INTEGRATING RADON DEFICIT, NAPL CONCENTRATION, AND DYNAMICS OF GROUNDWATER TABLE FOR EVALUATING SOIL AND AQUIFER POLLUTION FROM NAPLS

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September 16th – 18th, 2025, Prague, Czech Republic

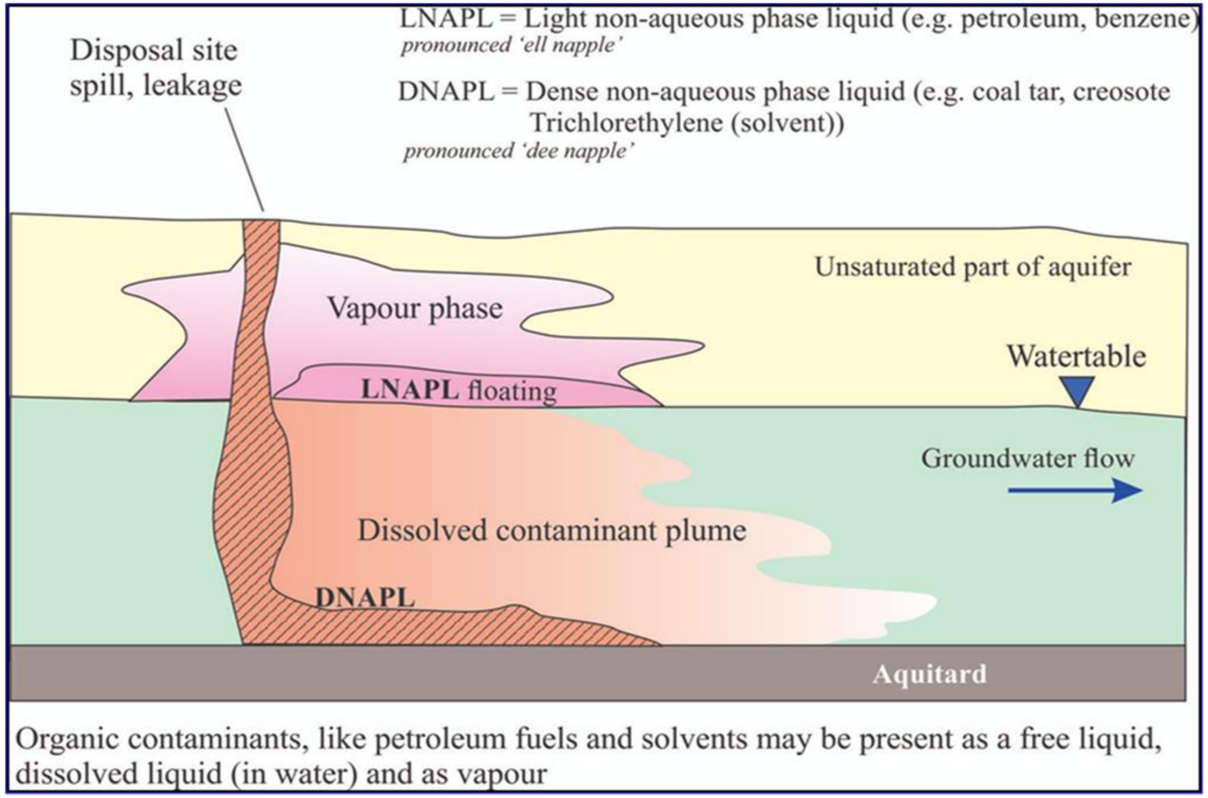
European Radon Association

17th INTERNATIONAL WORKSHOP GARRM

(on the GEOLOGICAL ASPECTS OF RADON RISK MAPPING)

Radon deficit technique for NAPLs contamination

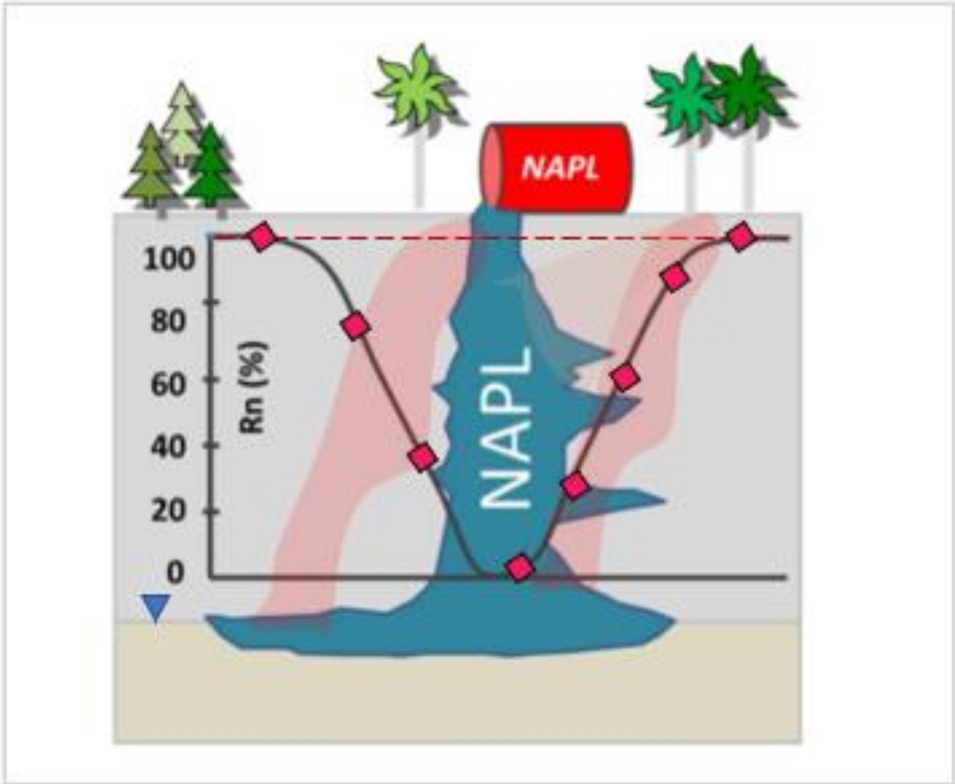
NAPLs (NON-AQUEOUS PHASE LIQUIDS)



(from the blog of Heron Instruments Inc, 2010)

LNAPL (ρNAPL < 1 g/cm^3);
DNAPL(ρNAPL >1 g/cm^3)

RADON DEFICIT TECHNIQUE



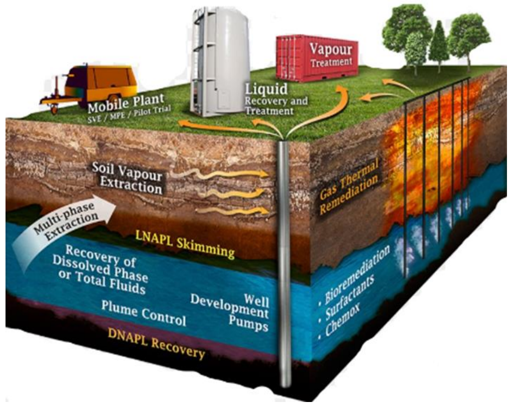
Conceptual model of the use of radon as a tracer of NAPL contamination (modified by De Simone et al.,2015)

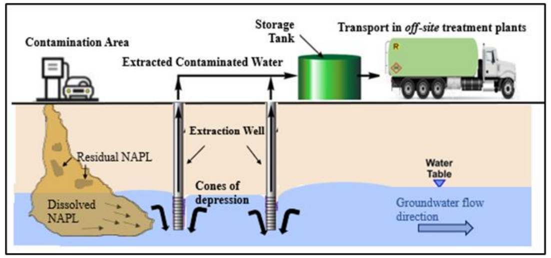
Rn=100 % **Reference value in the uncontaminated area**

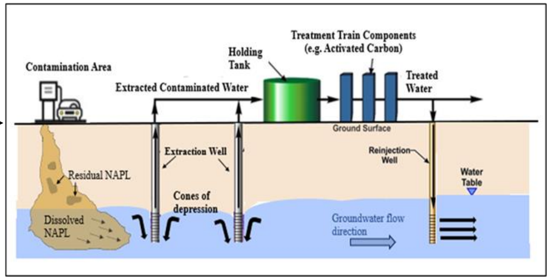
Mitigation

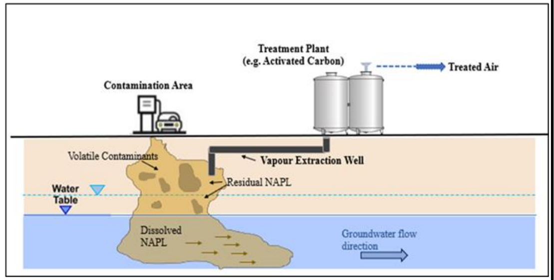
SOIL AND GROUNDWATER REMEDIATION SYSTEM

- ❑Pump and stock
- ❑Pump and treat
- ❑Soil vapour extraction
- ❑Air sparging
- ❑Augmentation



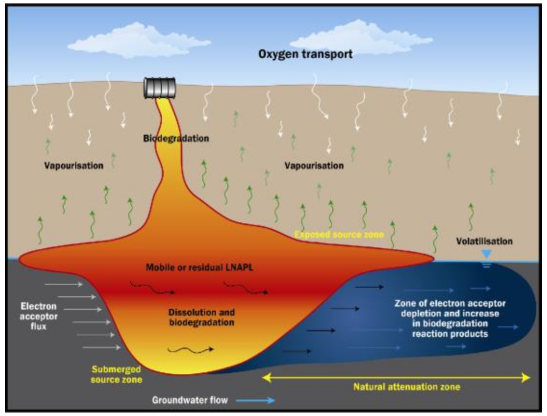




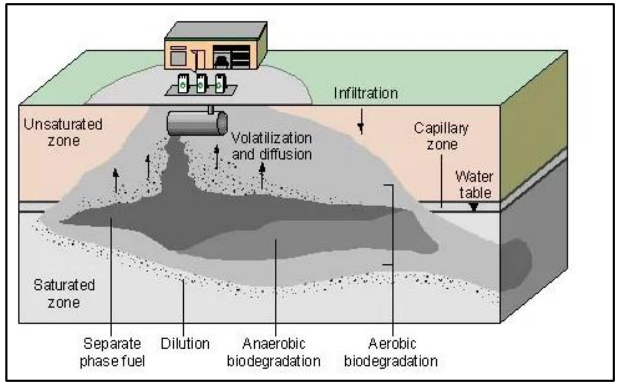


NATURAL ATTENUATION PROCESSES

- ❑Dilution
- ❑Volatilization
- ❑Solubility
- ❑Biodegradation



From "An Illustrated Handbook of LNAPL Transport and Fate in the Subsurface" (Rivett et al., 2014)



Conceptual modeling of natural attenuation processes that affect the fate of hydrocarbons in aquifers (modified by Bekins et al., 2001)

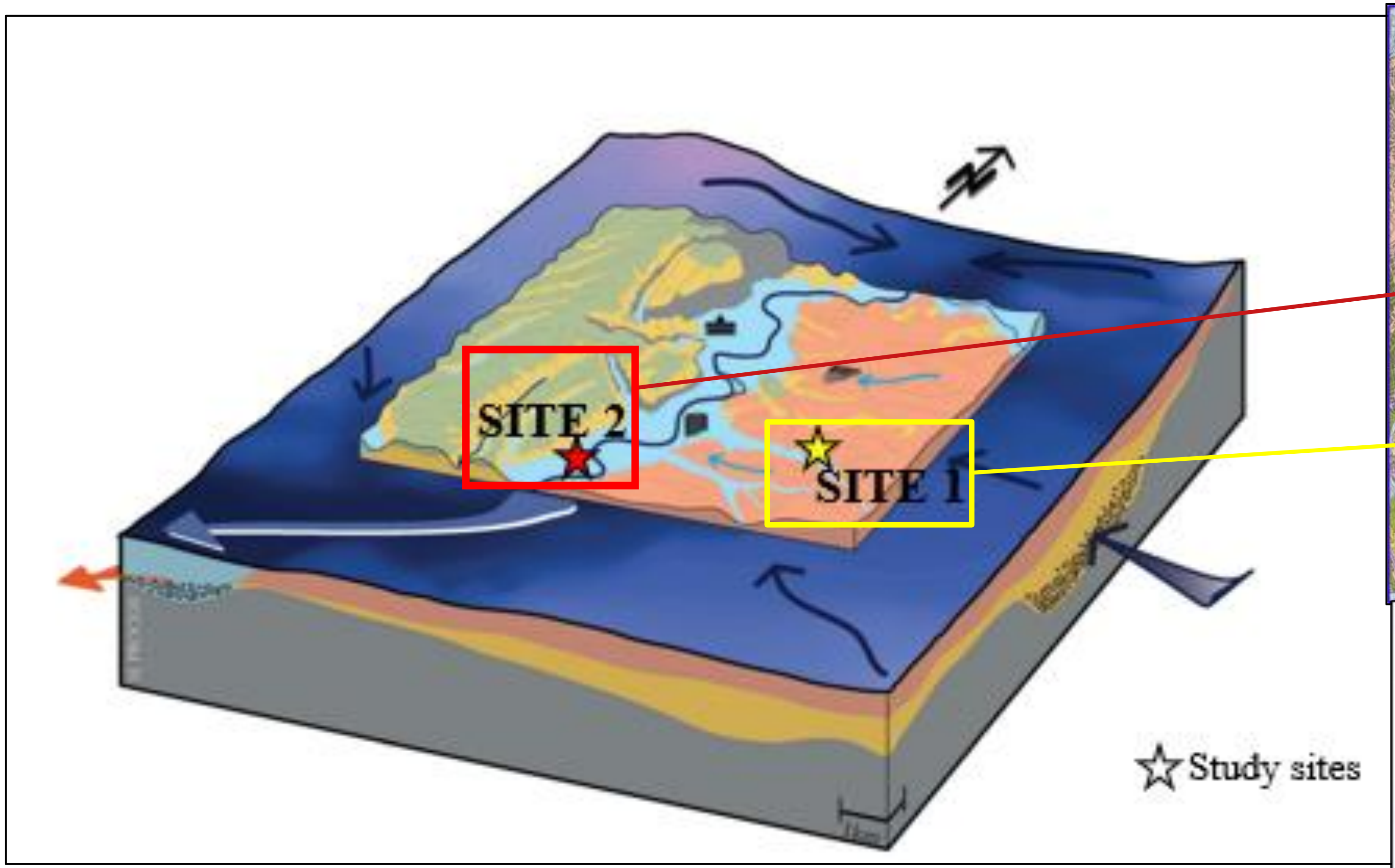
Aim of the research

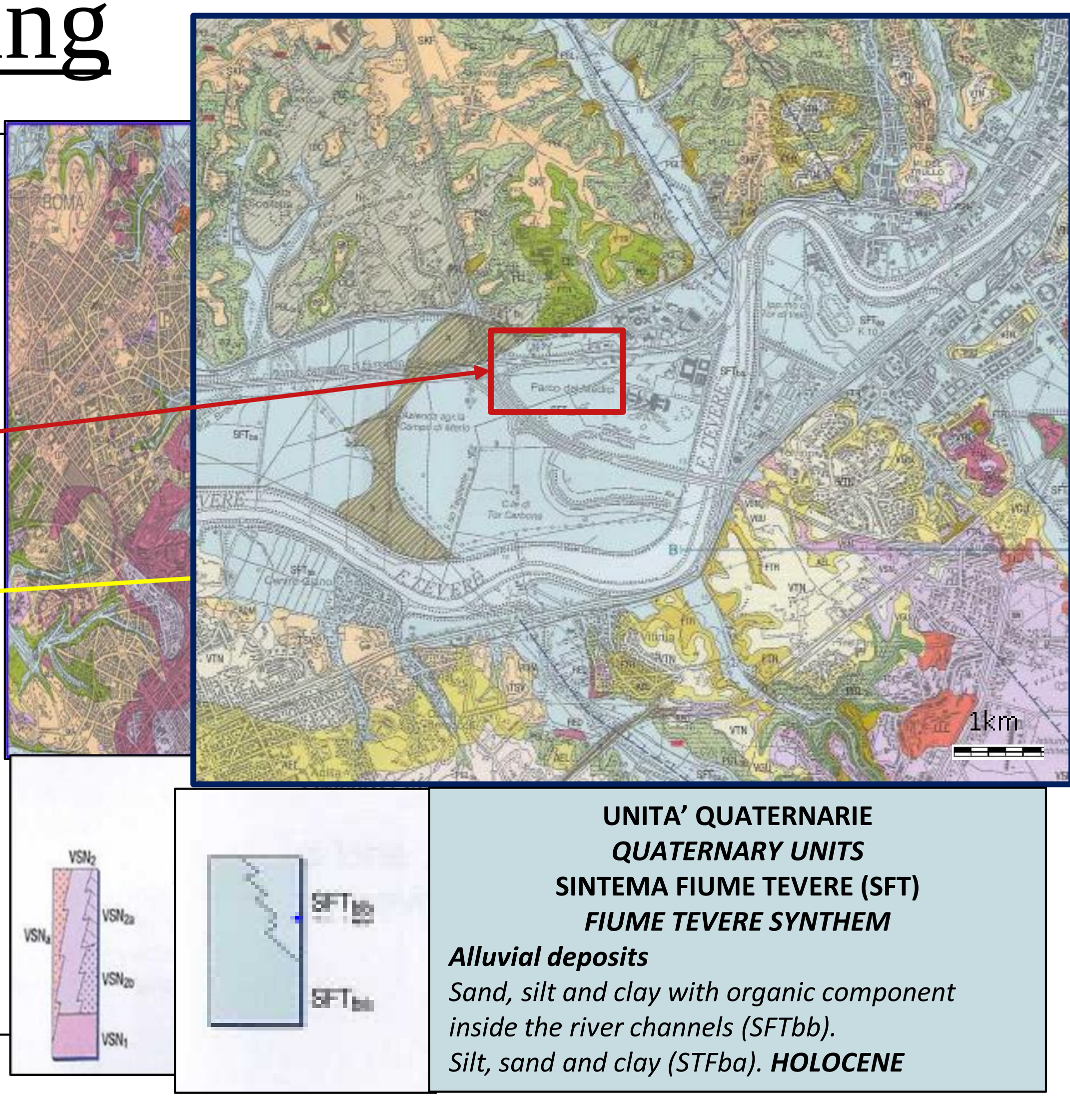
1. **TO VERIFY AND SUPPORT THE POTENTIAL OF THE «RADON DEFICIT» MONITORING TECHNIQUE** TO ASSESS THE CONTAMINATION BY NAPL

2. **TO SHOW THE LIMITS AND PREROGATIVES OF THE RADON DEFICIT TECHNIQUE** IN THE STUDY OF TWO REAL CASES CONTAMINATED BY NAPL

3. **TO CONTEXTUALIZE THE APPLICATION OF THE RADON DEFICIT TECHNIQUE** CONSIDERING ALL THE PARAMETER THAT PLAYED A KEY ROLE IN THE CONTAMINATION DYNAMICS

Geological setting





UNITA' QUATERNARIE
QUATERNARY UNITS
SINTEMA FIUME TEVERE (SFT)
FIUME TEVERE SYNTHEM
Alluvial deposits
Sand, silt and clay with organic component inside the river channels (SFTbb).
Silt, sand and clay (STFba). ***HOLOCENE***

New geological map of the municipality of Rome
(R. Funiciello, G. Giordano, M. Mattei; 2008)

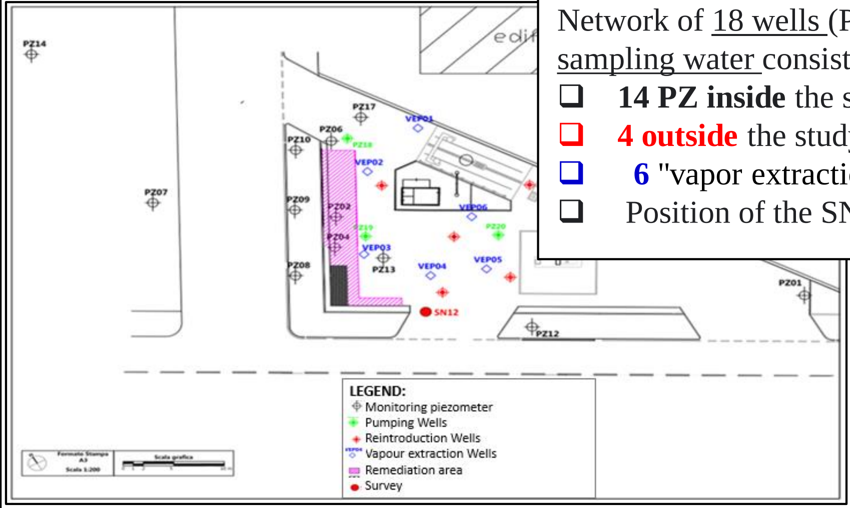
Main features, Monitoring and Remediation plant

SITE 1

- **OLD SPILL** (More than 25 years ago)
- Volcanic aquifer (Colli Albani Unit)

→ **HIGH RADON LEVELS**

- **WATER TABLE AT -18 m** below ground level
- LIMITED WATER LEVEL FLUCTUATION AND CONSTANT FLOW DIRECTION



Network of 18 wells (PZ) for water monitoring and sampling water consisting of:

- **14 PZ inside** the study area;
- **4 outside** the study area (background value);
- **6** "vapor extraction wells " (**VEP** ◇)
- Position of the SN12 survey (**SN12** ●)

Pump and Treat Remediation System

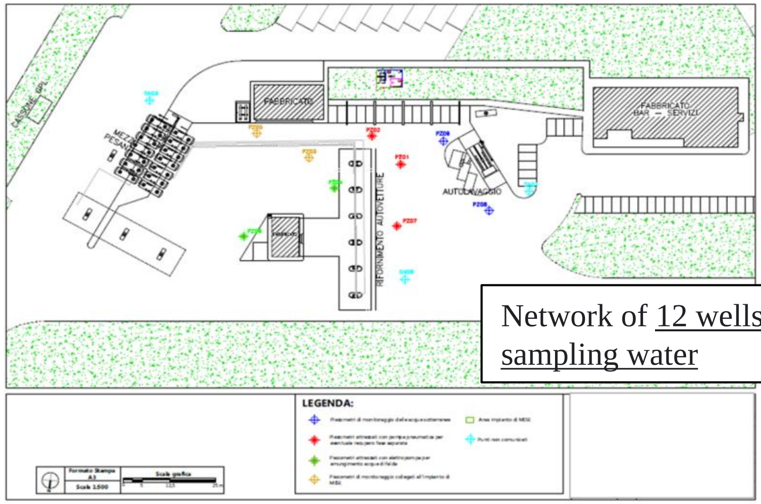
SITE 2

Fuelling station

- **RECENT SPILL** (About 5 years ago)
- Alluvial aquifer (Tevere River)

→ **LOW TO MODERATE RADON LEVELS**

- **WATER TABLE AT -2 m** below ground level
- RELEVANT WATER LEVEL FLUCTUATION (up to 70 cm) AND CHANGE OF FLOW DIRECTION SEASONALLY



Network of 12 wells (PZ) for water monitoring and sampling water

Pump and Stock Securing Activities

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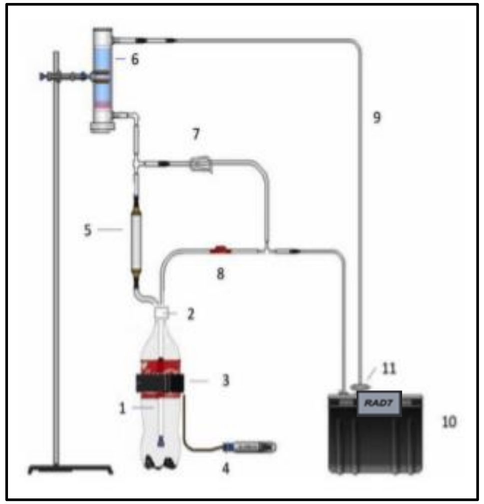
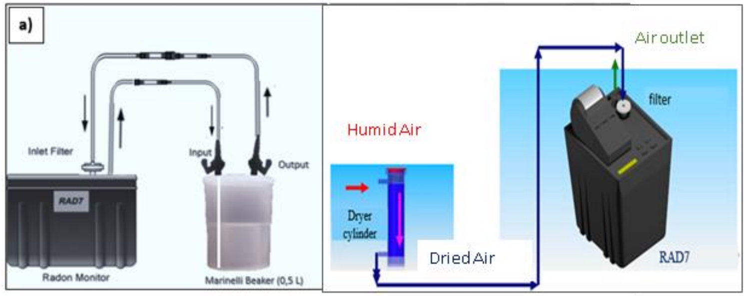
Field Work and Laboratory Methods

Groundwater Sampling

Experimental procedure of groundwater sampling

1) Measure of the piezometric level;
2) Purging of wells;
3) Sampling of water from monitoring wells

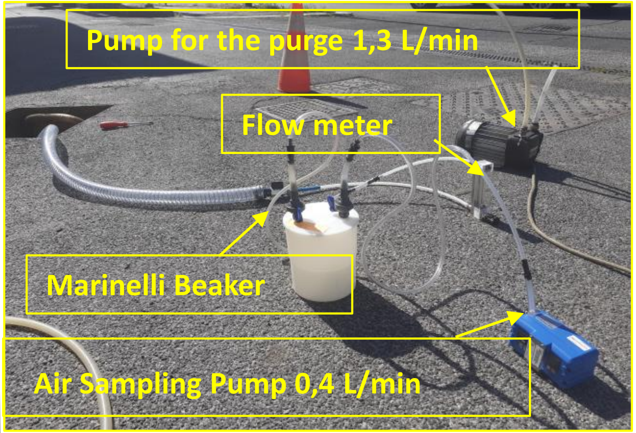
Radon Measurements in Groundwater and in Soil Gas

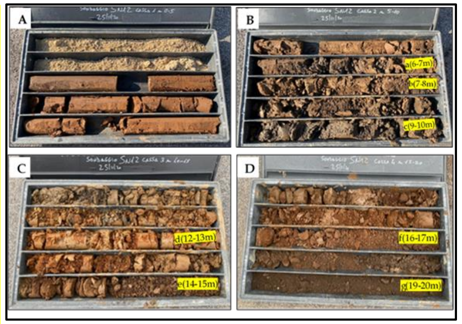
a) *Experimental set up;* ***b)*** *Schematic representation of the open circuit produced between the radonometer and the drying column (Tuccimei, 2019).*

RAD7 monitor with Big Bottle
RAD H2O accessory

Soil Gas Sampling

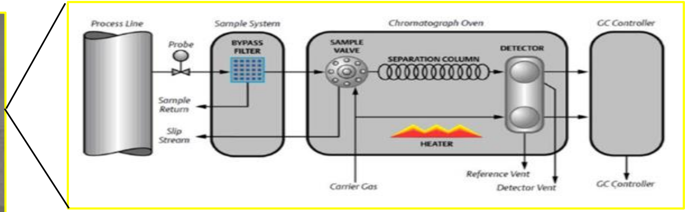


Soil Samples Collecting



Soil Samples collected on which VOC (PID) measurements were carried out

NAPL Measurements in Groundwater

Measurements performed by Mares with the ***gas chromatograph***

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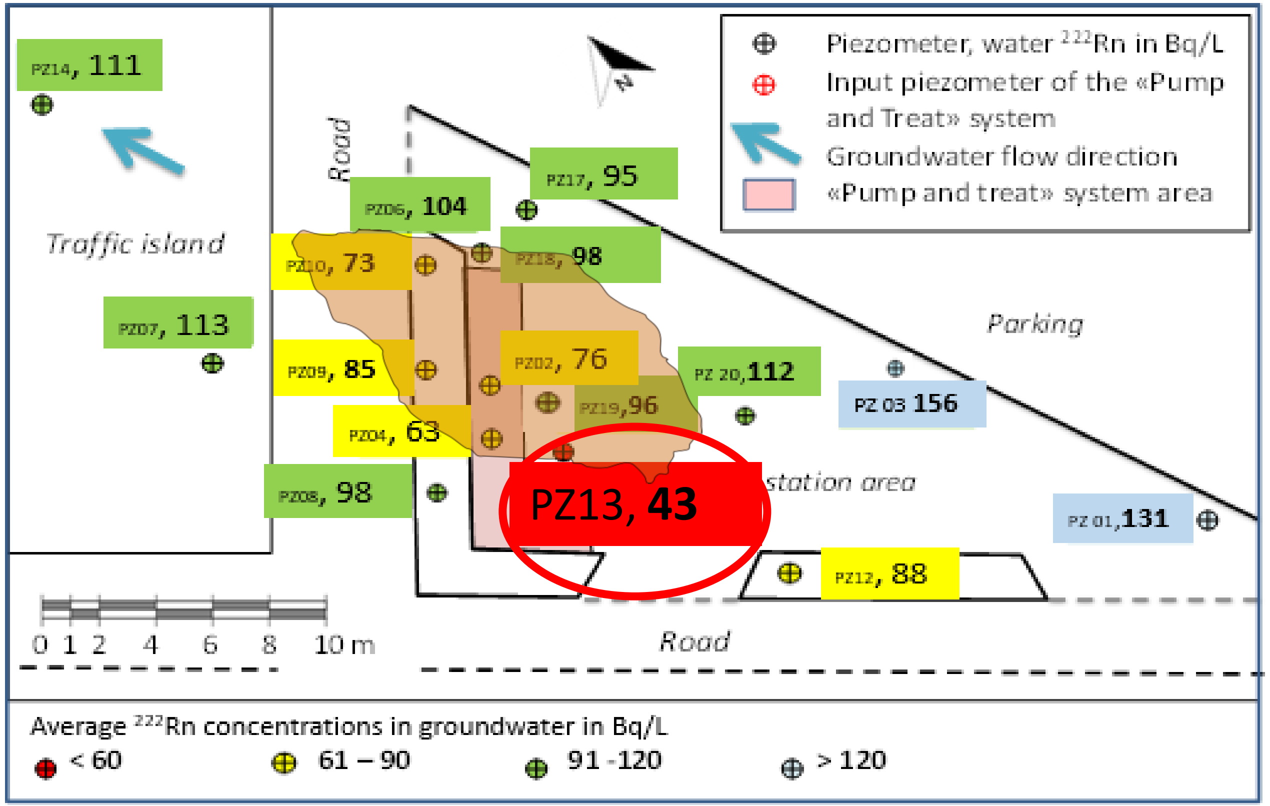
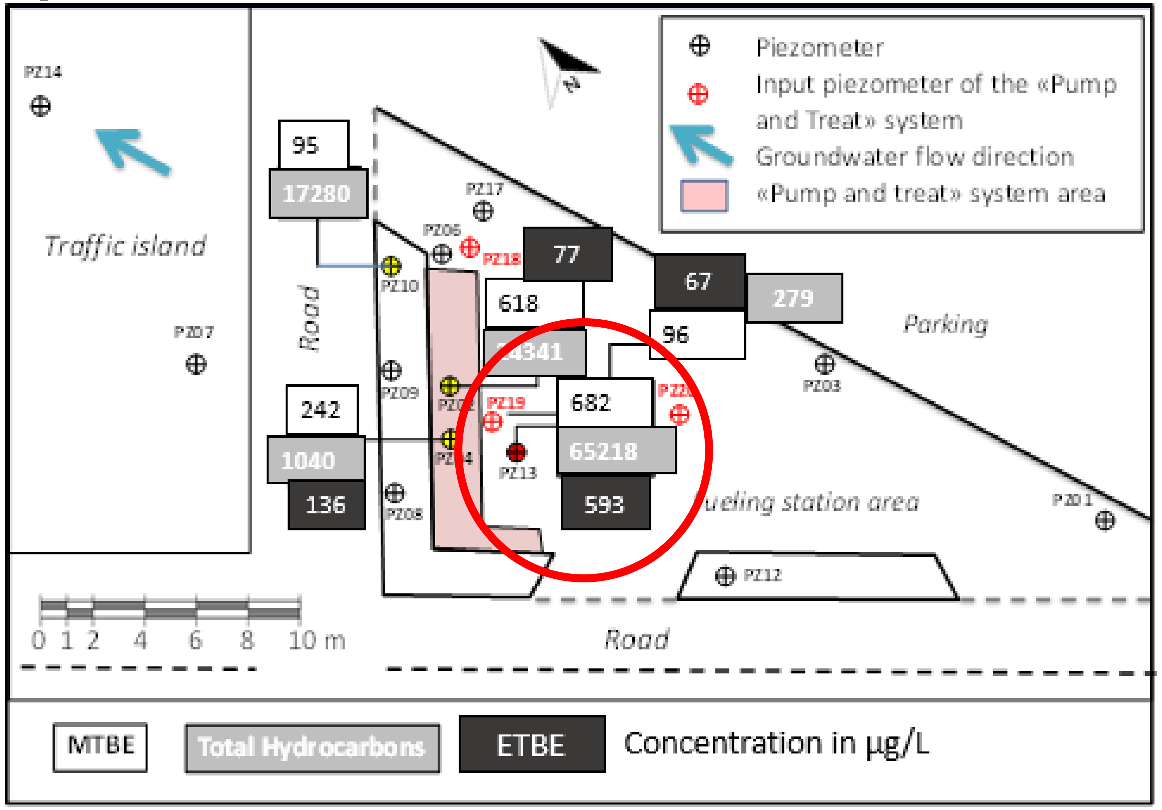
Site 1:Comparison of average radon and NAPLs concentration Dot Maps

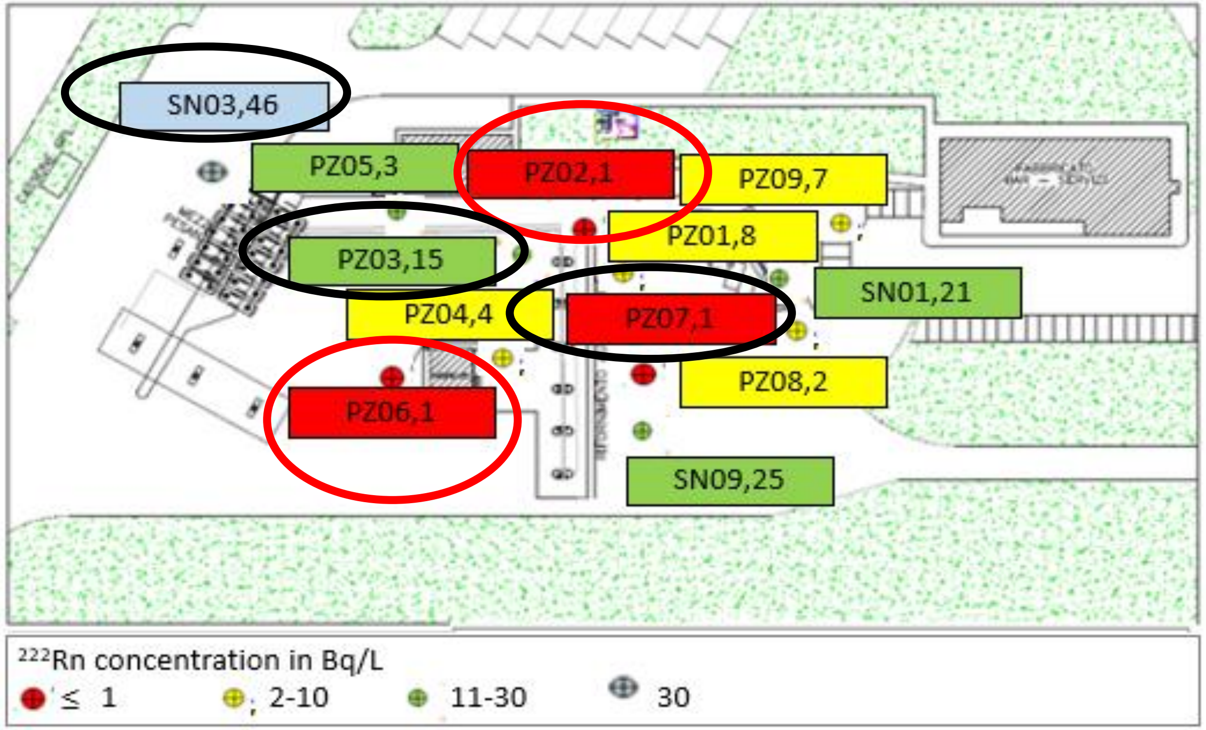


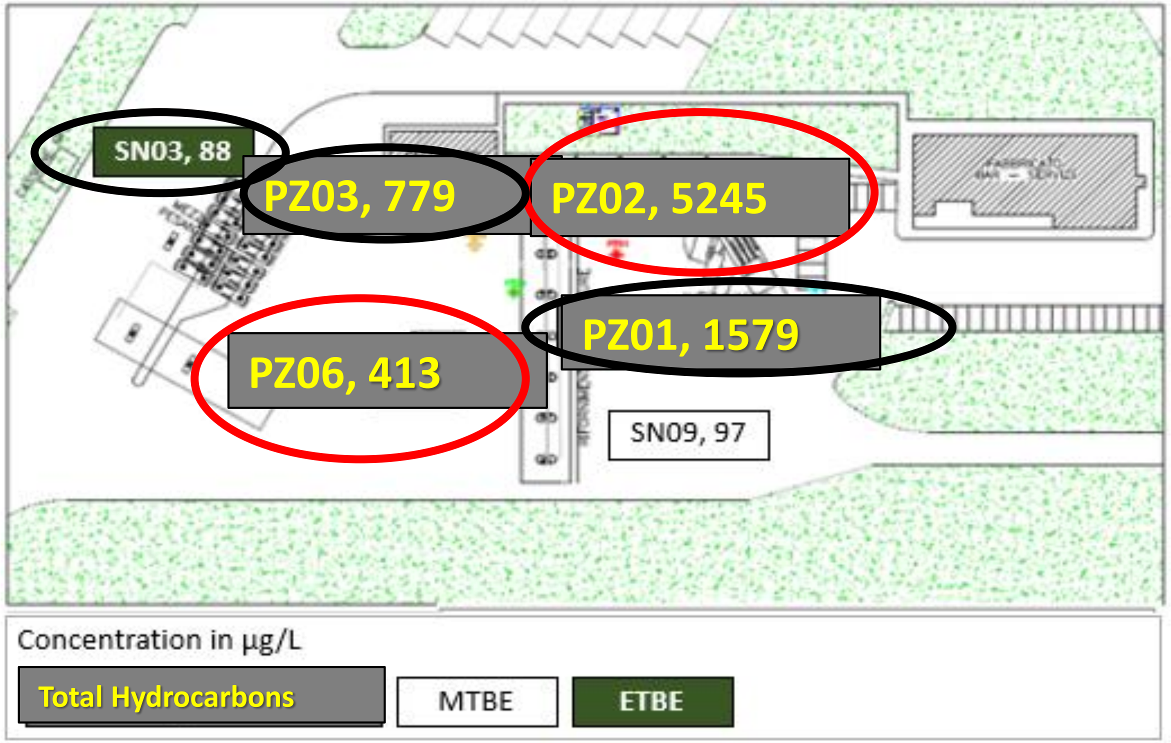


- Low radon abundances correspond to high NAPLs values in groundwater
- Low radon values identify the NAPLs source area
- After heavy rainfalls, a small temporaneous plume was detected

*Limits established by Italian Legislation:**40 µg/L** for MTBE/ETBE and **350 µg/L** for Total Hydrocarbons*

Site 2:Comparison of average radon and NAPLs concentration Dot Maps





LEGEND: PZn, **X** → X: Radon concentration in Bq/L

PZn: Piezometer name/number

LEGEND: PZn, **Y** → Y: NAPL concentration in µg/L

PZn: Piezometer name/number

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Statistical Approach for both sites

Summary statistics

Outliers analysis

Analysis of Variance (ANOVA)

Analysis of Covariance (ANCOVA)

Factorial Analysis

Regression Analysis

Outlier detection

Variable	Radon_Bq_L Radon Bq/L

Sample size	144
Lowest value	17,0000
Highest value	185,0000
Arithmetic mean	97,5972
Median	101,0000
Standard deviation	32,4680
Coefficient of Skewness	0,1725 (P=0,3845)
Coefficient of Kurtosis	0,3178 (P=0,3705)
Kolmogorov-Smirnov test[a] for Normal distribution	D=0,0604 accept Normality (P>0.10)

[a] Lilliefors significance correction

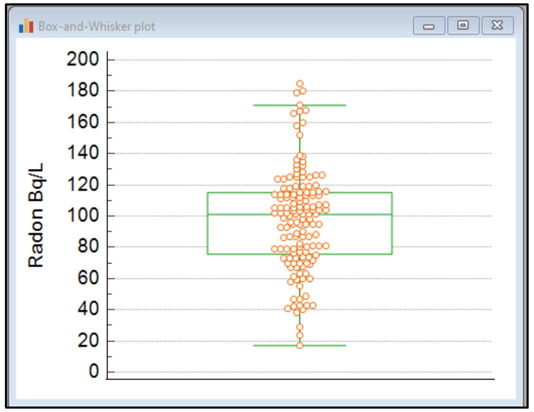
Suspected outliers

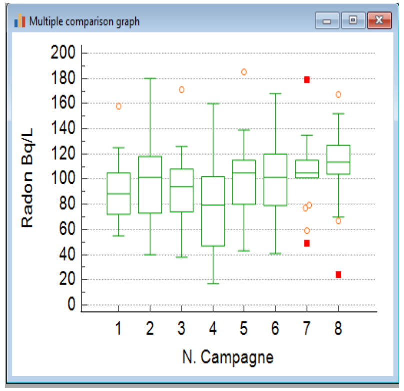
Grubbs - right-sided (alpha-level 0.05)
None

Tukey, 1977	
Outside values	179 180 185
Far-out values	None

Generalized ESD test (alpha-level 0.05)
None

Box-and-Whisker plot





Data	Radon_Bq_L Radon Bq/L
Factor codes	N._Campagne N. Campagne

Sample size	144

Levene's test for equality of error variances

Levene statistic	0,443
DF 1	7
DF 2	136
Significance level	P = 0,873

ANOVA

Source of variation	Sum of Squares	DF	Mean Square
Between groups (influence factor)	11046,7500	7	1578,1071
Within groups (other fluctuations)	139699,8889	136	1027,2051
Total	150746,6389	143	

F-ratio	1,536
Significance level	P = 0,160

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Factor Analysis

Variable	Factor1	Factor2	Factor3
Radon Bq/L	-0,635	0,007	-0,740
MTBE	0,782	0,056	-0,431
ETBE	0,840	-0,231	-0,153
Total Hydrocarbon	0,831	-0,113	-0,003
Groundwater level	-0,260	-0,957	0,007
Variance	2,4795	0,9859	0,7578
% Var	0,496	0,197	0,152

85% Var

Site 1

- **Factor 1** Radon deficit (rain+ leaks)
- **Factor 2** Aerobic degradation
- **Factor 3** Volatilization and degassing

- **The first factor** alone accounts for 50% and likely represents the radon deficit Here, radon and the groundwater level follow the same trend, while all contaminants show an opposite trend. The negative sign of the groundwater level indicates that water levels are rising due to rainfall. Although the water table is relatively deep, around 18 meters, rainfall combined with water losses from the pipes at this site likely mobilizes residual NAPLs in the vadose zone, between 6 and 11 meters below ground. This leads to increased contaminant concentrations in groundwater and a corresponding decrease in radon, consistent with the radon deficit phenomenon.
- The **second factor** explains about 20% of the variance. In this case, radon has very little influence and is not considered, while the groundwater table has the same trend of total hydrocarbons and ETBE. The negative sign of the water table reflects rainfall and rising groundwater levels. This factor could represent **aerobic degradation**: rainfall brings oxygen and nutrients into the aquifer, promoting the degradation of contaminants. This process is further enhanced by the SVE system and the use of biosurfactants. However, this degradation has little effect on MTBE, because it is more resistant to aerobic conditions, explaining its inverse trend compared to the other contaminants.
- The **third factor** accounts for about 15 % of the variance. In this factor radon is correlated with all contaminants. This factor could be explained by the volatilization of NAPL and the outgassing of radon, as we know from previous work that the soil vapor extraction system favors the volatilization phenomenon. In this case the water table has a very low factor score so it is not considered, also because the phenomenon concerns the vadose zone.

Factor Analysis

Variable	Factor1	Factor2	Factor3
Radon Bq/L	0,953	-0,014	-0,049
Total Hydrocarbons lim. Rif. 350	-0,128	0,726	-0,215
MTBE lim. Rif. 40 µg/l	0,219	-0,512	-0,790
ETBE lim. Rif. 40 µg/l	0,872	0,045	0,376
Groundwater level (m)	0,302	0,590	-0,450
Variance	1,8230	1,1391	1,0165
% Var	0,365	0,228	0,203

≈80% Var

Site 2

Factor 1 Radon deficit (rain)

Factor 2 Radon deficit (groundwater table)

Factor 3 Anaerobic degradation

Factor 1 and Factor 2 likely represent the **radon deficit.**

- **Factor 1**, which explains about 37% of the variance, shows an inverse relationship between radon and total hydrocarbons, a pattern not observed with ETBE and MTBE. It is important to note that total hydrocarbons are the most abundant contaminants at this site. Here, the groundwater table is much shallower, around 2 meters, so variations in water level play a key role in the phenomenon.
- **Factor 2,** accounting for about 23% of the variance, also reflects the radon deficit, primarily associated with changes in groundwater depth. When the water table lowers, it remobilizes NAPLs located at shallow depths (around 3 meters), increasing total hydrocarbons and ETBE concentrations. Conversely, MTBE shows a decrease, likely because it is more soluble and tends to migrate to greater depths, leaving residual NAPLs at shallow depths depleted of MTBE, which explains its opposite trend.
- **Factor 3**, which explains about 20% of the variance, is characterized by a rising water table (indicated by decreasing depth) and a common trend among most parameters, except ETBE. This factor is assumed to represent **biodegradation under anaerobic conditions**. Similar to the first site, rainfall introduces nutrients that promote contaminant degradation. However, in this case, water table fluctuations flood part of the subsurface where residual NAPLs were previously above the water table, creating partially anaerobic conditions. Previous studies have shown that ETBE does not degrade under anaerobic conditions, which is consistent with its distinct trend in this factor.

Regression Analysis of both sites as predictive tool

Site 1

Regression Equation

Radon (Bq/L)	=	8,2 - 0,000485 Total Hydrocarbons + 0,00440 MTBE - 0,0495 ETBE + 5,28 Groundwater level (m)

Coefficients

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	8,2	76,1	0,11	0,914	
Total Hydrocarbons	-0,000485	0,000160	-3,03	0,003	1,71
MTBE	0,00440	0,00838	0,52	0,601	1,72
ETBE	-0,0495	0,0211	-2,34	0,021	1,97
Groundwater level (m)	5,28	4,25	1,24	0,216	1,06

Site 2

Regression Equation

Radon (Bq/L)	=	-6,85 - 0,000101 Total Hydrocarbons + 0,1366 MTBE + 0,4514 ETBE + 5,15 Groundwater level (m)

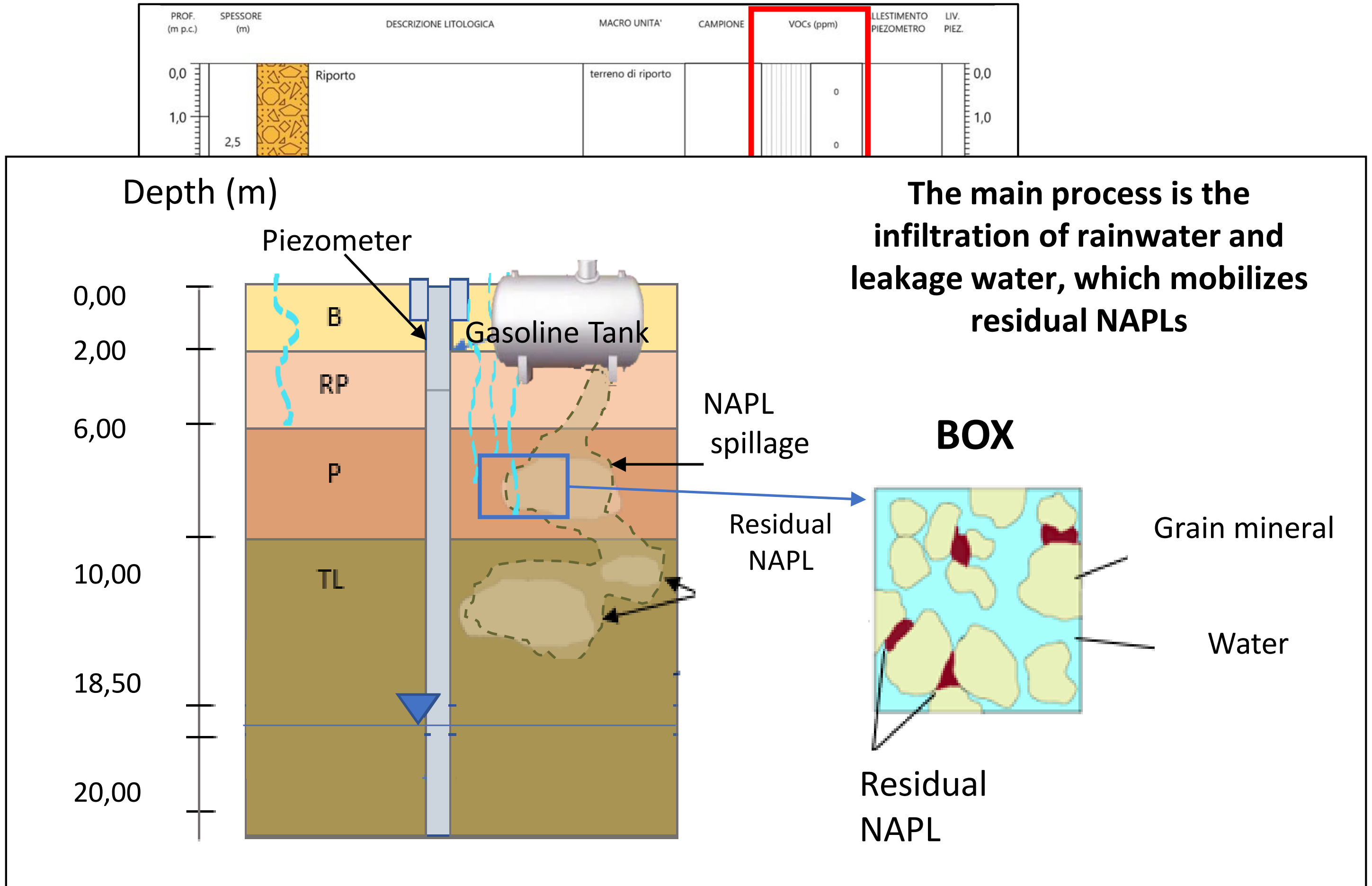
Coefficients

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	-6,85	4,30	-1,59	0,117	
Total Hydrocarbons	-0,000101	0,000276	-0,37	0,714	1,02
MTBE	0,1366	0,0350	3,90	0,000	1,01
ETBE	0,4514	0,0444	10,16	0,000	1,01
Groundwater level (m)	5,15	1,82	2,83	0,006	1,01

equation of a curve that best describing how one variable is related to another. It also can be used as a predictive tool.

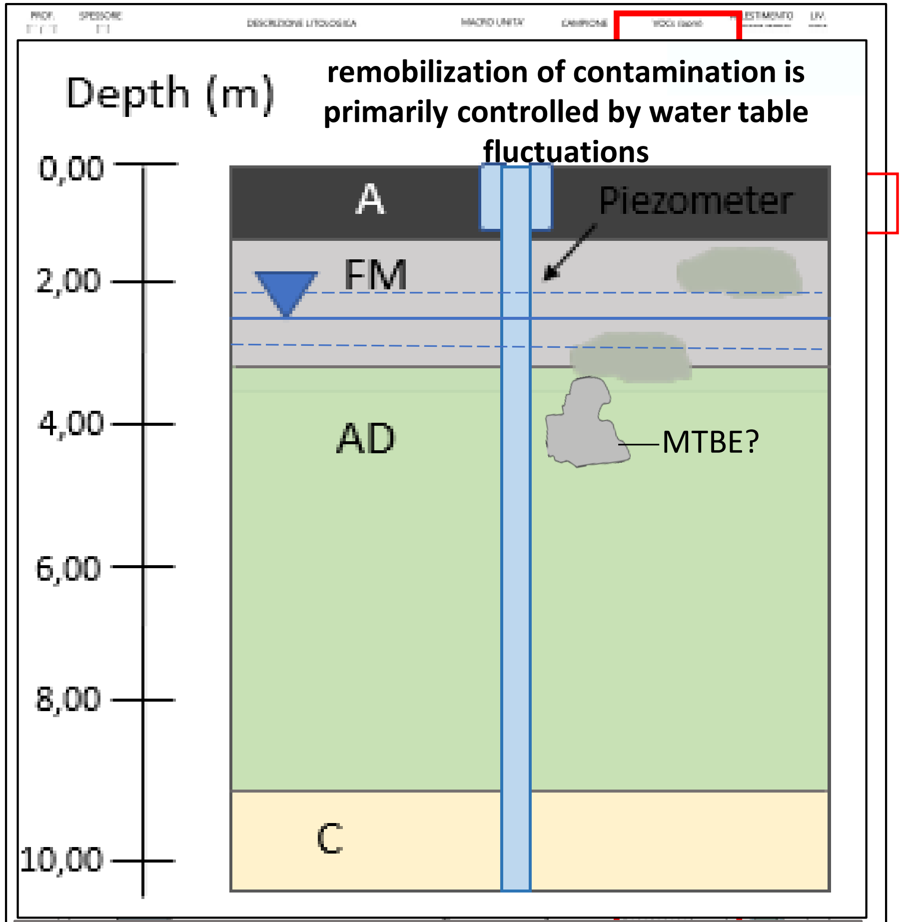
→ by knowing the value of one variable, we can estimate or forecast the value of the other.

Conceptual models of the two case studies



B is backfill; RP is reworked pozzolan; P is pozzolan belong to Villa Senni formation and TL is “Tufo Lionato” formation.

Site 1



A is Asphalt; FM is filling material; AD is alluvial deposit; C is Clay. The solid line indicates the average depth level of the aquifer in sampled wells

Site 2

Conclusion

- Low radon in soil gas and groundwater allowed to identify the location of residual NAPLs.

- Radon deficit approach was validated with a COMBINED METHOD consisting of multi-parameter monitoring (radon, NAPLs and groundwater levels), chemical analysis, mapping and statistical treatment of data collected for two study sites with different geological setting and contamination conditions.

➡ Groundwater table depth and fluctuations, location of residual NAPLs and mitigation techniques resulted crucial to outline the different significance of radon deficit and that of main natural and induced attenuation processes (degradation in aerobic and anaerobic environment and volatilization) in the two sites

- The statistical treatment of the data collected for both sites was an innovative and original survey approach. In fact, factor analysis had never been used to study the processes that come into play at a contaminated site

- Regression models may be used as a predictive tool in these sites and in others with similar features, where not all data are available.

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water MDPI

Article

Radon as a Natural Tracer for Monitoring NAPL Groundwater Contamination

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Water: Ecology and Management

Book Chapter

Tracing NAPL Contamination of Groundwater Using Natural Radon: A Case-Study in Roma (Central Italy)

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applied sciences MDPI

Article

Combining Radon Deficit, NAPL Concentration, and Groundwater Table Dynamics to Assess Soil and Groundwater Contamination by NAPLs and Related Attenuation Processes

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THANK YOU FOR YOUR ATTENTION