $(NH_4)_2SO_4$ + 0.375 g/L NP-sol • microorganisms (after ca. 1 month adaptation) • SURF : 100 µl/L	Heterotrophic	2.0×10^3	12	2.6×10^4	23 500
		Degrading*	2.9×10^5			
		TPH	26 600			
20	• ca. 200 g of SOIL2 (dry weight) • sodium azide • N,P nutrients: 0.9 g/L $(NH_4)_2SO_4$ + 0.375 g/L NP-sol • microorganisms (after ca. 1 month adaptation) • SURF: 100 µl/L	Heterotrophic	0.0	9	1.2×10^4	23 400
		Degrading*	2.9×10^5			
		TPH	23 200			
21	• ca. 100 mL mixed water medium • N,P nutrients: 0.9 g/L $(NH_4)_2SO_4$ + 0.375 g/L NP-sol • microorganisms (after ca. 1 month adaptation) • SURF: 100 µl/L	Heterotrophic	8.0×10^2	0	0.1×10^4	0.31
		Degrading*	3.5×10^5			
		TPH	0.35			

* = bioaugmentation

After 6-d cultivation

BIO – discussion

- None of the obtained samples is suitable for bioremediation without pre-processing

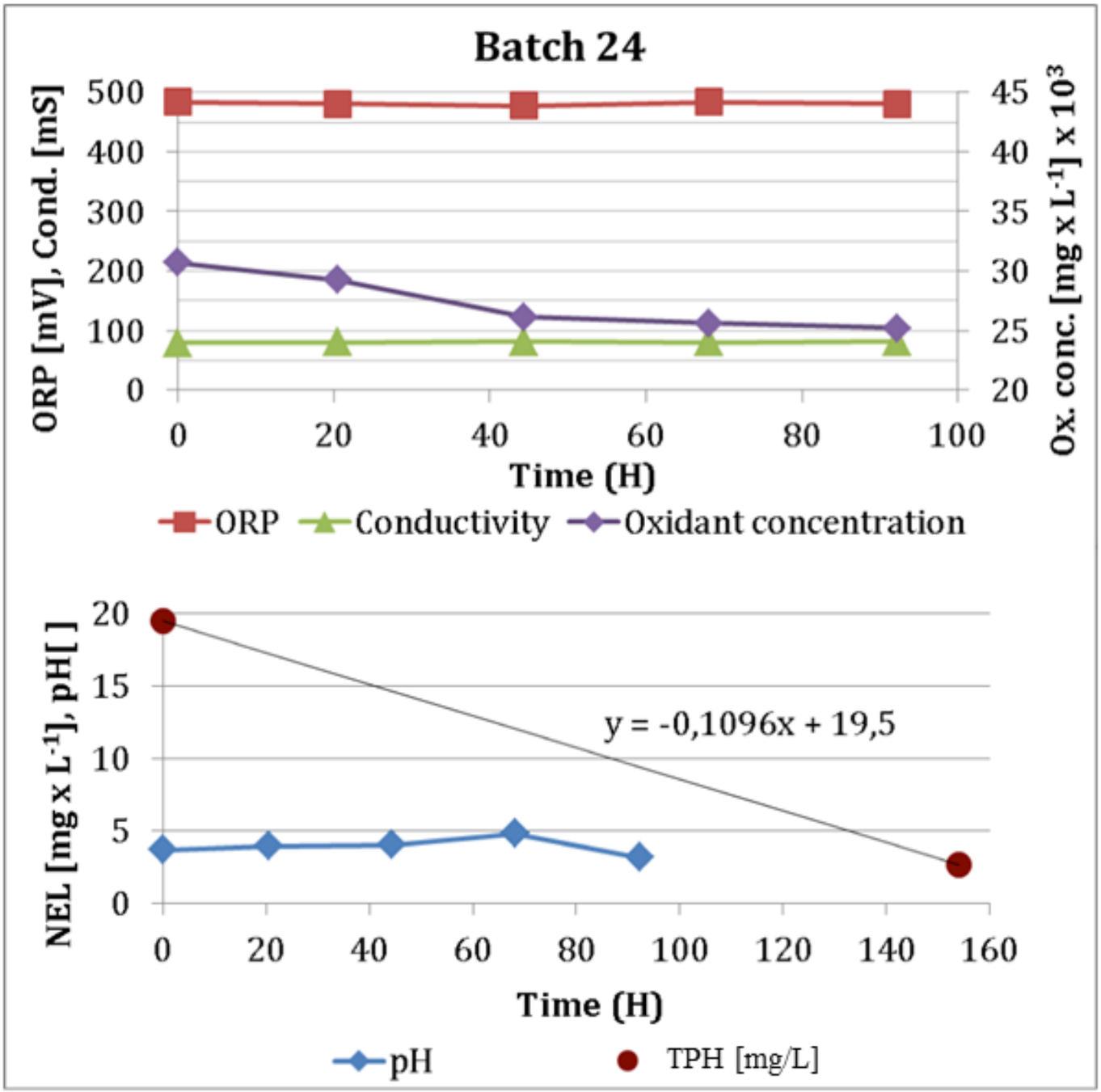
- Desert soil (sand):
  - Low water activity,
  - Lack of nutrients (C, N, P, S)
  - => biomass development prevention

- Low initial TPH concentration in gw.
- Low TPH bioavailability in soils (strongly bound to soil-grains – long term weathering?)
  - => generation of biodegrading enzymes not induced…

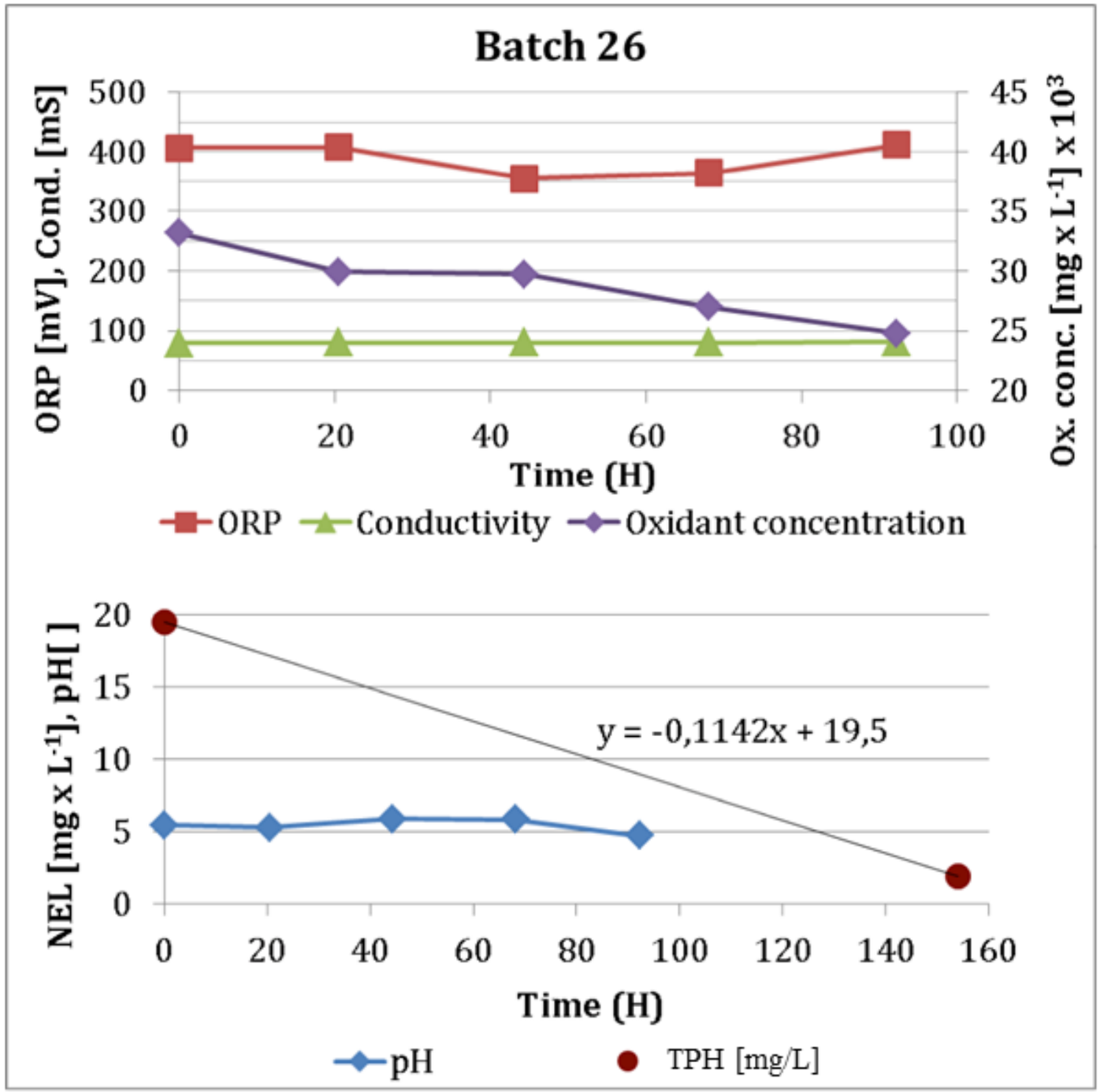
ISCO – methodology

Batch	Label	Ox.	Model seawater	H_2O_2 20%	SURF	$Na_2S_2O_8$	Agent1	Agent2
		[%]	[ml]	[ml]	[ml]	[g]	[g]	[g]
22	Blank	0.0	1000	0	0	0	0	0
23	MFR_1	1.5	925	75			0.1	0.1
24	MFR_2	3.5	833	167			0.1	0.1
25	MFR_3	3.5	833	167			0.2	0.1
26	MFR_4	3.5	833	167			0.4	0.2
27	MFR_5	7.0	666	334			0.1	0.1
28	MFR_SURF	3.5	833	167	0.5		0.1	0.1
29	APDS_SURF	0.5	1000		0.5	5		0.1
30	APDS_1	0.5	1000			5		0.1
31	APDS_2	1.0	1000			10		0.1

ISCO – results



ISCO – results

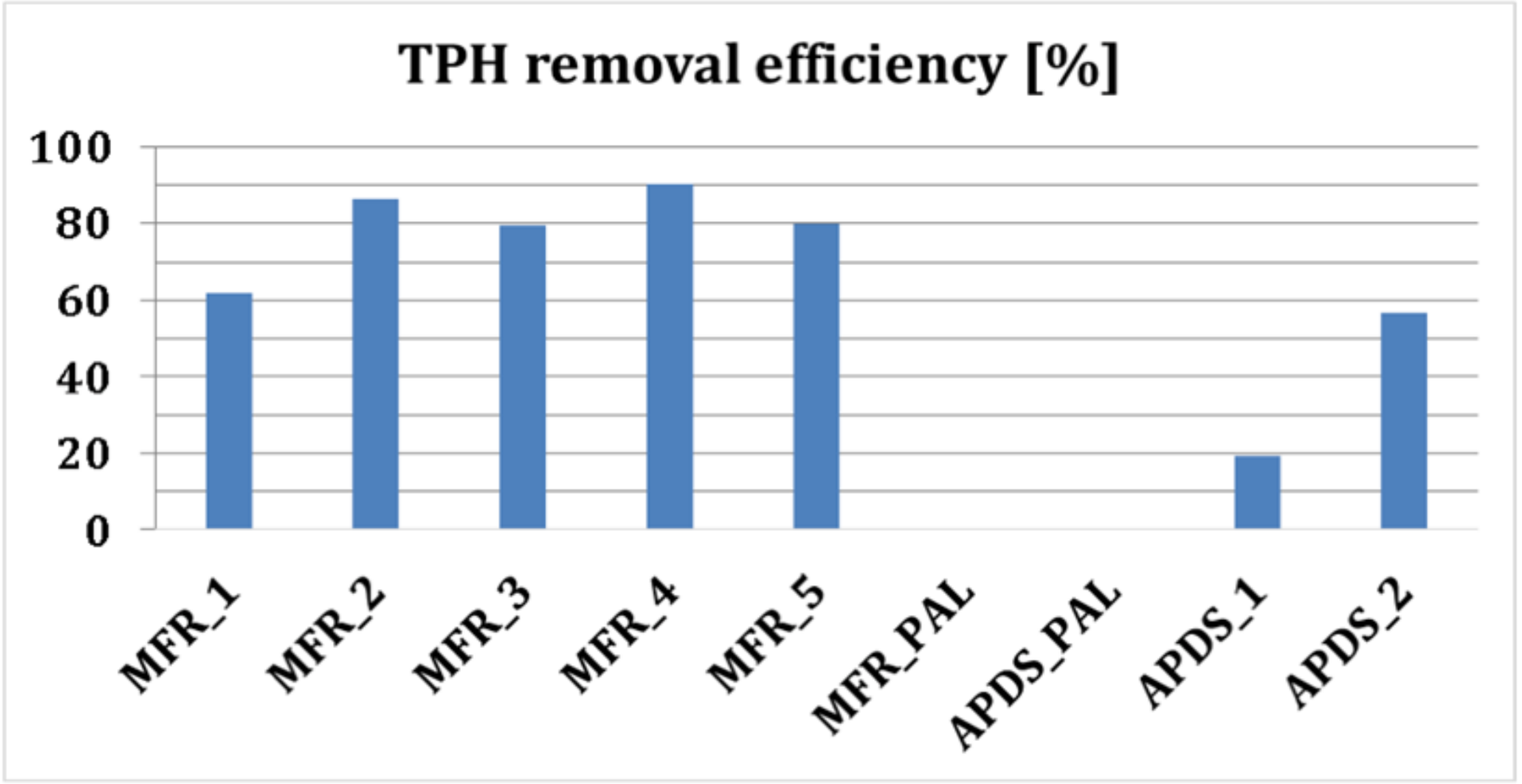


ISCO – Results (TPH degradation kinetics)

Batch	Batch Label	Coeff a	$T_{1/2}$ [h]	$T_{(c-0)}$ [h]	T [°C]
23	MFR_1	-0,0784	124	249	21
24	MFR_2	-0,1096	89	178	21
25	MFR_3	-0,1008	97	193	21
26	MFR_4	-0,1142	85	171	21
27	MFR_5	-0,1014	96	192	21
28	MFR_PAL	NR*			
29	APDS_PAL	NR*			
30	APDS_1	-0,0247	395	789	21
31	APDS_2	-0,0716	136	272	21

NR*, no results

ISCO – results



ISCO – discussion

- Despite the substantial salinity of the model sea water (EC ≈ 3,4 mS/cm), no extinguishing by the present salt ions (typical for H_2O_2oxidations) was observed in MFR reactions.

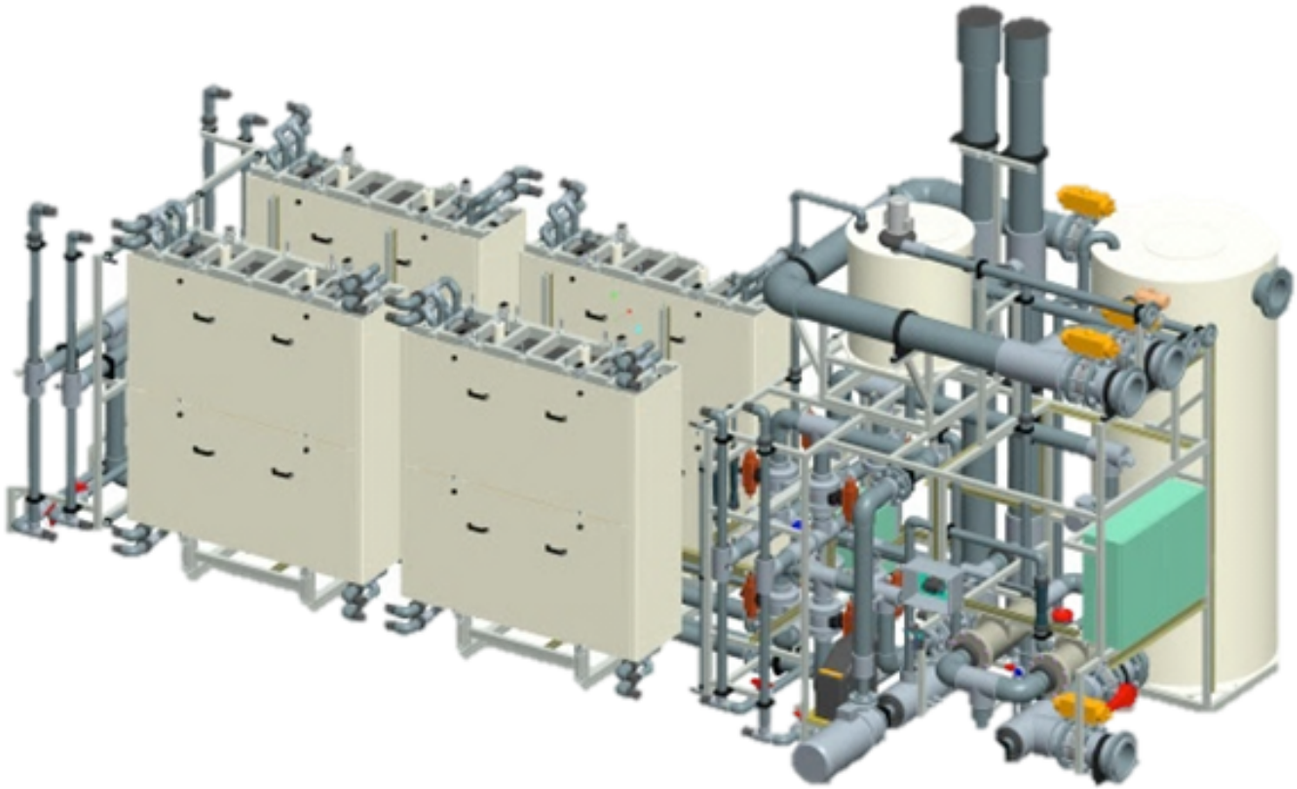
- Highest efficiency observed in MFR batches no. 24 and 26, potentially capable to mineralize the present TPH in 178, or 171 hours, respectively.

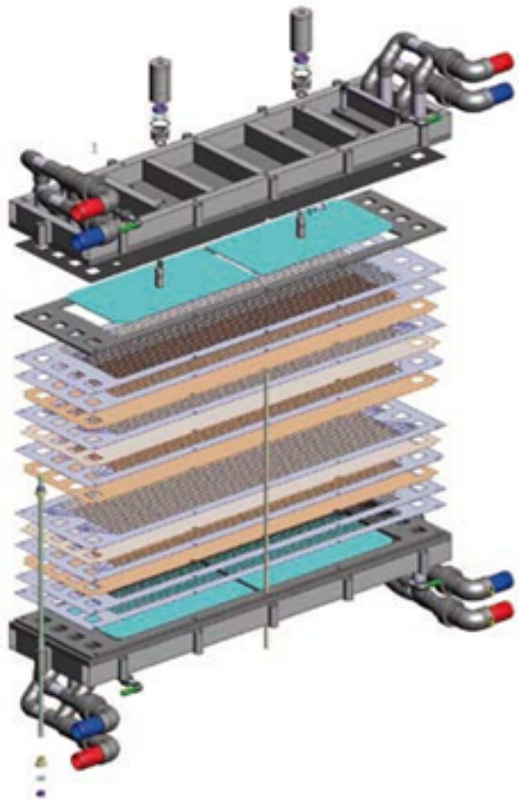
- Groundwater salinity of the Umm Al-Aish aquifer is lower (diluted by fresh gw., filtered during the formation percolation, …)

- => GOOD POTENTIAL FOR *IN SITU* PILOT TEST

Salinity – discussion

- Desalination targets the tap water quality …
- Required desalination unit discharge is equivalent to discharge of WW treatment plants in small-medium settlements =>
- An electrodiaysis unit **RALEX® EWTU M90** equipped with three **EDR-III** modules (MEGA a.s.) was recommended.





Conclusion:

1. Geochemical character of the gw. samples does not allow bioremediation without pre-processing.

2. *In-situ* chemical oxidation of TPH is feasible without pre-processing.

3. Desalination technology of sufficient capacity is available (= a way of pre-processing?).

Literature

- Akbar SA (2011) Remediation of Oil Polluted Groundwater Resources of Northern Kuwait: Challenges and Solutions. The 20th Joint GCC-Japan Environment Symposium. Abu Dhabi, UAE.
- Alloway BJ, Ayres DC (1996) Schadstoffe in der Umwelt. Spektrum, Heidelberg
- Al-Rashed M, Al-Senafy MN, Viswanathan MN, Al-Sumait A (1998) Groundwater Utilization in Kuwait: Some Problems and Solutions. Water Resources Development 14: 91-105
- Al-Sarawi M, Massoud MS, Al-Abdali F (1998) Preliminary assessment of oil contamination levels in soils contaminated with oil lakes in the Greater Burgan Oil Fields, Kuwait. Water, Air and Soil Pollution 106: 493-504
- Al-Sulaimi J, Viswanathan MN, Szťkely F (1993) Effect of oil pollution on fresh groundwater in Kuwait. Environmental Geology 22: 246-256
- Hamed MM (2004) Screening level modeling of long-term impact of petroleum hydrocarbon contamination on fresh groundwater lenses in the Arabian Gulf Region. Environmental Modeling and Assessment 9: 253-264
- Mukhopadhyay A, Akber A. (2018) Sustainable Water Management in Kuwait: Current Situation and Possible Correctional Measures, Int. Journal of Sustainable Development and Planning 13(3): 425–35, doi: 10.2495/SDP-V13-N3-425-435
- Schlösser, U. G. (1982). Sammlung von Algenkulturen. *Berichte Der Deutschen Botanischen Gesellschaft*, 95(1), 181–276. Doi: 10.1111/j.1438-8677.1982.tb02862.x


got rabbit?