Using Radon as a Tracer for Mapping NAPL Contamination

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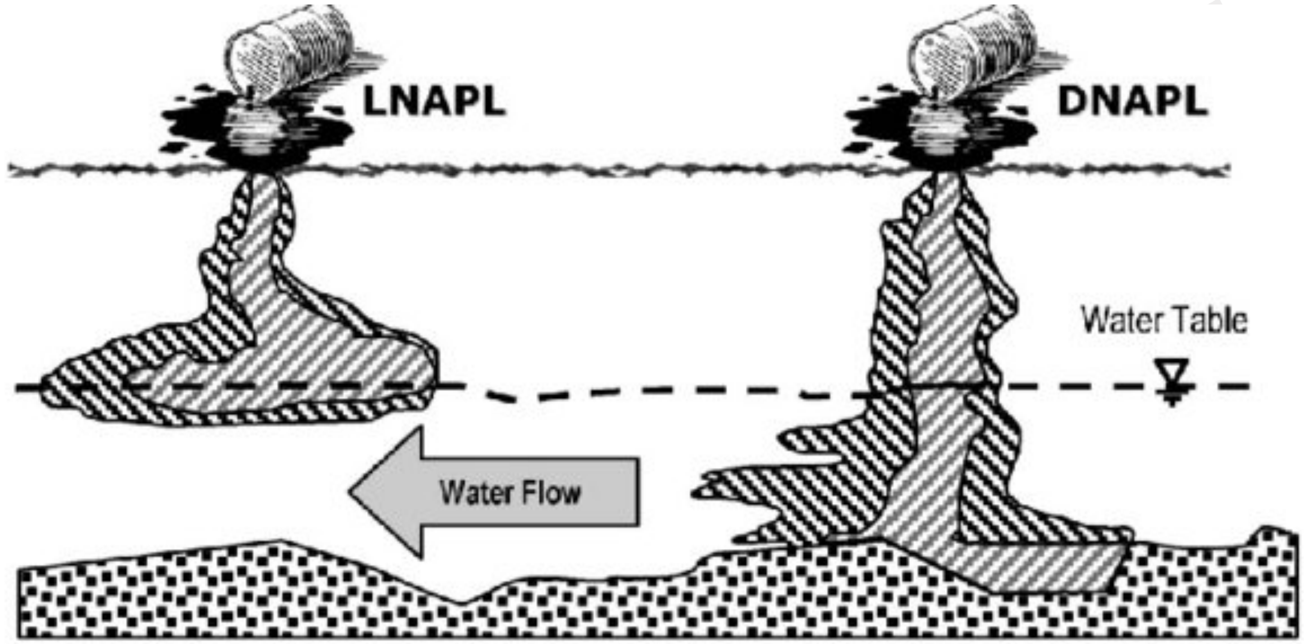
13 Jan 2021

Contents

What Is NAPL?

Image from Flores et al. 2011 [Flores2011]



- NAPL = Non-Aqueous-Phase Liquids
- Environmental contaminants.
- Immiscible in water.
- Examples: diesel, kerosene, gasoline, chlorinated solvents, mineral oils.

Two types:

1. LNAPL (lighter than water), which occupies the vadose zone, but may penetrate the saturated zone.

2. DNAPL (denser than water, > 1 g/cm^3), which sinks down to the bottom of the saturated zone.

Goals & Applications of NAPL Contamination Measurements

- Map the spatial extent and degree of recent or historical NAPL contamination, for the purposes of remediation planning and risk assessment.
- Examples of sites: military, industrial, airports, petrol stations, etc. (in-use or abandoned).

Traditional Solutions & Their Drawbacks

Technique	Drawback
Direct detection, either directly of NAPL (‘drive-point profiling’ or ‘core sampling’), or organic carbon vapours (e.g. BTEX).	Expensive, as many samples needed to cover ‘patchy’ spills. Samples must be taken to a lab for off-site analysis.
Detection of organic vapours biologically derived from NAPL.	Take time to accumulate and are therefore not useful for new spills.
Injection of artificial Tracers: SF_6.	Perturbation of the system you are trying to measure. Possible legal hurdles. Costly.

Alternative: Radon

- Colourless, odourless naturally occurring radioactive gas. Produced from the decay of radium-226 (ubiquitous in the earth's crust).
- Chemically inert (noble gas).
- Short (3.8 day) half life: ideal tracer of short-term environmental processes.
- Non-destructive and non-invasive.
- Strong affinity for NAPL.

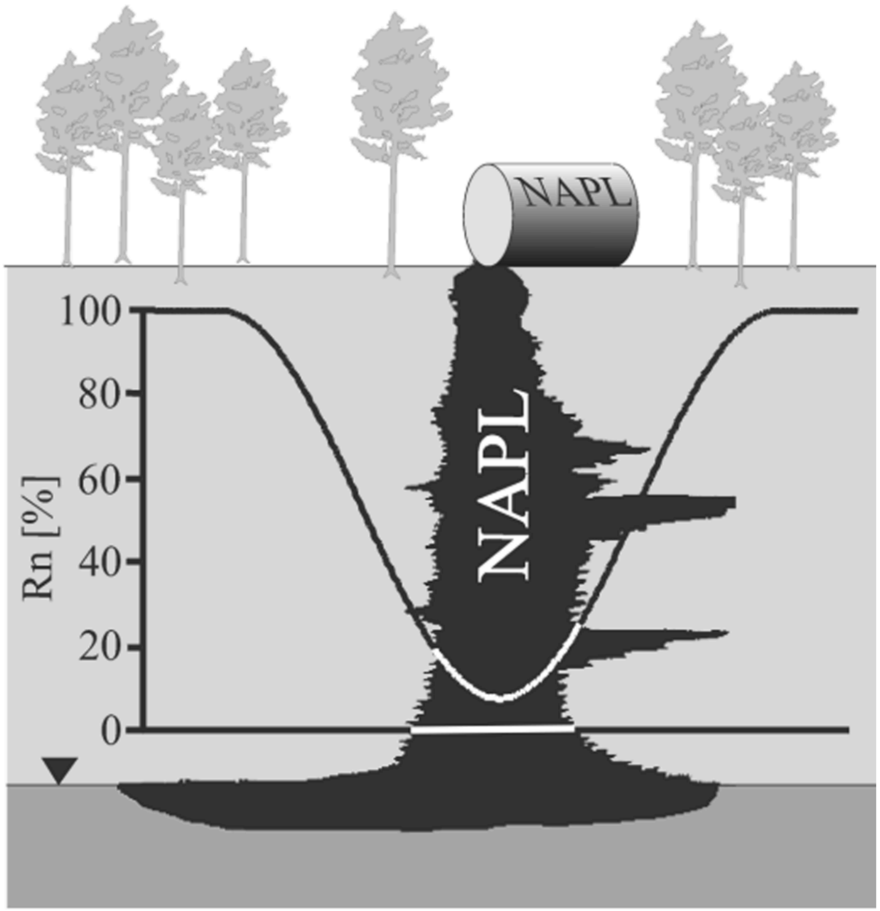


Image from Schubert 2002 [Schubert2002]

Two Techniques

- 1) Map and measure NAPL contamination in the vadose zone by measuring radon deficit in soil gas using a continuous radon monitor + soil gas probe.

- 2) Map and measure NAPL contamination in the saturated zone (aquifer) by measuring radon deficit in water samples using a continuous radon monitor + air-water radon exchanger.

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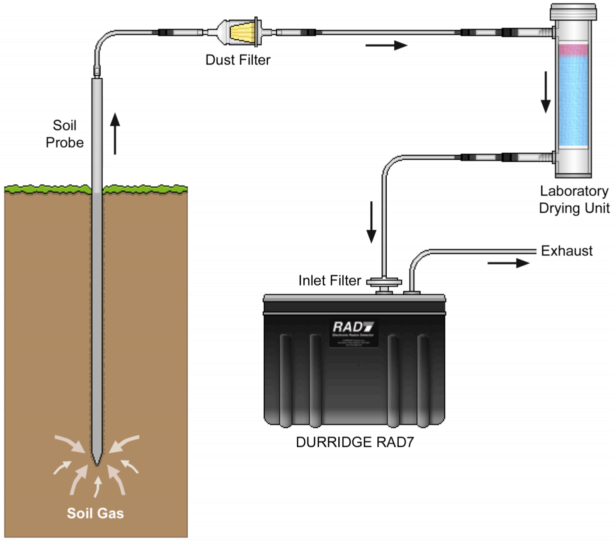
1) Soil Gas Measurements (Vadose Zone)

- Continuous radon monitor (e.g. DURRIDGE RAD7) + soil gas probe.
- Want high sensitivity (for high precision), coupled with accurate results (background discrimination, radon/thoron discrimination, etc.)
- Make precise (~ +/- 10%) readings every half-hour.



Mapping NAPL in the soil

- White dashed lines are known extent of NAPL (diesel) contamination from soil core sampling.
- Black dots are soil sampling points (n=209).
- Greyscale is radon concentration in soil gas at 70 cm depth.
- Strong negative correlation.

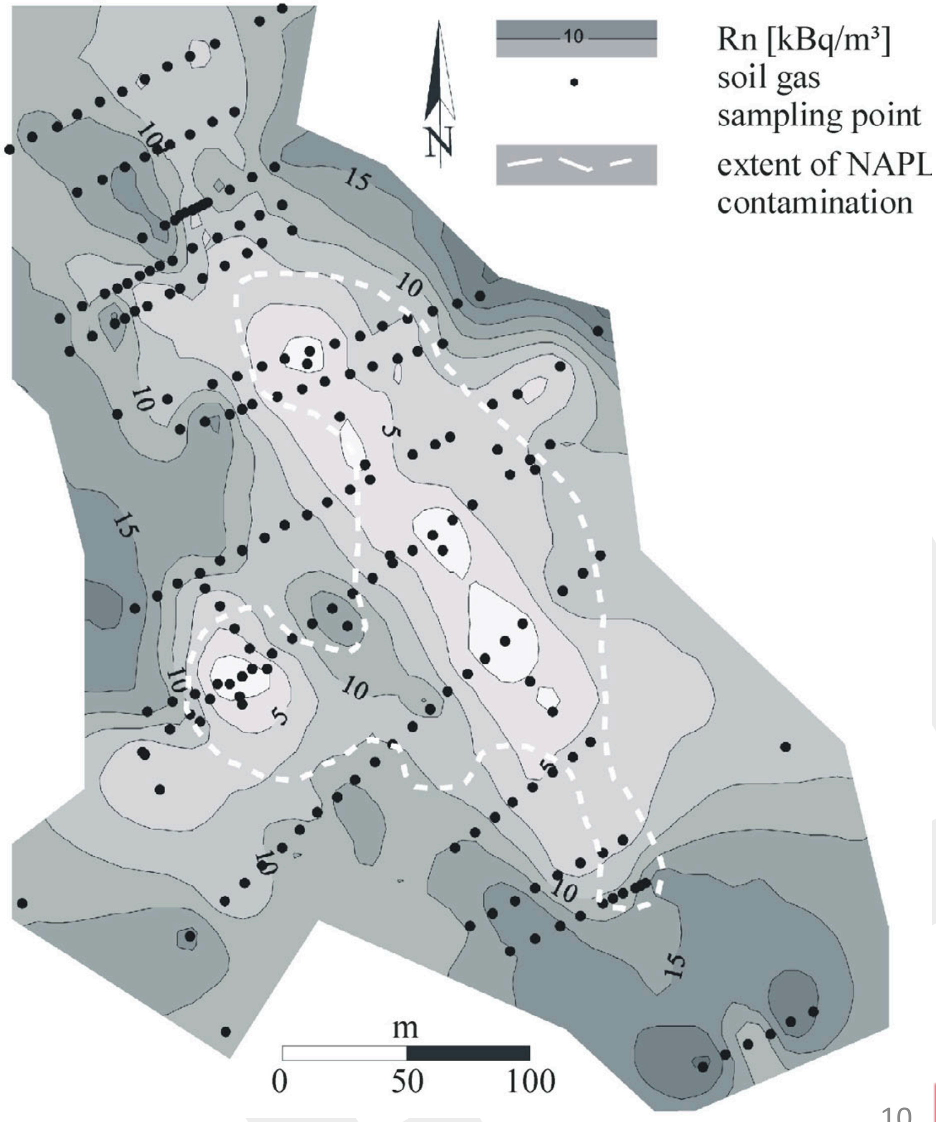


Image from Schubert 2002 [Schubert2002]

Quantifying Soil NAPL Contamination

- Can write equations like this one that relate the measured radon concentration in soil gas to the amount of NAPL contamination.
- $K_{NAPL/SG}$ and $K_{water/SG}$ (radon partition coefficients between NAPL and soil gas or water) are important parameters to know. Theoretical values agree well with the results of experiments done in the lab.

$$C_\infty = \varepsilon A_{Ra} \rho_d / n \Big(1 - S_F + K_{W/SG} S_F (1 - X_{NAPL}) + K_{NAPL/SG} X_{NAPL} S_F\Big) \quad (3)$$

where:

C_∞: radon concentration in the soil pore space (Bq/m^3)
ε: emanation coefficient = 0.2
A_{Ra}: ^{226}Ra activity concentration of the mineral matrix (31.4 ± 0.6 Bq/kg)
ρ_d: bulk density of the mineral matrix (2650 kg/m^3)
n: porosity of the mineral matrix = 0.37
S_F: total fluid saturation of the pore space
X_{NAPL}: NAPL fraction of S_F
$K_{W/SG}$: radon partition coefficient between water and soil gas, quantified by Weigel (1978)
$K_{NAPL/SG}$: radon partition coefficient between NAPL and soil gas

Source: De Simone et al. (2017)

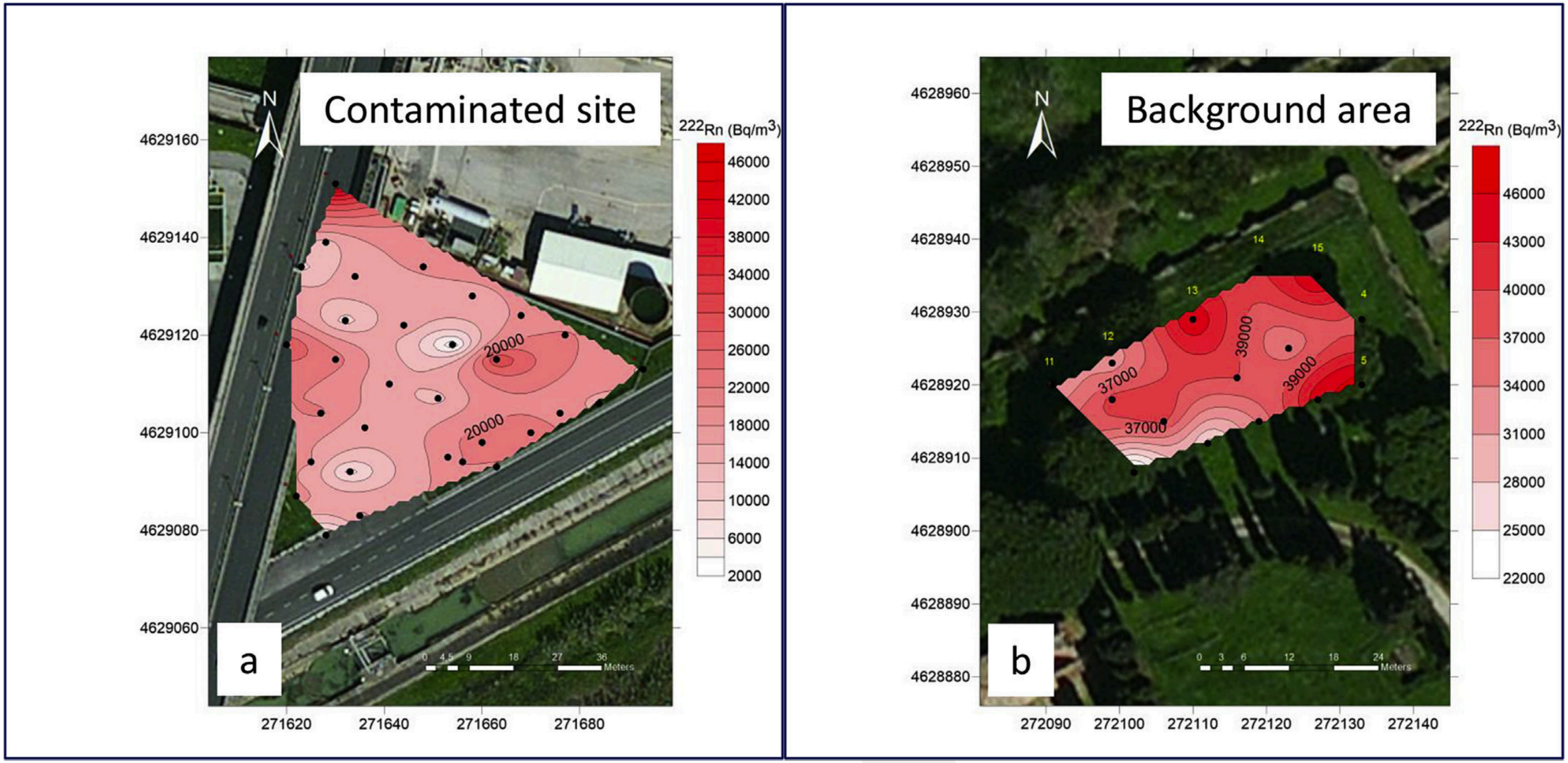
Pitfalls & Limitations

NAPL	$K_{NAPL/w}$	$K_{NAPL/air}$
Gasoline	50.9 ± 5.8	13.2 ± 1.5
Diesel fuel	43.8 ± 4.6	11.4 ± 1.2
Kerosene	40.6 ± 8.3	10.6 ± 2.1

From Schubert et al. (2001)

- Mineralogical heterogeneity of soil.
- Permeability heterogeneity.
- Meteorological interference – sink probes deeper than 70 cm to avoid this.
- Rain can affect radon concentrations below 70 cm, but its effect is understood and can be accounted for.
- Since the coefficient of partitioning between the soil gas and the NAPL is similar for a wide range of NAPLs, the technique can't tell you precisely what is there (a few soil samples still needed for that).
- Limited to NAPL contamination within the diffusion length of radon in soil (~ 2 m in dry, sandy soil). Radon diffusion length in water is only a few cm, so this technique cannot detect NAPL below the water table.

Heterogeneity of Minerology / Permeability



Source: *De Simone et al. (2017)*

Two Techniques

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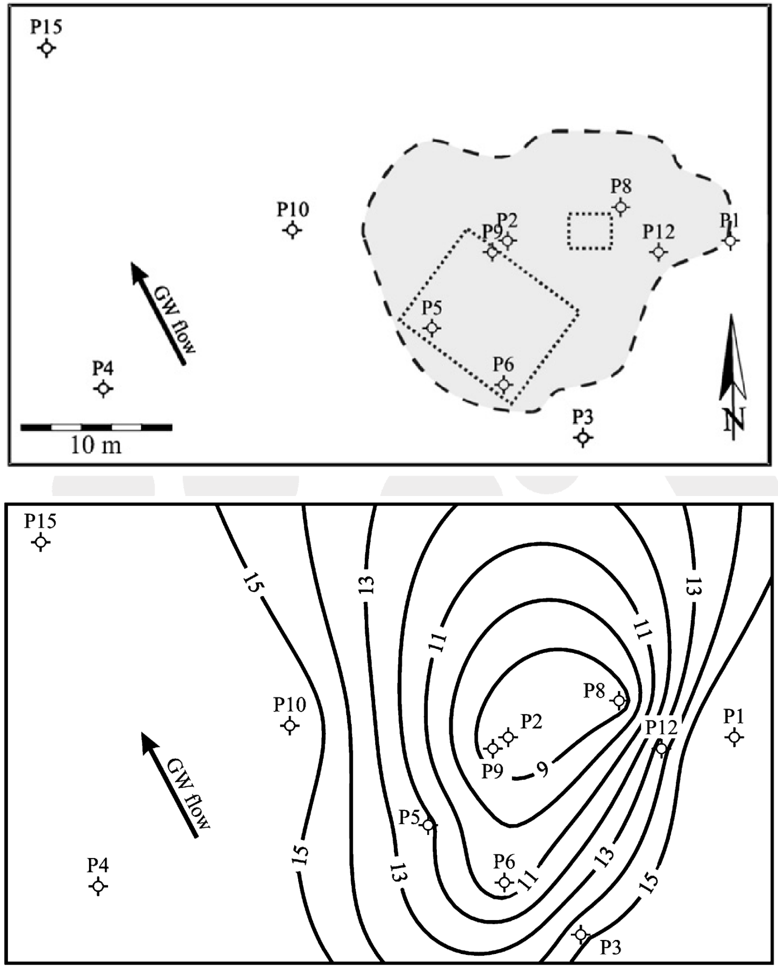
2) Aquifer Water Sample Measurements

- Continuous radon monitor + water-air radon exchanger (e.g. DURRIDGE RAD7 + RAD H2O).
- Collect water samples from sampling wells.
- Bubble air in a closed loop through water sample and measure the radon in the air loop (RAD H2O accessory, right).
- Measure in the field or take the samples away for later analysis.
- Precise and accurate results in 30 minutes.

NAPL Contamination of Aquifers

- Example: measure radon in water from sampling wells at a contaminated disused petrol station.
- Top - Dashed line and grey shaded area: extent of NAPL spill determined by traditional core sampling technique.
- Bottom - Contours represent radon concentration in groundwater as reconstructed from measurements at a set of sampling wells P[X].



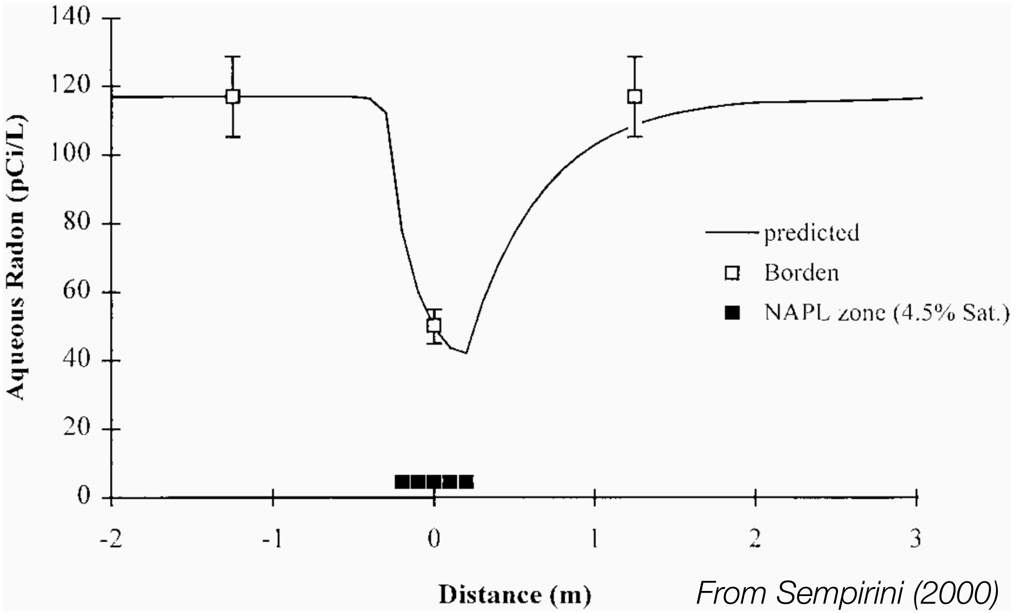
From Schubert (2007)

Modeling the Effect of NAPL on radon in Aquifers

$$\frac{C_{w(NAPL)}}{C_{w(background)}} = \frac{1}{1 + S_{NAPL}(K_C - 1)}$$

- Similar model parameters as the equations we saw for radon in soil gas.
- However, now advective transport of radon must be considered due to groundwater flow.
- Right: 1D models e.g. by Sempirini et al. show good agreement with data.
- Radon drops by a factor of ~ 3 at the source zone, then recovers to equilibrium value after ~ 2 metres (in direction downgradient of groundwater flow).
- Again, estimate or measure all other model parameters, then adjust the level of NAPL contamination until the model fits the data.
- Equation above is for steady state. Things get a bit trickier when groundwater flow is considered.

- $C_{W(NAPL)}$ = radon concentration in groundwater sample from contaminated zone.
- $C_{W(background)}$ = radon conc. in background groundwater sample.
- S_{NAPL} = NAPL saturation in contaminated zone.
- K_C = NAPL/water partition coefficient.



From Sempirini (2000)

Pitfalls & Limitations

- Mineralogical heterogeneity of aquifer.
- Permeability heterogeneity.
- Still need to drill sampling wells.
- Since the coefficient of partitioning between the water and the NAPL is similar for a wide range of NAPLs, the technique can't tell you precisely what is there.
- Mixing of groundwater between contaminated and uncontaminated zones can lead to an underestimation of the contamination.

Summary

- Radon measurements are an alternative to direct core sampling for mapping and estimating the amount of NAPL contamination in soil and aquifers.
- Plenty of real-world examples in the scientific literature over the past two decades.
- Complicated by factors including heterogeneities in minerology and permeability.
- Cannot tell you the exact nature of the NAPL, because different NAPLs have similar radon affinities.
- Even if quantitative measurements are not possible, radon maps can precisely target remediation efforts to the most contaminated locations.
- Can be much faster, cheaper and more convenient than traditional methods.

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Radon Capture & Analytics

Thanks for your attention!

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