

# SESSIONE 2 - Approcci innovativi alla caratterizzazione e metodi di bonifica verdi e sostenibili

## Applicazione della caratterizzazione multilivello e del fingerprinting isotopico in acquiferi contaminati da DNAPL

*Alessandro Gargini*

*Alma Mater Studiorum - Università di Bologna  
Dipartimento di Scienze Biologiche, Geologiche ed Ambientali*

*alessandro.gargini@unibo.it*



# INQUINANTI TIPO DNAPL



## Metodi

- Una elevata complessità multifase
- Gli acquitardi
- Caratterizzazione multi-livello
- Fingerprinting isotopico

## Applicazioni

Il caso di Ferrara

Il caso di Bussi sul Tirino



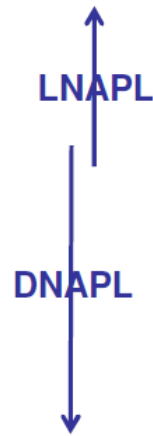
## Chemical

## Density, $\rho$ (kg/L)

gasoline	0.7 to 0.76
benzene	0.88
methyl isobutyl ketone (MIBK)	0.80
coal tar	0.9 to 1.2
1,4-dioxane	1.03
chlorobenzene	1.11
pyrene	1.27
trichloroethene (TCE)	1.46
tetrachloroethene (PCE)	1.63
<i>tetraethyl lead</i>	1.65
tribromoethane (bromoform)	2.89

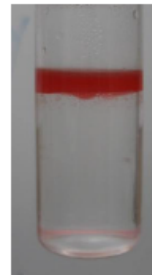
mixtures ?

$$\rho_{\text{mixture}} = \sum_i \rho_i * \text{vol fraction}_i$$



# LNAPL (Light)

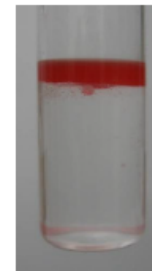
# DNAPL (Dense)



Gasoline  
0.75 g/cm<sup>3</sup>



TCE  
1.46 g/cm<sup>3</sup>

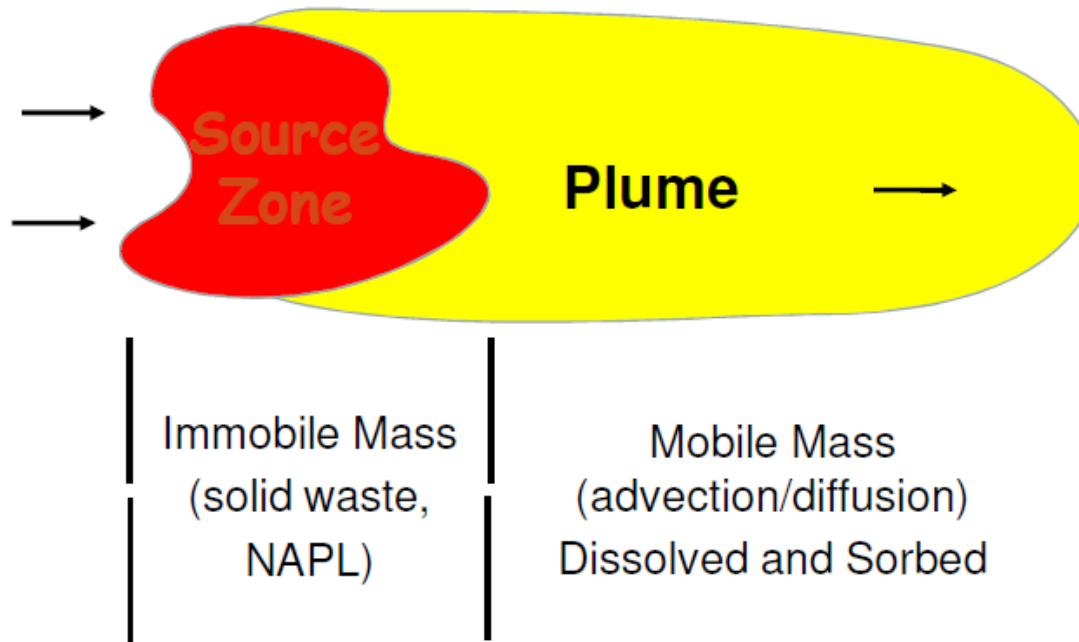


Gasoline + TCE  
ratio 2:1  
( $\approx$  0.9 g/cm<sup>3</sup>)

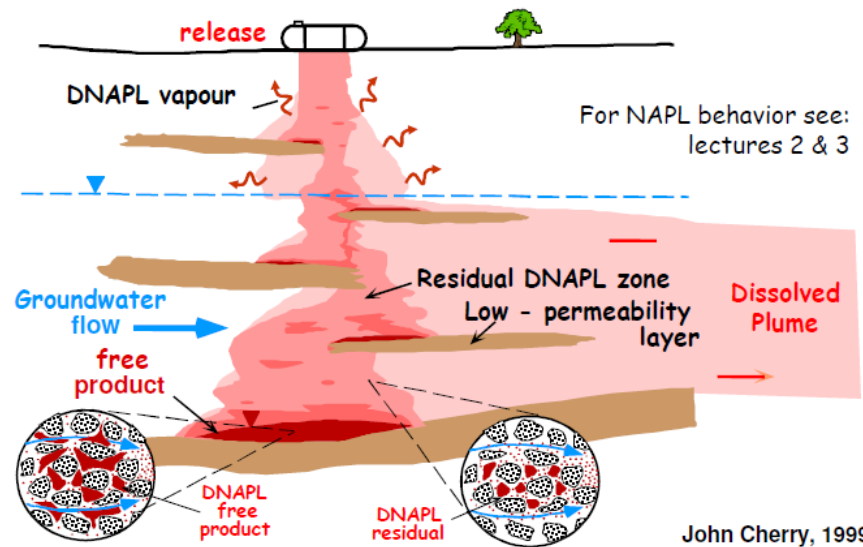


Gasoline + TCE  
ratio 1:2  
( $\approx$  1.2 g/cm<sup>3</sup>)



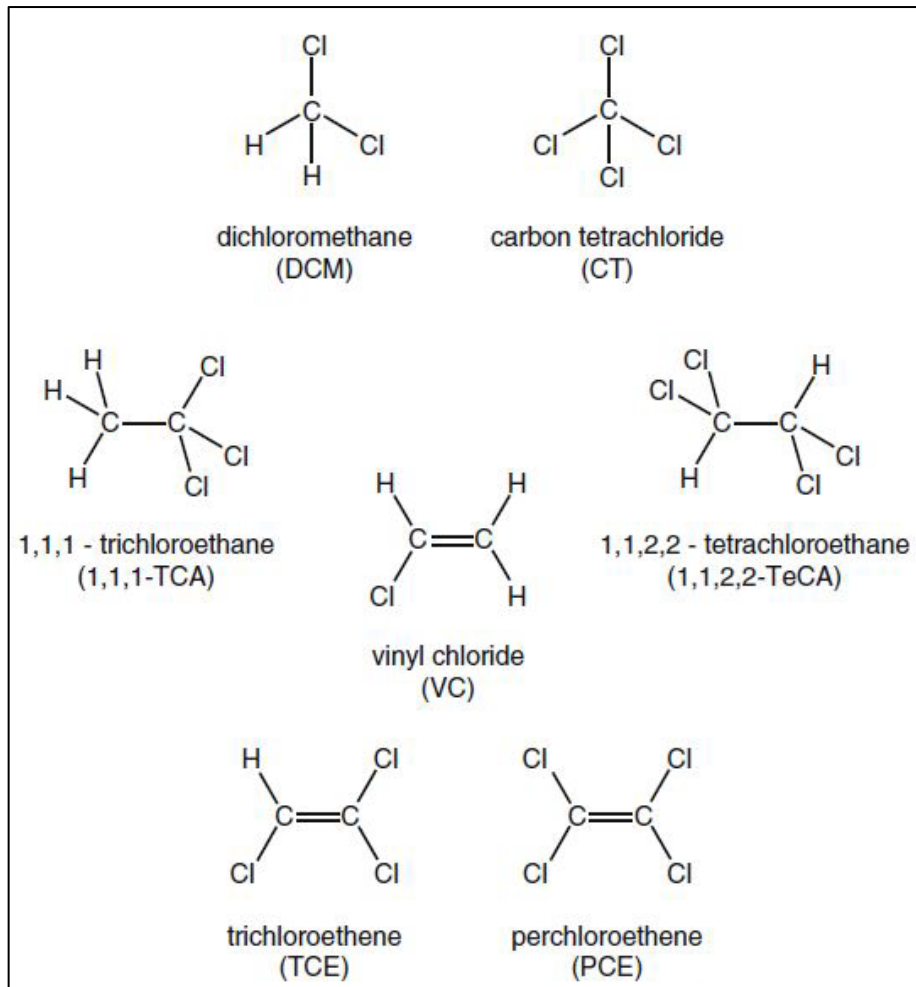


Una estrema complessità

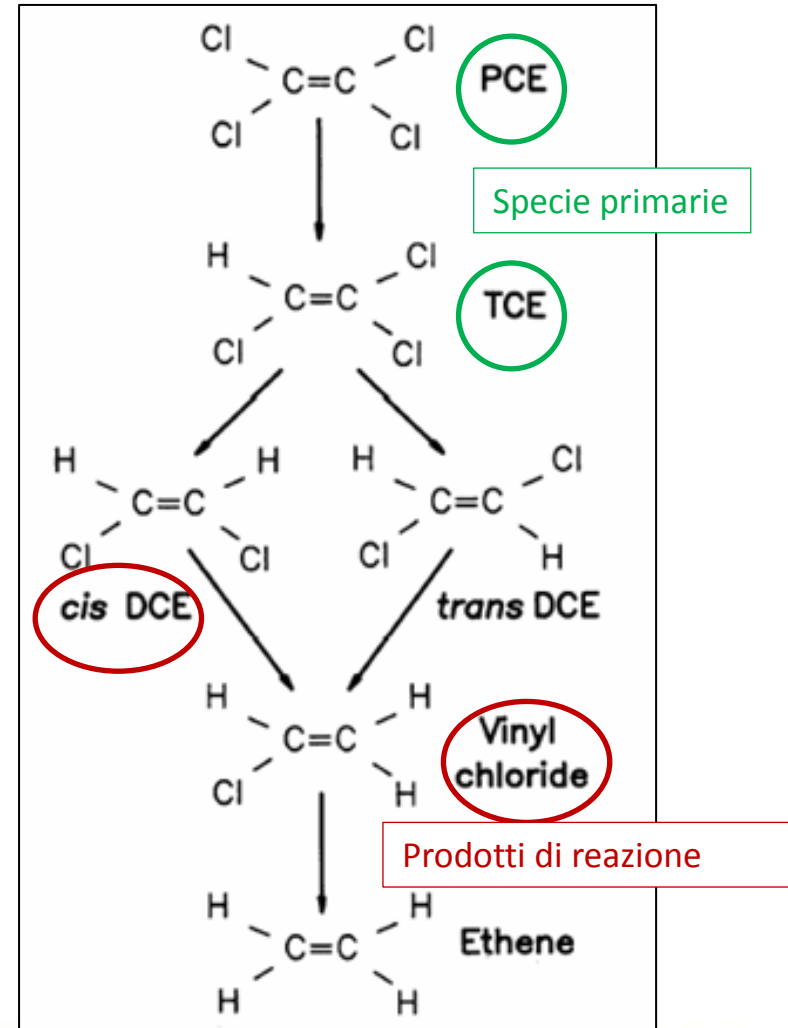


# PRODOTTI DI DEGRADAZIONE

## Formule di struttura di alcuni alifatici clorurati

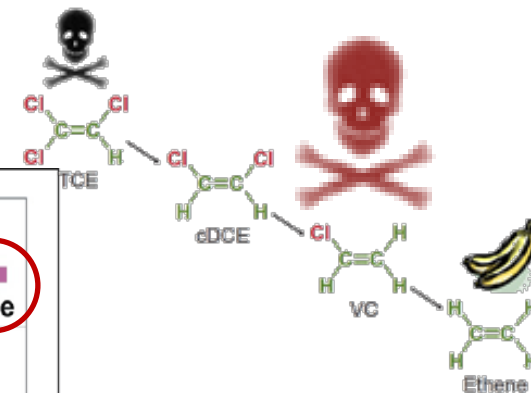
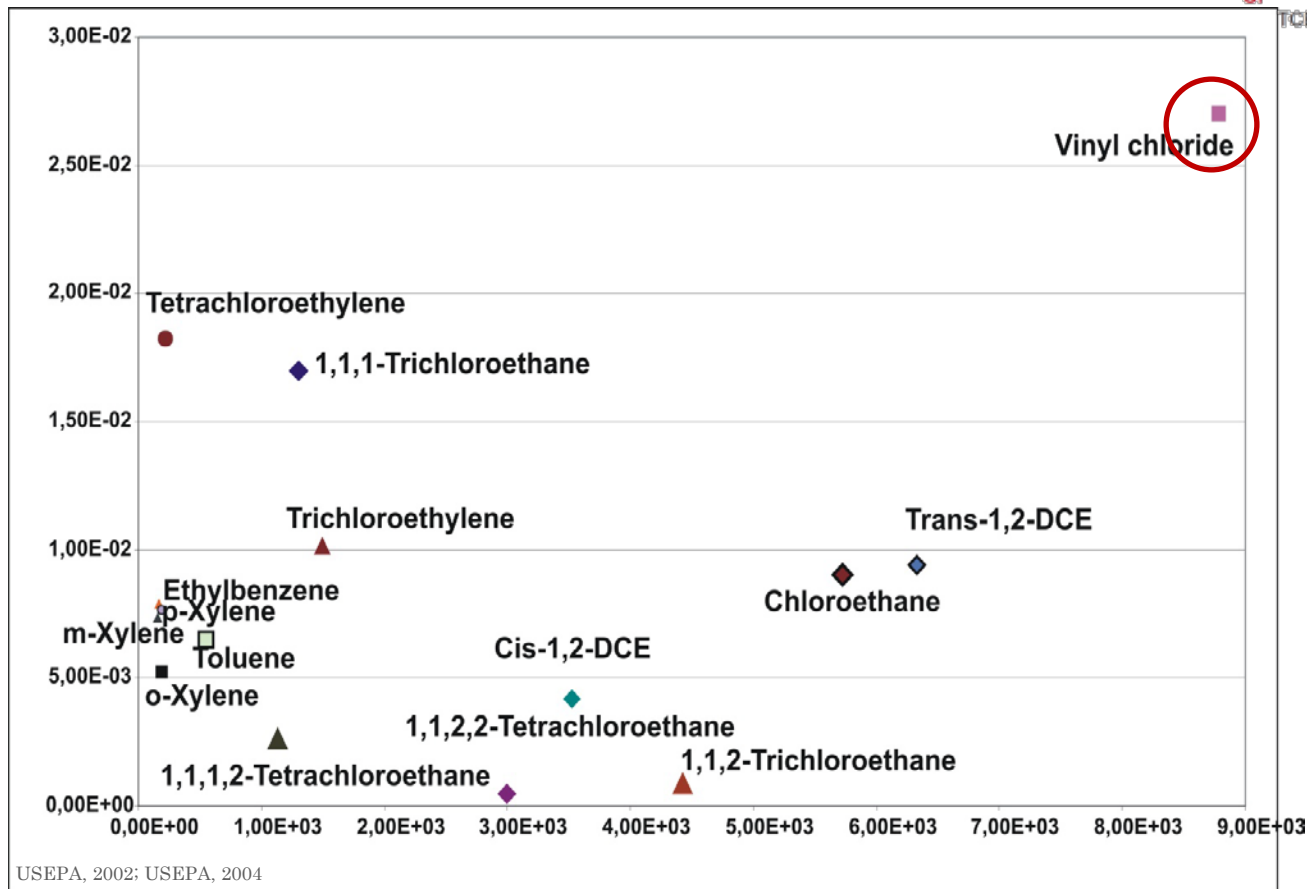


## Declorurazione riduttiva



# Cloruro di Vinile – Criticità maggiore in contaminazioni da DNAPL

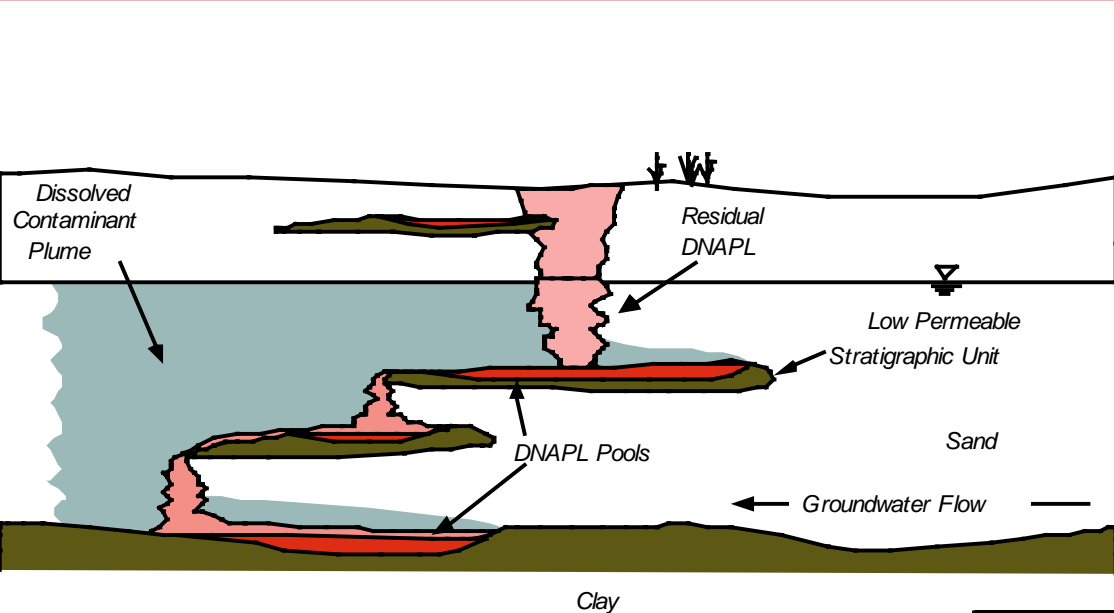
Henry Constant a 25°C (atm\*m<sup>3</sup>/mol)



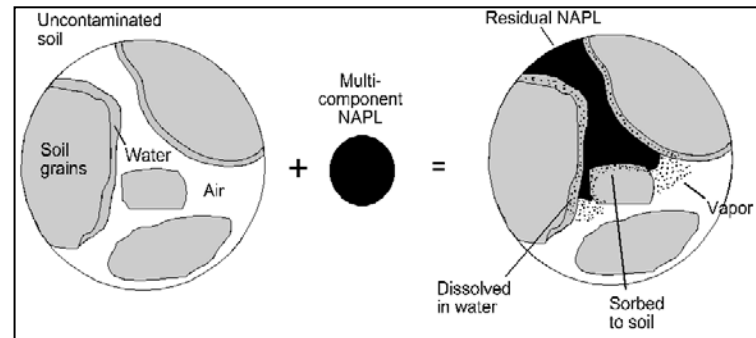
Solubility in water @ 25°C (mg/L)



# Disaccoppiamento con gli approcci classici di valutazione della vulnerabilità

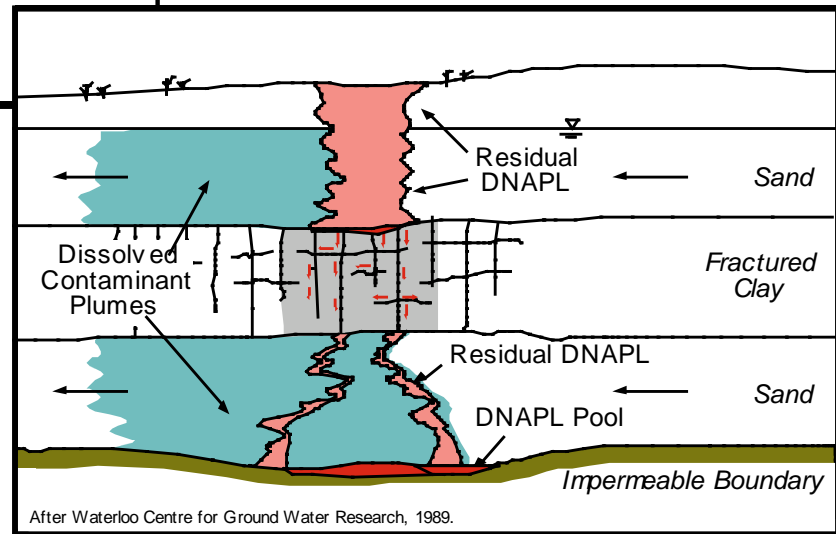


After Waterloo Centre for Groundwater Research, 1989.



$\rho > \text{acqua}$   
 $\mu < \text{acqua}$

Acquitrando

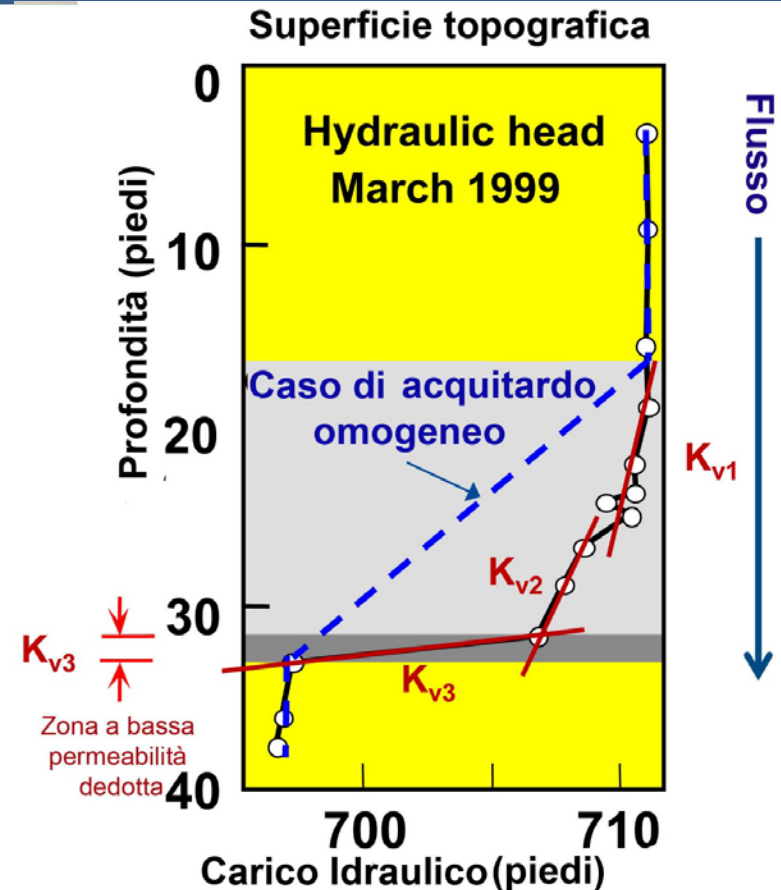


After Waterloo Centre for Ground Water Research, 1989.

# Barriere di permeabilità su minimi spessori

La larga inflessione rappresenta una resistenza relativamente significativa al flusso, quindi:

$$K_{v1} > K_{v2} \gg K_{v3}$$





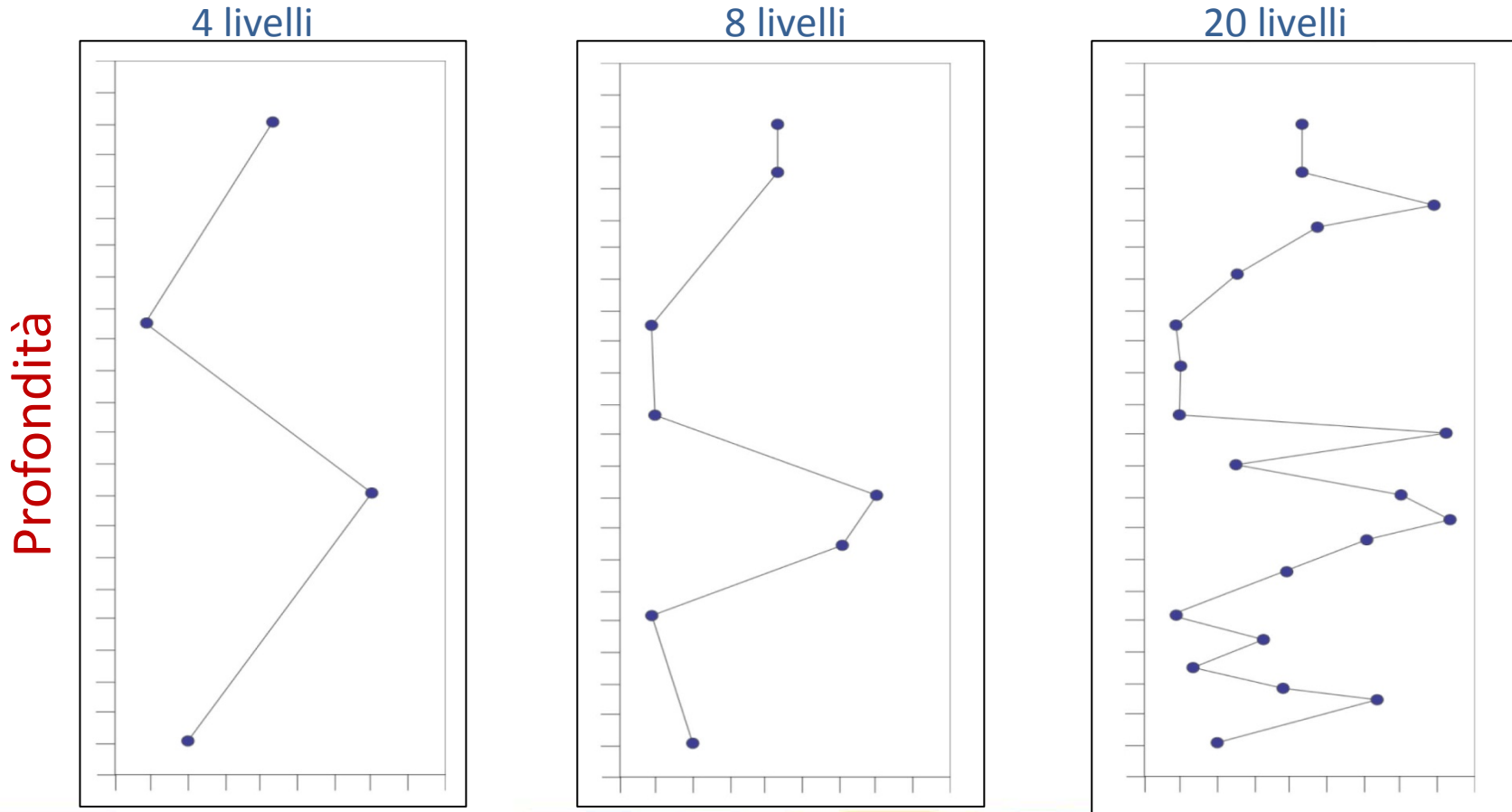
*Elevata complessità del fluido e del mezzo poroso*

*Modo migliore per caratterizzare??*



# Profili verticali di dati

*"The shape of the head profile is everything" J.A.Cherry*



# Fondamento di Idrogeologia dei Contaminanti

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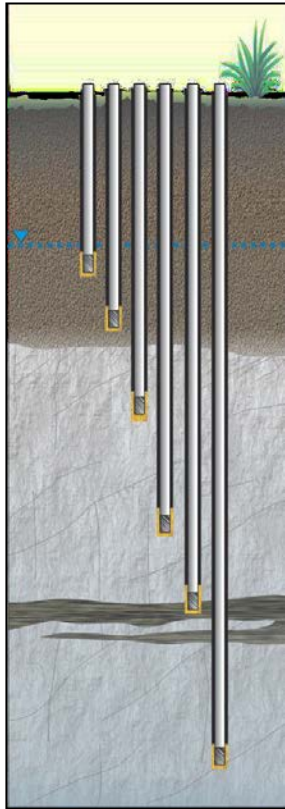
“To exploit at the most one single borehole is better than use several simple boreholes”

J.A. Cherry and B.L. Parker

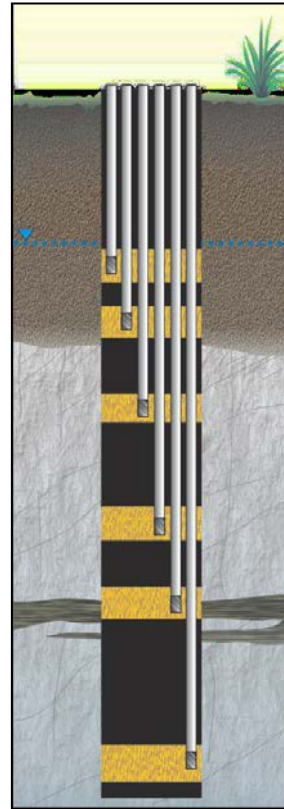


# Diversi approcci multilivello per ottenere profili verticali

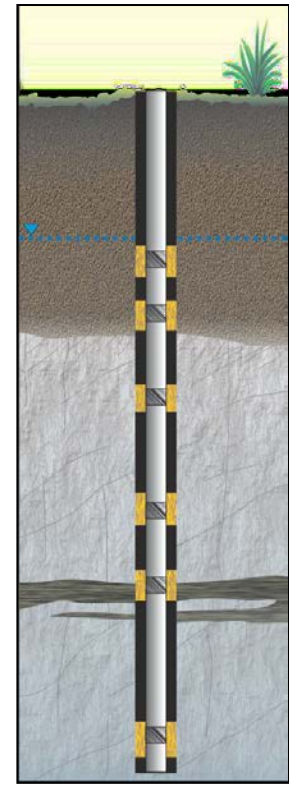
Pozzi "a grappolo" (*well cluster*)



Pozzi "a nido" (*well nest*)

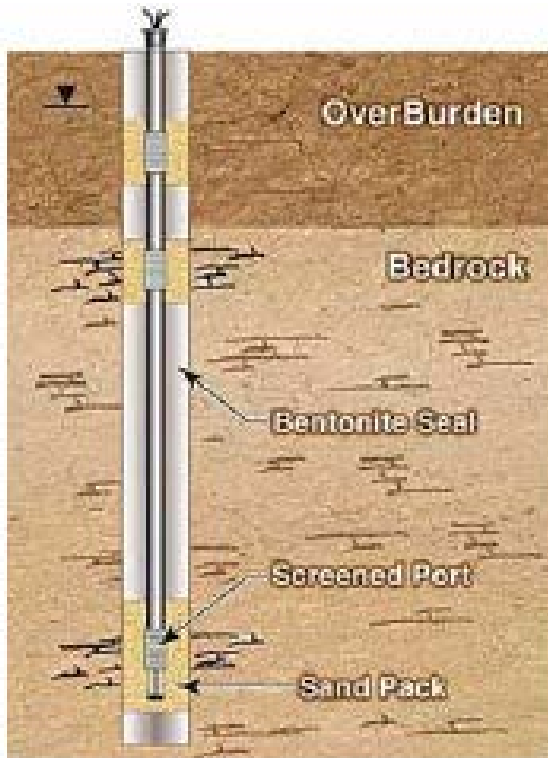


Sistemi multilivello (MLS)

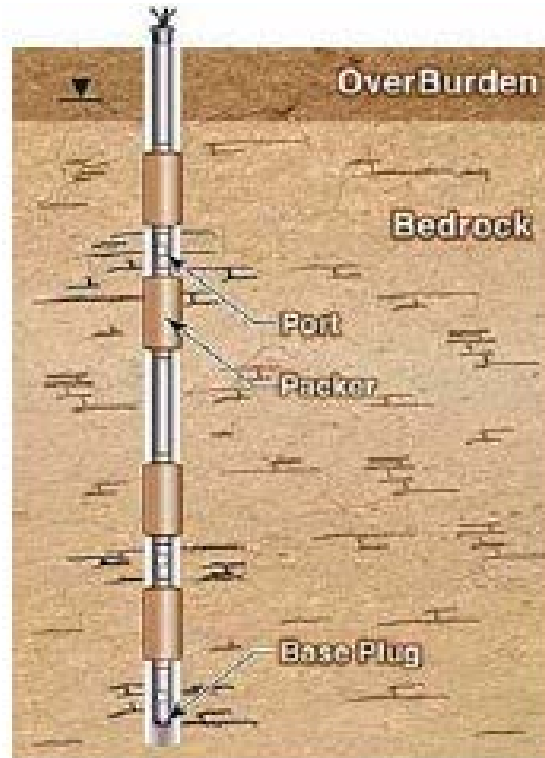


# Approcci Sistemi Multilivello

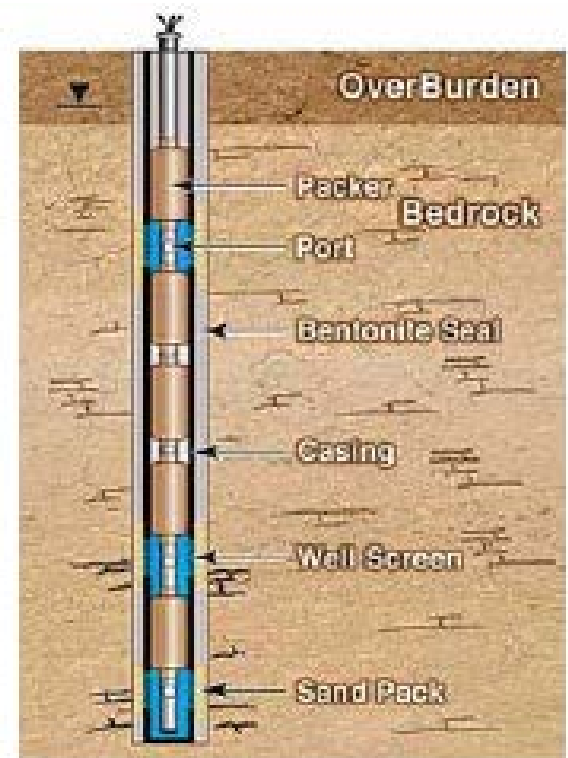
Riempimento  
(foro non rivestito)



Packers  
(foro non rivestito)



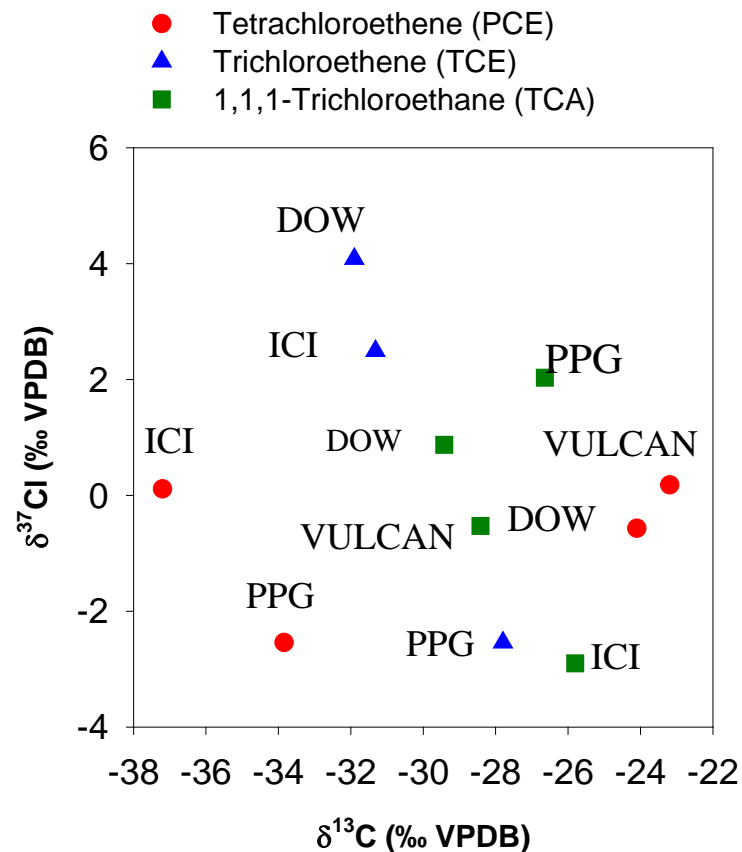
Packers  
(foro rivestito)



# FINGERPRINTING ISOTOPICO DEI COMPONENTI MISCELE DNAPL



Firma isotopica della boccetta di smacchiatore (trielina) che compriamo al supermercato



Van Warmerdam et al., 1995



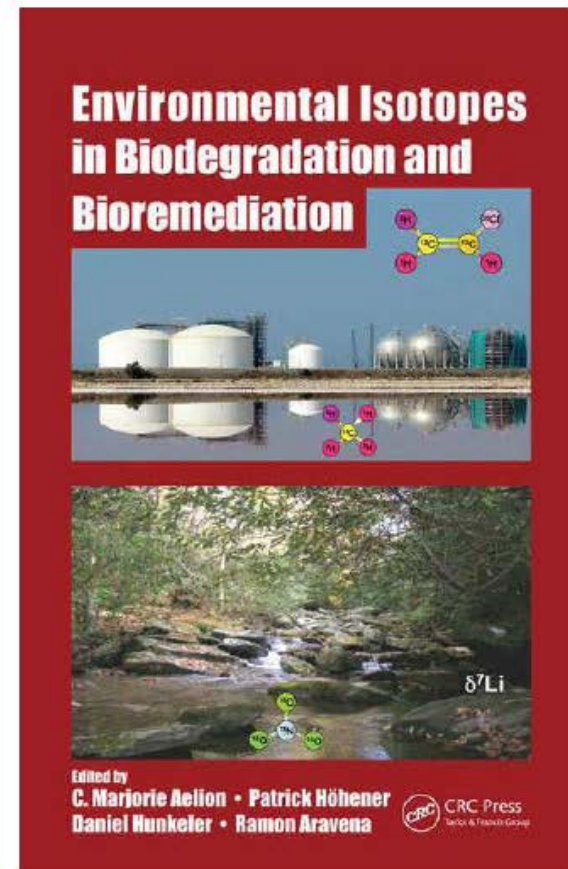
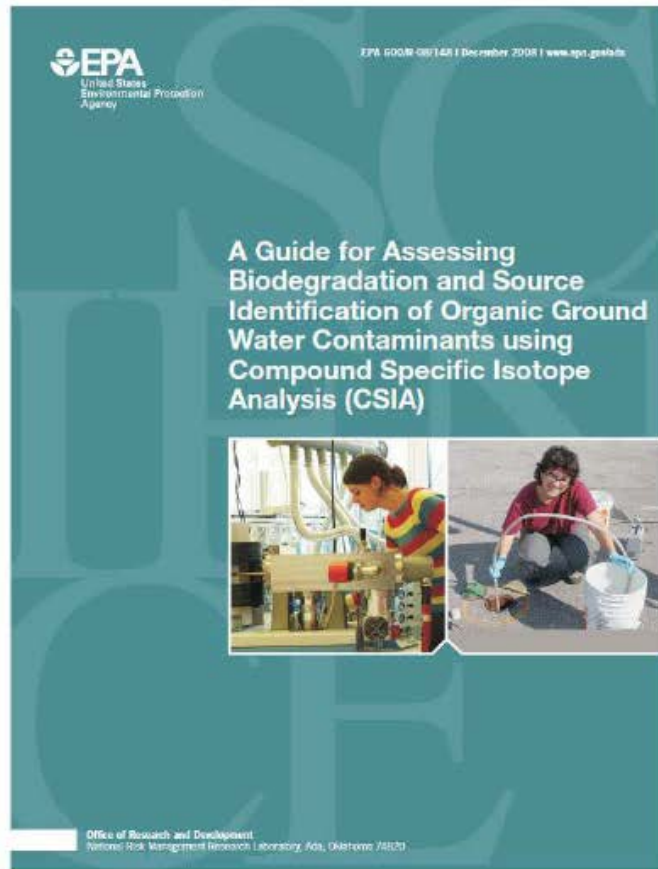
# RAPPORTO ISOTOPICO MEDIO DI COMPOSTI NATURALI DEL CARBONIO

$$\delta^{13}\text{C} = \left( \frac{{}^{13}\text{C}/{}^{12}\text{C}_{\text{Sample}}}{{}^{13}\text{C}/{}^{12}\text{C}_{\text{Standard}}} - 1 \right) \cdot 1000 \quad (\text{‰ VPDB})$$

	${}^{13}\text{C}/{}^{12}\text{C}$	$\delta^{13}\text{C}$	
Carbonati	0.01124	0	↑ more ${}^{13}\text{C}$
CO <sub>2</sub> atmosferica	0.01116	-7	
Biomassa	0.01096	-25	
Metano biogenico	0.01045	-70	



# CSIA Compound Specific Isotope Analysis

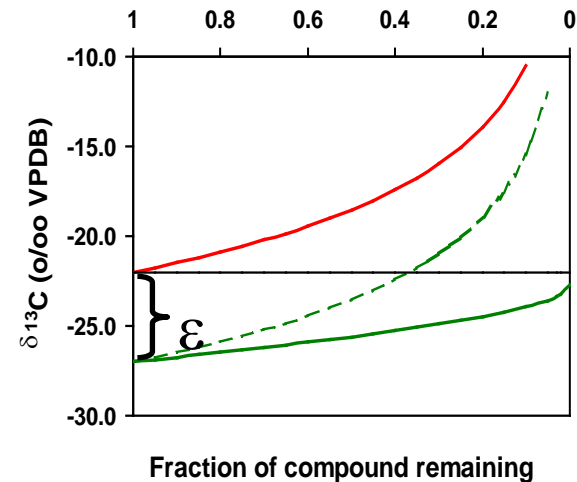
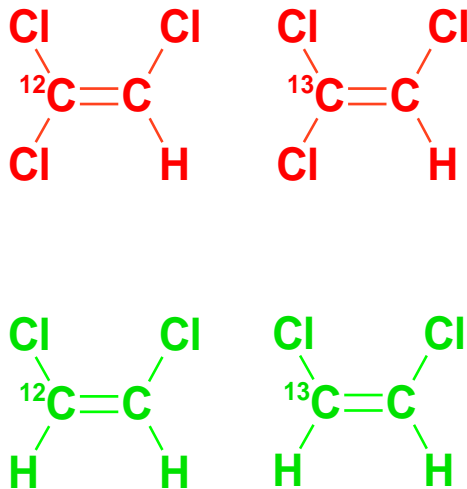


<http://nepis.epa.gov/Exe/ZyPDF.cgi?Dockey=P1002VAI.PDF>



# Impiego CSIA in Contaminant Hydrogeology

- Fingerprinting: identificazione della sorgente (*source apportionment*)
- Vie e processi di biodegradazione
- Valutare performance bonifica: ISCO (*In Situ Chemical Oxidation*);
- PRB (*Permeable Reactive Barriers*); *Air sparging, etc.*
- Valutare biodegradazione nell'insaturo



# *Come studiare tale complessità?*

## *Approccio sperimentale: Borden site, Ontario (Canada)*

Iniettati 770 litri di DNAPL  
PCE nel luglio 1991



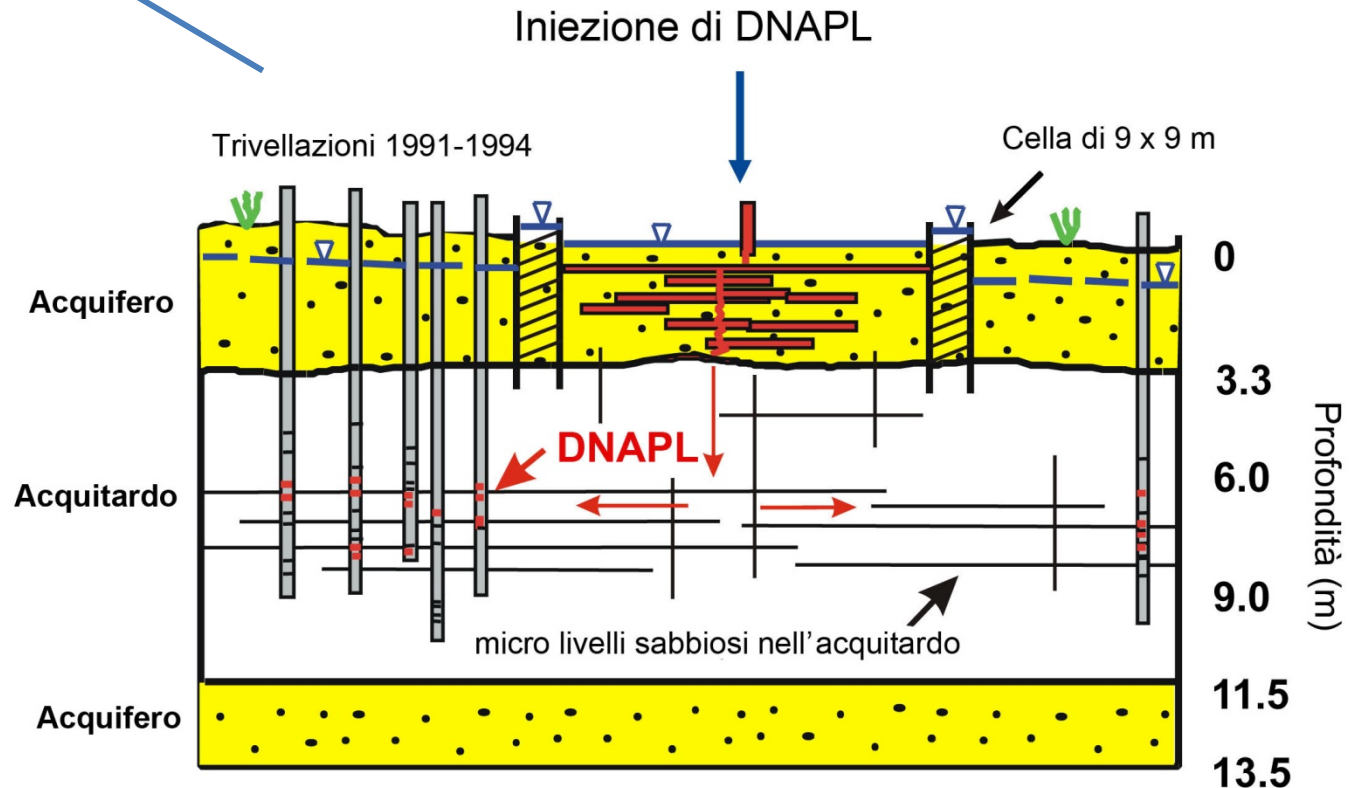
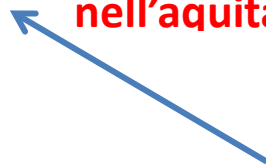
**DNAPL colorato in  
rosso**



# Evidenze sperimentali su DNAPL presente nei micro livelli permeabili dell'acquitrardo



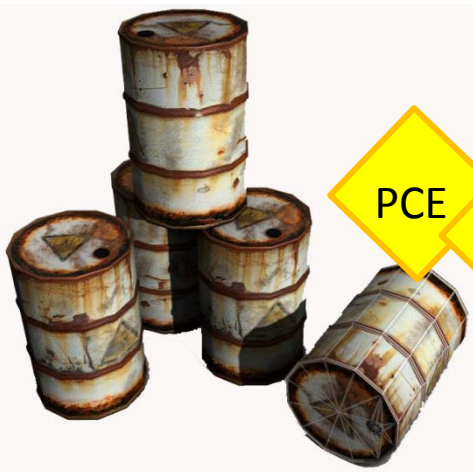
**DNAPL rosso riportato  
in superficie dalle  
trivellazioni  
nell'aquitrardo**





Approccio «geologico»: studiare i  
siti contaminati reali  
Dove è abbondanza di fase pura  
DNAPL?  
Petrolchimici ma non solo..

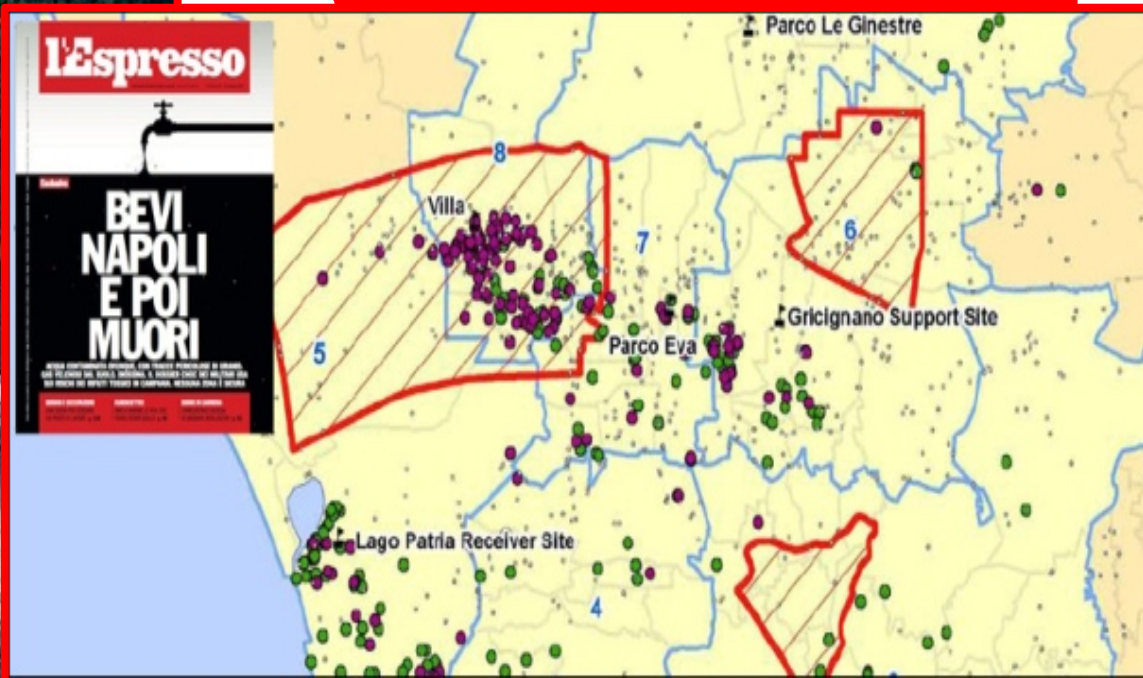
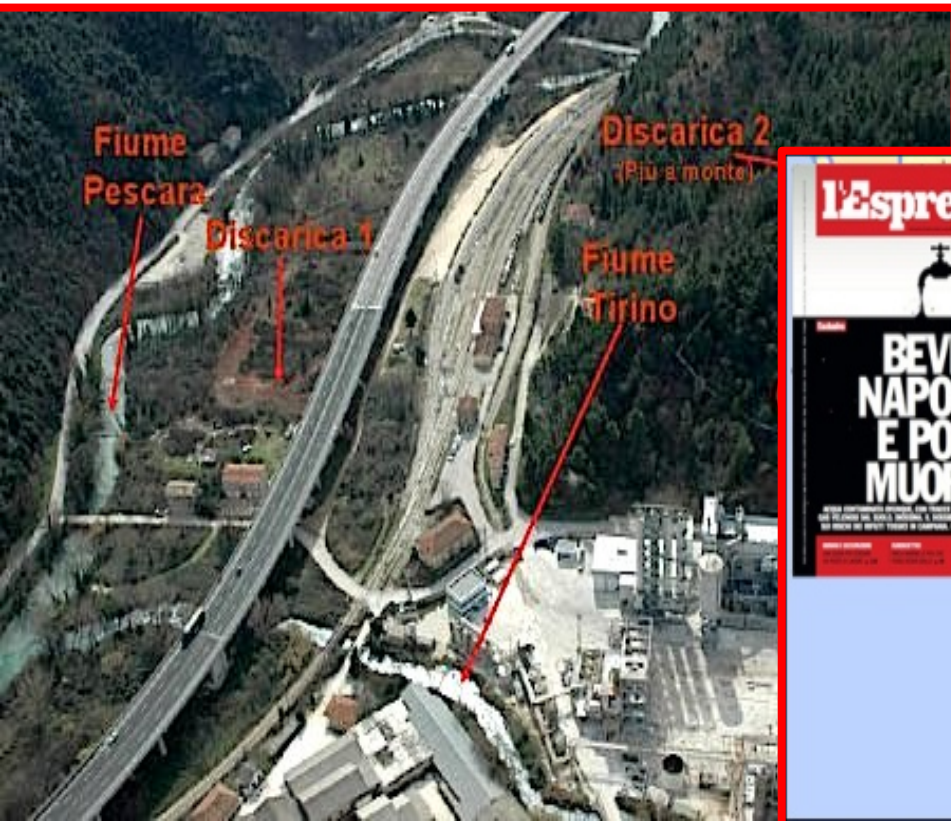
# Are contaminated by DNAPL also in urbanized areas, for agricultural use or in fluvial channels



PCE

TCE

**Ferrara**  
**Terra dei Fuochi**  
**Bussi sul Tirino**





SITO "CARETTI"  
ED ALTRI SITI  
(FERRARA)

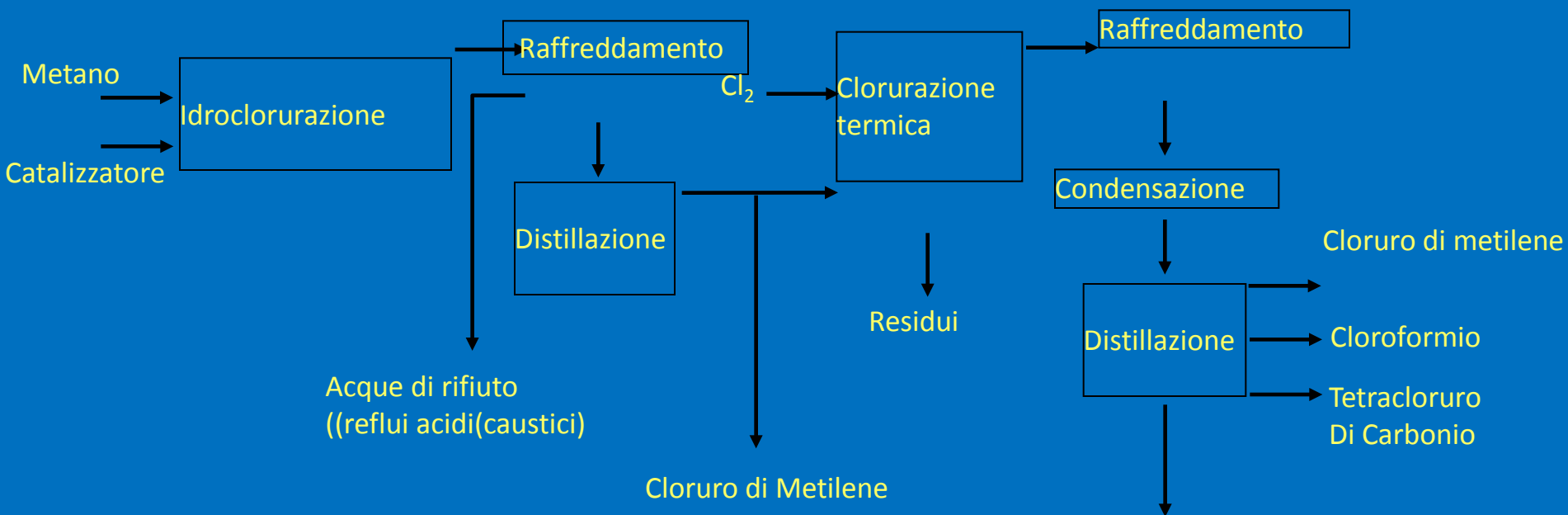


DISCARICA  
"I TRE MONTI"  
(BUSSI SUL TIRINO, PE)



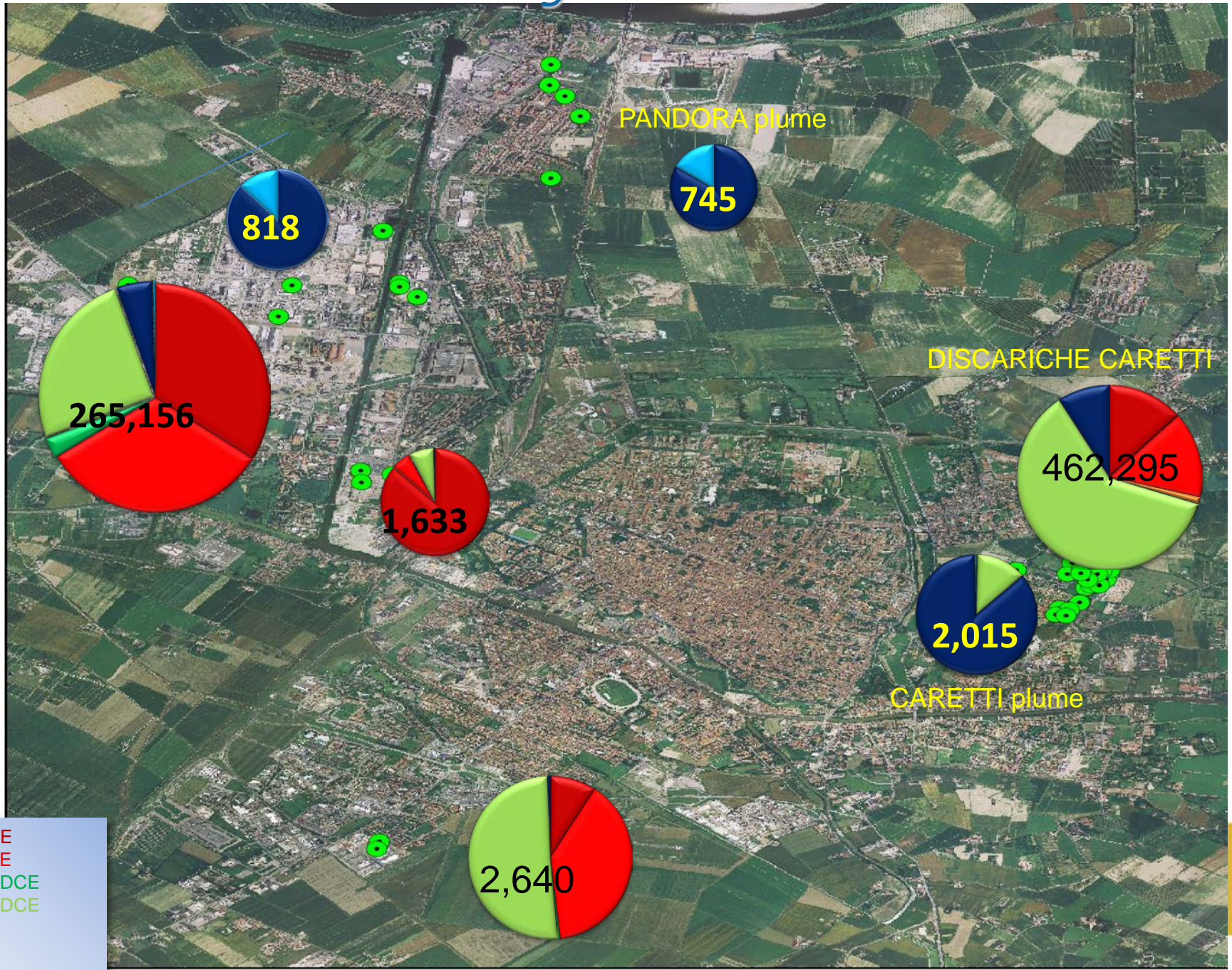
# PROCESSO PRODUTTIVO TIPICO DI UNO STABILIMENTO DI CLORO-METANI

*Si parte da Metano e Cloro e si producono cloro-metani*



**RIFIUTI: Peci clorurate  
Morchie liquido/oleose ricche di  
PCE, TCE, Esacloroetano,  
Tetracloruro di carbonio  
Etc..**

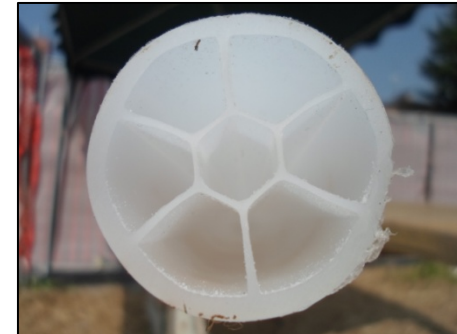
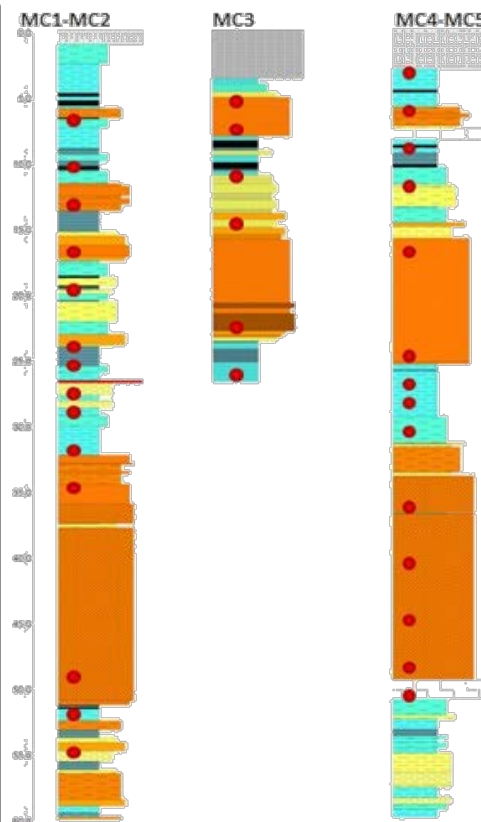
# Ferrara e gli etileni clorurati

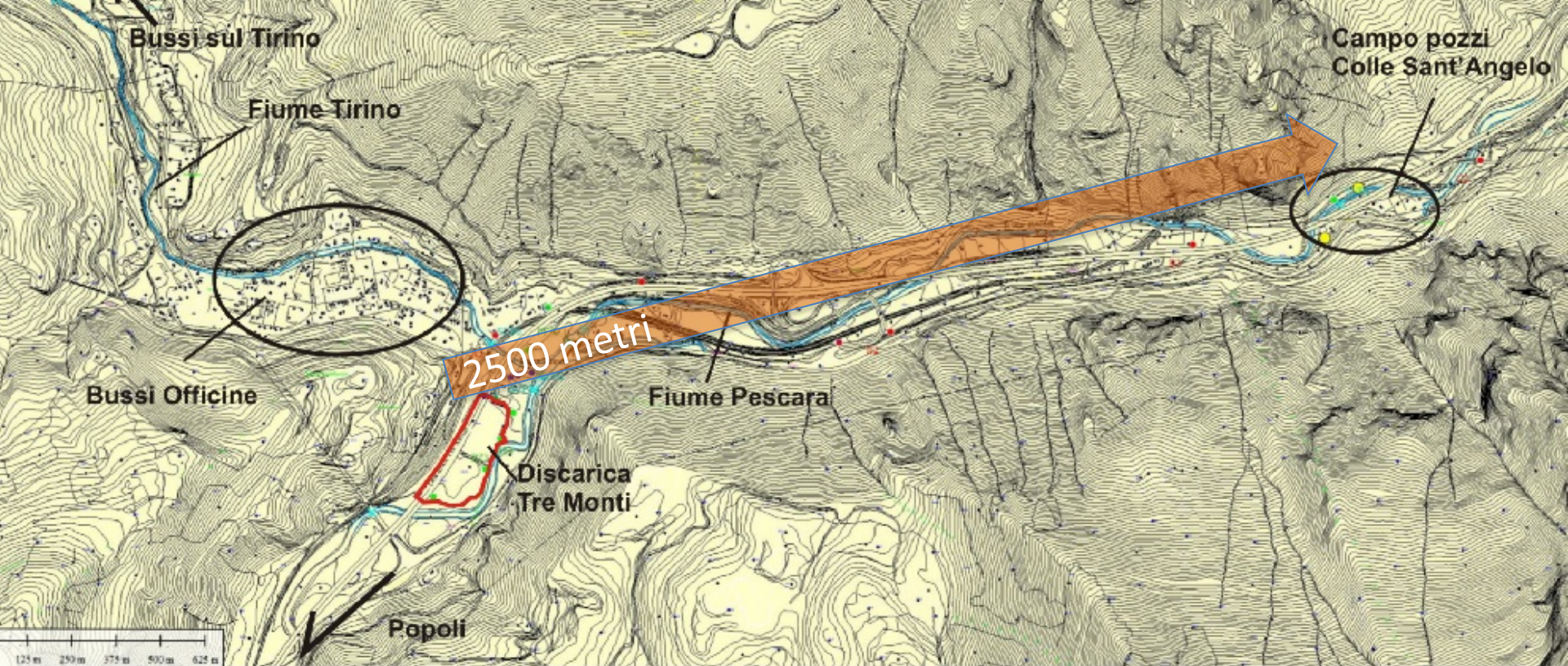


- PCE
- TCE
- 1,1DCE
- 1,2DCE
- VC
- E







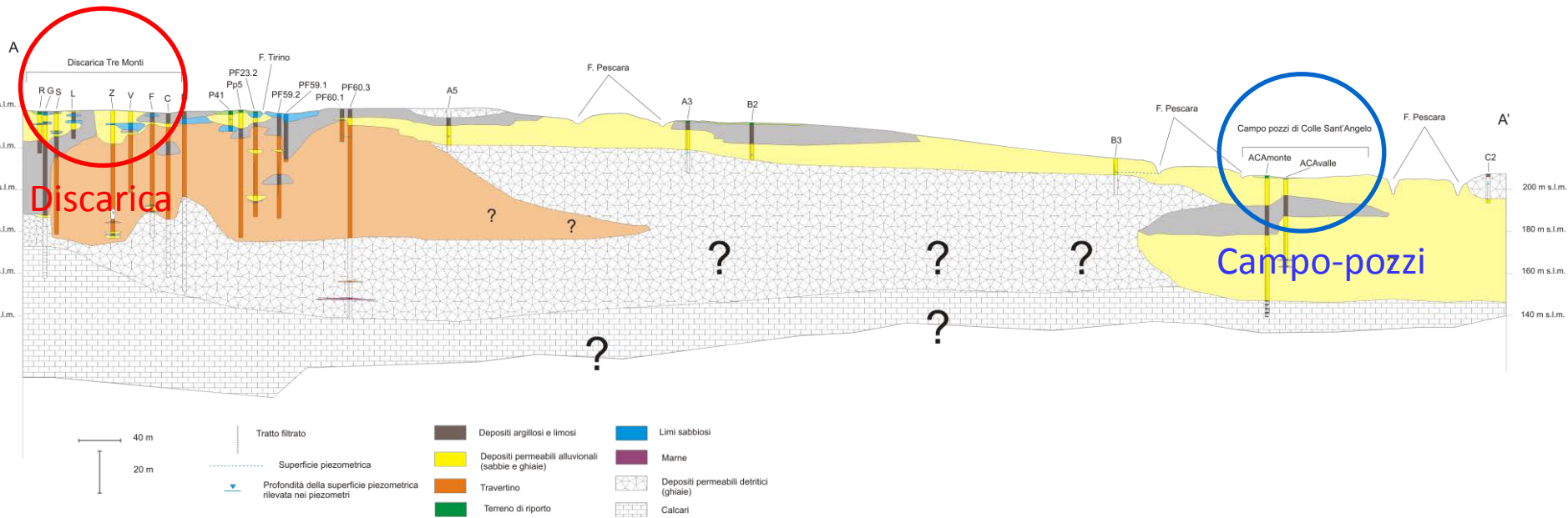


# Sito di Bussi sul Tirino (Pescara)



# Sezione longitudinale della Val Pescara

Sezione longitudinale delle Gole di Popoli

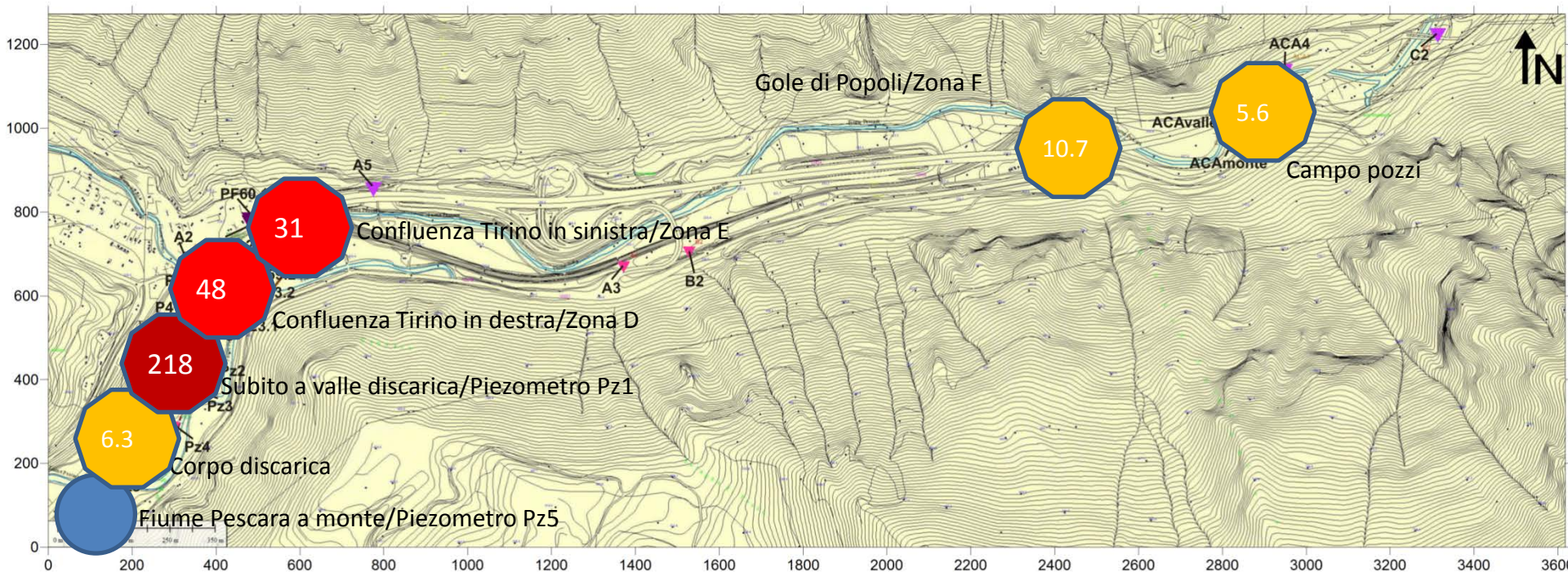


# Distribuzione degli inquinanti - 2012

## Tetracloroetilene - PCE

(Concentrazione Soglia Contaminazione-DLGS 152/2006: 1,1 microgrammi/litro )

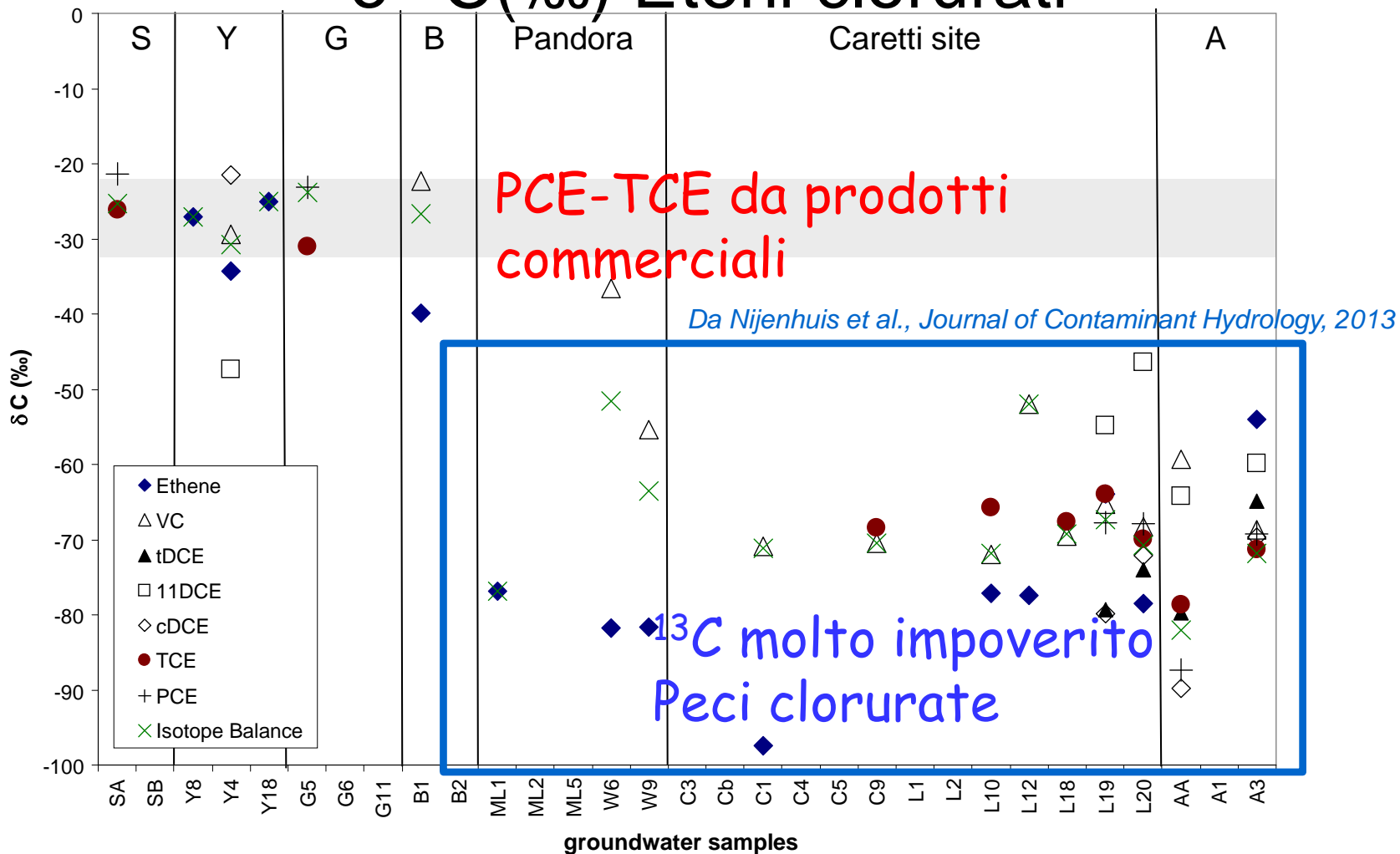
PCE - acque di falda



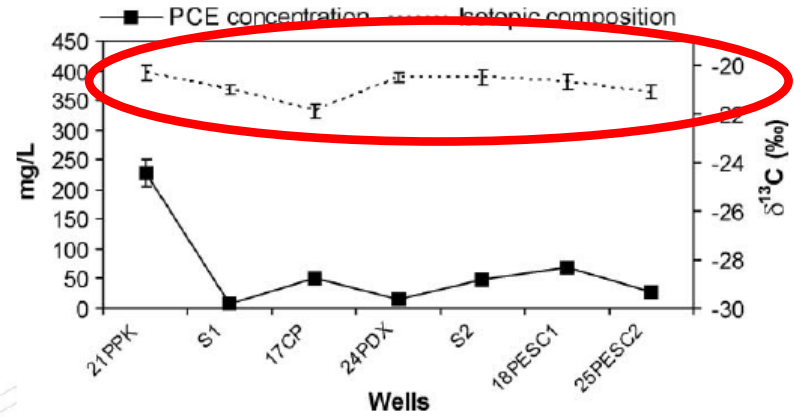
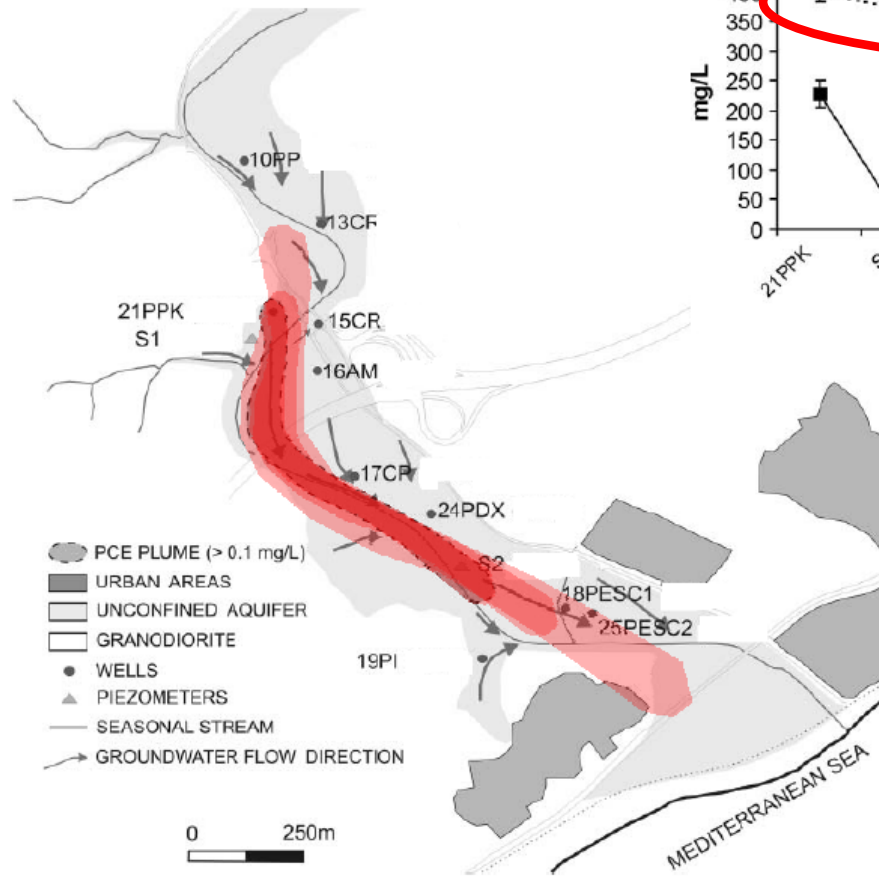
Gradiente di concentrazione da monte a valle secondo il flusso di falda

# Fingerprinting isotopico siti di Ferrara

## $\delta^{13}\text{C}$ (‰) Eteno clorurati



# Is $^{13}\text{C}$ conservative?



1 Km plume

Eh > 200 mV  
DO > 2-3 mg/l

AEROBIC CONDITIONS

(Modified from Palau et al., 2010)

# CONCLUSIONI TRATTE DAI CASI DI STUDIO

- 1) La caratterizzazione multilivello permette di definire con dettaglio la distribuzione della contaminazione DNAPL e individuare i processi chiave (perforazione acquitardi, datazione, accumulo cloruro di vinile)*
- 2) La presenza di torbe favorisce la declorurazione riduttiva a cloruro di vinile*
- 3) Le peci clorurate determinano una firma isotopica peculiare, aspetto essenziale nel source apportionment in siti complessi*



# Ringraziamenti

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*UFZ LEIPZIG*

*Beth Parker*

*Università di Guelph*





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## HYDROGEOLOGY: BACK TO THE FUTURE!

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1. Groundwater, food and health
2. Sustainable use of groundwater resources
3. Urban and contaminant hydrogeology
4. Ground / Surface Water: an integrated view
5. From recharge to discharge
6. Groundwater management in coastal areas
7. New tools and new frontiers

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