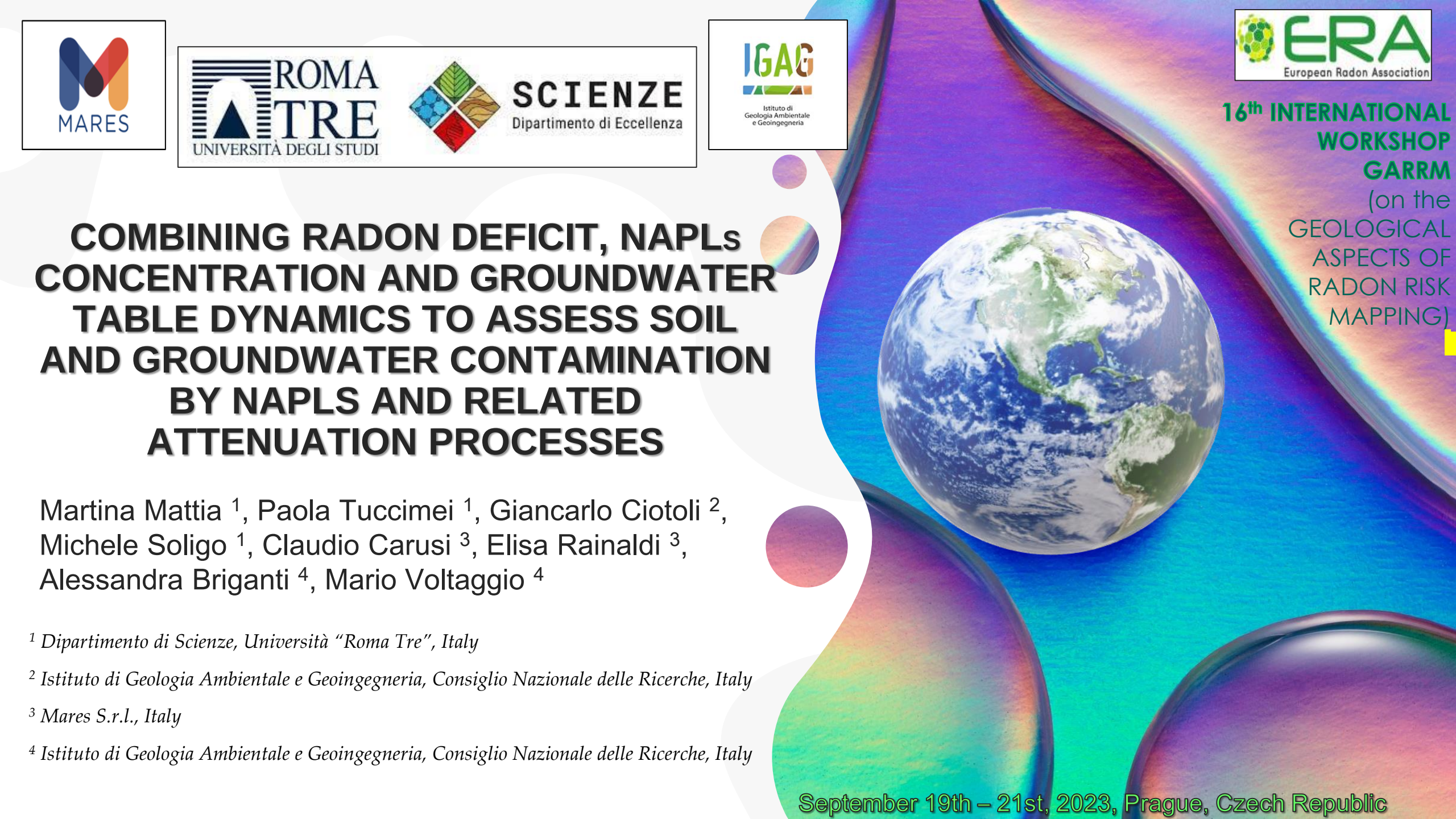

16th INTERNATIONAL WORKSHOP GARRM (on the GEOLOGICAL ASPECTS OF RADON RISK MAPPING)

September 19th – 21st, 2023, Prague, Czech Republic

COMBINING RADON DEFICIT, NAPLs CONCENTRATION AND GROUNDWATER TABLE DYNAMICS TO ASSESS SOIL AND GROUNDWATER CONTAMINATION BY NAPLS AND RELATED ATTENUATION PROCESSES

Martina Mattia [1], Paola Tuccimei [1], Giancarlo Ciotoli [2], Michele Soligo [1], Claudio Carusi [3], Elisa Rainaldi [3], Alessandra Briganti [4], Mario Voltaggio [4]

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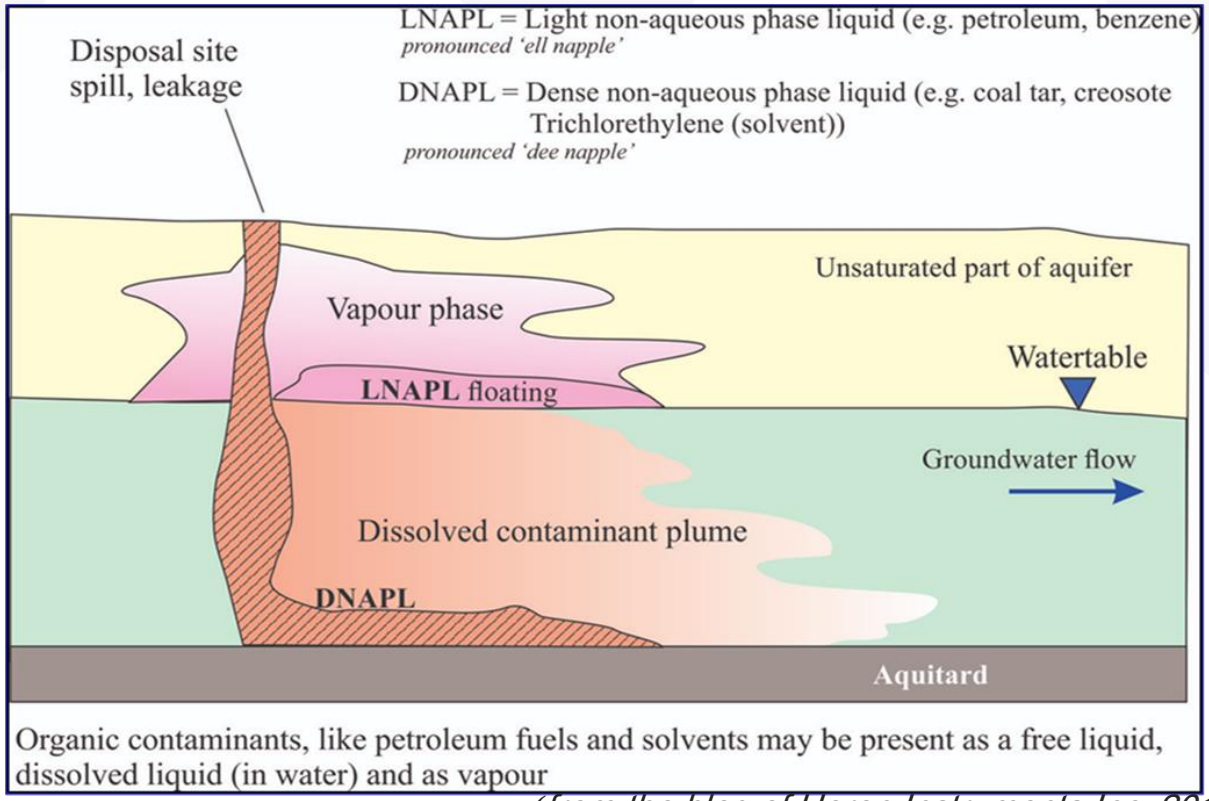
Radon deficit technique for NAPLs contamination

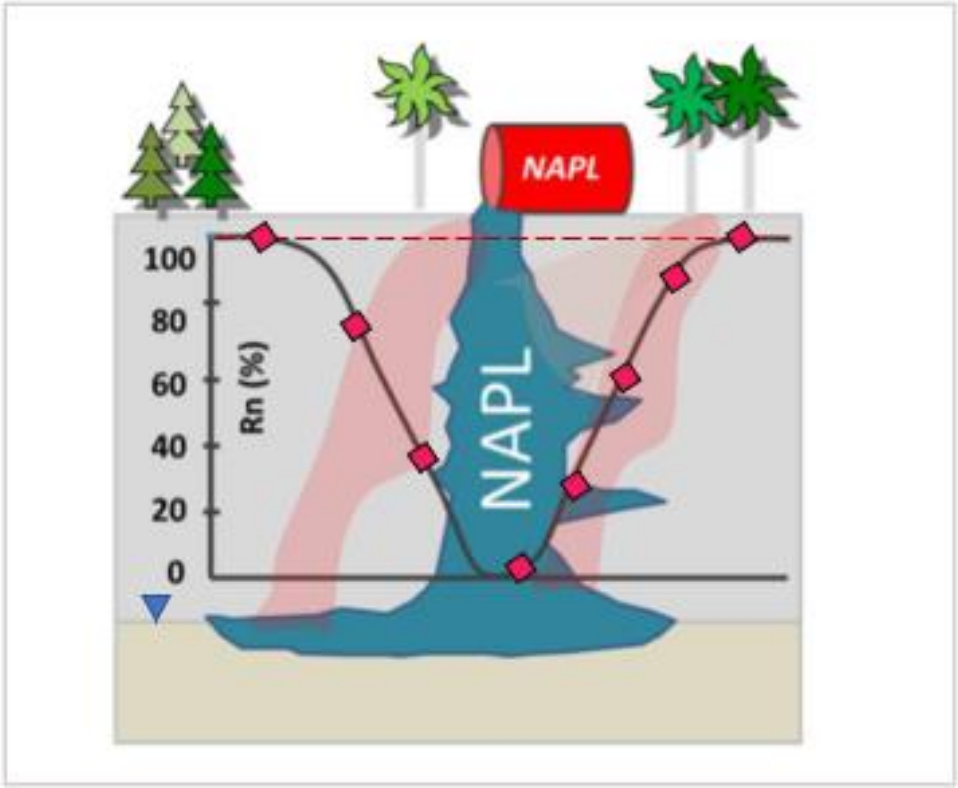
NAPLs (NON-AQUEOUS PHASE LIQUIDS)



(from the blog of Heron Instruments Inc, 2010)

LNAPL ($\rho_{NAPL} < 1$ g/cm^3);
DNAPL($\rho_{NAPL} > 1$ 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

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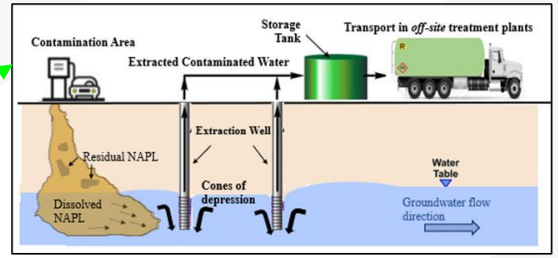
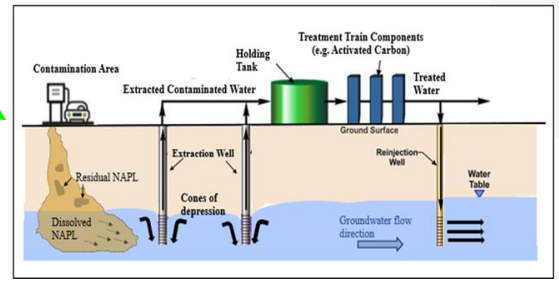
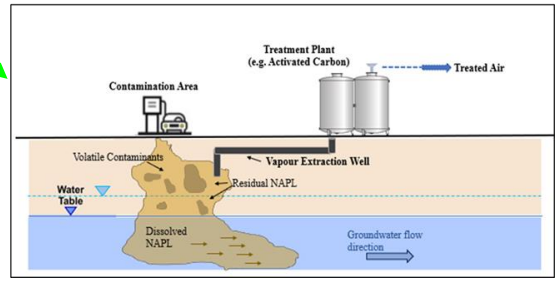
Mitigation

SOIL AND GROUNDWATER REMEDIATION SYSTEM

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

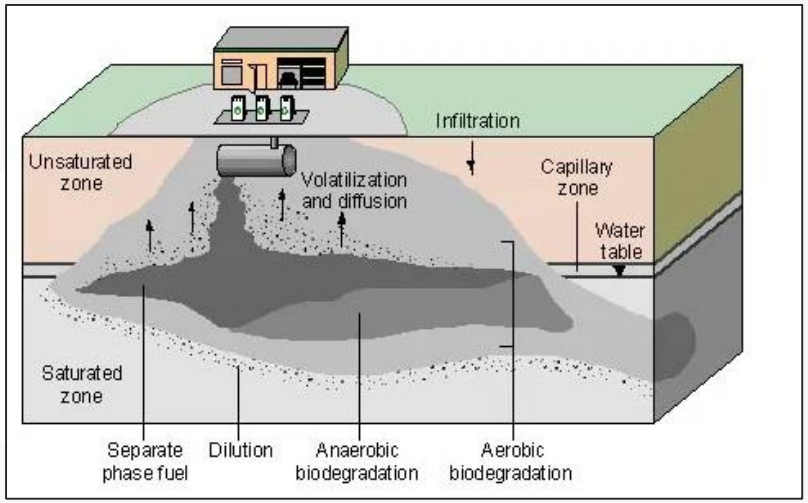






NATURAL ATTENUATION PROCESSES

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



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Aim of the research

- ✓ **TO VERIFY AND SUPPORT THE POTENTIAL OF THE «RADON DEFICIT»** MONITORING **TECHNIQUE** TO ASSESS THE CONTAMINATION BY NAPL
- ✓ **TO SHOW THE LIMITS AND PREROGATIVES OF THE RADON DEFICIT TECHNIQUE** IN THE STUDY OF TWO REAL CASES CONTAMINATED BY NAPL
- ✓ **TO CONTEXTUALIZE THE APPLICATION OF THE RADON DEFICIT TECHNIQUE** CONSIDERING ALL THE PARAMETER THAT PLAYED A KEY ROLE IN THE STUDY OF SPECIFIC CONTAMINATED SITES

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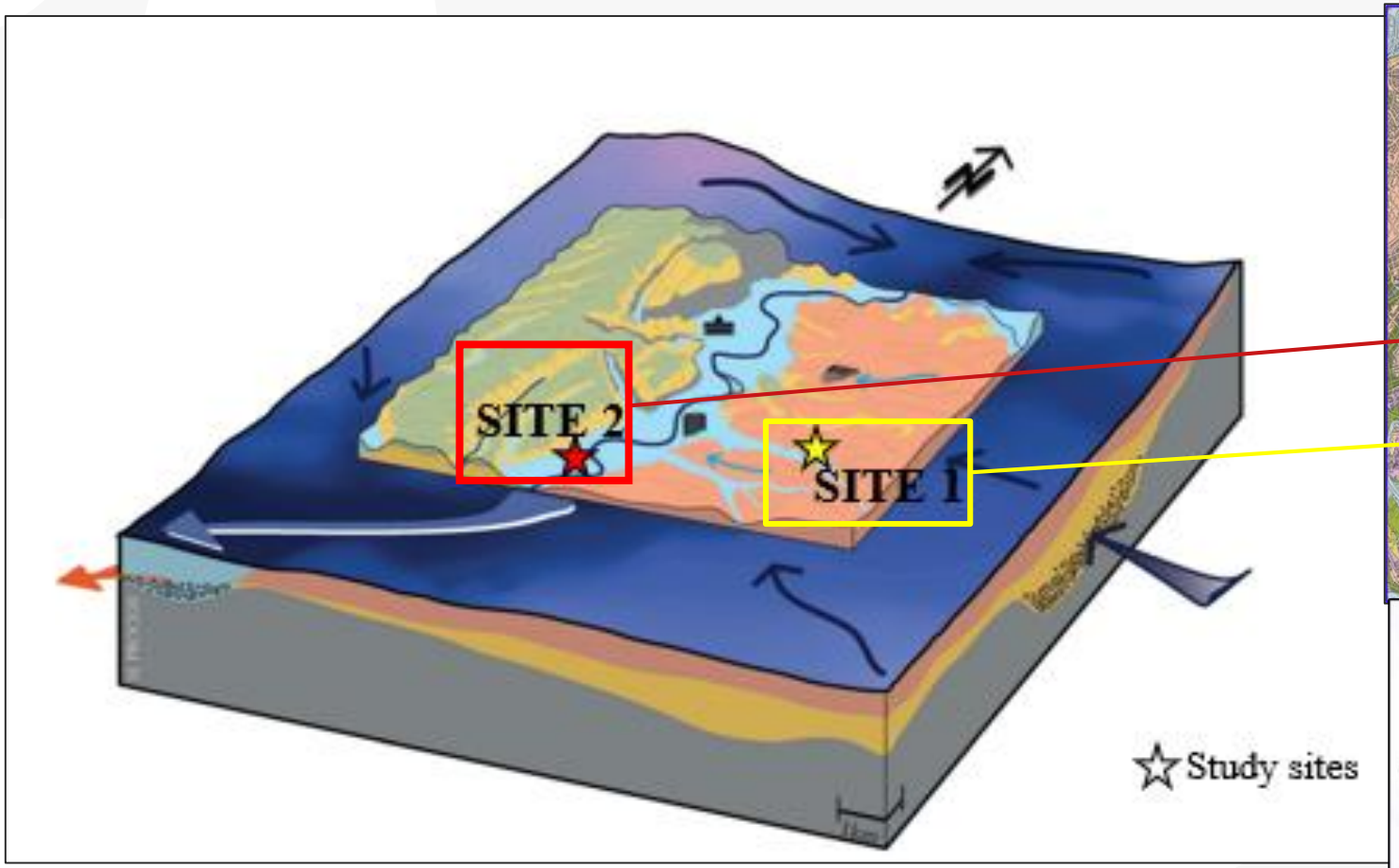
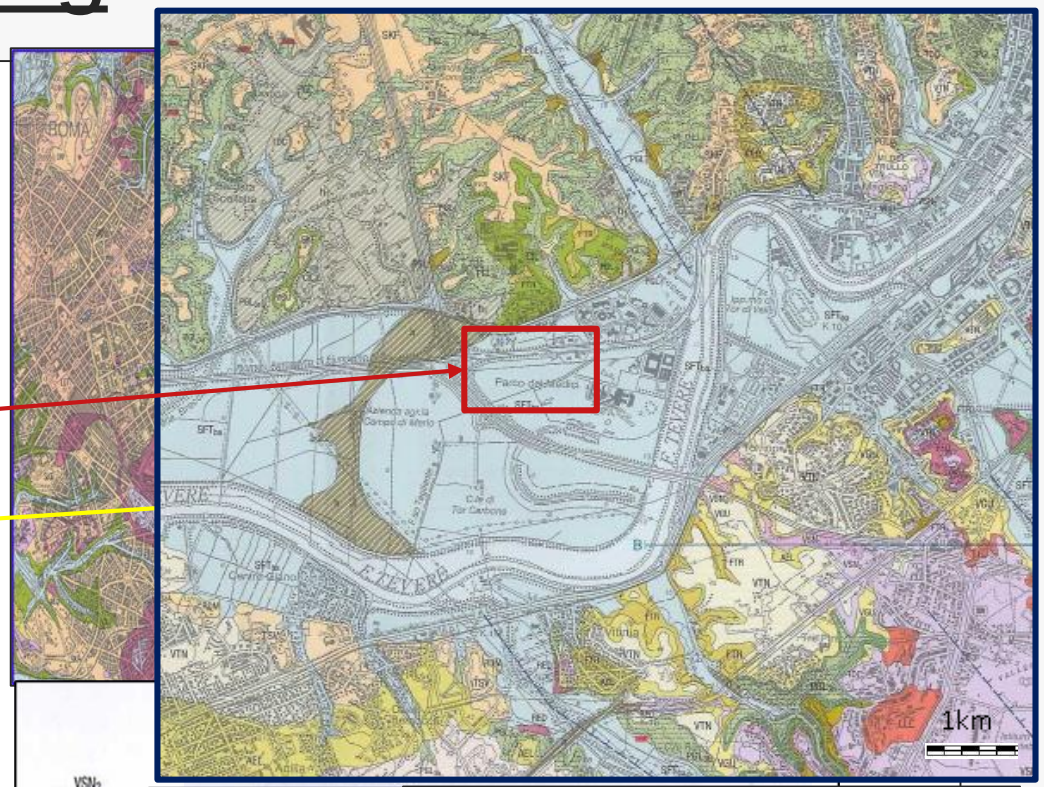
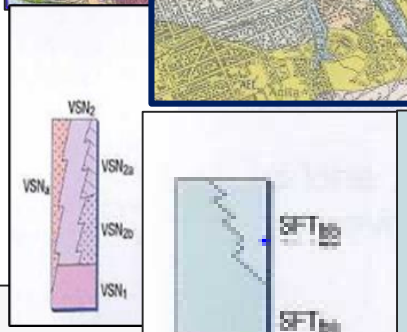
Geological setting







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 g
Rome
(R. Funiciello, G. Giordano, M. Mattei; 2008)

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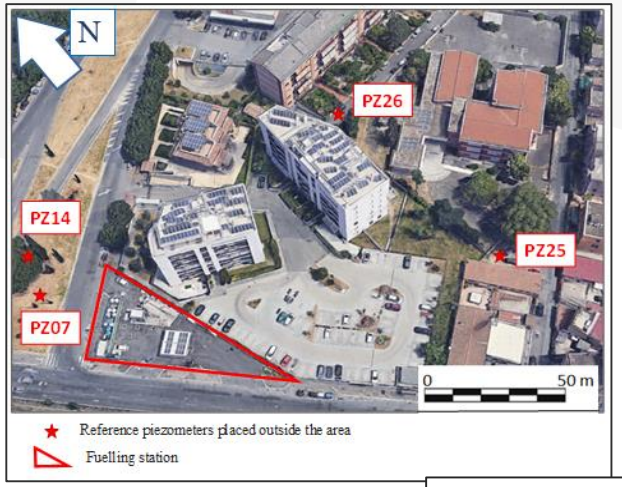
Main features, Monitoring and Remediation plant

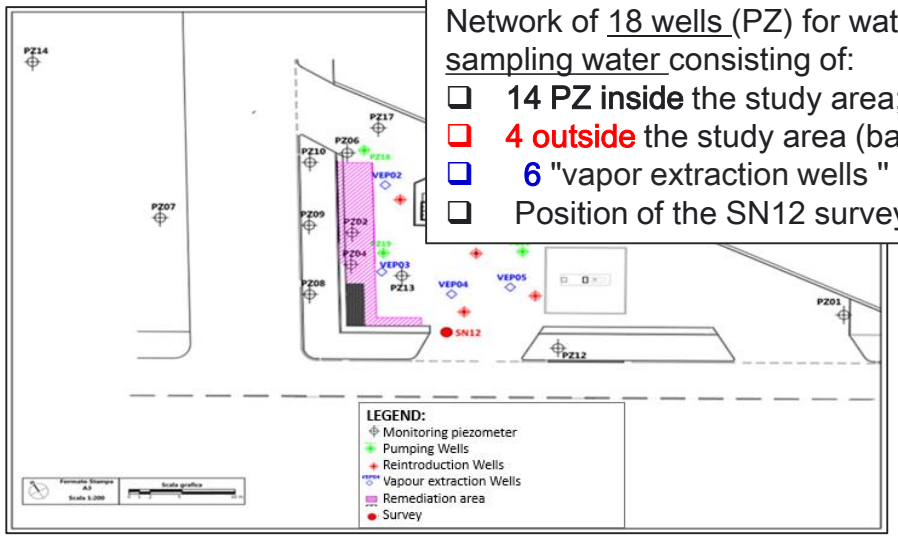
SITE 1



- **OLD SPILL** (About 20 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

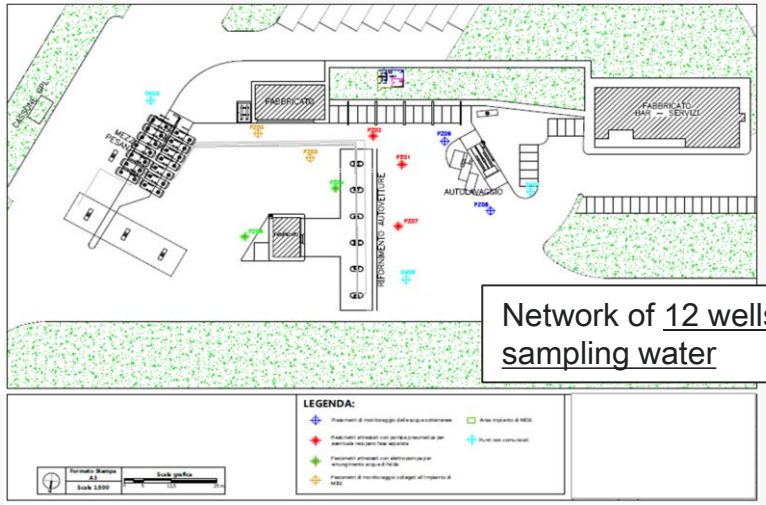
SITE 2

Fuelling station

- **RECENT SPILL** (About 3 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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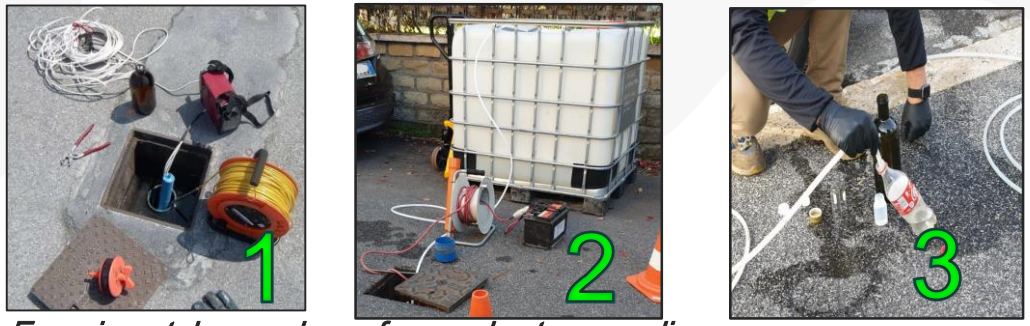
Field Work and Laboratory Methods

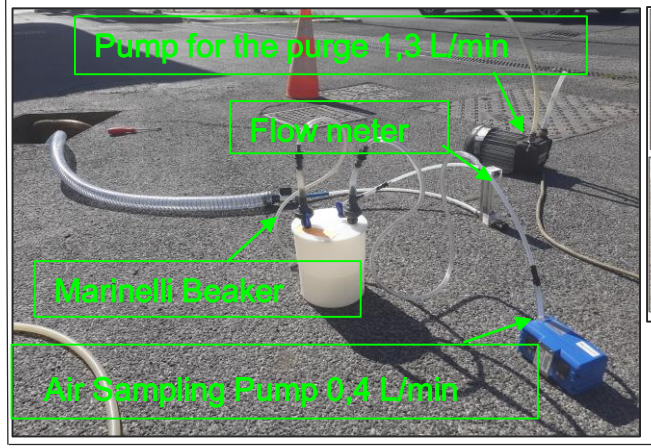
Groundwater Sampling



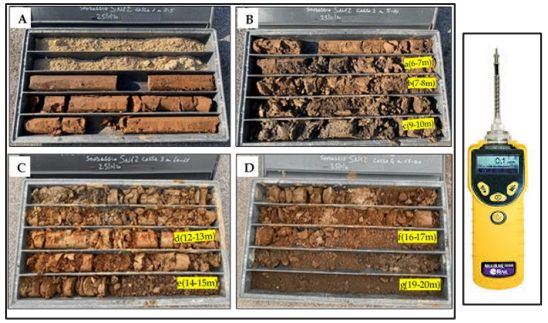
Experimental procedure of groundwater sampling

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

Soil Gas Sampling

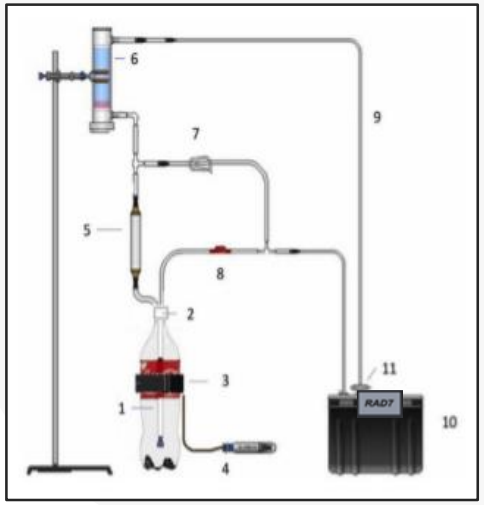


Soil Samples Collecting

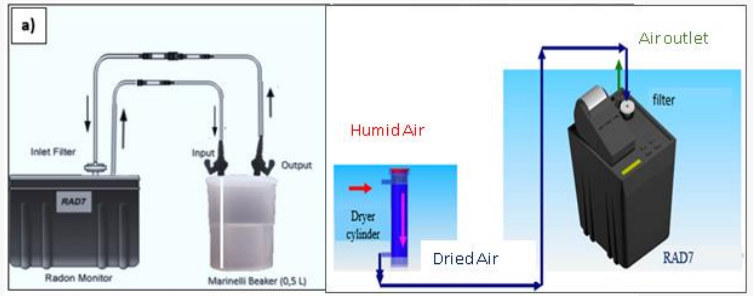


Soil Samples collected on which VOC (PID) measurements were carried out

Radon Measurements in Groundwater and in Soil Gas

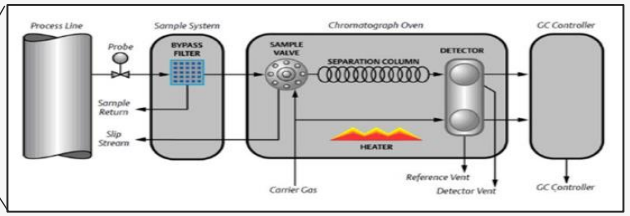


RAD7 monitor with Big Bottle RAD H2O accessory



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

NAPL Measurements in Groundwater



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

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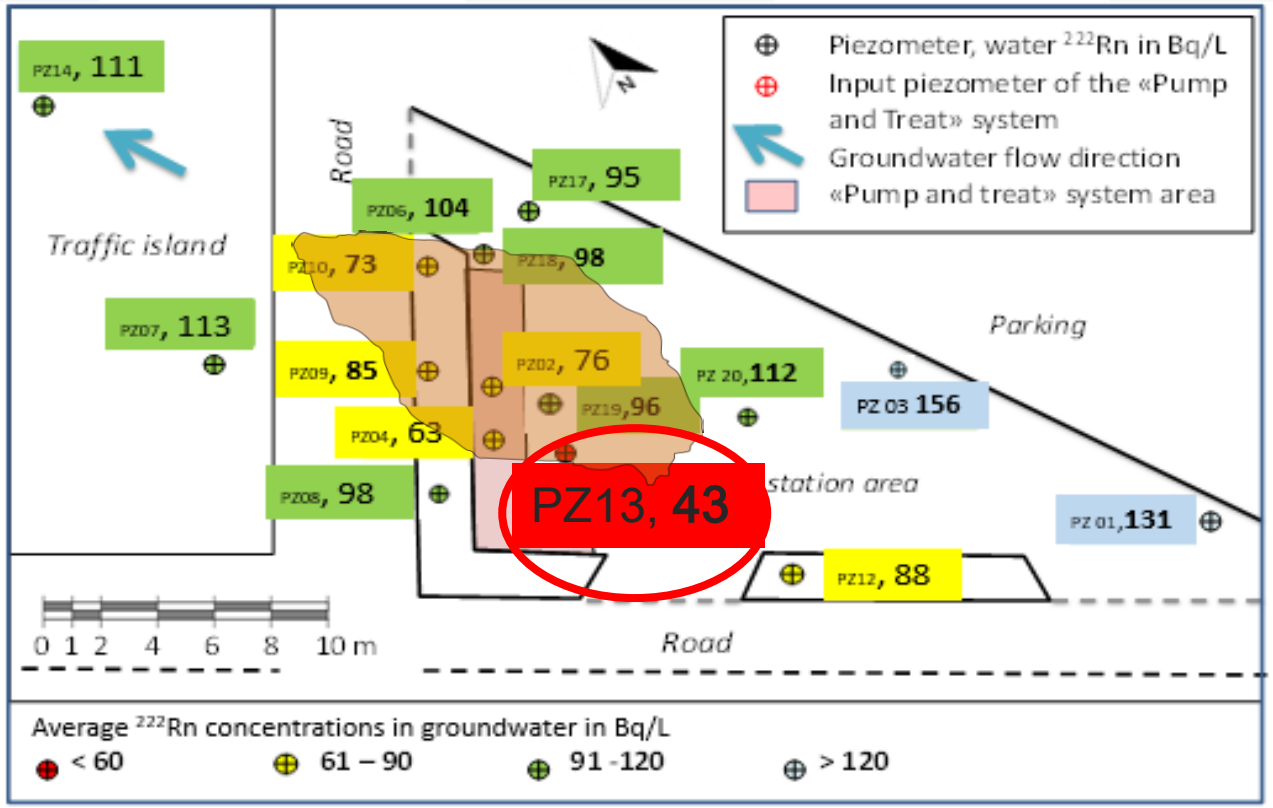
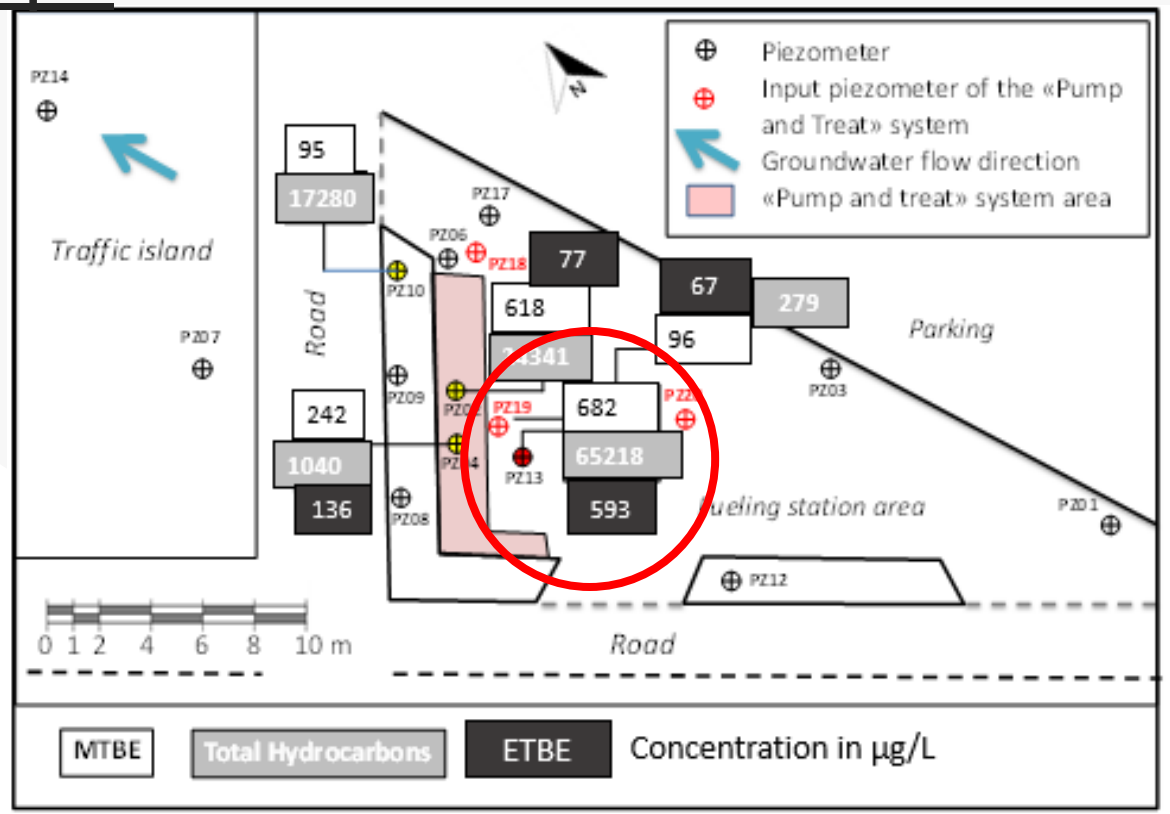
Site 1:Comparison of average radon and NAPLs concentration Dot Maps





- 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*

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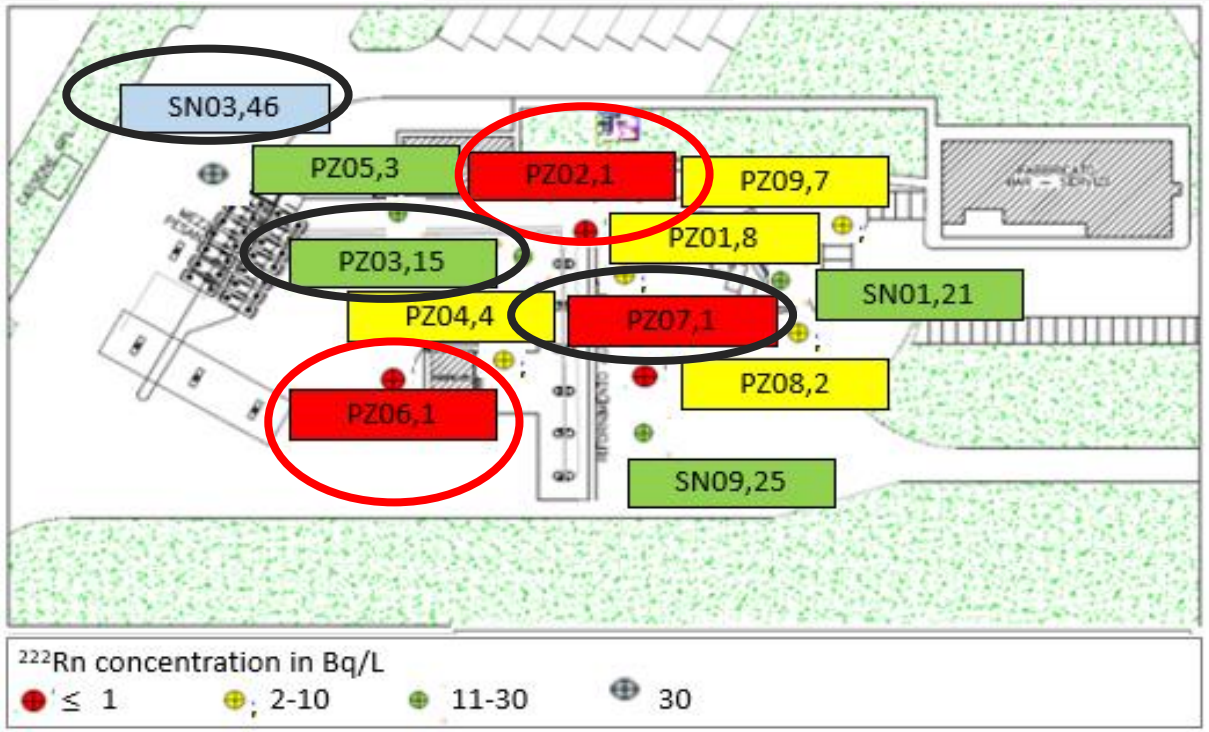
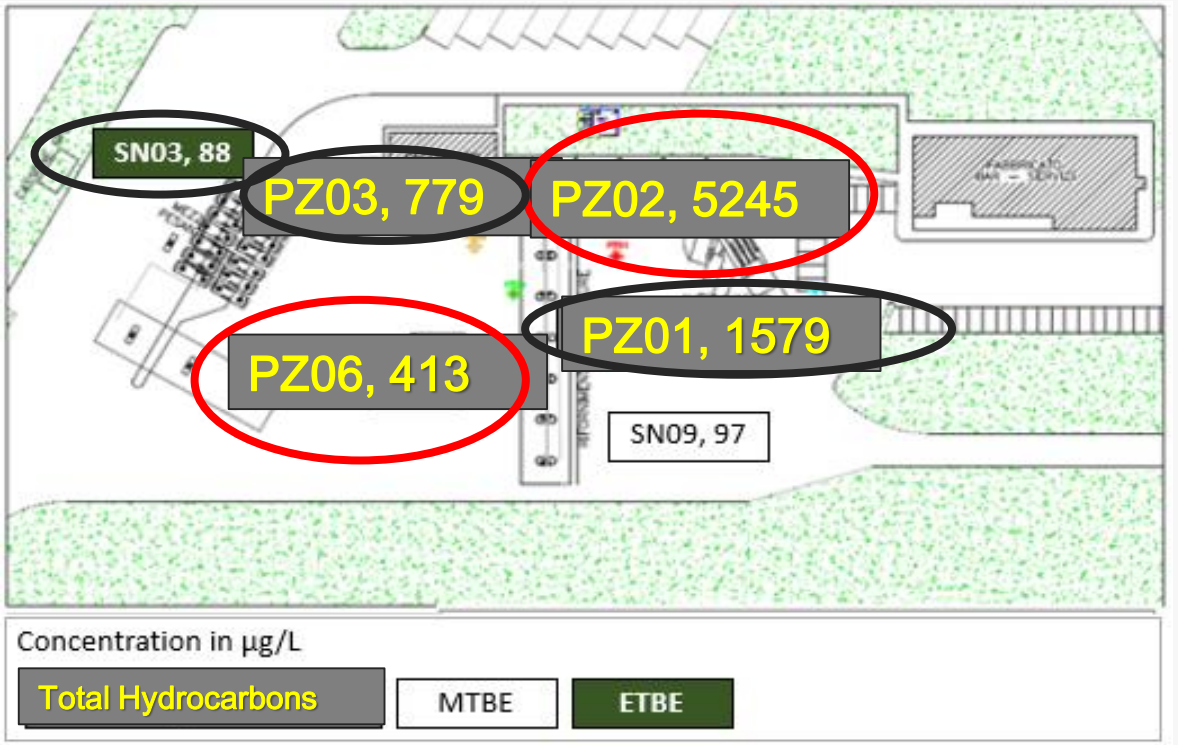
Site 2:Comparison of average radon and NAPLs concentration Dot Maps





LEGEND:

PZn, → X: Radon concentration in Bq/L

PZn: Piezometer name/number

LEGEND:

PZn, → Y: NAPL concentration in µg/L

PZn: Piezometer name/number

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Statistical Approach for both sites

- Summary Statistics
- Outlier 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

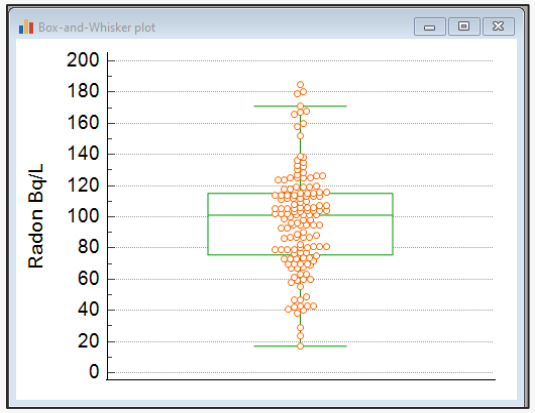
Suspected outliers

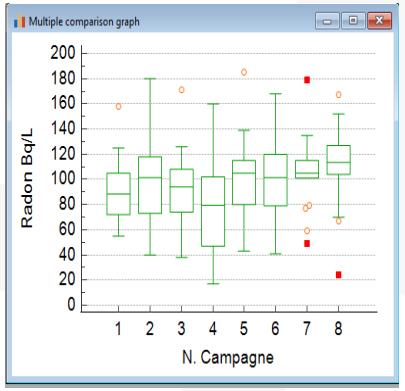
Grubbs - right-sided (alpha-level 0.05)
None

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

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

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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

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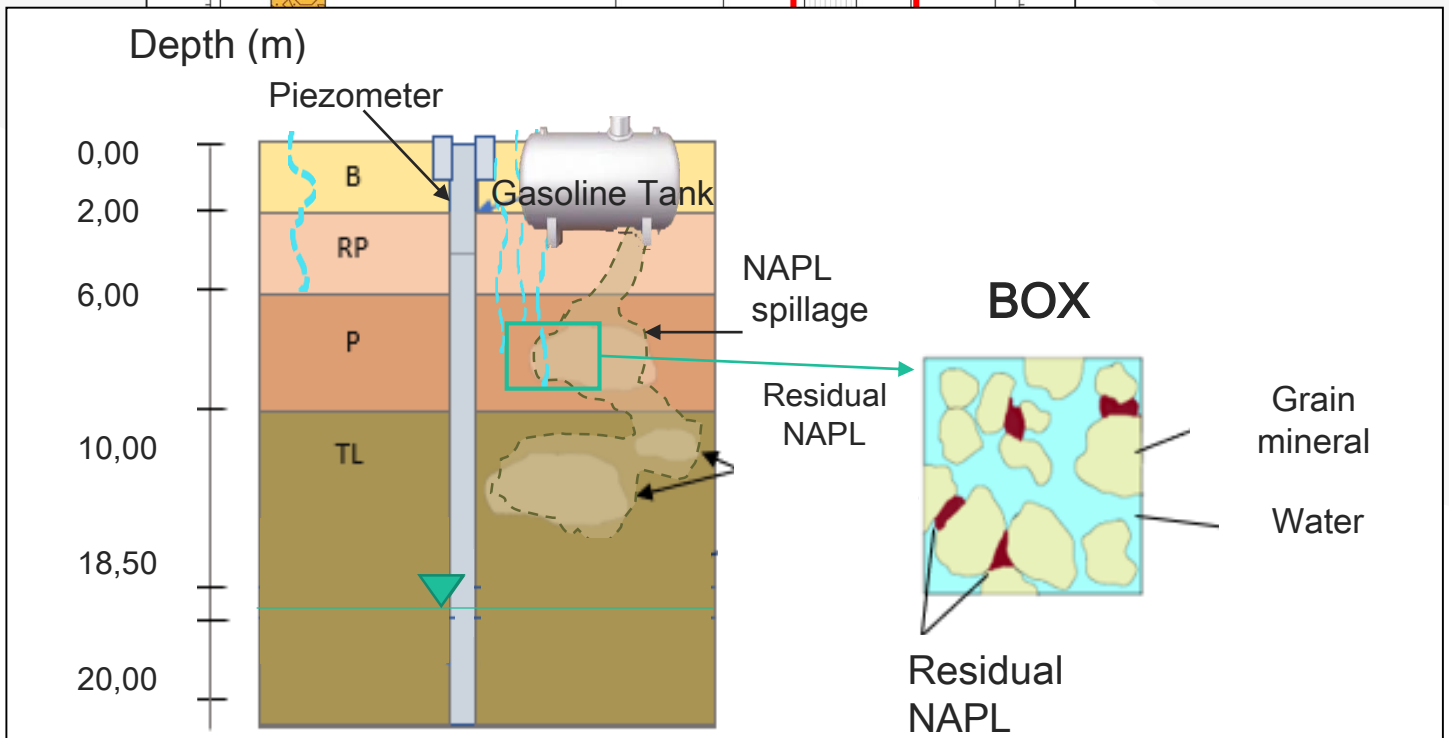
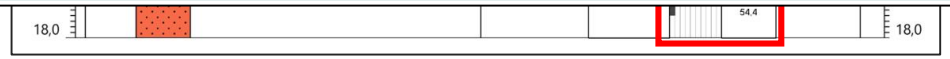
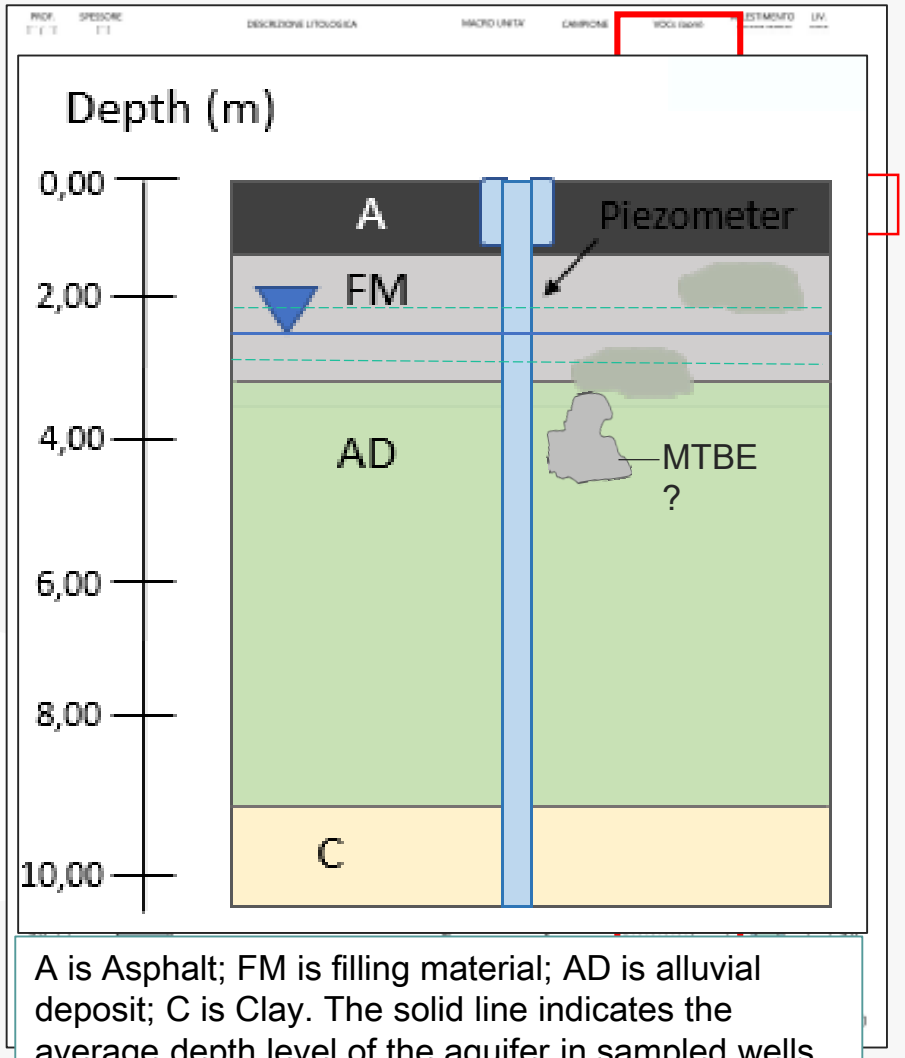
Conceptual models of the two case studies



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

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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.

water

MDPI

Article

Radon as a Natural Tracer for Monitoring NAPL Groundwater Contamination

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check for updates

Water: Ecology and Management

Book Chapter

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

Martina Mattia[1], Paola Tuccimei[1]*, Michele Soligo[1], Claudio Carusi[2] and Manuela Portaro[1]

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THANK YOU FOR YOUR ATTENTION