

## Urban gasoline stations: new techniques for early leak detection from USTs and removal of low concentration pollutants from groundwater

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- Activities in support to Eni Refining & Marketing Division
  - Environmental monitoring at Service Stations
- Hydrocarbon leak detection in soils (SOIL ALERT)
  - Principles and main characteristics
  - Application to USTs (Underground Storage Tanks)
- Groundwater remediation by Pump & Treat (EN-Z-LITE)
  - Laboratory tests
  - Pilot plant
  - Full scale application
- Future activities and developments

# Eni Refining & Marketing Division

Fuel retail leader in Italy with ~ 5,000 Agip service stations.  
Reorganization of the distribution network, ~ 1000 small size urban area service stations ceded or removed.  
Enitecnologie involved in subsoil quality assessment and, where necessary, in remediation and environmental restoration actions.



# Scope of the work

Development of a combined monitoring – remediation system capable to provide early warning for hydrocarbon leaking and effective groundwater treatment

Two Enitecnologie patents:

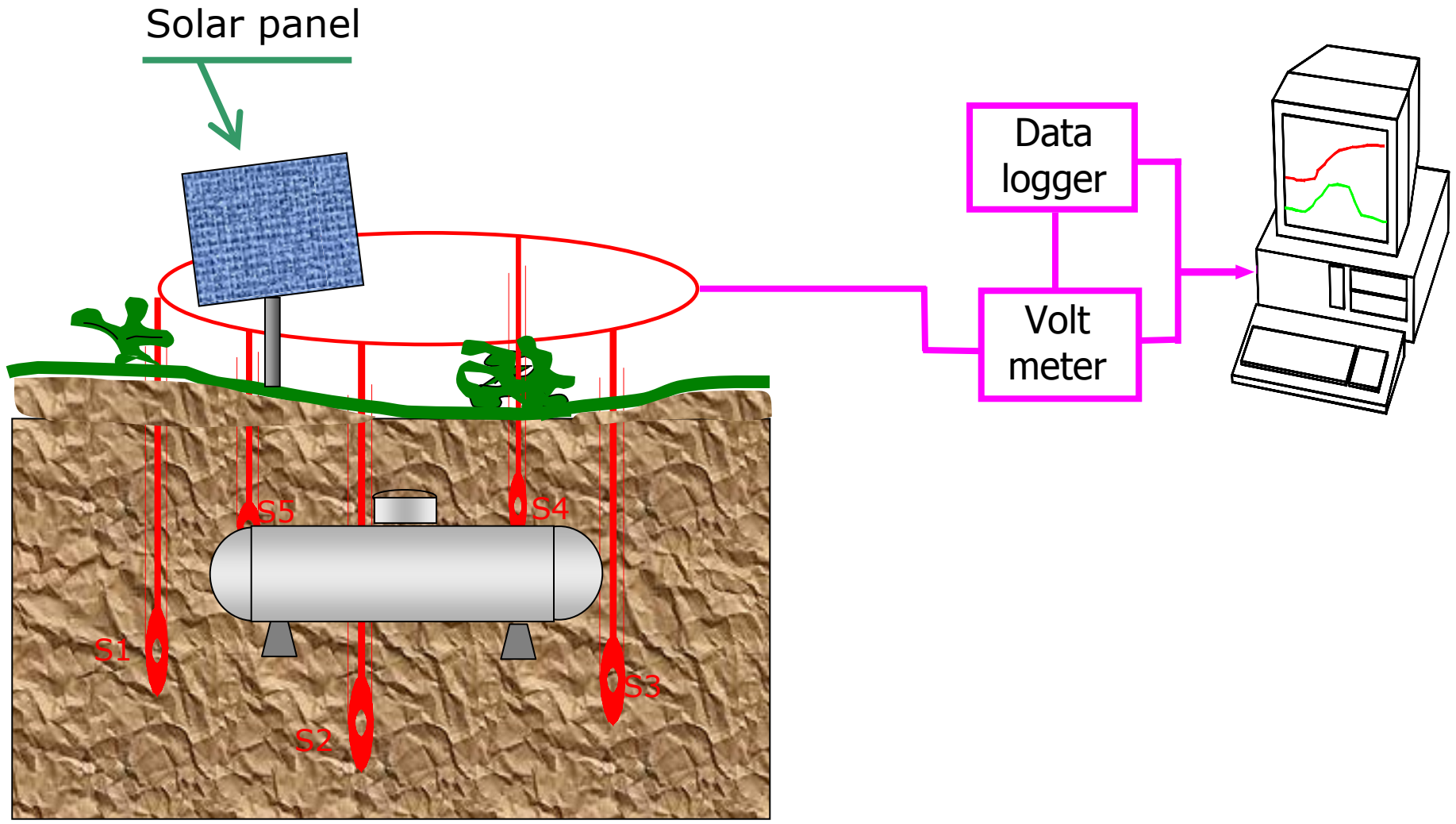
1. **SOIL ALERT**: a leak detector based on a resistive gas sensor
2. **EN-Z-LITE**: an adsorbent for effective groundwater removal of hydrocarbons, including BTEX and MtBE, associated to Pump & Treat technology



# SOIL ALERT

- SOIL ALERT is an alarm system for tank leakage control.
- It consists of a probe for interstitial gas detection in subsoil.
- The probe contains two sensors, one at the micro-holed bottom tip and one at the top for aboveground air referencing.
- Can take continuous measurements, without use of extraction systems and chemical analysis.
- ATEX explosion proof certification (EEX d II B T5) allows for use in hazardous zones.
- Applications:
  - Service stations and aboveground storage tank fields (AST)
  - Remediation monitoring

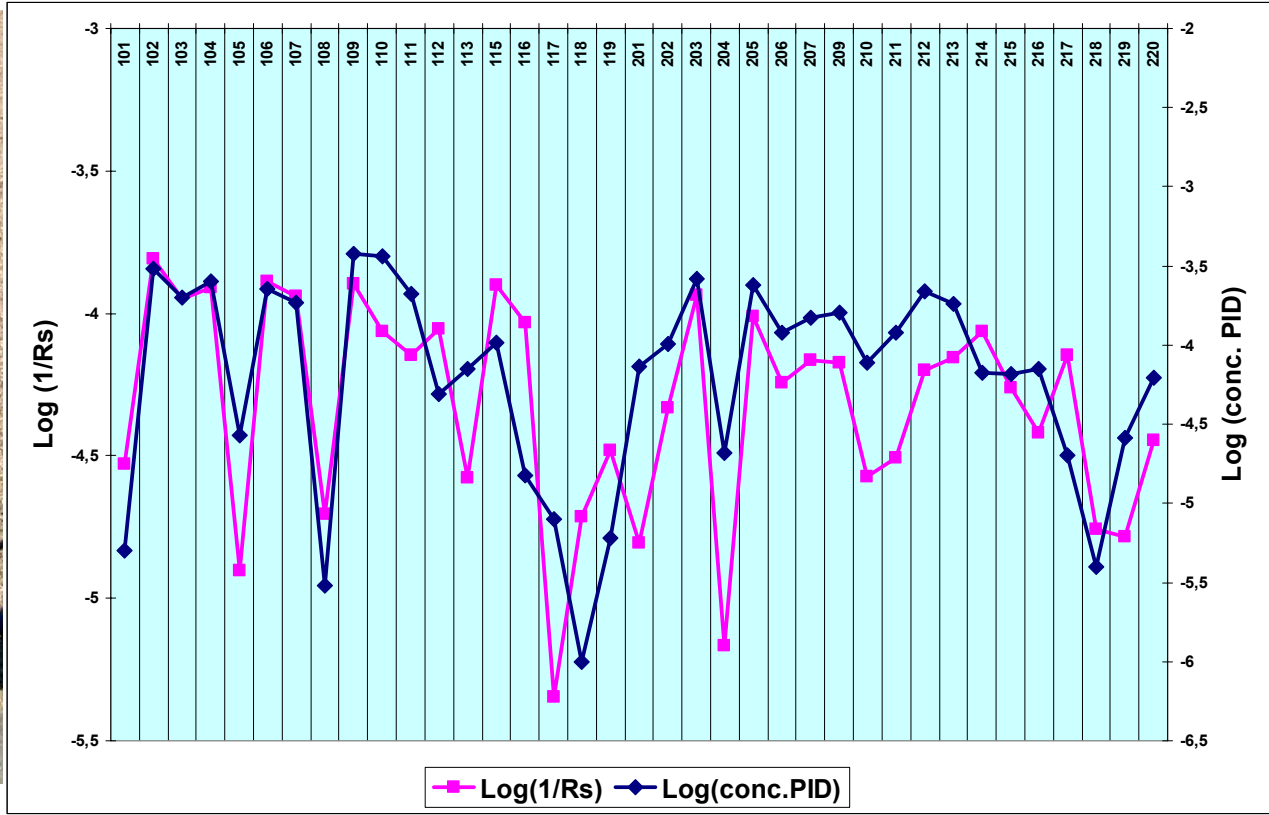
# SOIL ALERT: Leak detection of USTs



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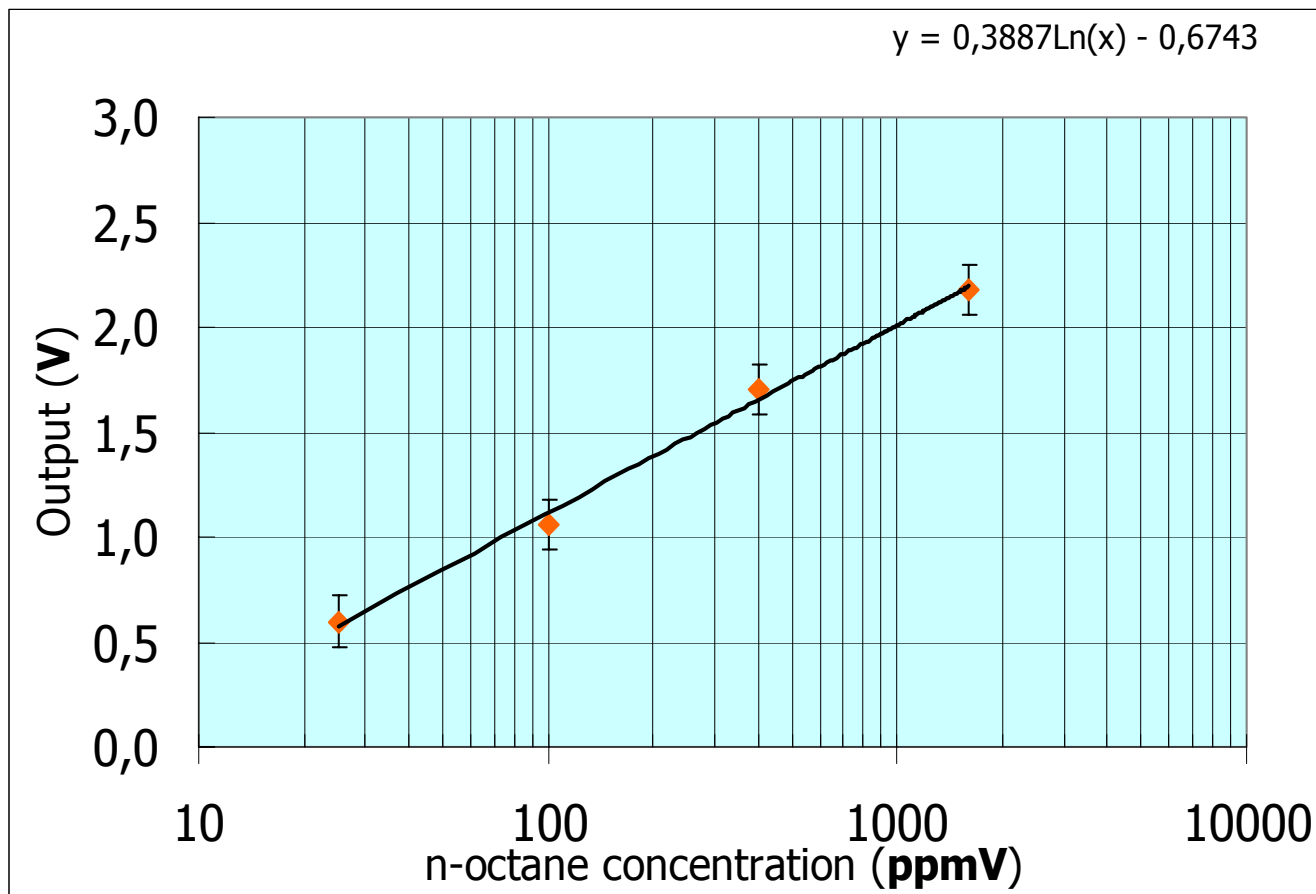
## Comparison of SOIL ALERT Probe and PID signals

External part of probe



Same day measurements on 37 probes

# Calibration of gas sensors

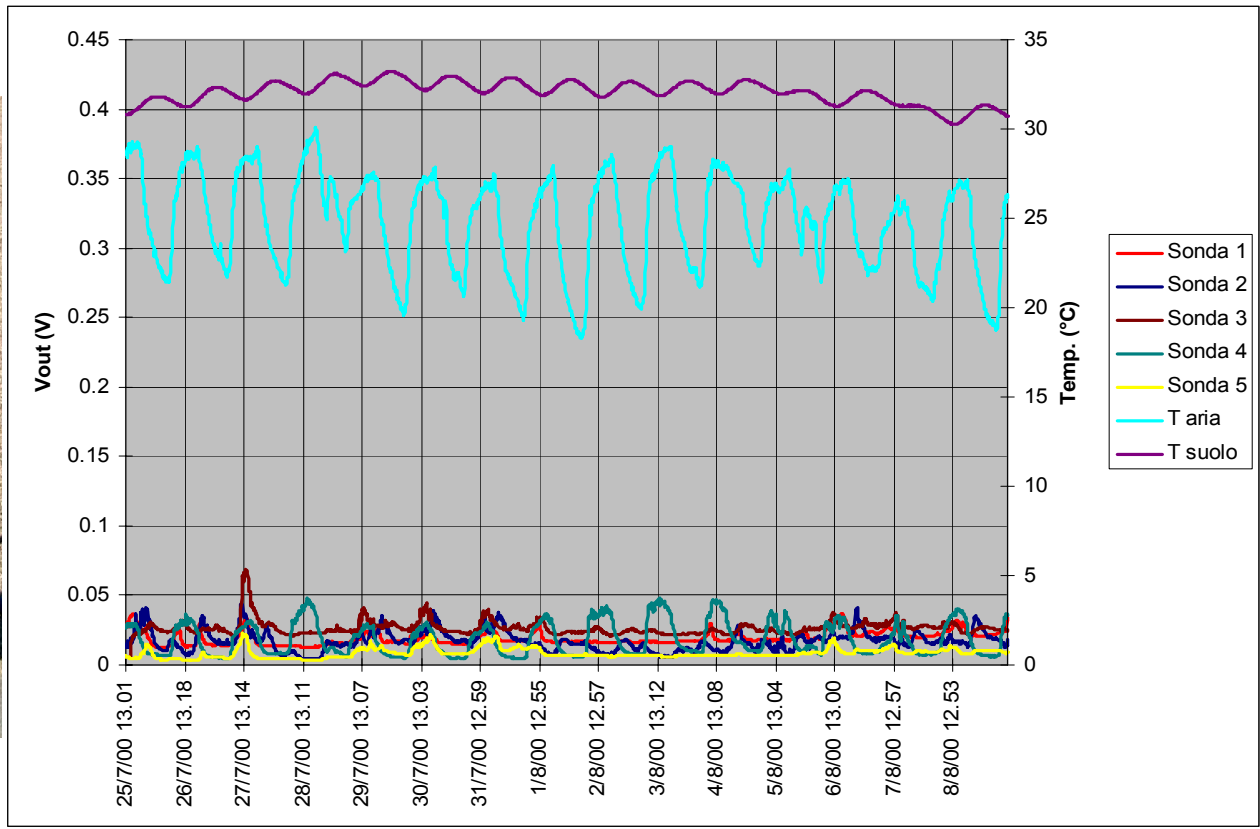
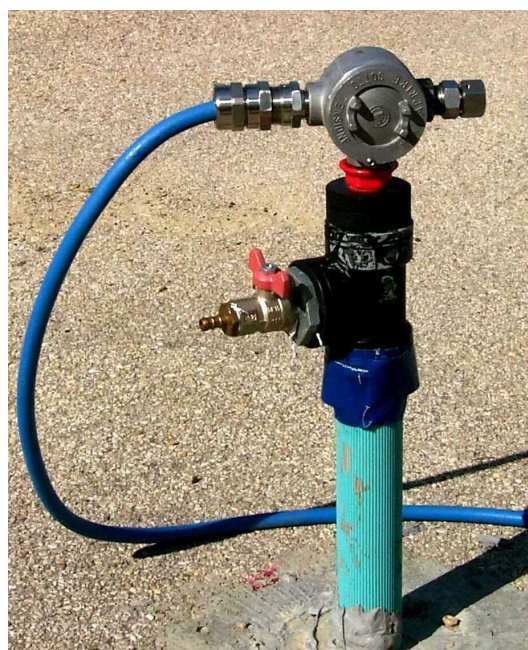


<b>Volts</b>	<b>ppmV</b>
<b>0,6</b>	<b>25</b>
<b>1,1</b>	<b>100</b>
<b>1,7</b>	<b>400</b>
<b>2,2</b>	<b>1600</b>

# SOIL ALERT: Leak detection of USTs

- Monitoring campaign at an Agip service station in central Italy

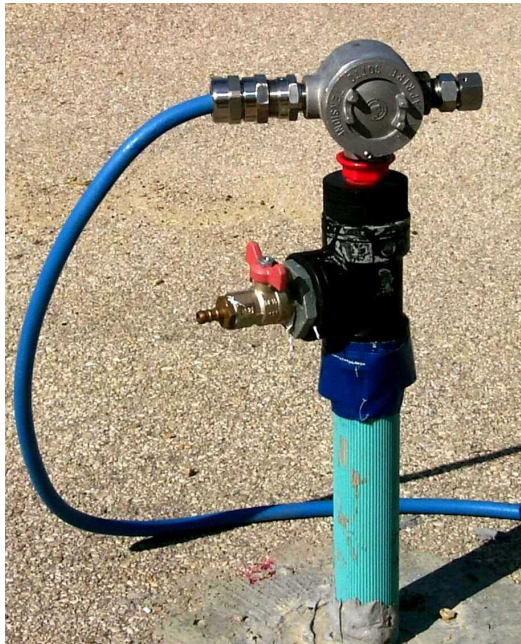
15 days monitoring



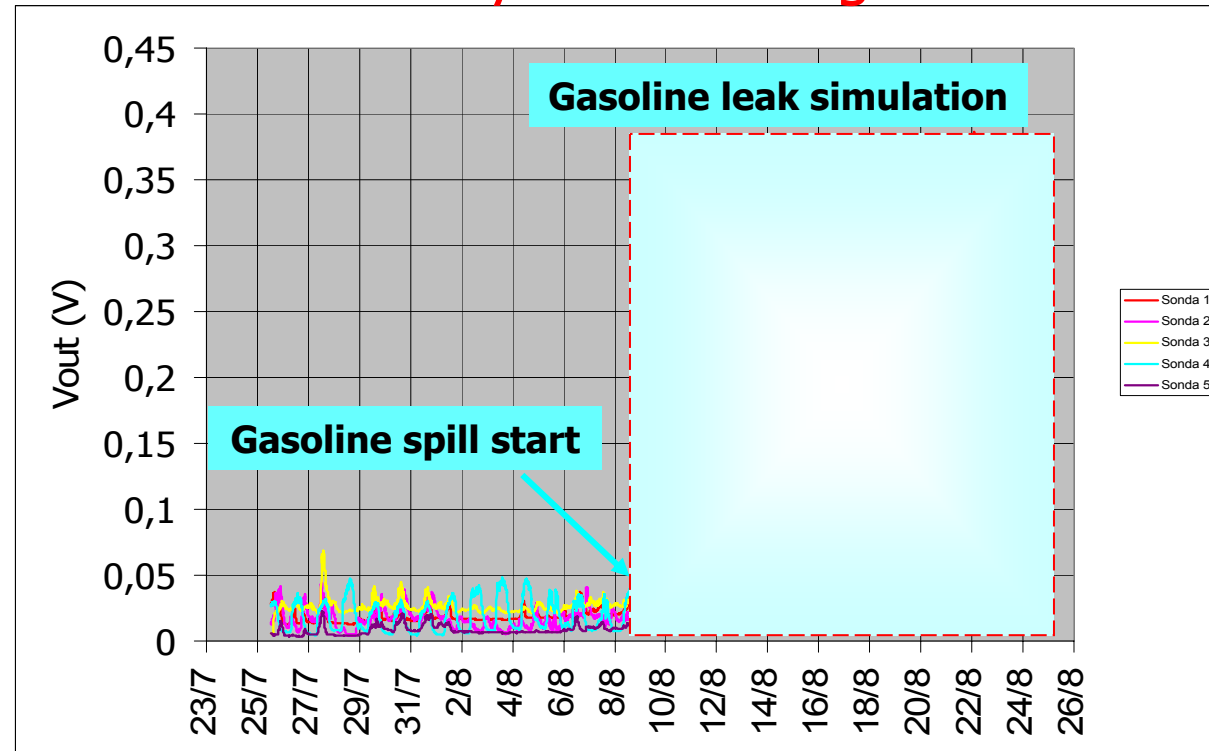


# SOIL ALERT: Leak detection of USTs

- A field simulation was carried out by spilling small amounts of gasoline and diesel



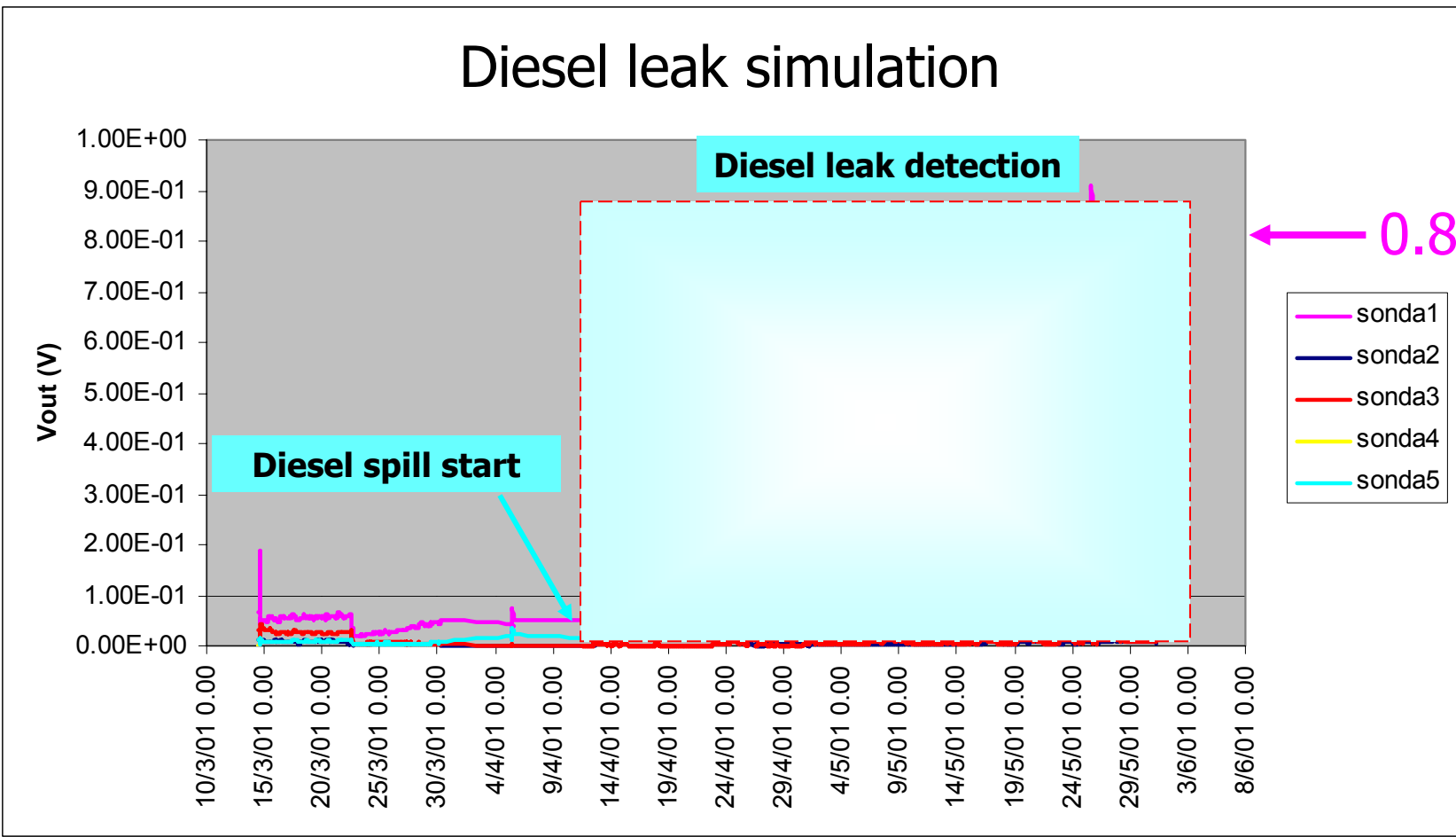
## 30 days monitoring



# SOIL ALERT: Leak detection of USTs

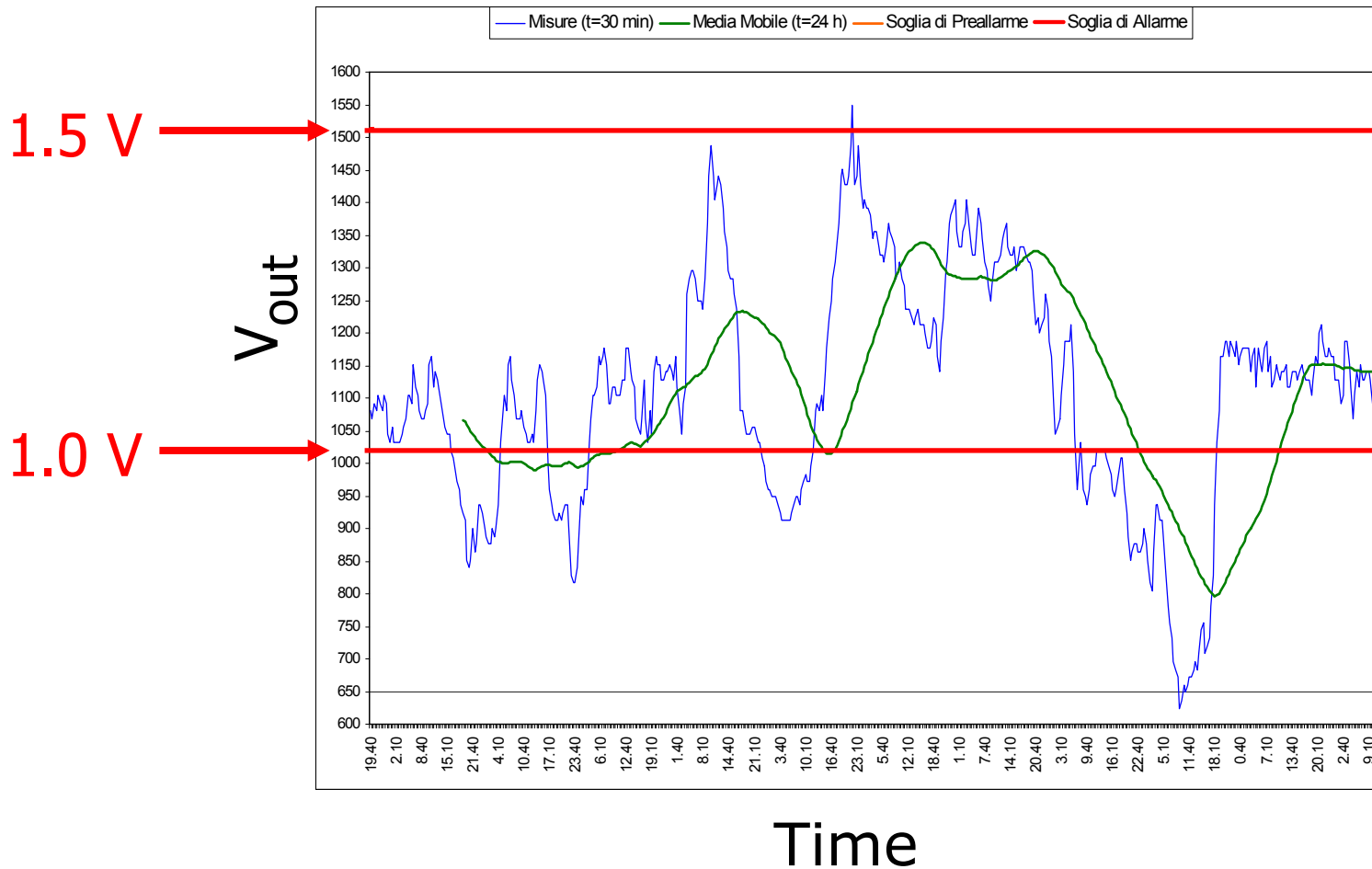
80 days monitoring

## Diesel leak simulation



# SOIL ALERT: Leak detection of USTs

## 11 day monitoring at a dismissed service station

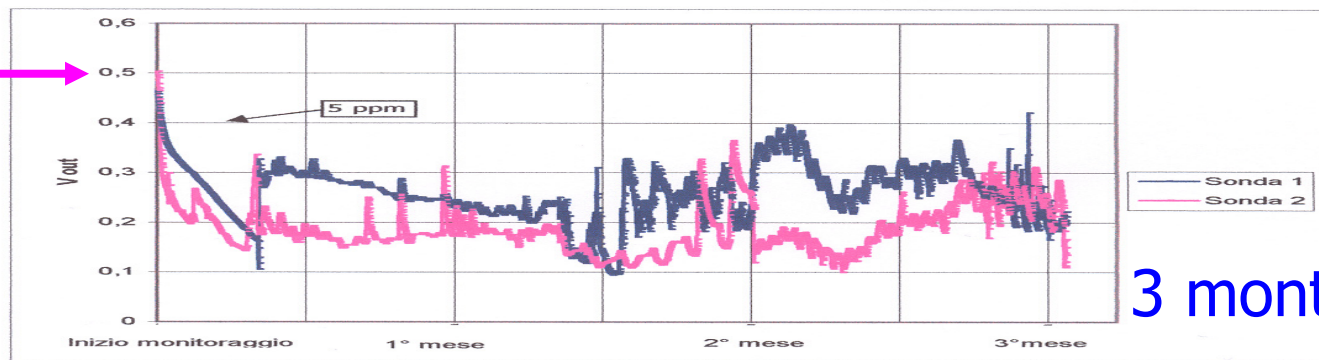




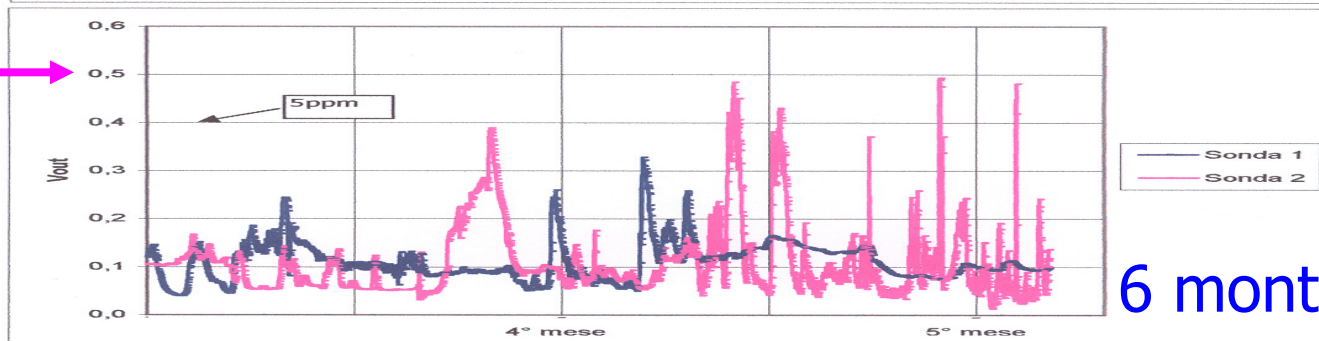
# SOIL ALERT: Leak detection of USTs

## 1 year monitoring

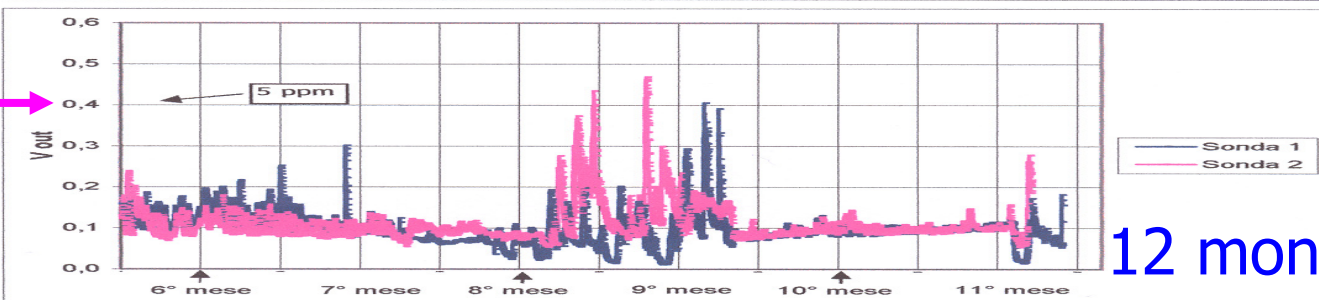
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3 months




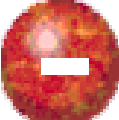
6 months



12 months

# SOIL ALERT: Advantages and limitations

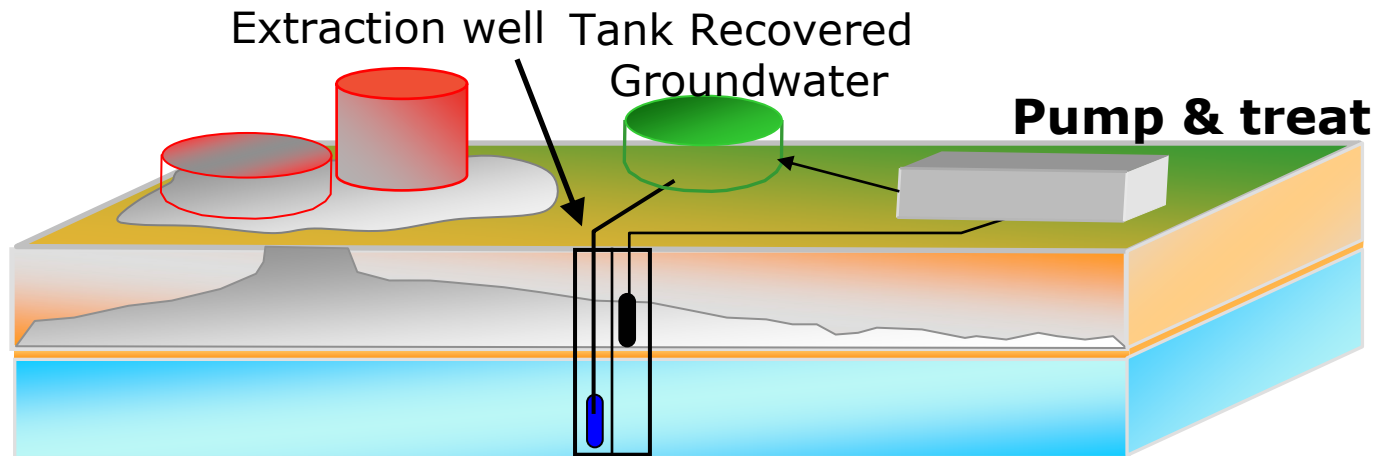
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- Sensor output is an electrical signal, easily manageable for automatic and continuous remote control
  - Large HC concentration range (10 - 5000 ppmV)
  - Leak detection is fast compared to normal monitoring systems

- 
- Low selectivity: these sensors respond, although to a different extent, to many reducing gases
  - Signal fluctuates with changes in water table level
  - Signal saturates in severely contaminated soils
  - Require soil perforation for positioning

# Groundwater remediation

Pump & Treat is the most common form of groundwater remediation. It is often associated with treatment technologies such as Air Stripping or Adsorption.

In adsorption systems, granular activated carbon (GAC) is mainly used as sorbent material



# Adsorption: Granular Activated Carbon (GAC)

With GAC, organic molecules as well as certain metal and inorganic ions are attracted and adsorbed in the porosity of the sorbent

## Limitations and Concerns

GAC not efficient with small organic molecules and water soluble contaminants like MtBE

If humic acids are present GAC adsorption capacity is rapidly decreased

If treated water has high salinity (eg. marine coastal sites), GAC regeneration and recycling becomes very difficult or not applicable

# EniTecnologie EN-Z-LITE approach

EN-Z-LITE (Enitecnologie US Patent 20040206705) for the removal of groundwater contaminants based on synthetic zeolites

## Advantages of zeolites used for water treatment:

1. selectivity (based on physical-chemical affinities of adsorbate and adsorbent)
2. good adsorption capacity (up to 15%)
3. higher efficacy towards MtBE
4. easy regeneration by thermal desorption
5. no effects of salts and interfering compounds such as humic acids and inorganic ions

## Successfully proven applications

### Simulation apparatus operating with sampled groundwater:

- different hydrocarbon contaminants: chlorinated, aromatic hydrocarbons (BTEX), MtBE, etc. at high concentration

### Mobile pilot scale plant:

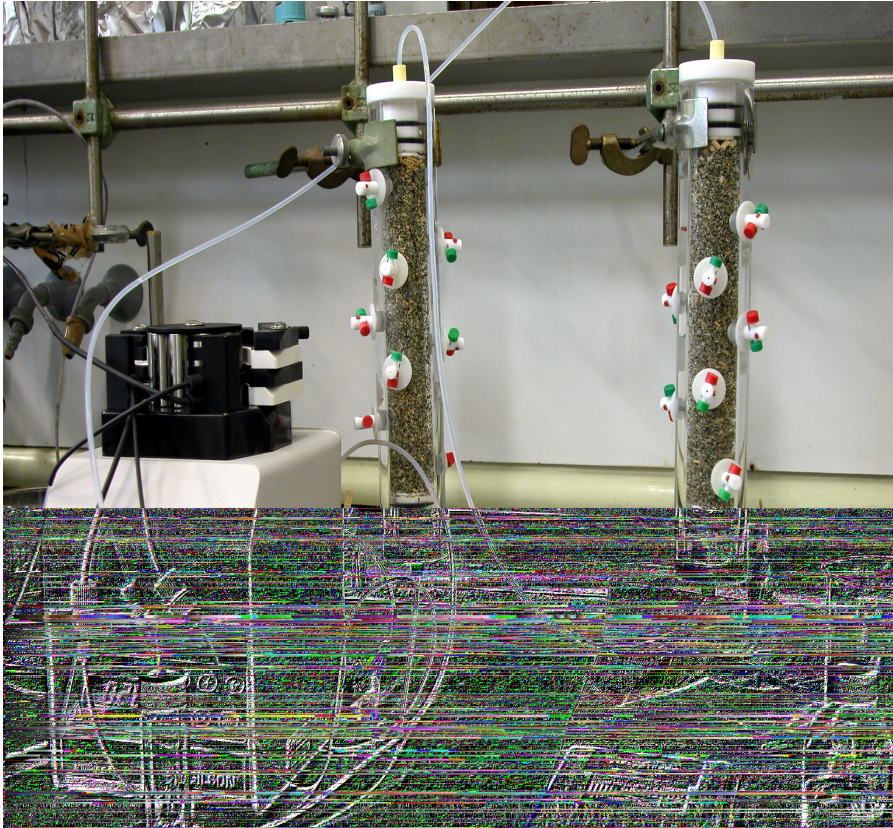
- Field tested for various kinds of contaminants

### Full scale plant at an Agip Service Station

- Automotive fuels (gasoline, diesel) and MtBE



# Laboratory Simulation Apparatus



200 mL columns

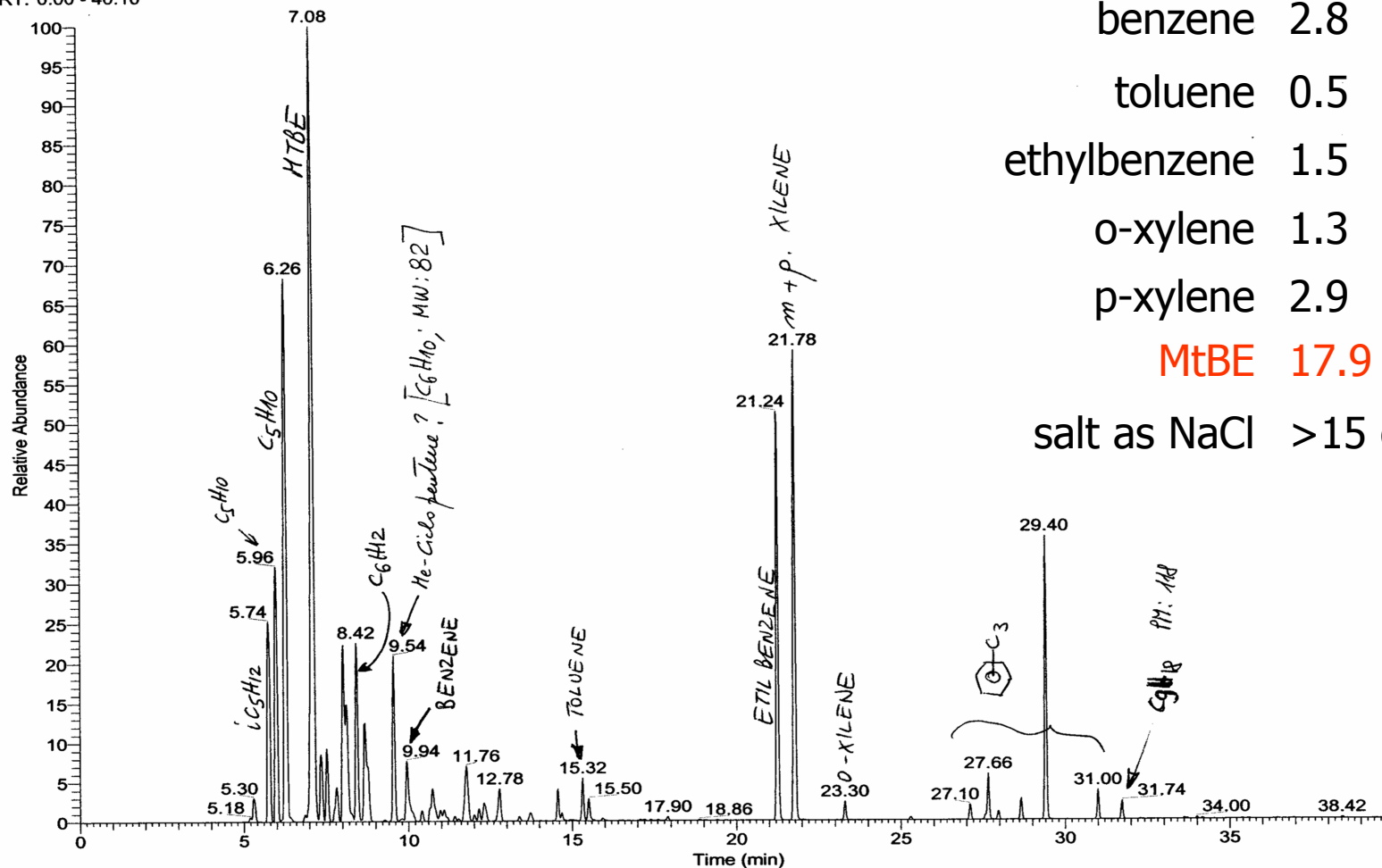


2 L column

# EN-Z-LITE application: high concentration of MtBE and BTEX

## GC-MS inlet of simulation apparatus

gcms col. Rtx-5MS Met.rvignola  
RT: 0.00 - 40.10



Compound mg/l

benzene 2.8

toluene 0.5

ethylbenzene 1.5

o-xylene 1.3

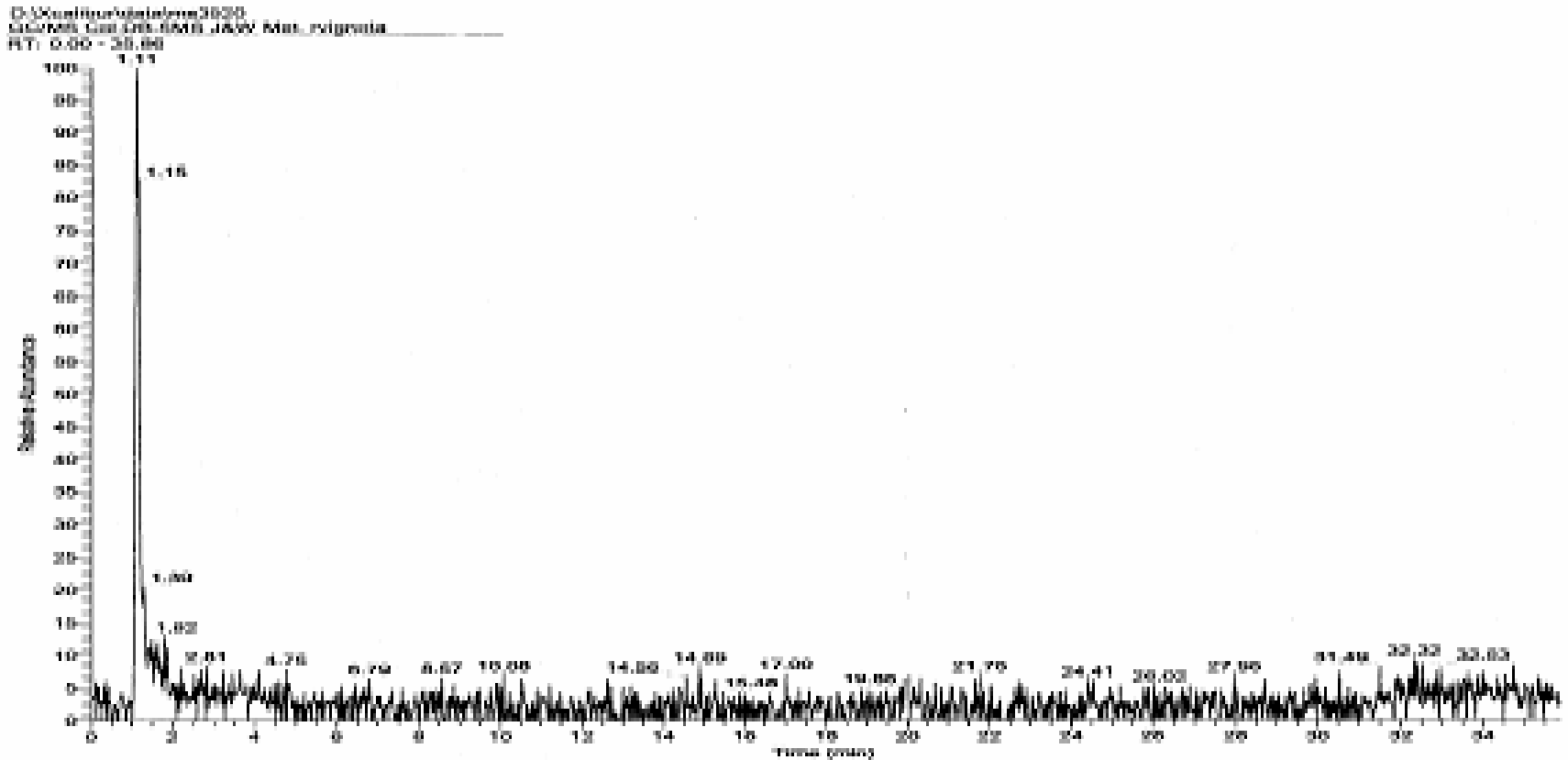
p-xylene 2.9

**MtBE 17.9**

salt as NaCl >15 g/L



# EN-Z-LITE application: high concentration of MtBE and BTEX



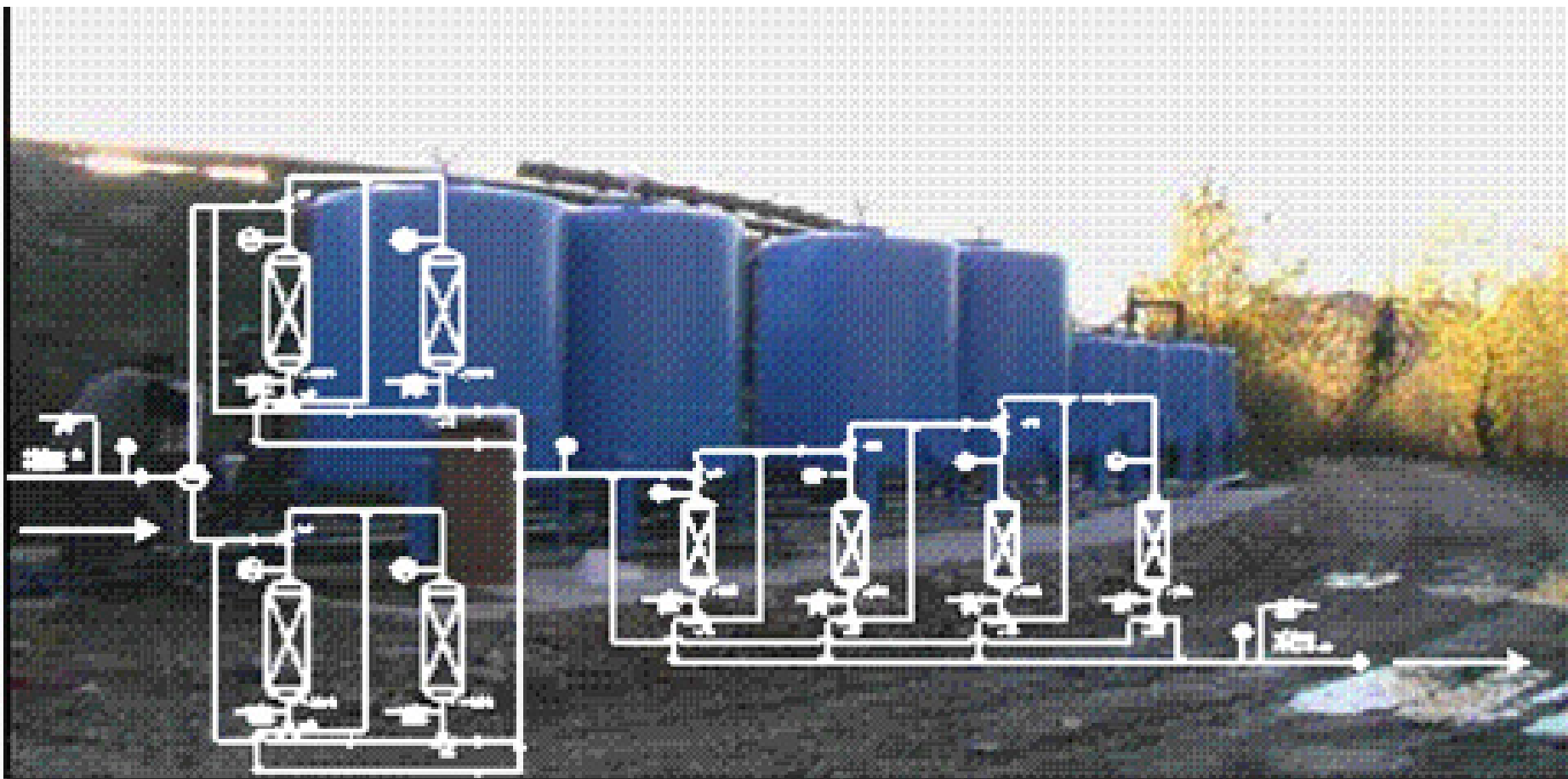
MtBE and aromatics (BTEX) outlet concentrations < 1 ppb

# EN-Z-LITE pilot plant



Mobile unit with 4 x 75 kg, water flux of  $\sim 1\text{m}^3/\text{h}$ , trucked to field sites for differently contaminated waters

# Full scale application: Agip service station



Pump and Treat system using GAC and EN-Z-LITE to reduce outlet TPH, BTEX and MtBE concentration below the limit imposed by controlling authority

# Full scale application: operating conditions

## Remediation plant dimensions

GAC pretreatment vessels:	4 x 1300 kg
EN-Z-LITE vessels:	4 x 350 kg
Water flow:	17 m <sup>3</sup> /h (max)
GAC replacement:	~ 2 tons/month
Zeolite replacement:	~ 100 kg/month

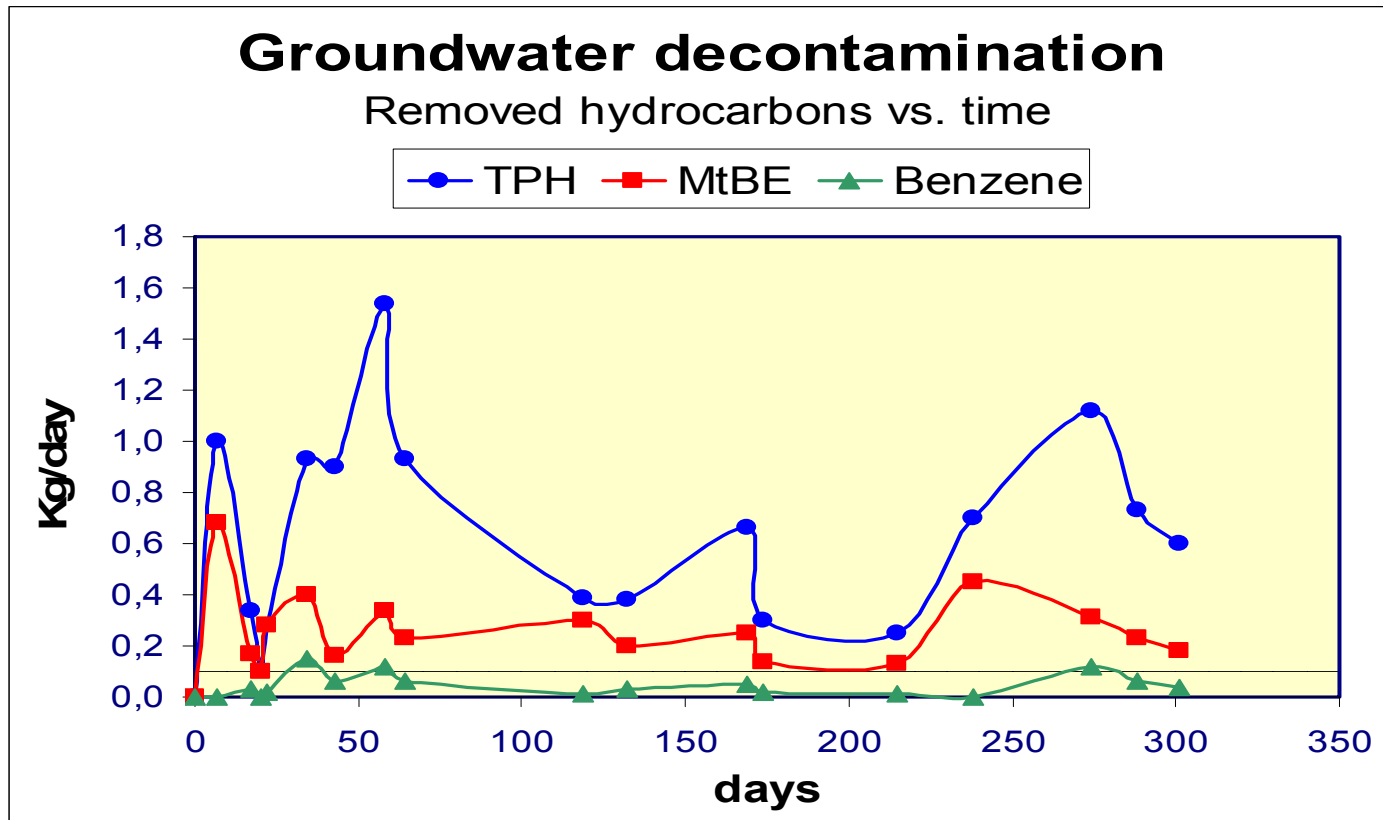
## Costs

Water treatment total	0.85 Euro/m <sup>3</sup> of treated water
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# Full scale application: results

Groundwater decontamination figures (ppb)			
	Inlet	EN-Z-LITE outlet	Controlling authority
TPH	500 – 9000	< 1	≤ 10
MtBE	500 - 3000	< 10	≤ 10
BTEX	0 - 900	< 1	Benzene ≤ 1 Ethyl-benzene ≤ 50 Toluene ≤ 15 p-Xylene ≤ 10

# Full scale application: results



EN-Z-LITE provides a technological improvement since it allows more effective removal of contaminants

# SOIL ALERT and EN-Z-LITE: Future development

SOIL ALERT can be used in water media also

Upgrade by means of a protective polymeric membrane in the probe micro-holed section, selectively permeable to contaminant vapors

## Benefits:

1. Measurements in water
2. Measurements in saturated zone

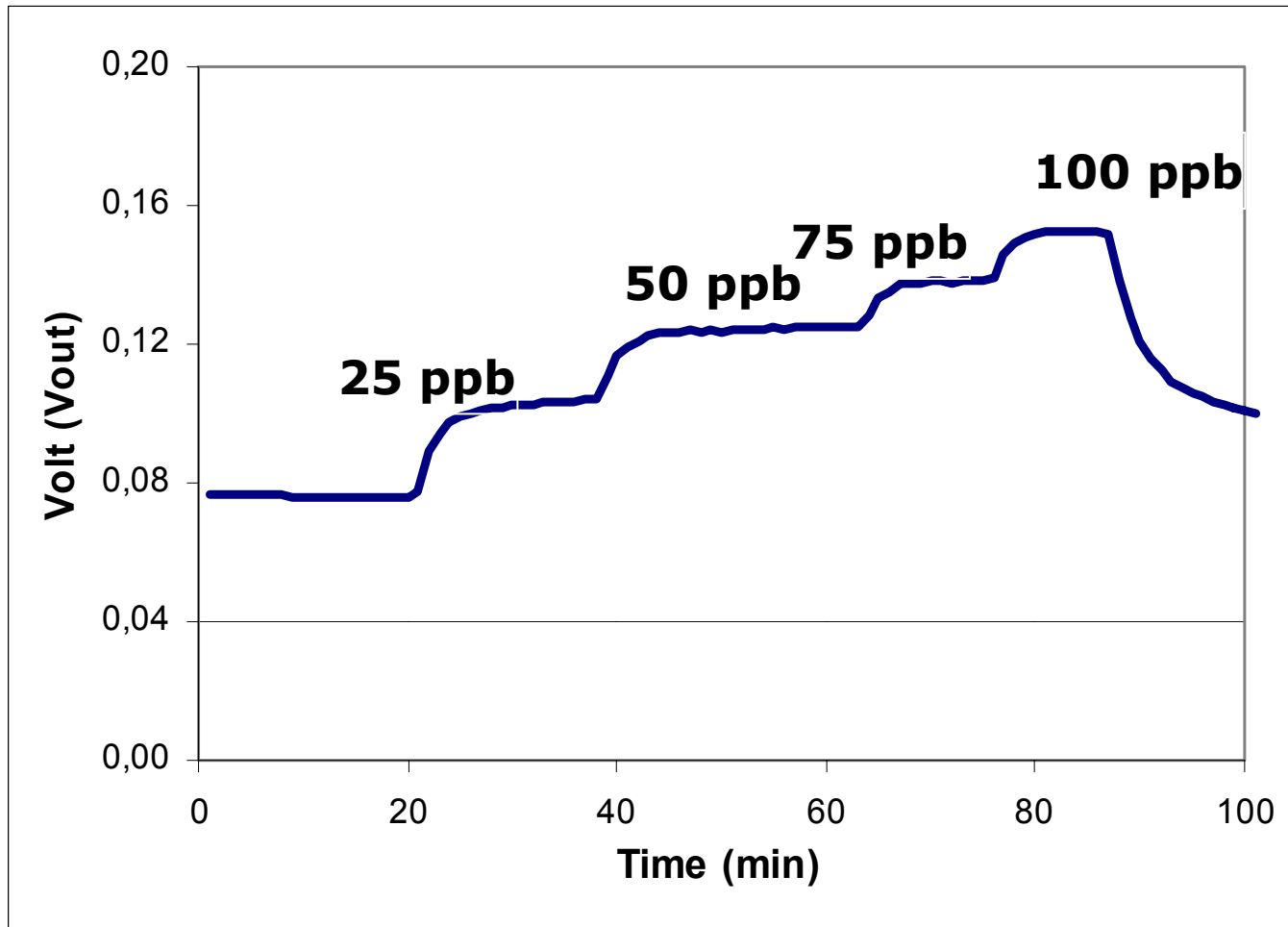
## Future development:

SOIL ALERT sensor switches for the EN-Z-LITE groundwater remediation system



# SOIL ALERT: tests in water

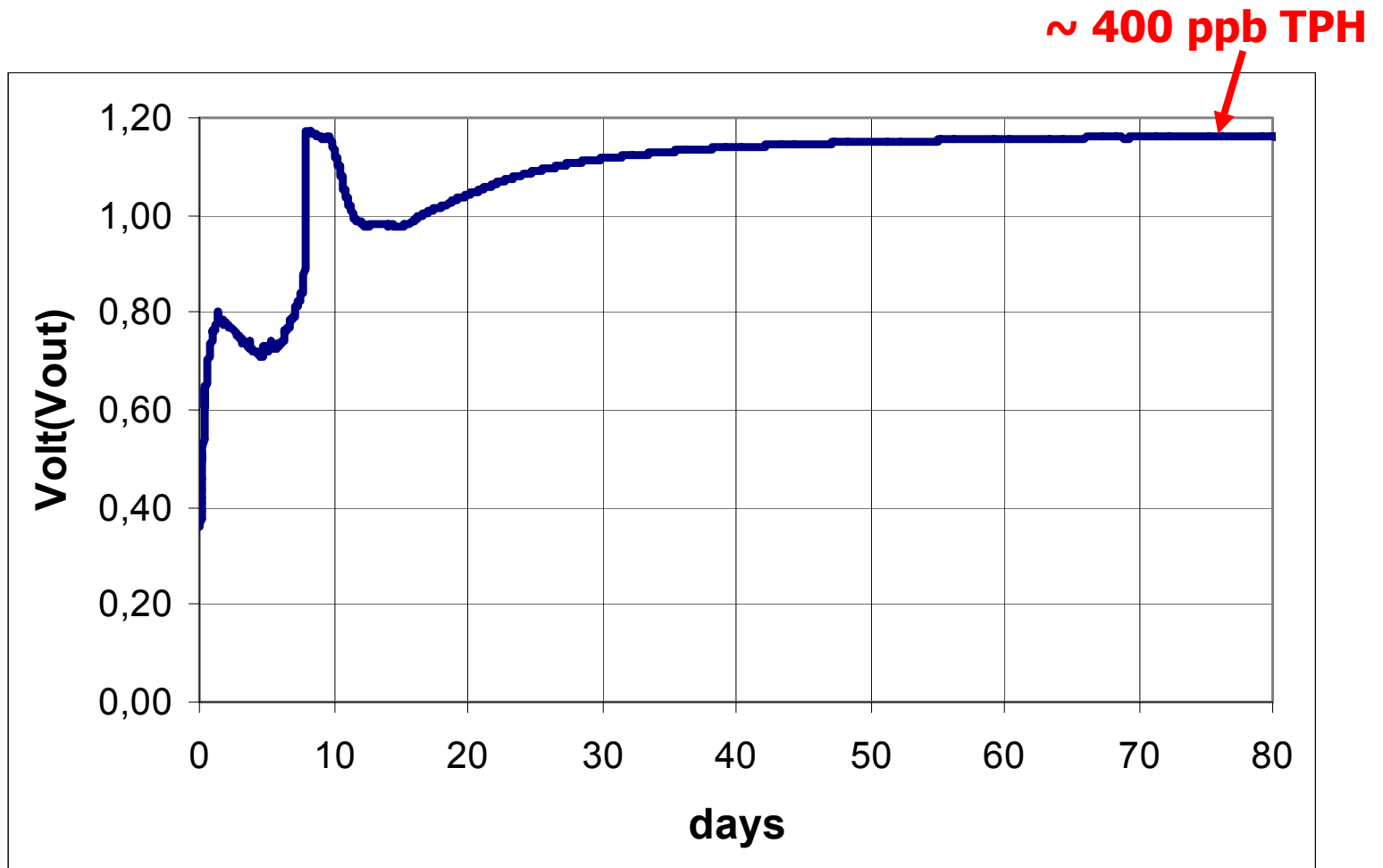
Laboratory tests in water containing toluene from 25 to 100 ppb



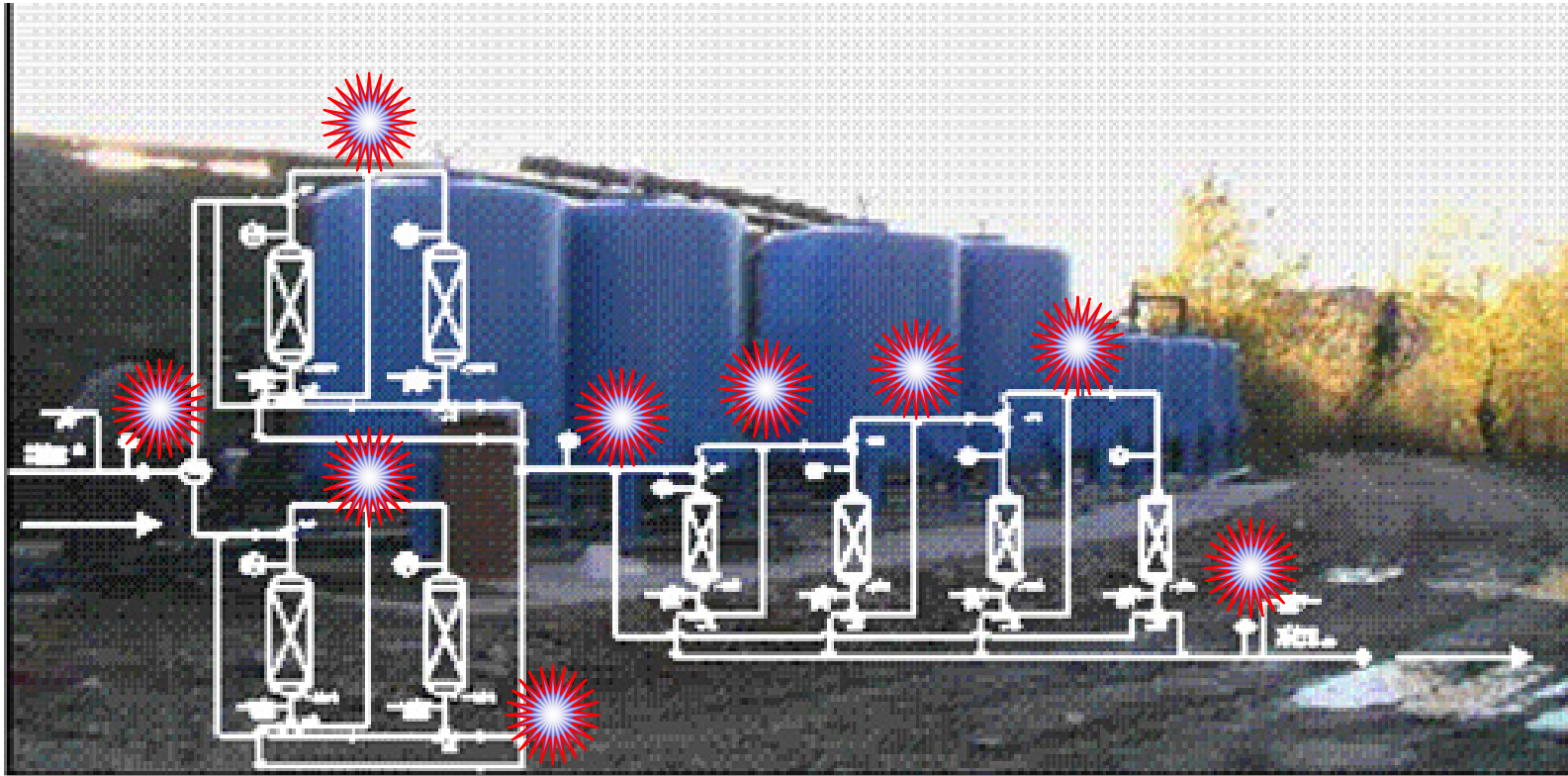


# SOIL ALERT: field tests in saturated soil

continuous measurements for 80 days



# Development of the combined SOIL ALERT and EN-Z-LITE remediation system



SOIL ALERT will be applied to continuous monitoring of groundwater remediation plants. Placed on vessels outlets, it can provide better timing for exhaust adsorbent replacement

# Acknowledgements

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