

Seminario tecnico

ORGANO-CLORURATI ED IDROGEOLOGIA DELLE AREE URBANE: INQUINAMENTO PUNTUALE O DIFFUSO ?

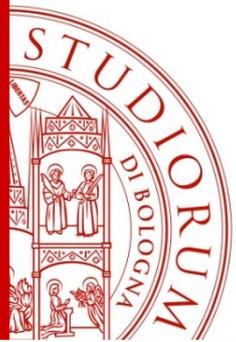
Bologna, 11 Giugno 2015

Idrogeologia dei solventi clorurati: chiavi di lettura alternative rispetto agli approcci classici

Maria Filippini, Alessandro Gargini

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

*maria.filippini3@unibo.it
alessandro.gargini@unibo.it*

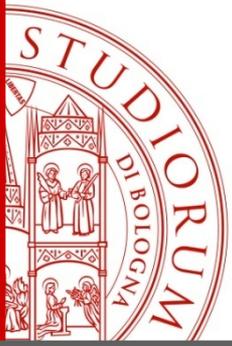


IDROGEOLOGIA DEI DNAPL

Dalla sorgente al piezometro



- Una elevata complessità multifase
- Contaminant hydrogeology-La ricerca
- Fattori geologici di controllo
(eterogeneità, acquitardi, torbe)
- Sfide
caratterizzazione
individuazione del responsabile
assimilation capacity



DNAPL

Dense Non - Aqueous Phase Liquid

DNAPL = affonda (trielina)

LNAPL = galleggia (idrocarburi)

«AFFONDARE» IN UN BICCHIER D'ACQUA



DENSITÀ ACQUA = 1

DENSITÀ OLIO D'OLIVA = 0,92



GALLEGGIA!!!!



7° giorno sotto effetto, l'esperimento è concluso, l'acqua è completamente separata dal petrolio

DENSITÀ PETROLIO = 0,73

GALLEGGIA!!!!!!!!!!

DENSITÀ TRICLOROETILENE = 1,46
TCE

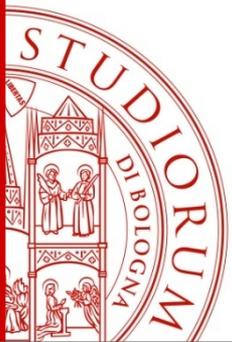
AFFONDA!!!!!!!!!!



DENSITÀ TETRACLOROETILENE = 1,63
PCE

AFFONDA!!!!





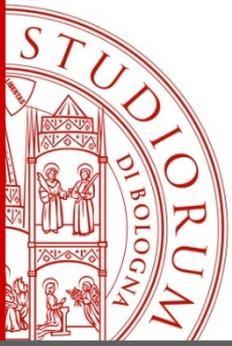
Raro esempio di "cattura" di fase pura in piezometro

Produzione armamenti
nucleari -
Savannah River site
(North Carolina)

Jackson & Mariner,
1995 (Groundwater)

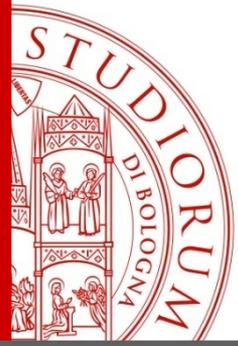


DNAPL
entro
un
bailer



PRINCIPALI DNAPLs

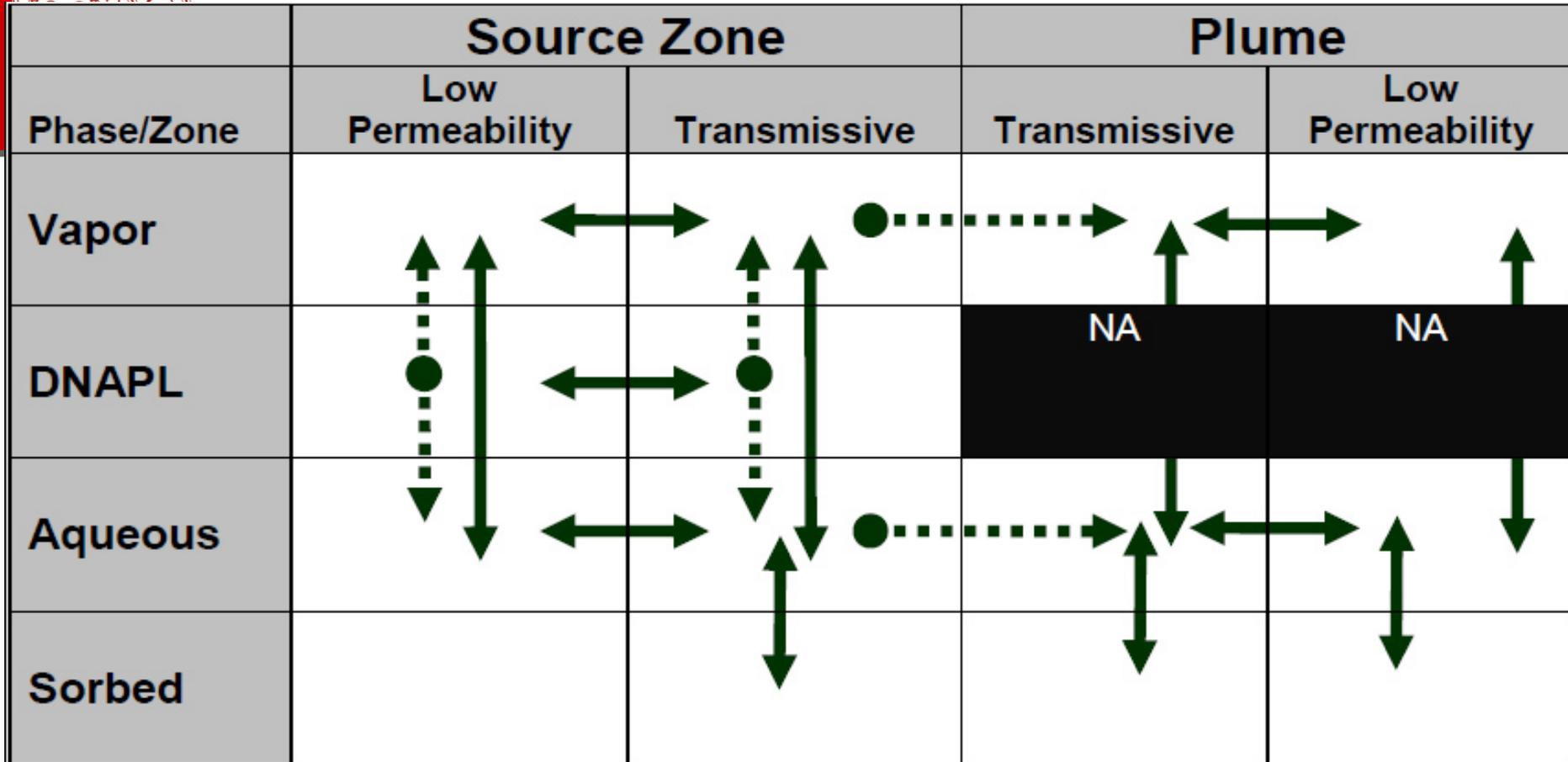
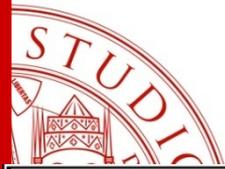
- Solventi, sgrassanti e detergenti
- Creosoto/catrame di carbone
- Miscugli di rifiuti industriali (es. peci clorurate)
- Oli Policlorobifenili
- Alcuni pesticidi in stato non diluito in acqua



Fenomeno idrogeologico "recente" ed incremento delle conoscenze "assai recente"

- Produzione industriale dei solventi cresce enormemente dopo Seconda Guerra Mondiale
- Fino alla fine anni'70 plume non riconosciuti come un pericolo
- Fase DNAPL non riconosciuta come la causa dei plume fino alla seconda metà anni '80

Complessità multi-fase, multi-zona, multi-K



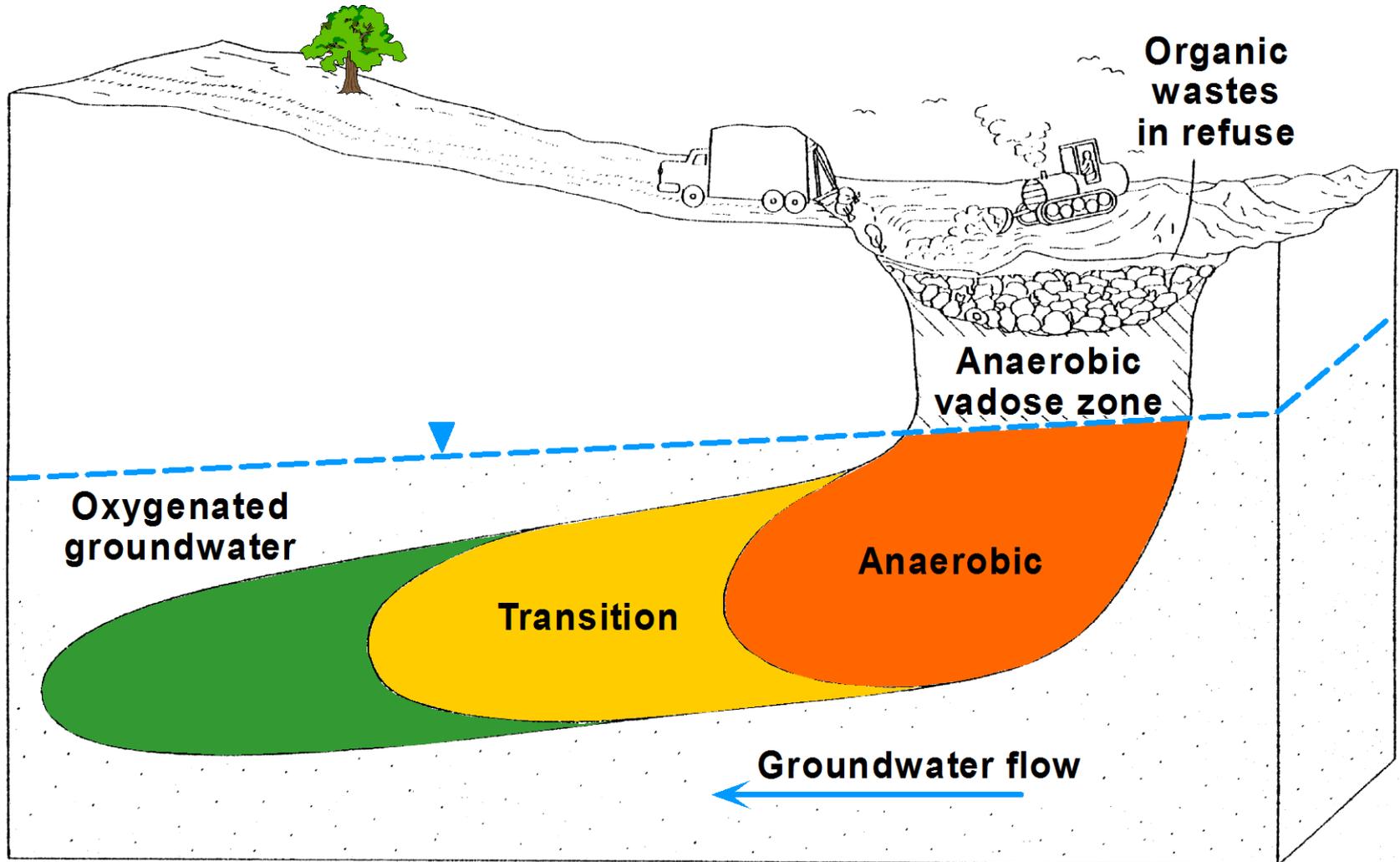
4 fasi, 2 zone (sorgente, plume), 2 tipi di permeabilità (acquifero, acquitardo)
13 compartimenti

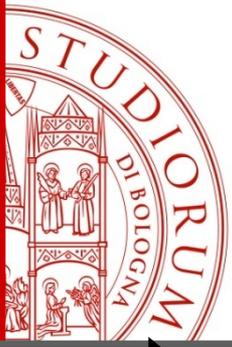
Sale & Newell 2011 (US Department of Defense, ESTCP)

ALMA MATER STUDIORUM - UNIVERSITÀ DI BOLOGNA

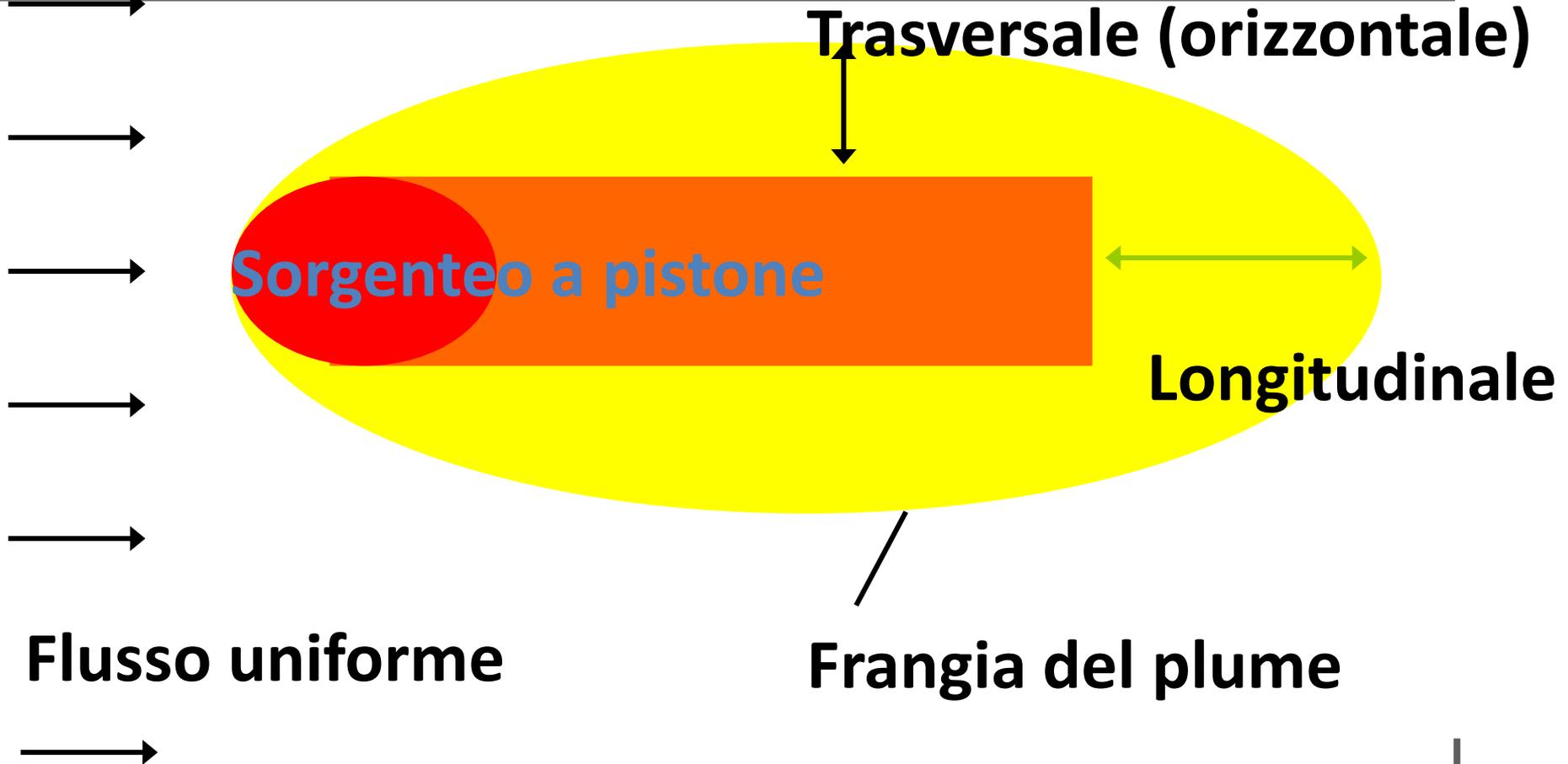
IL PRESENTE MATERIALE È RISERVATO AL PERSONALE DELL'UNIVERSITÀ DI BOLOGNA E NON PUÒ ESSERE UTILIZZATO AI TERMINI DI LEGGE DA ALTRE PERSONE O PER FINI NON ISTITUZIONALI

Plume "classico" da rifiuti non industriali





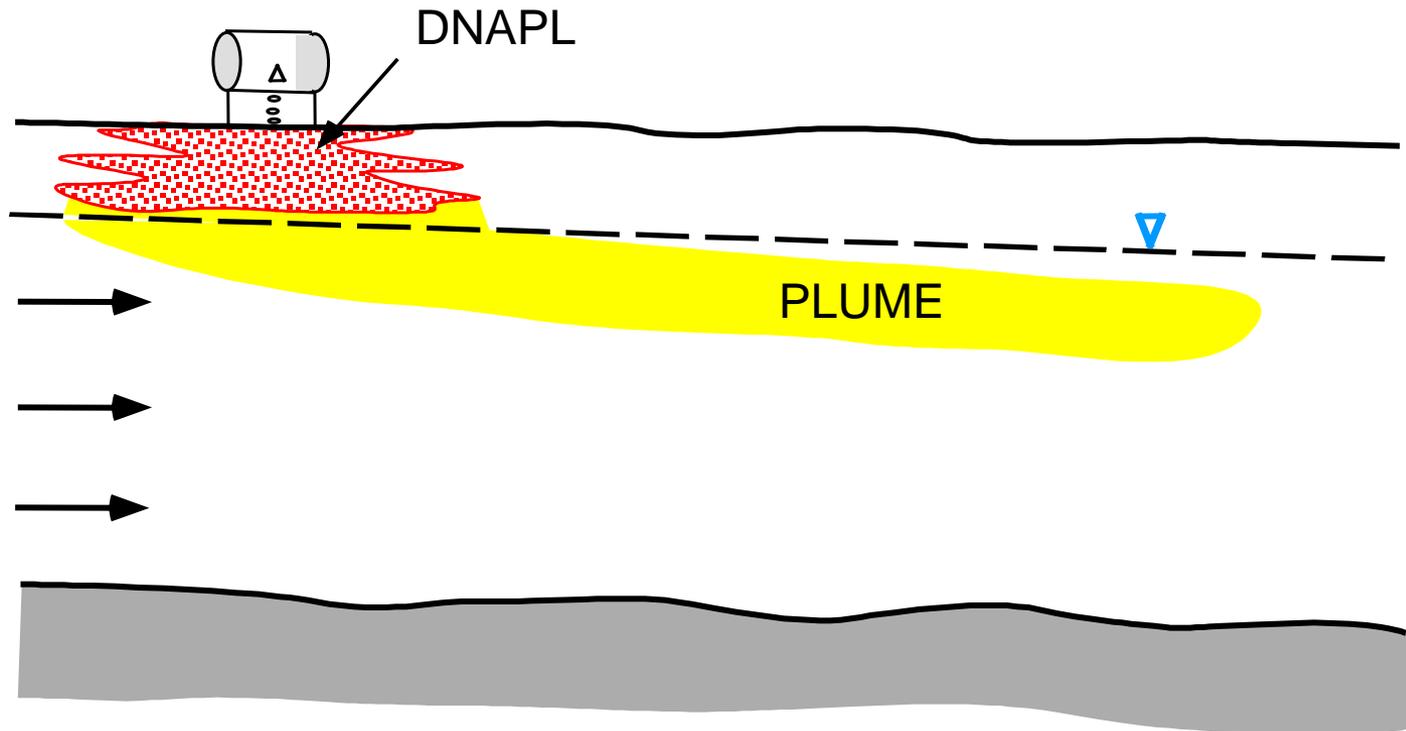
Diluizione classica per Dispersione Meccanica

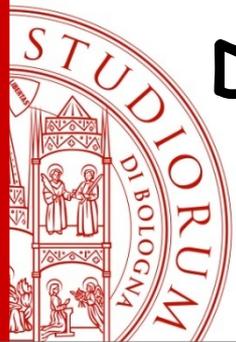


Flusso uniforme

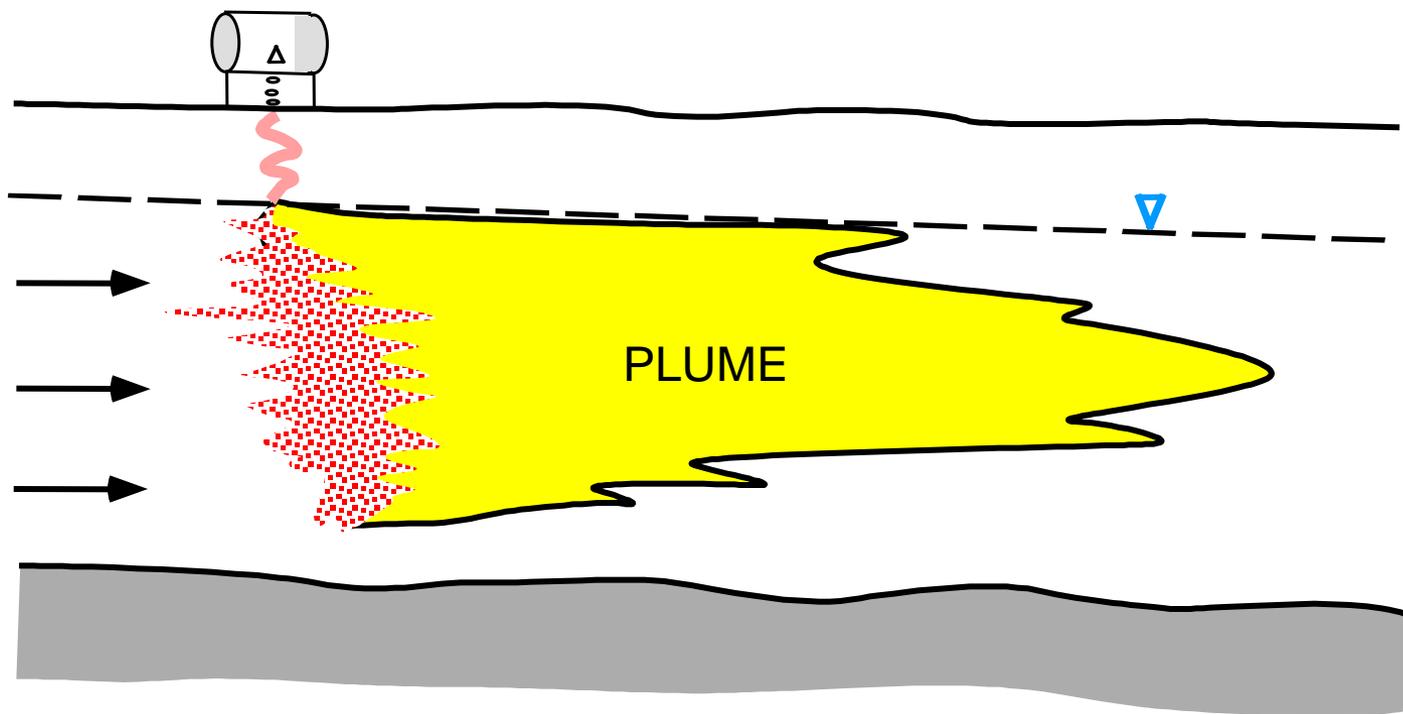
Frangia del plume

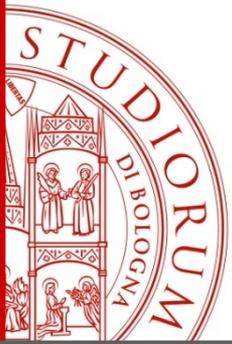
DNAPL RESIDUO NELL'INSATURO



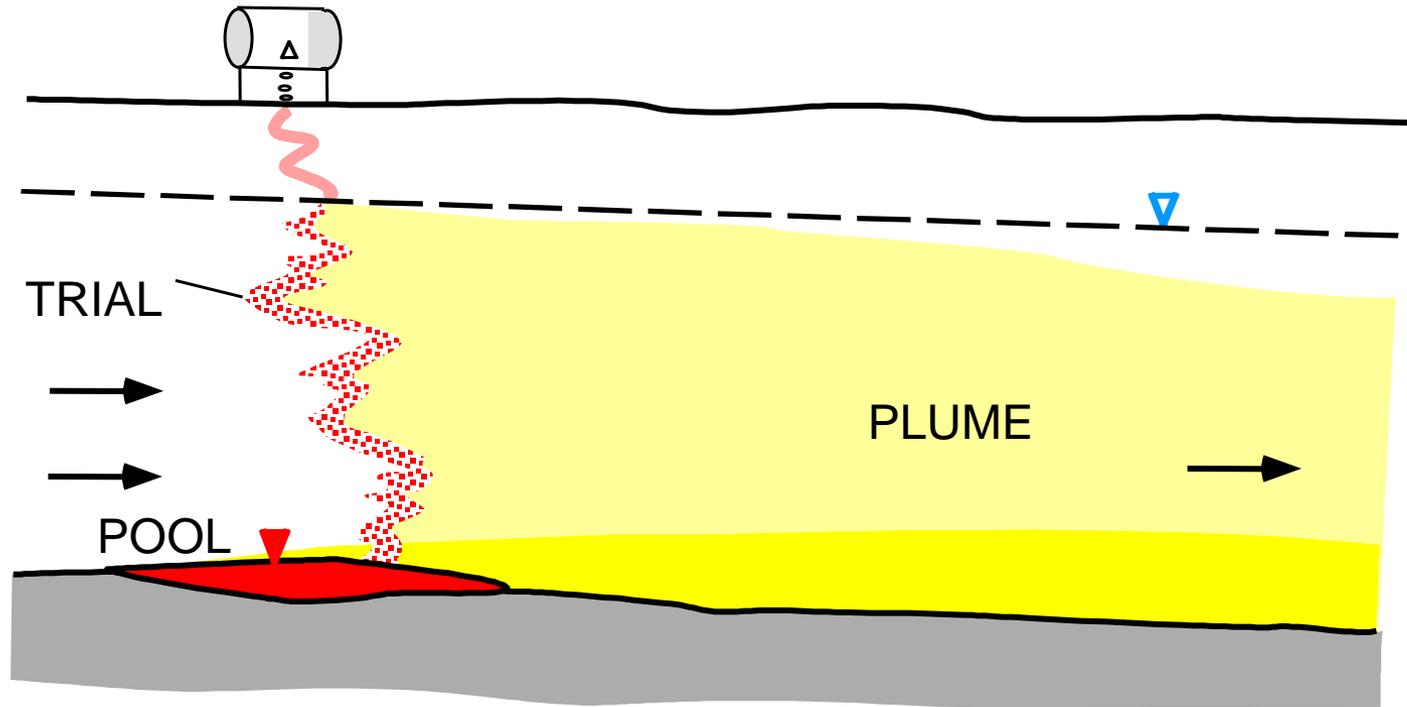


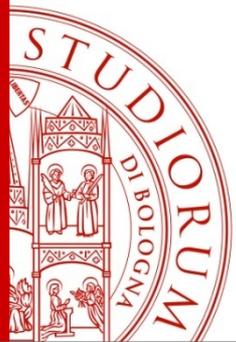
DNAPL RESIDUO SOTTO FALDA ("trail")



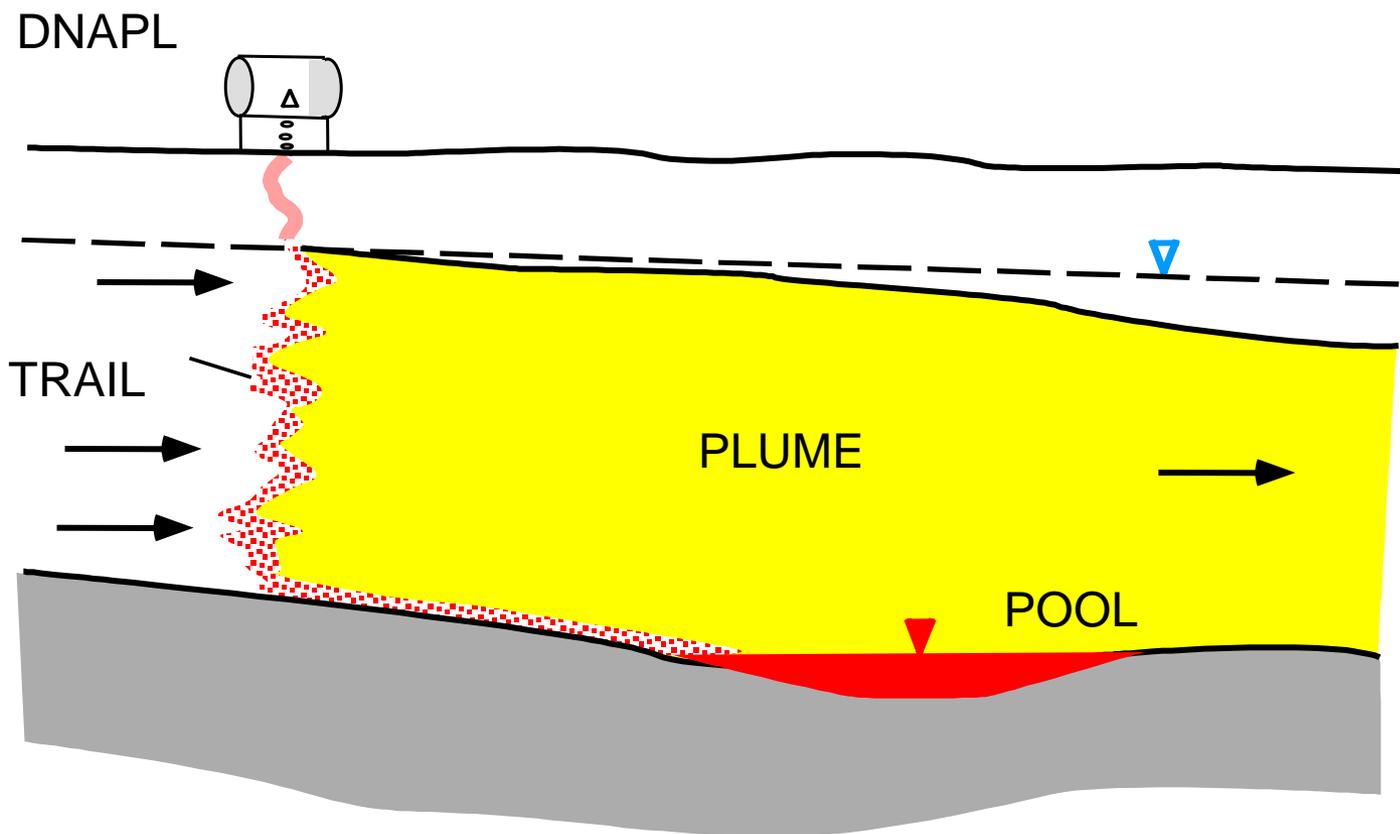


"TRAIL" SOTTO FALDA E "POOL" FASE PURA

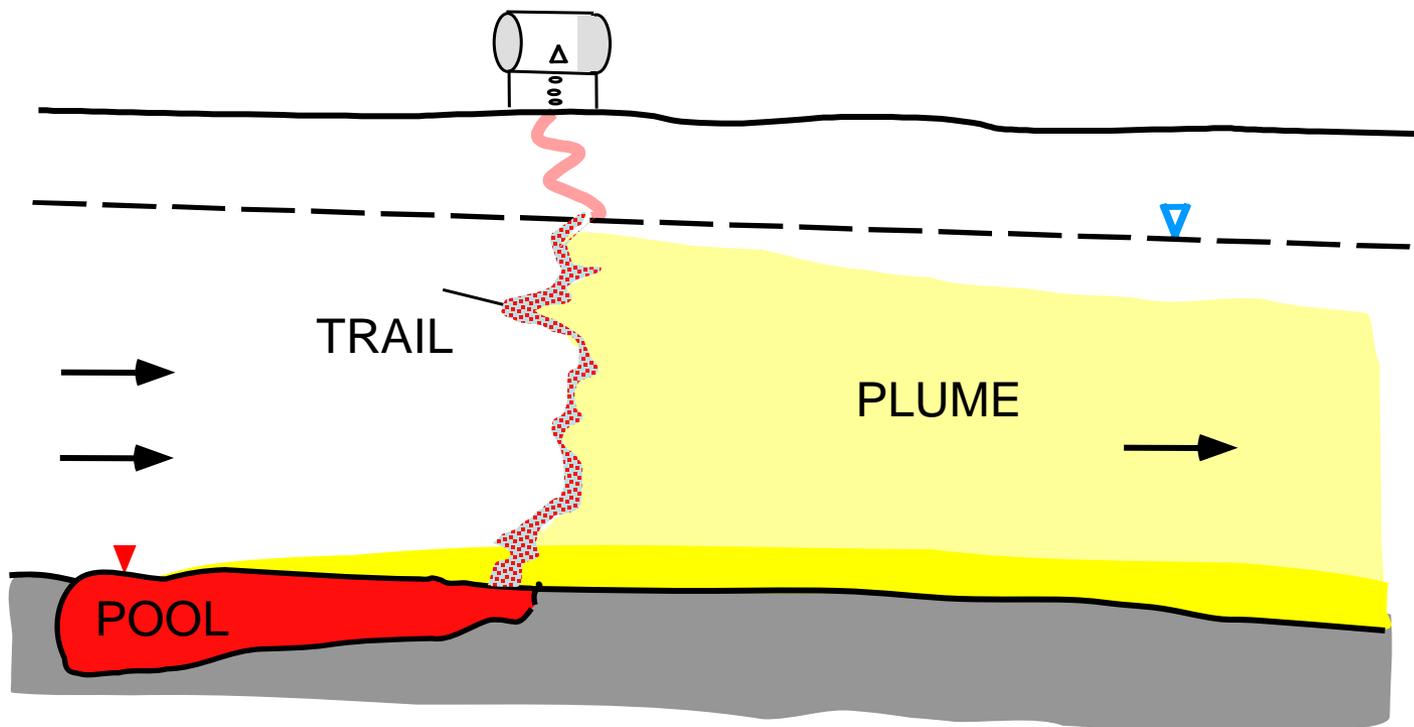


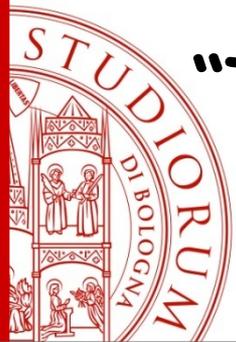


"POOL" MIGRA VALLE FLUSSO

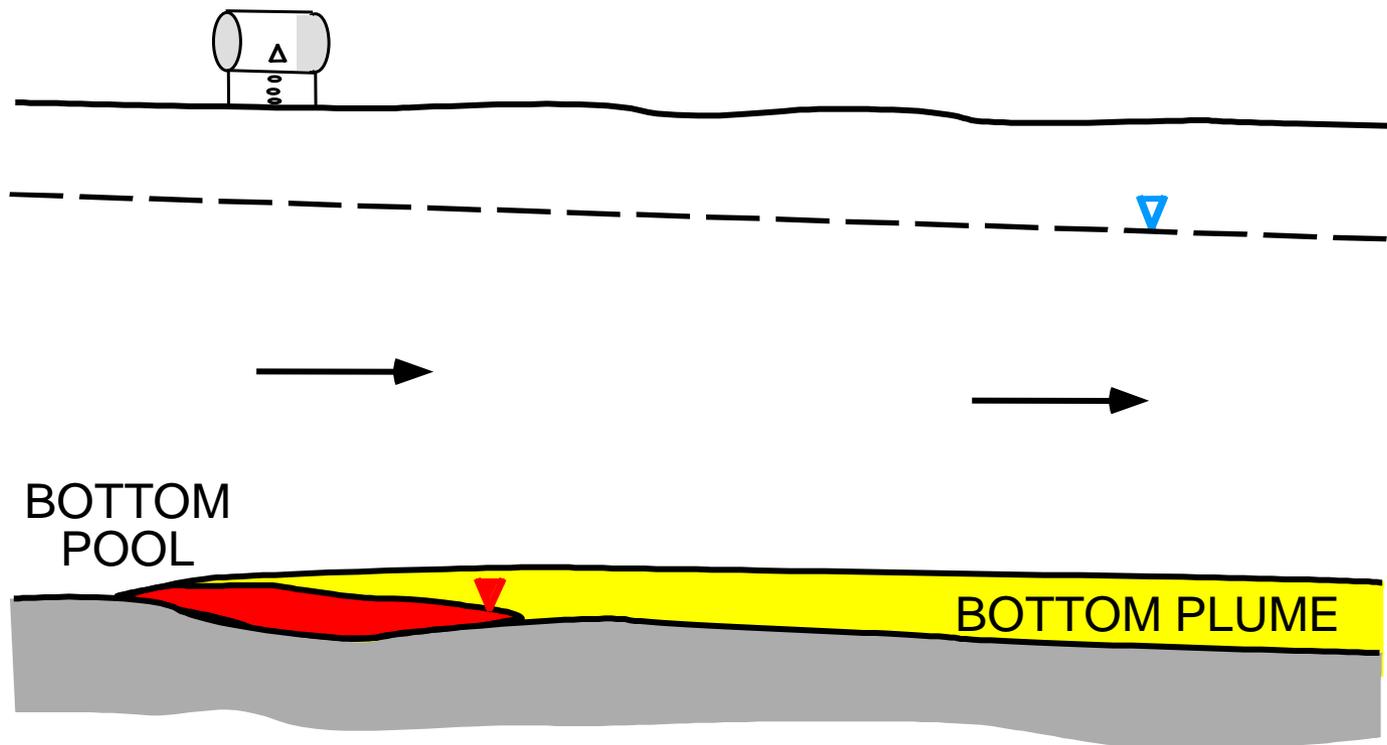


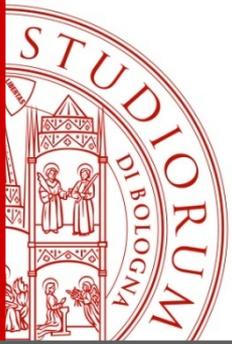
"POOL" MIGRA MONTE FLUSSO



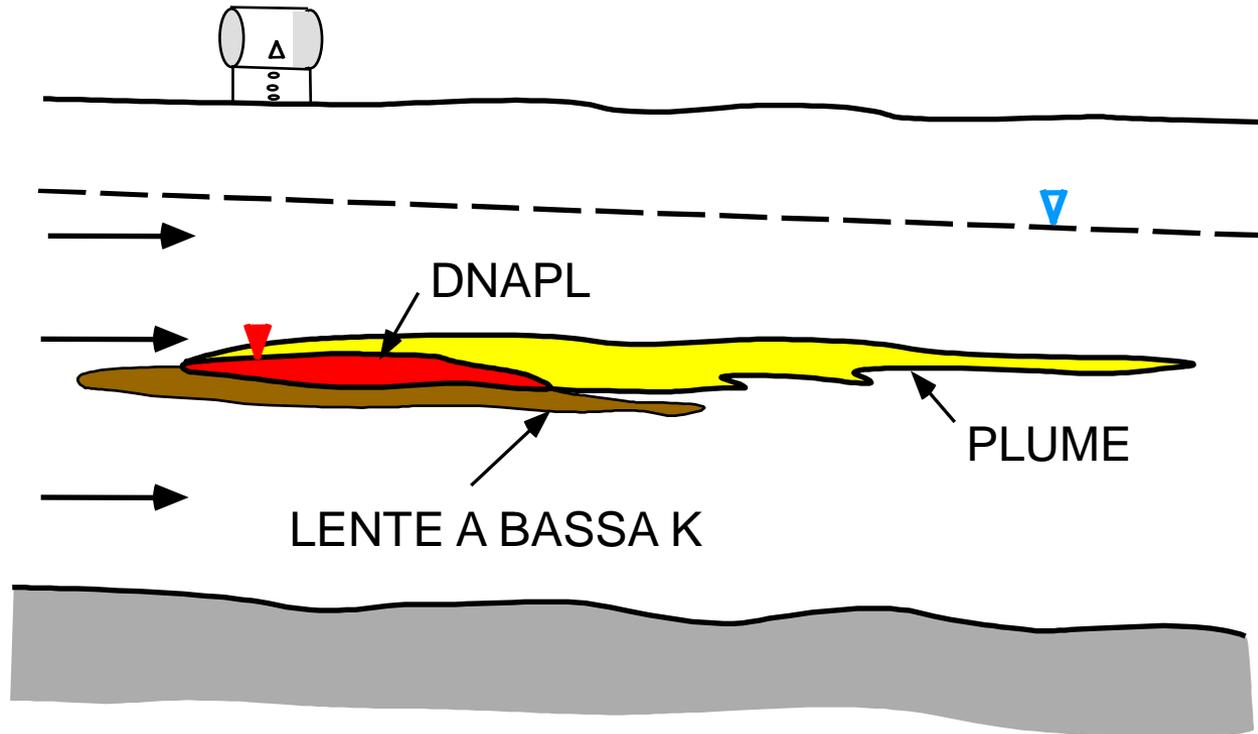


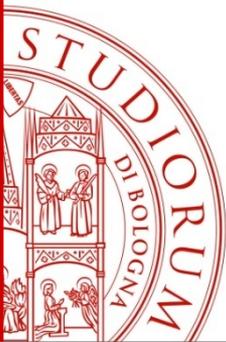
"TRAIL" ASSIMILATO PER DISSOLUZIONE





"POOL" SOSPESO

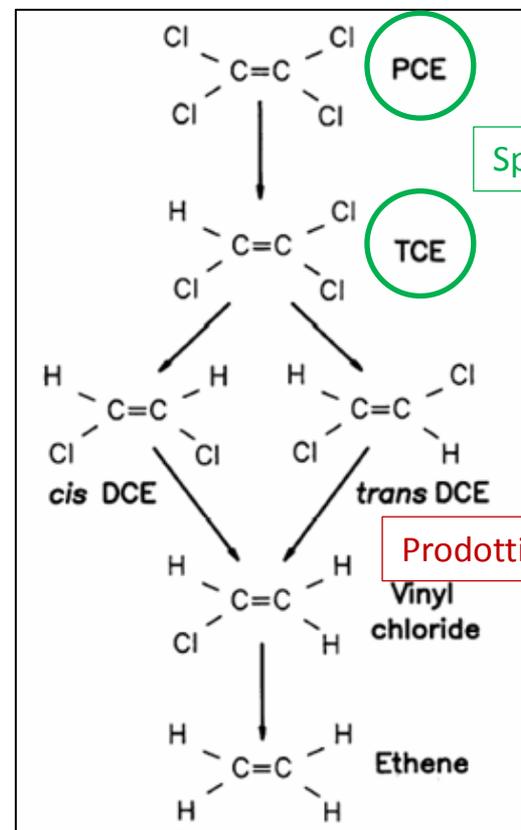
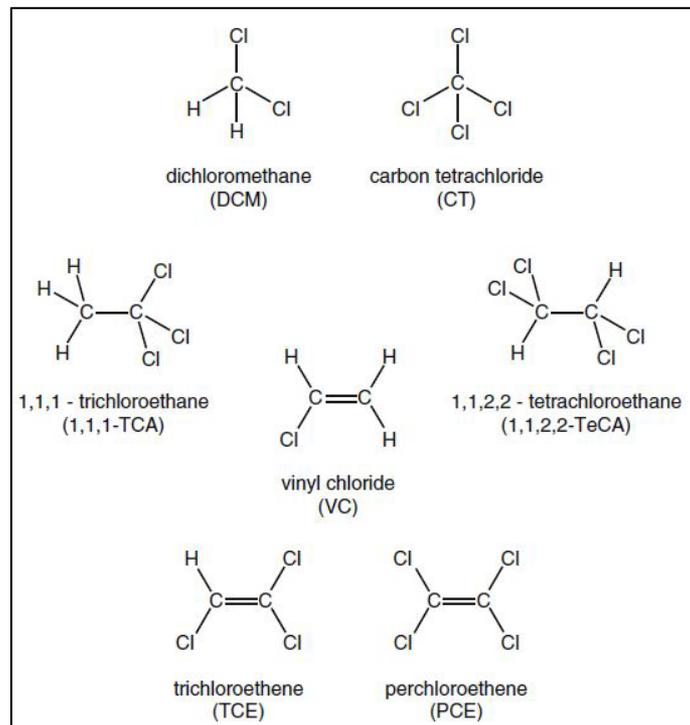




CHIMICA E DEGRADAZIONE

Declorurazione riduttiva degli etileni

Composti alifatici clorurati



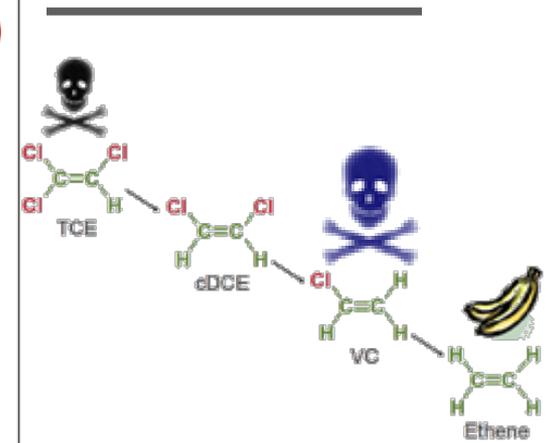
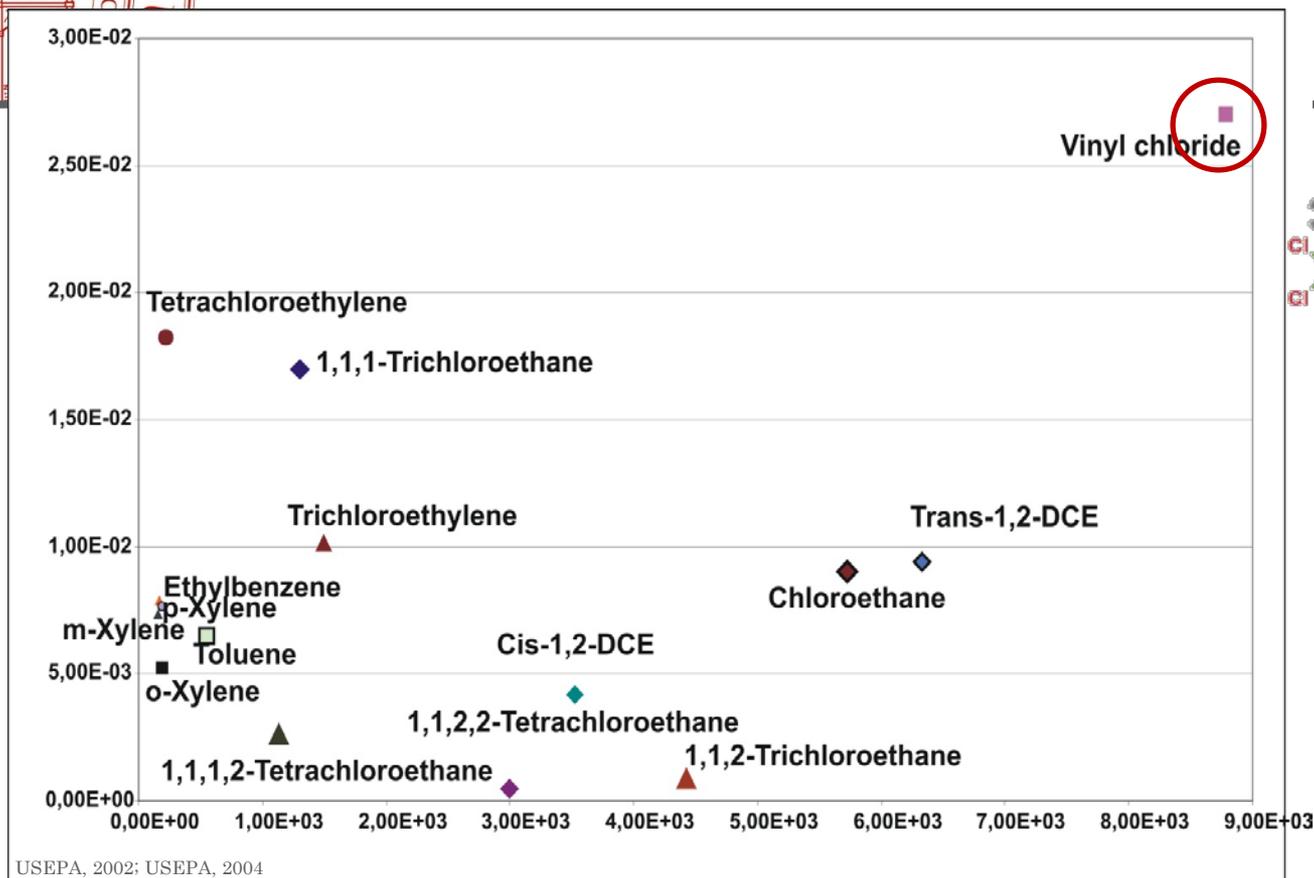
Specie primarie

Prodotti di reazione

Cloruro di Vinile - Criticità maggiore in contaminazioni da DNAPL

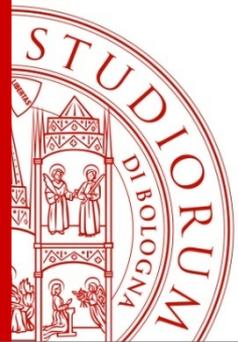


Henry Constant a 25°C (atm*m³/mol)

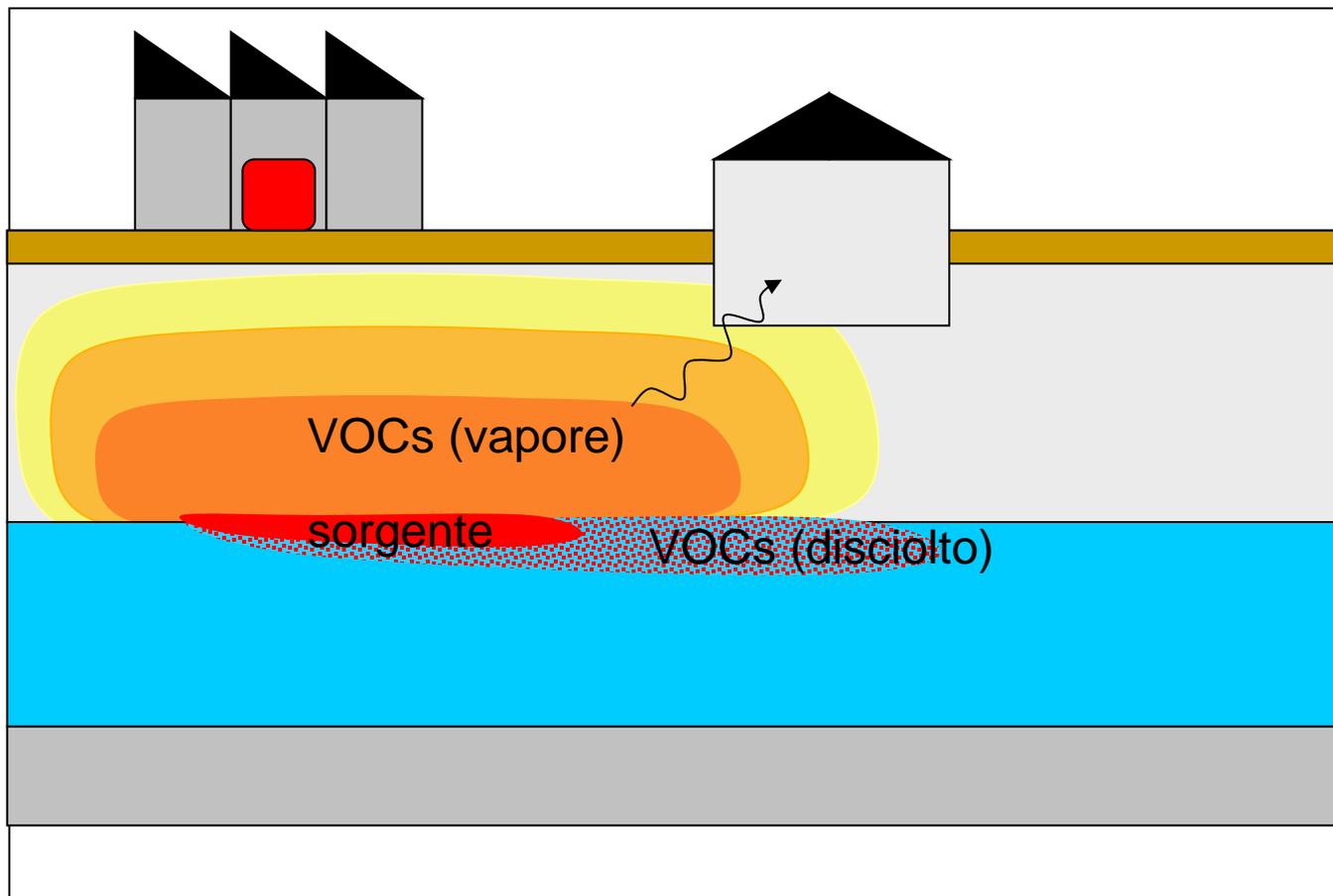


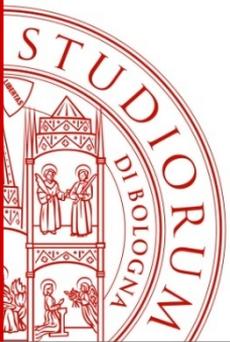
Solubility in water @ 25°C (mg/L)

USEPA, 2002; USEPA, 2004



Problema dell'intrusione di vapori indoor





Tipologia della sorgente

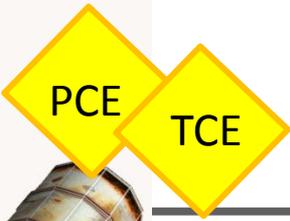




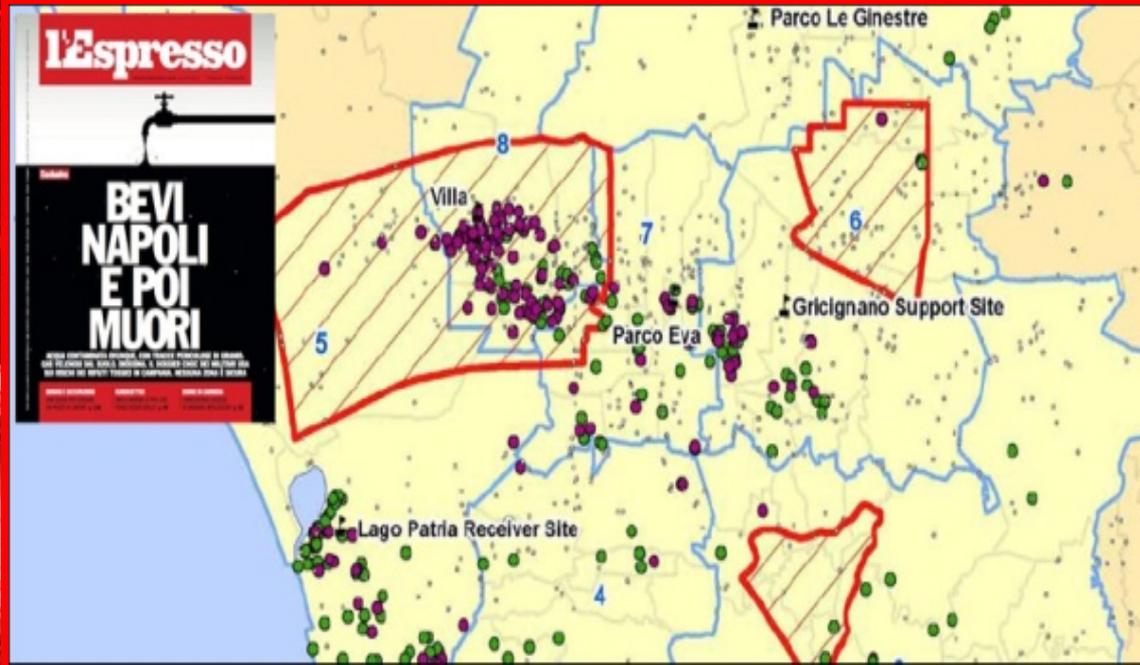
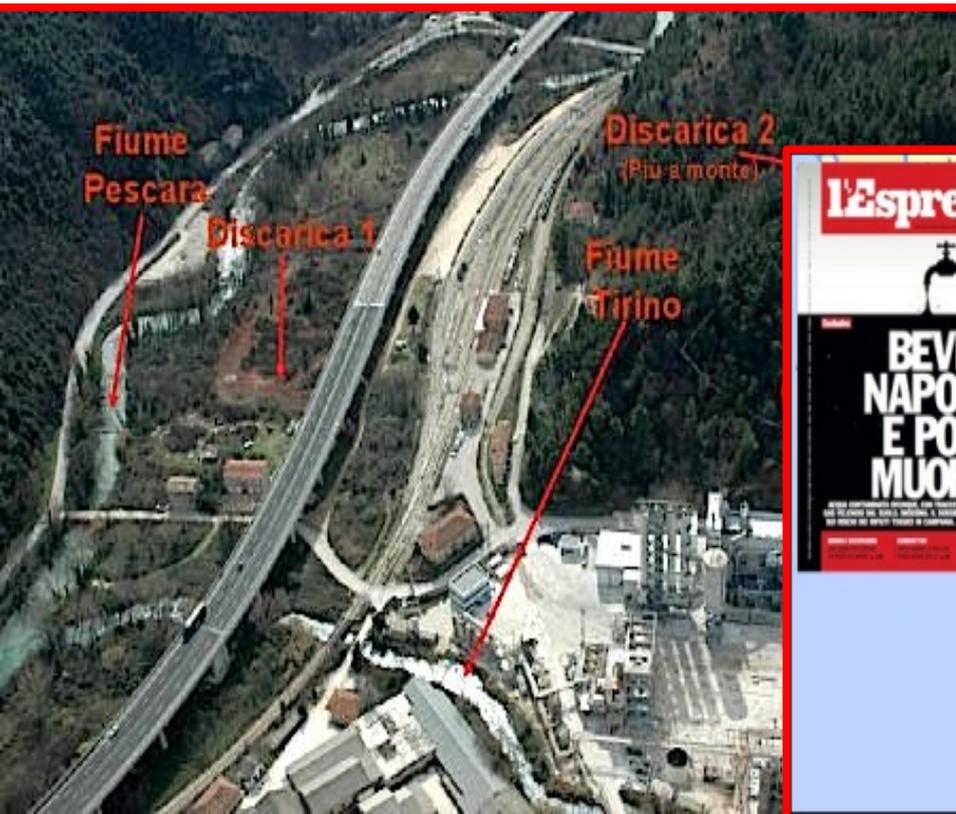
In molti siti petrolchimici diverse sorgenti puntuali si sono succedute nello spazio e nel tempo, stratificandosi e coalescendo:

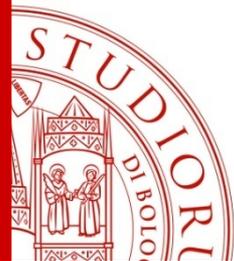
EFFETTI DIFFUSI DA
SORGENTI PUNTUALI

Aree contaminate da DNAPL anche in zone urbanizzate, ad uso agricolo o in aree golenali



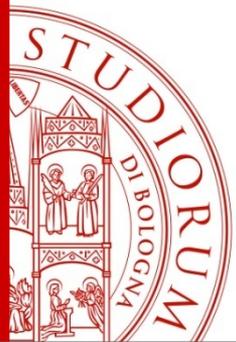
Ferrara
Terra dei Fuochi
Bussi sul Tirino





Duplicità di sorgenti puntuali ed incertezza sulle relazioni causa-effetto

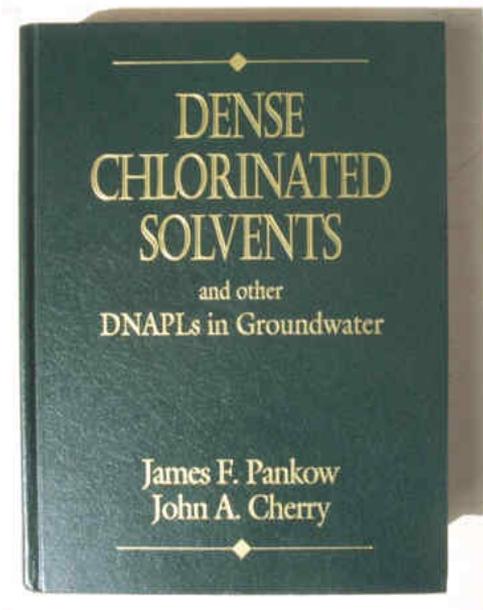
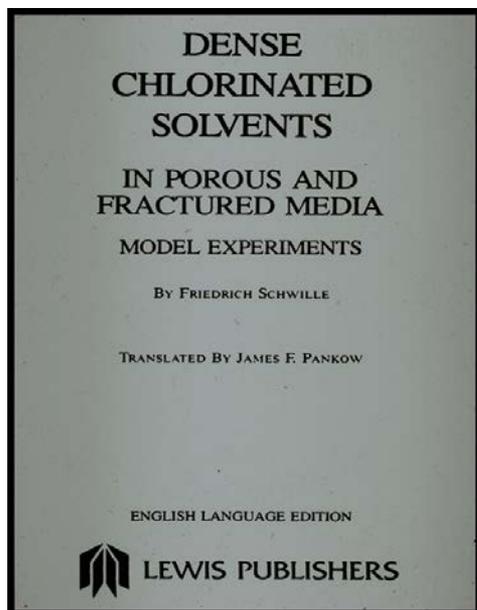


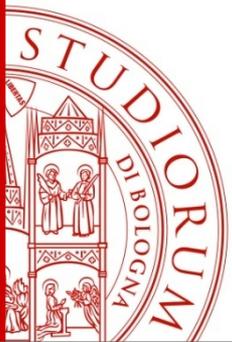


LA RICERCA (assai recente) CONTAMINANT HYDROGEOLOGY

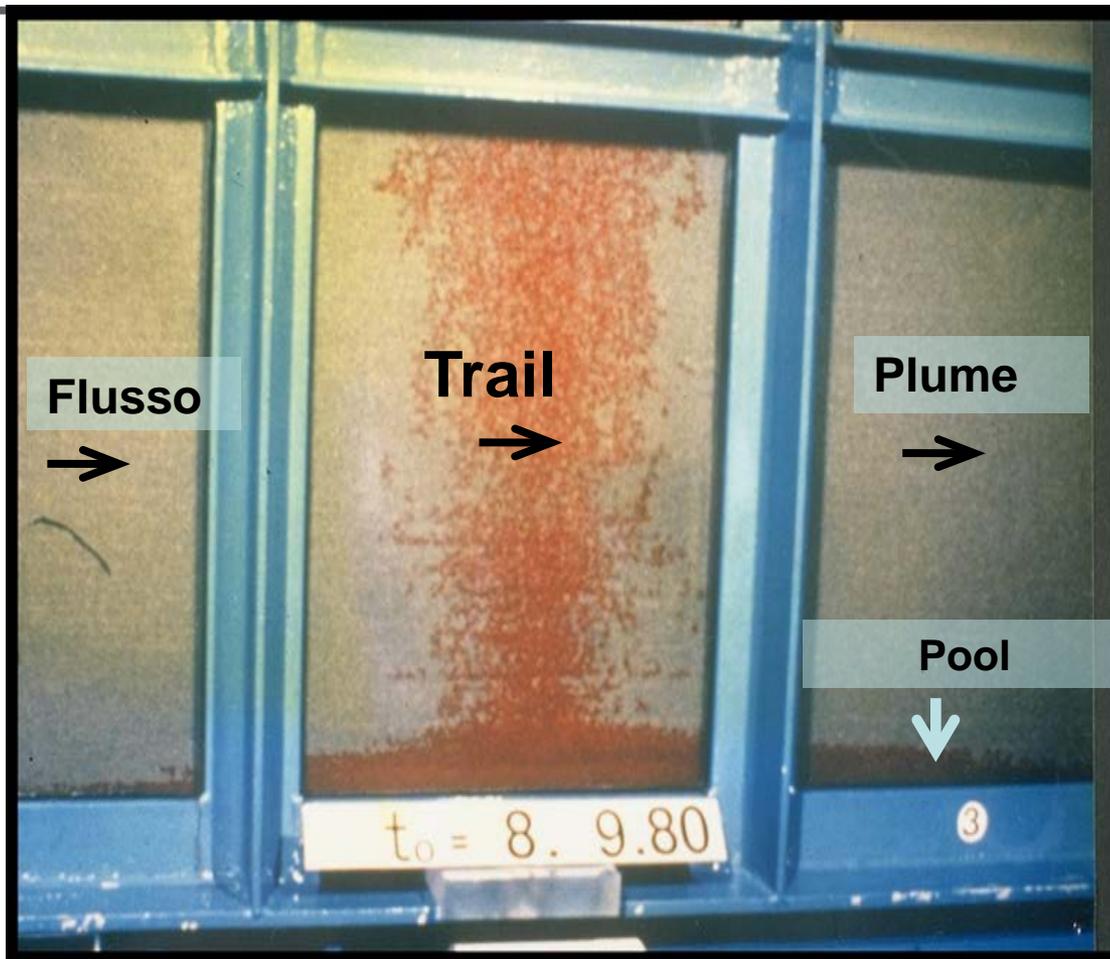
Germania: 1977-1984 (traduzione in inglese nel 1988)

Nord America (Canada): metà anni '80



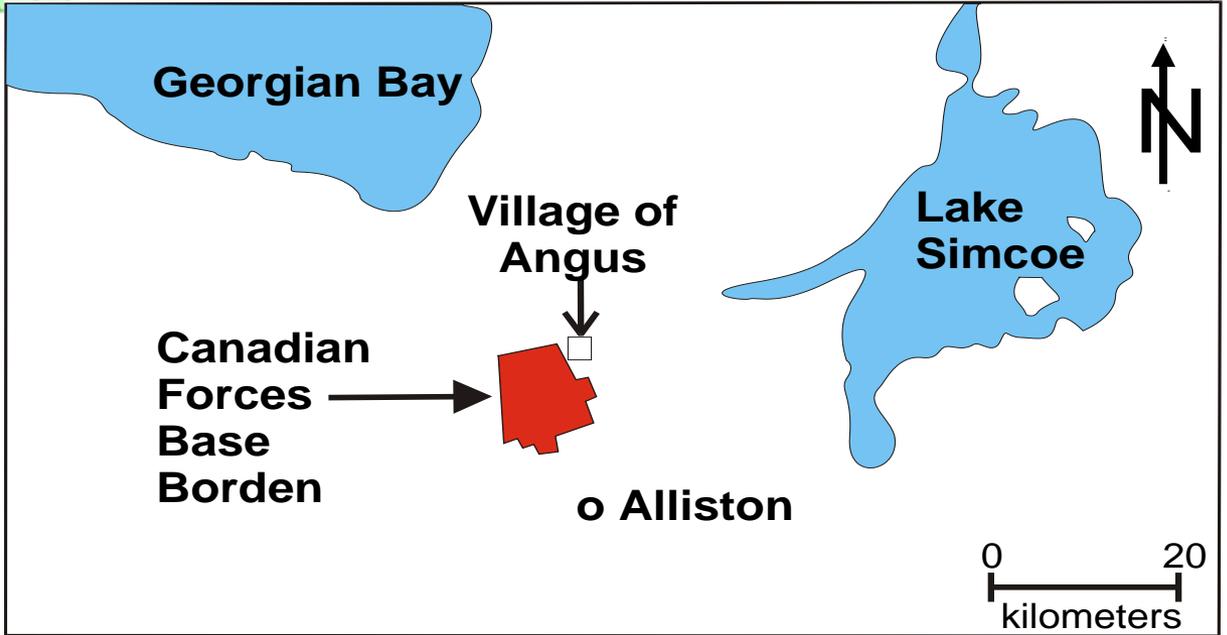


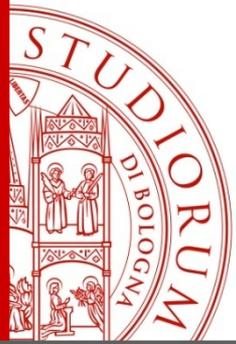
ESPERIMENTO DI SCHWILLE





Borden site Sito sperimentale





PRIMO ESPERIMENTO SUI DNAPLs A BORDEN: 1989

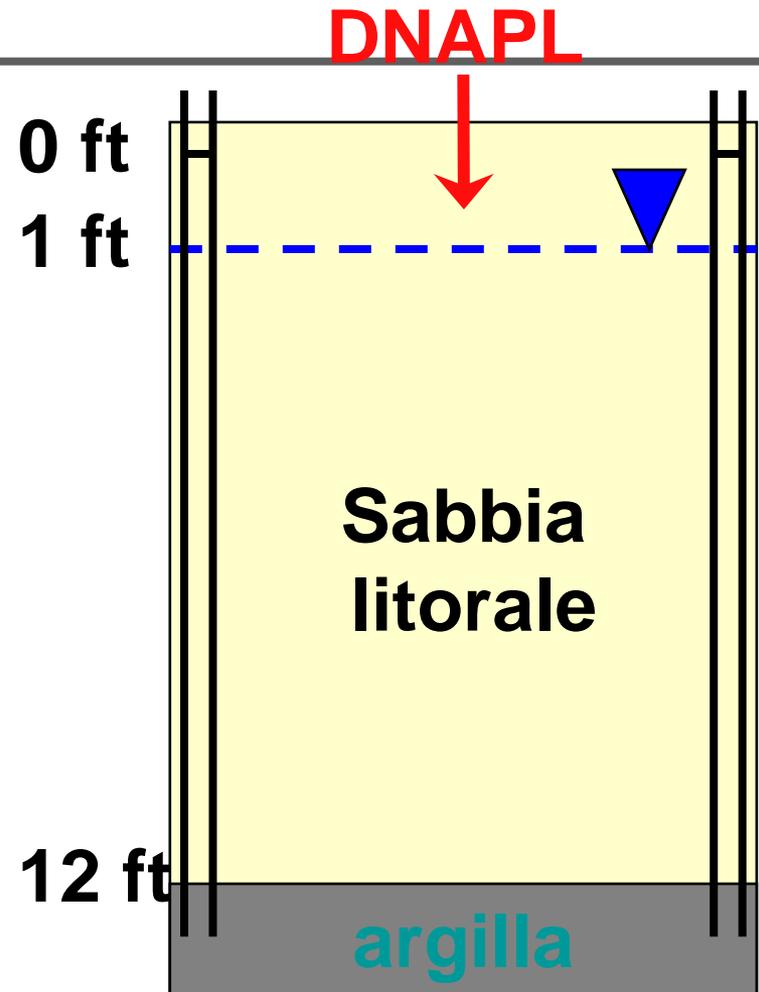
**A Field Experiment to Study the
Behaviour of Tetrachloroethylene in
Unsaturated Media**

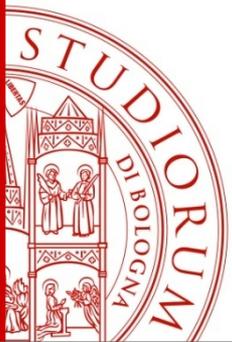
by

Mette M. Poulsen and Bernard H. Kueper

Environmental Science and Technology

Vol. 26, 1992





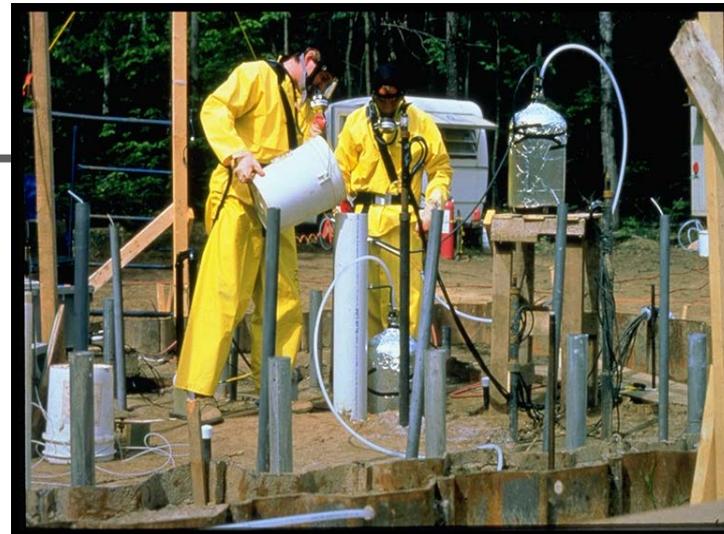
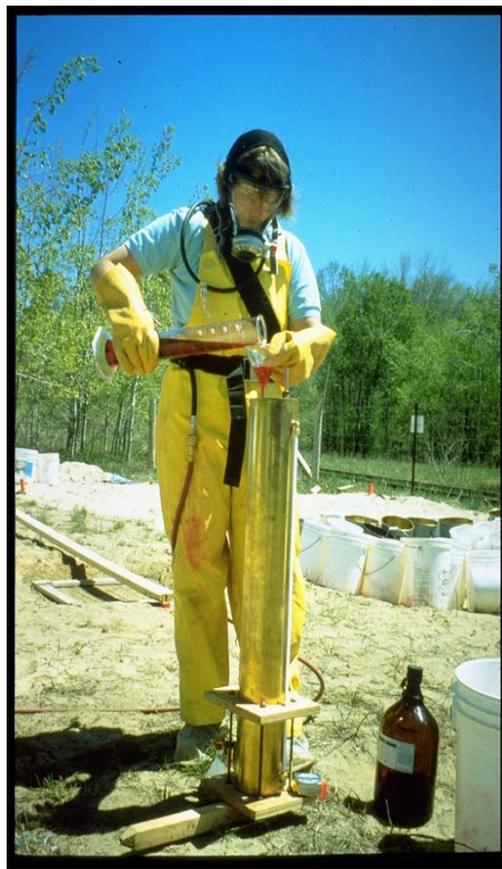
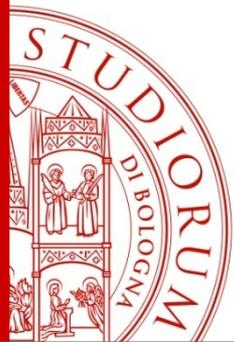
Borden site

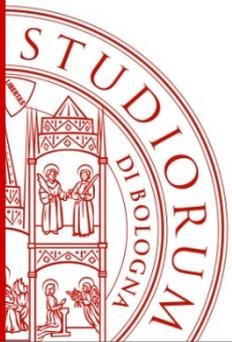
Foreste di alberi e di piezometri



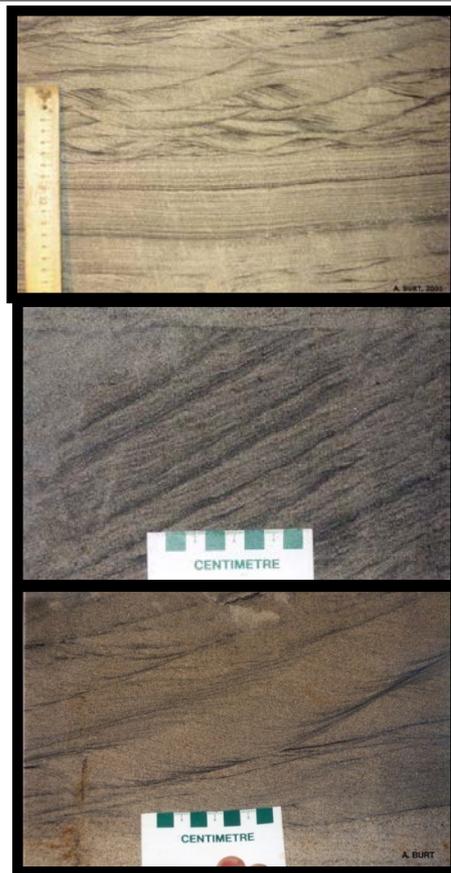
Rilasci controllati e definiti

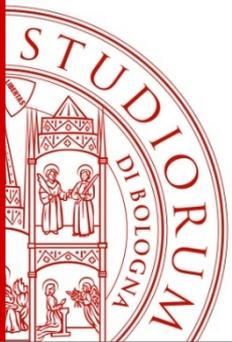
Sorgente totalmente controllata



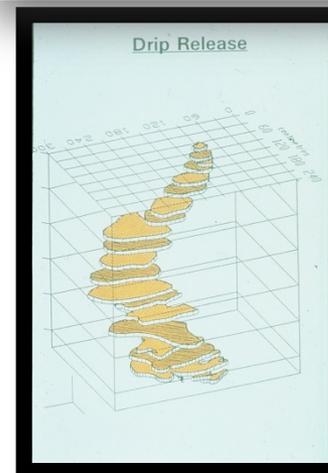
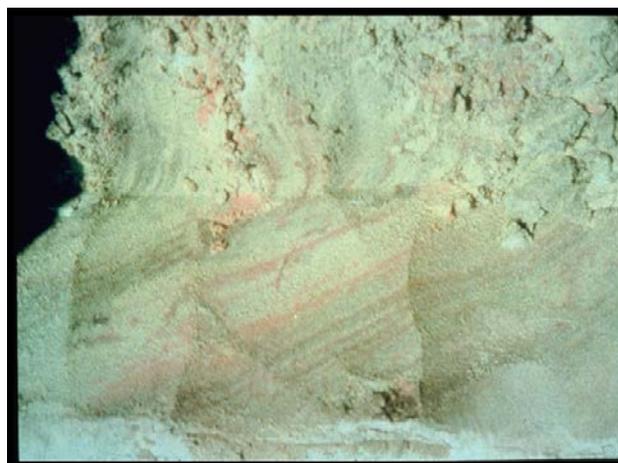
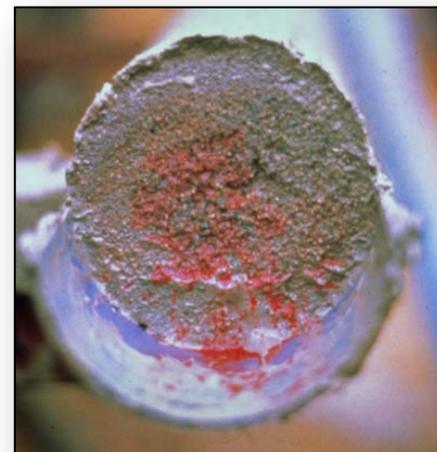
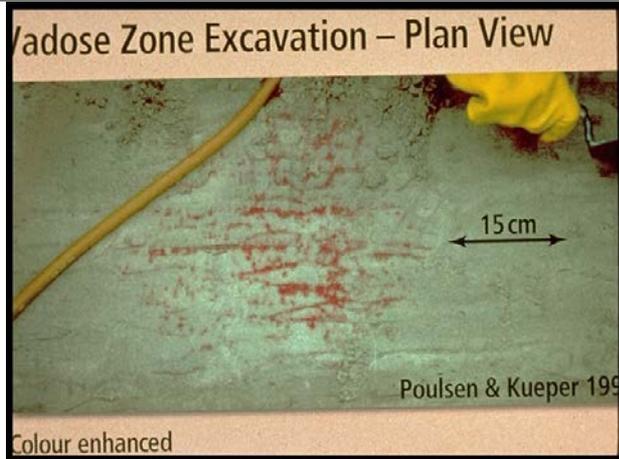


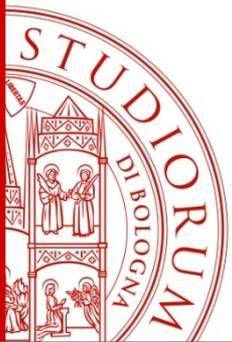
Caratterizzazione geologica ad altissima risoluzione



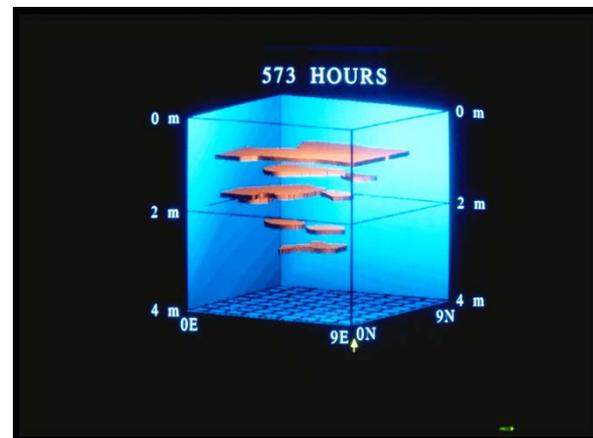
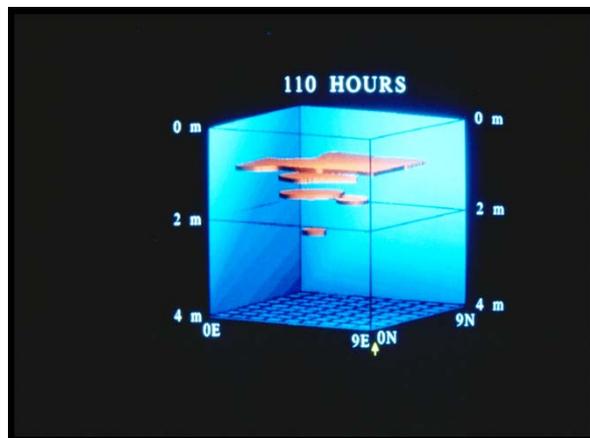
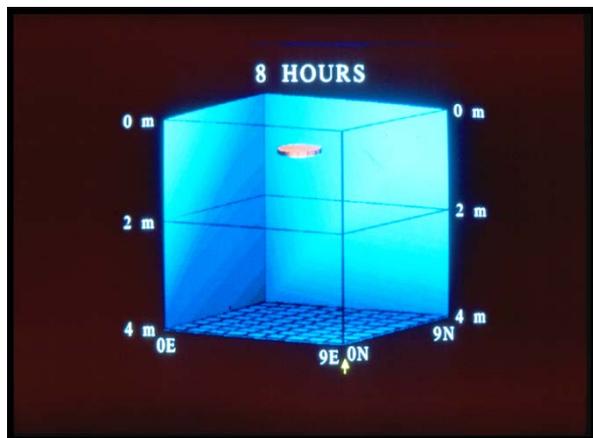
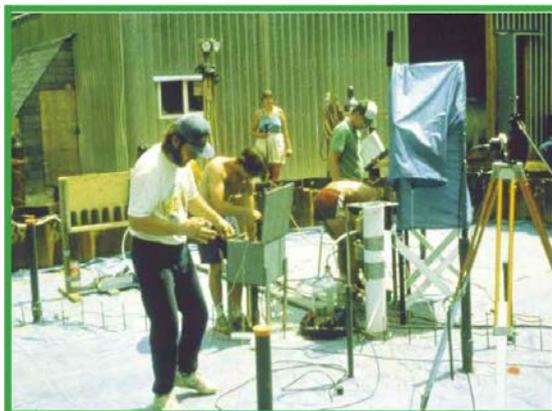


Tracciamento diretto del DNAPL





Tracciamento indiretto del DNAPL

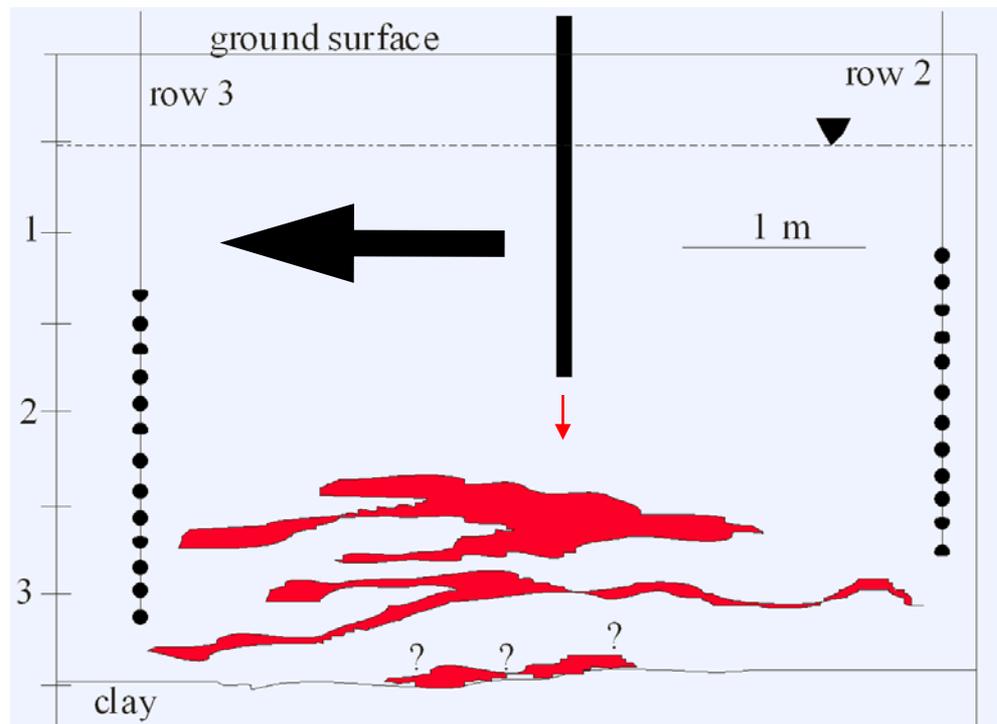
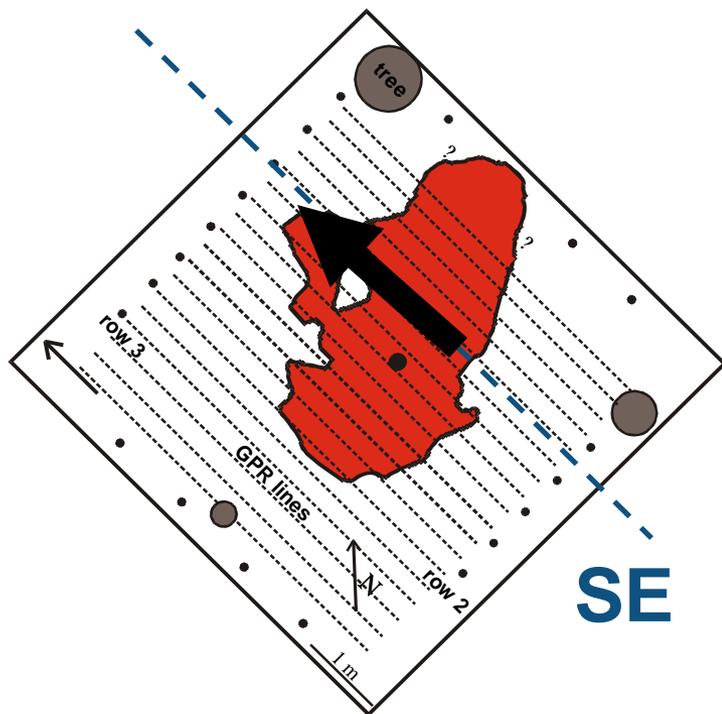


Geometria della sorgente

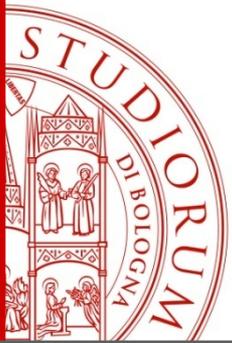
DNAPL riflettore geo-radar

NW

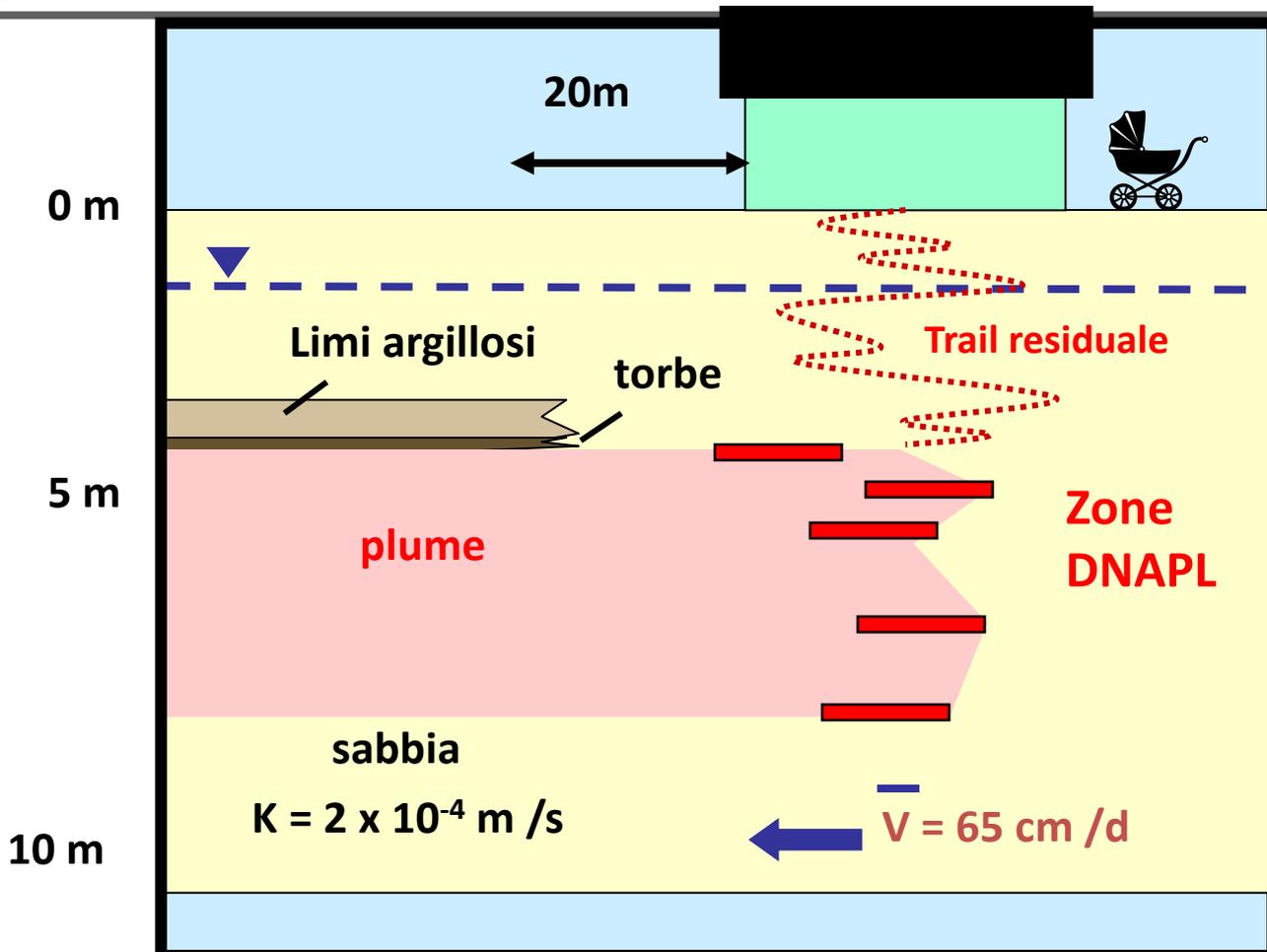
SE



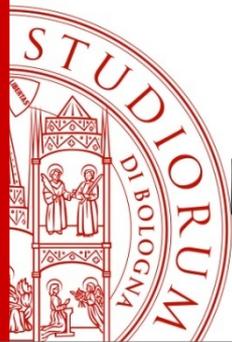
K. Laukonen, 2001



Fattori geologici Eterogeneità per stratificazione

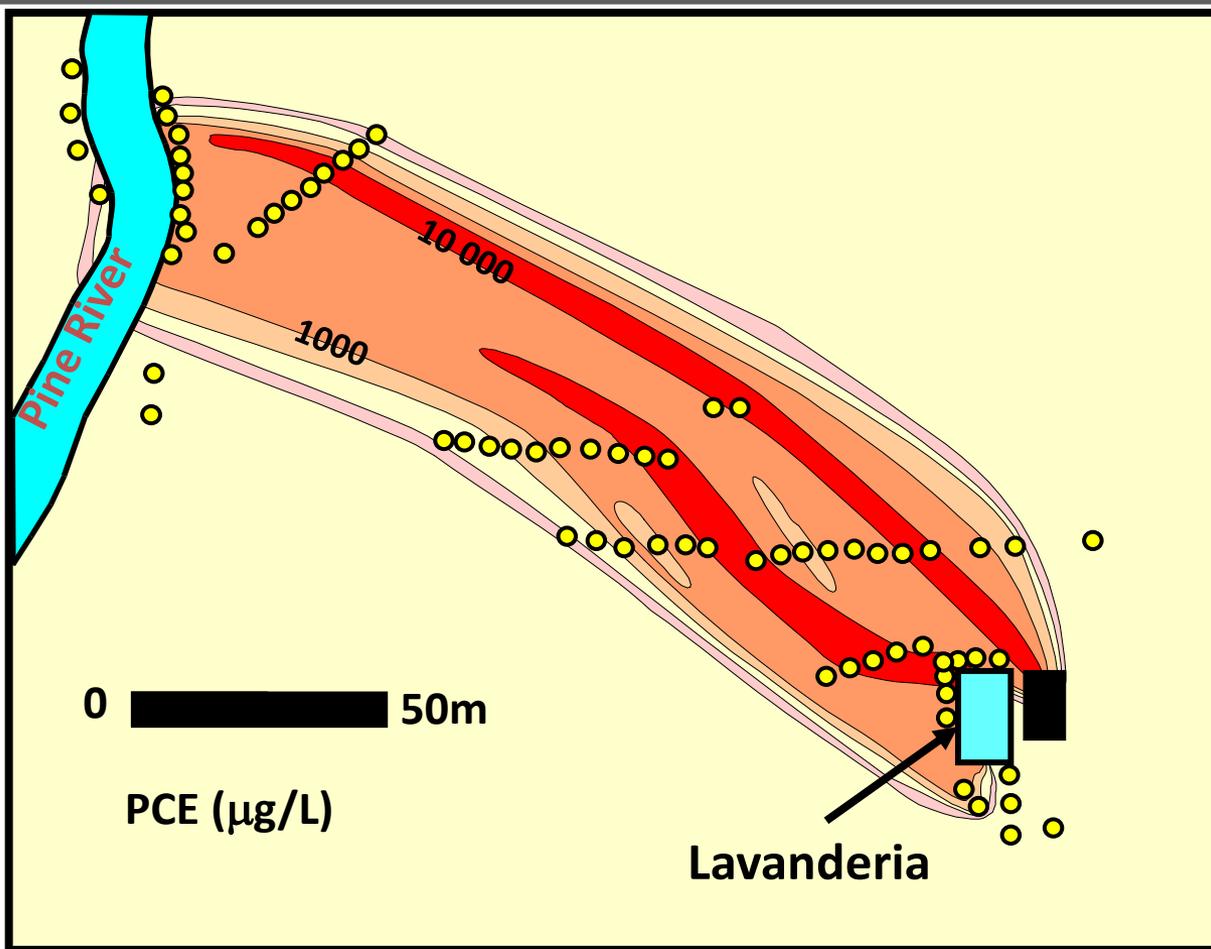


Guilbeault, 1999

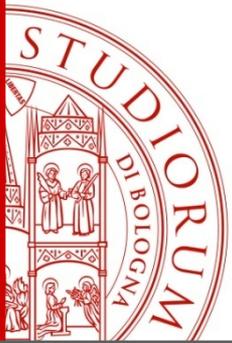


Plume di Angus (Ontario)

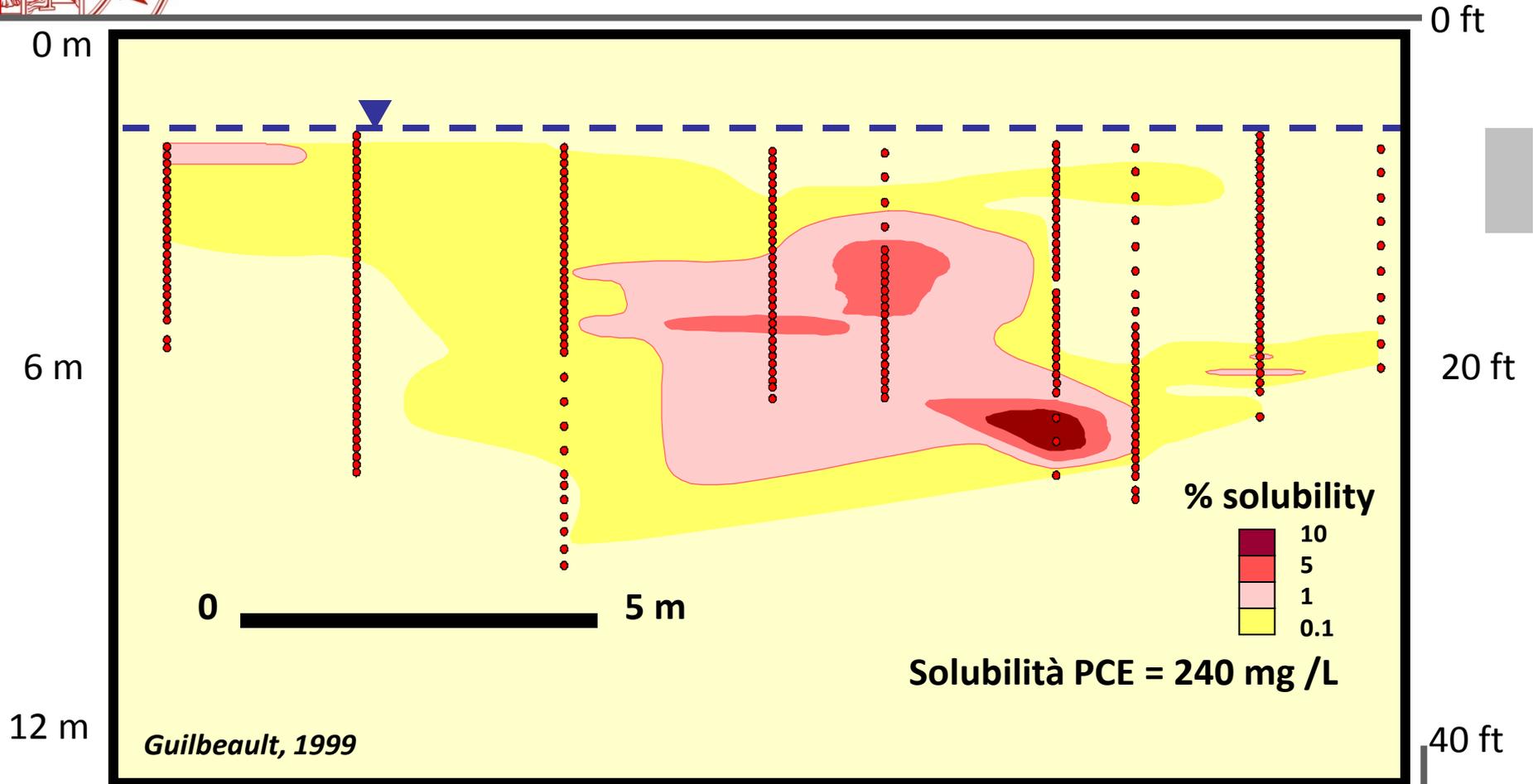
Formazione di mini-plumes ("pencil plumes")

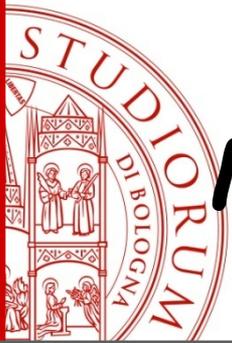


Dati da Pitkin (1994),
Writt (1996),
Conant (2001),
Guilbeault (1999)

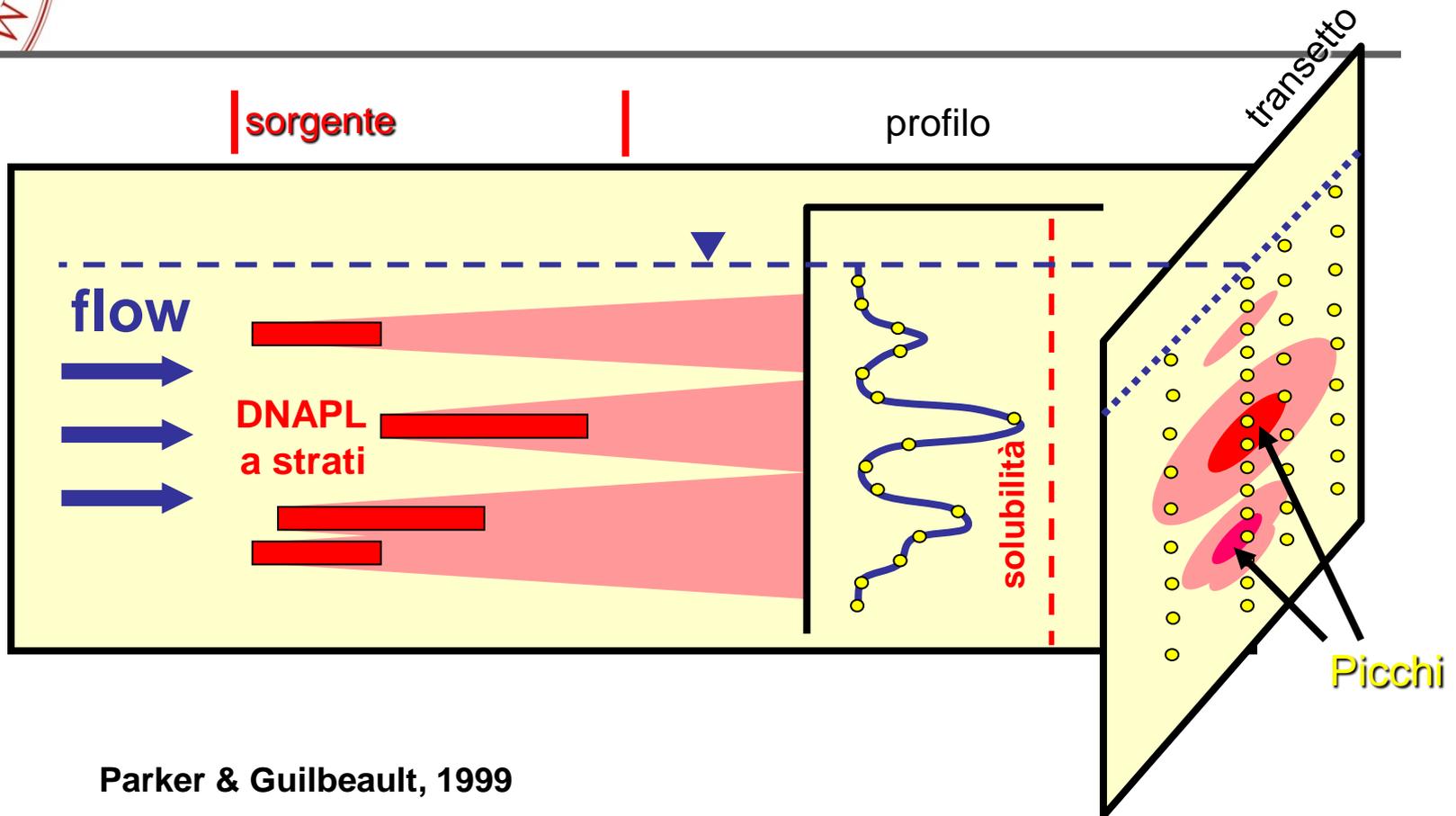


Transetto

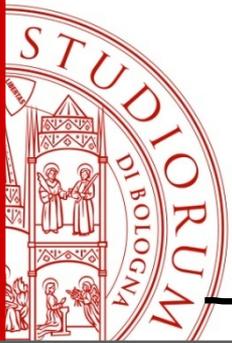




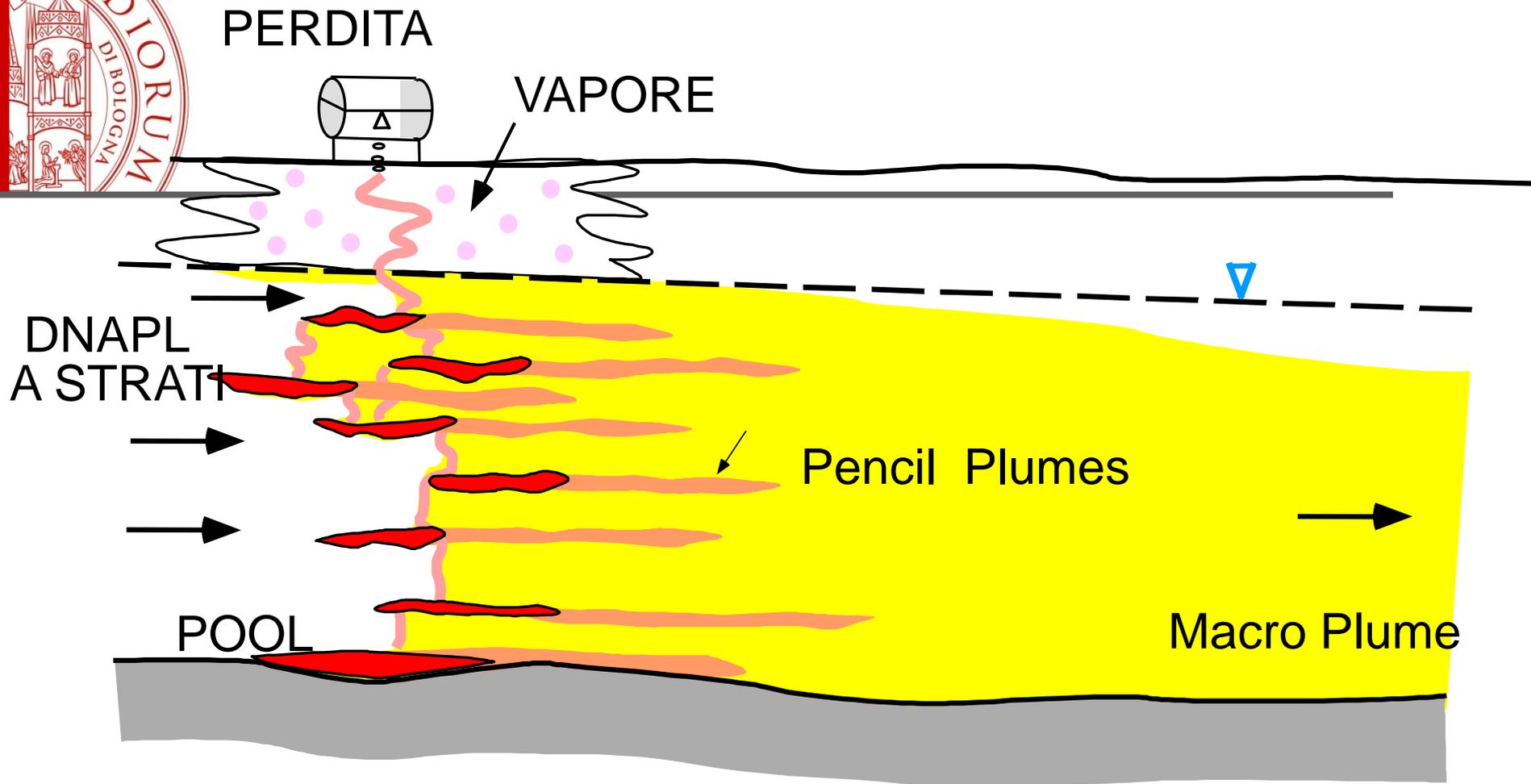
Modello concettuale alternativo



Parker & Guilbeault, 1999



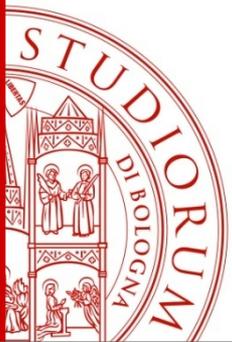
Pencil plumes



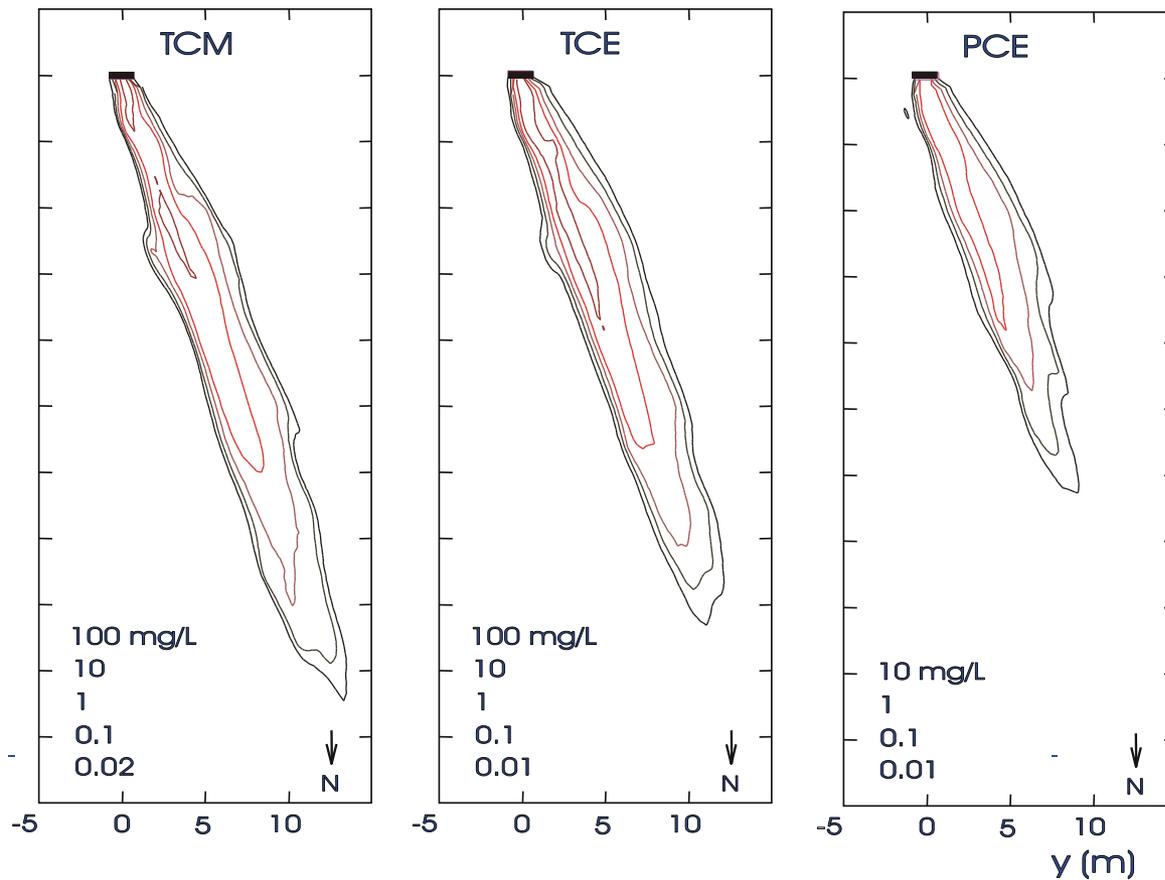
SORGENTE

MIXING

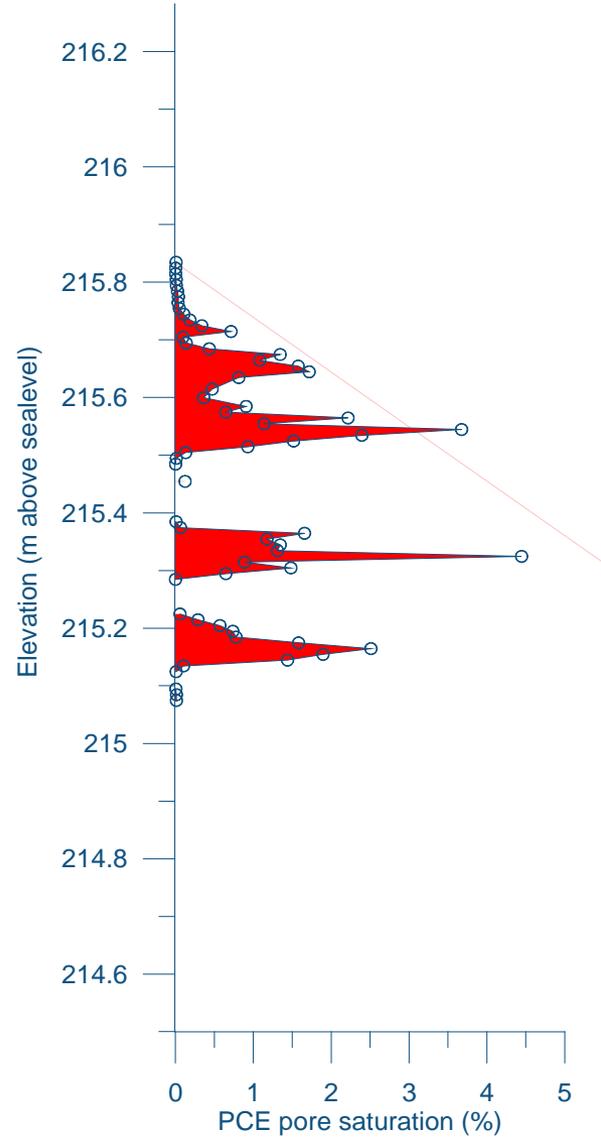
DISPERSIONE DEL PLUME

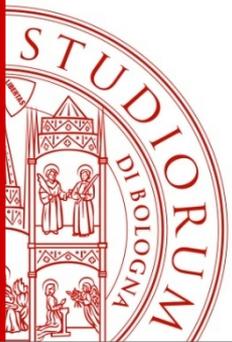


PENCIL PLUMES RICREATI A BORDEN



Elevata variabilità nella distribuzione del grado di saturazione relativo con passo di campionamento 1 cm



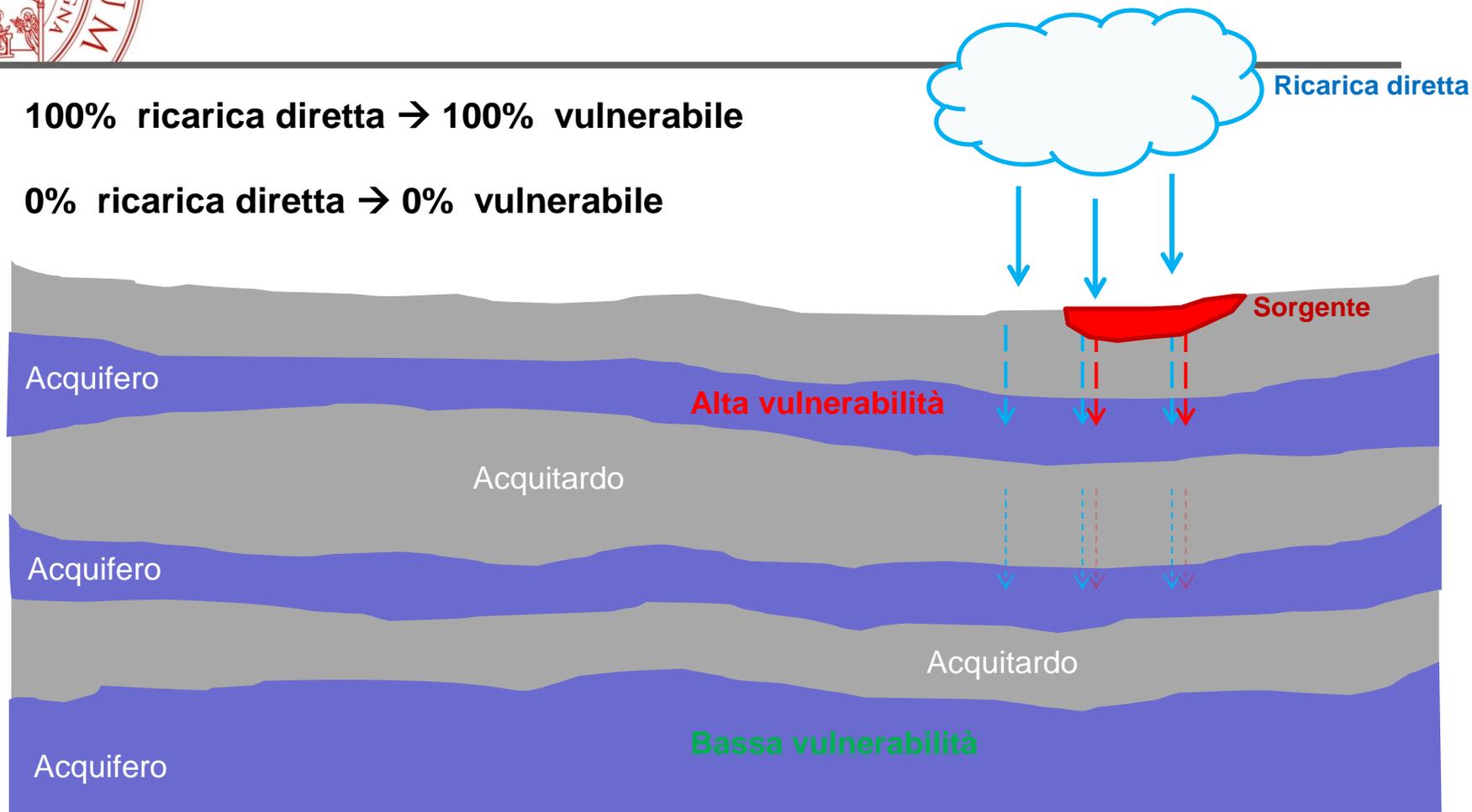


DNAPL ed acquitardi

Il modello classico è adeguato?

100% ricarica diretta → 100% vulnerabile

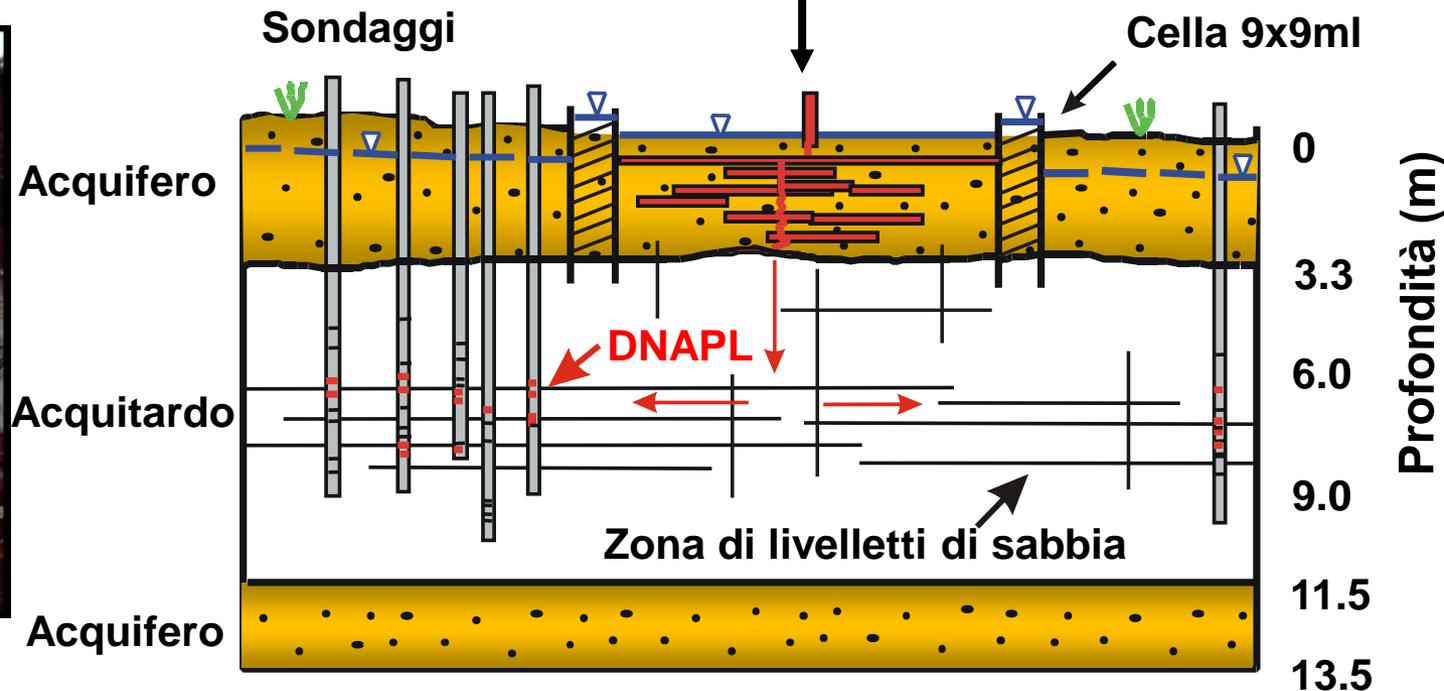
0% ricarica diretta → 0% vulnerabile

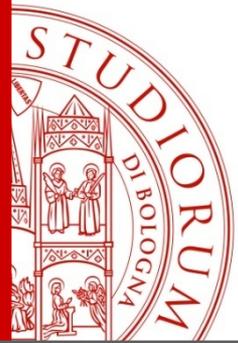


Approccio sperimentale al Borden site



INIEZIONE





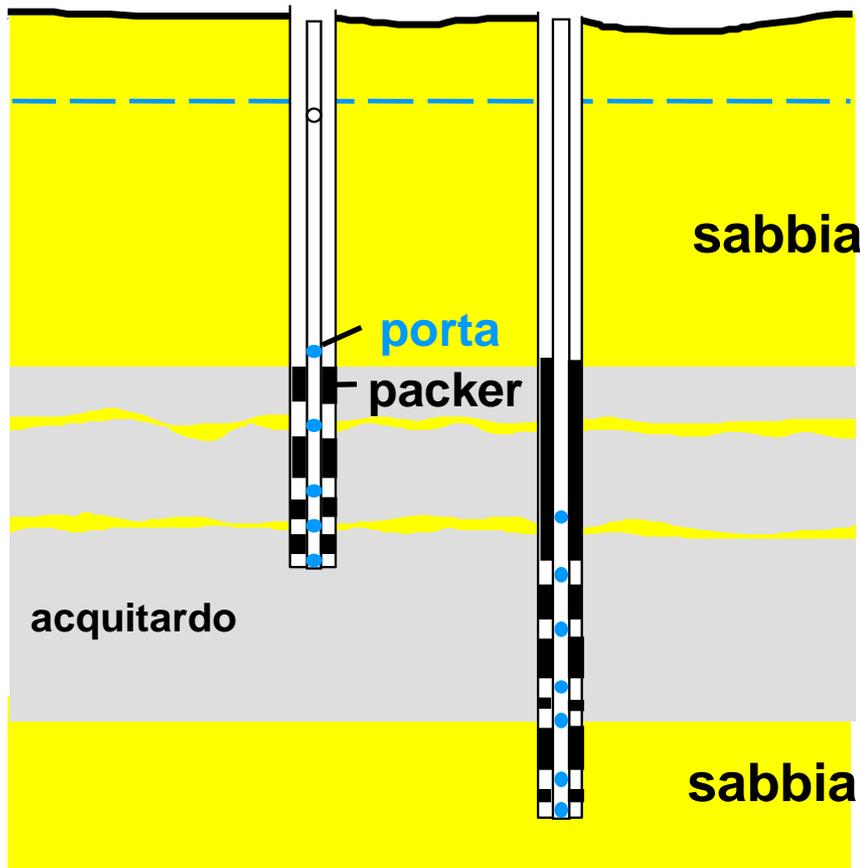
Borden site

Profilo di carico idraulico

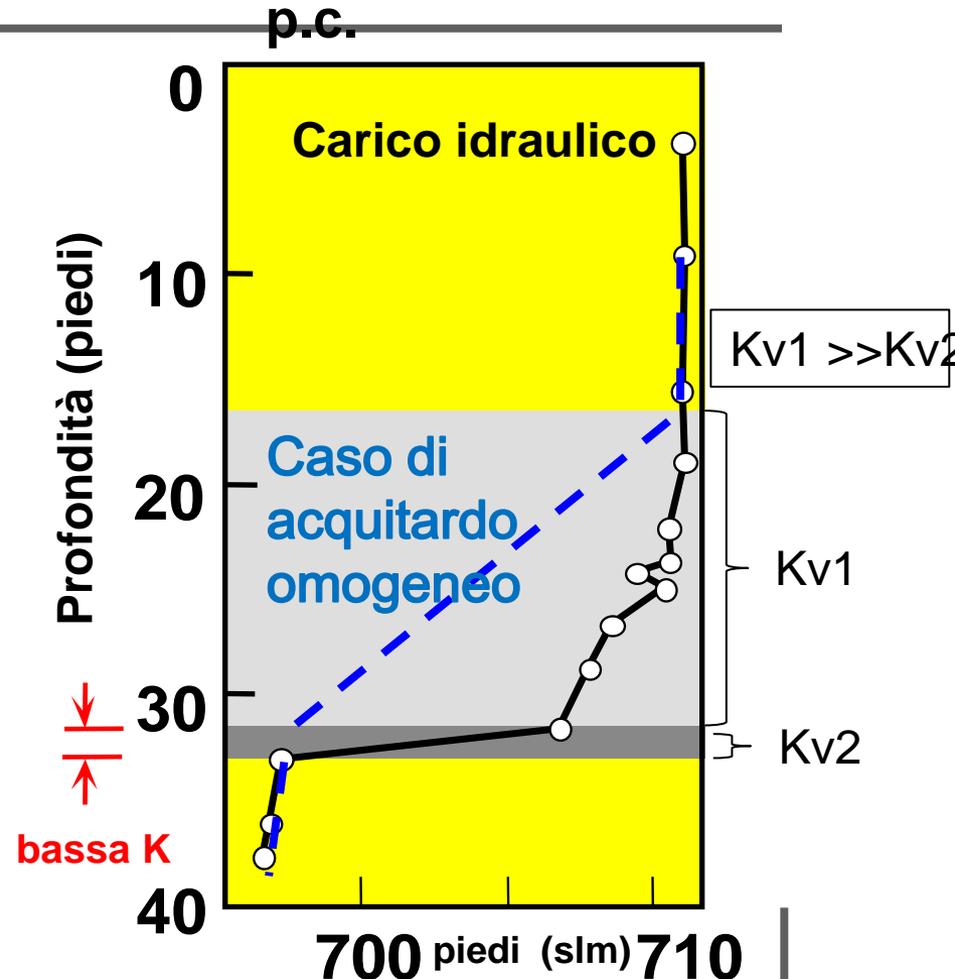
La resistenza idraulica è concentrata in 60 cm

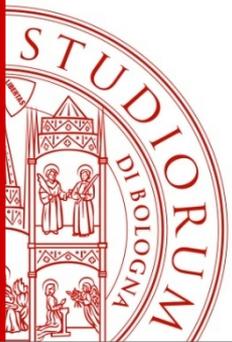
"The shape of the head profile is everything" J.A.Cherry

CMT MLS

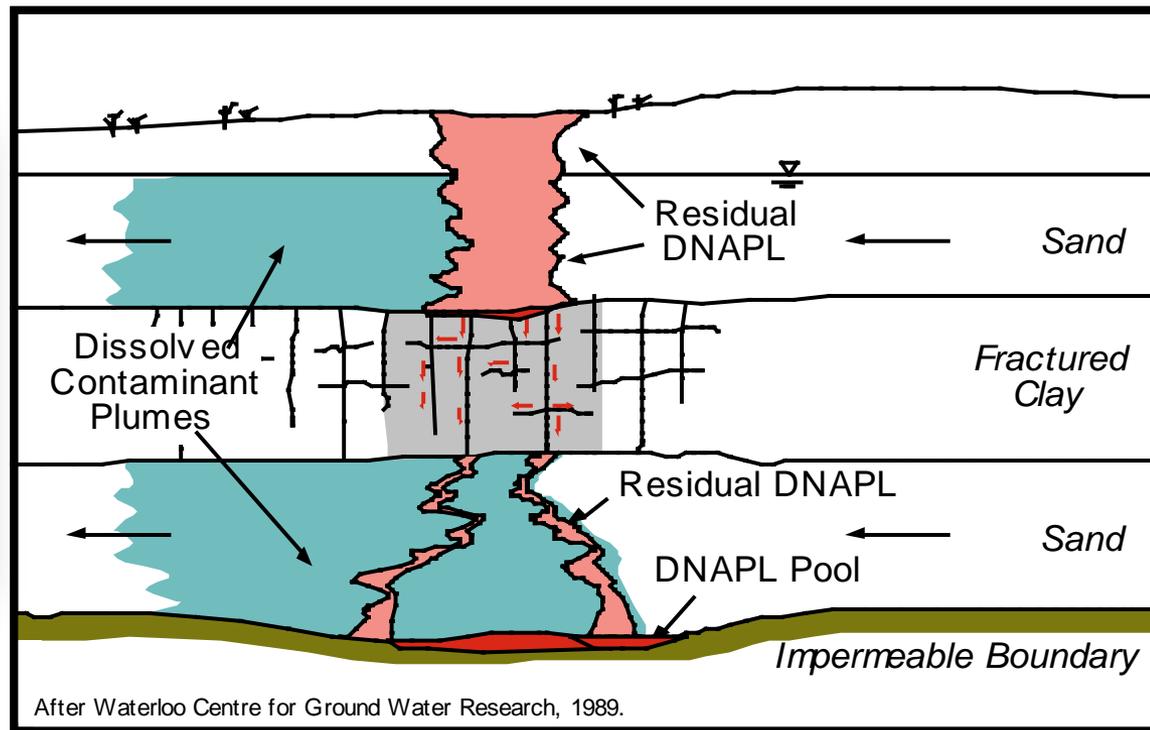
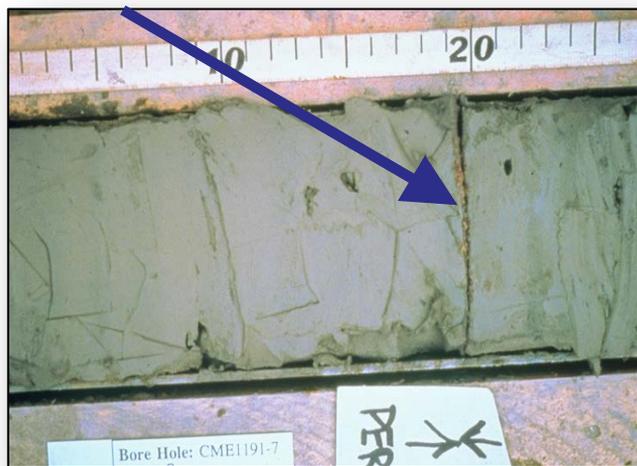


(Meldrum, 1999)

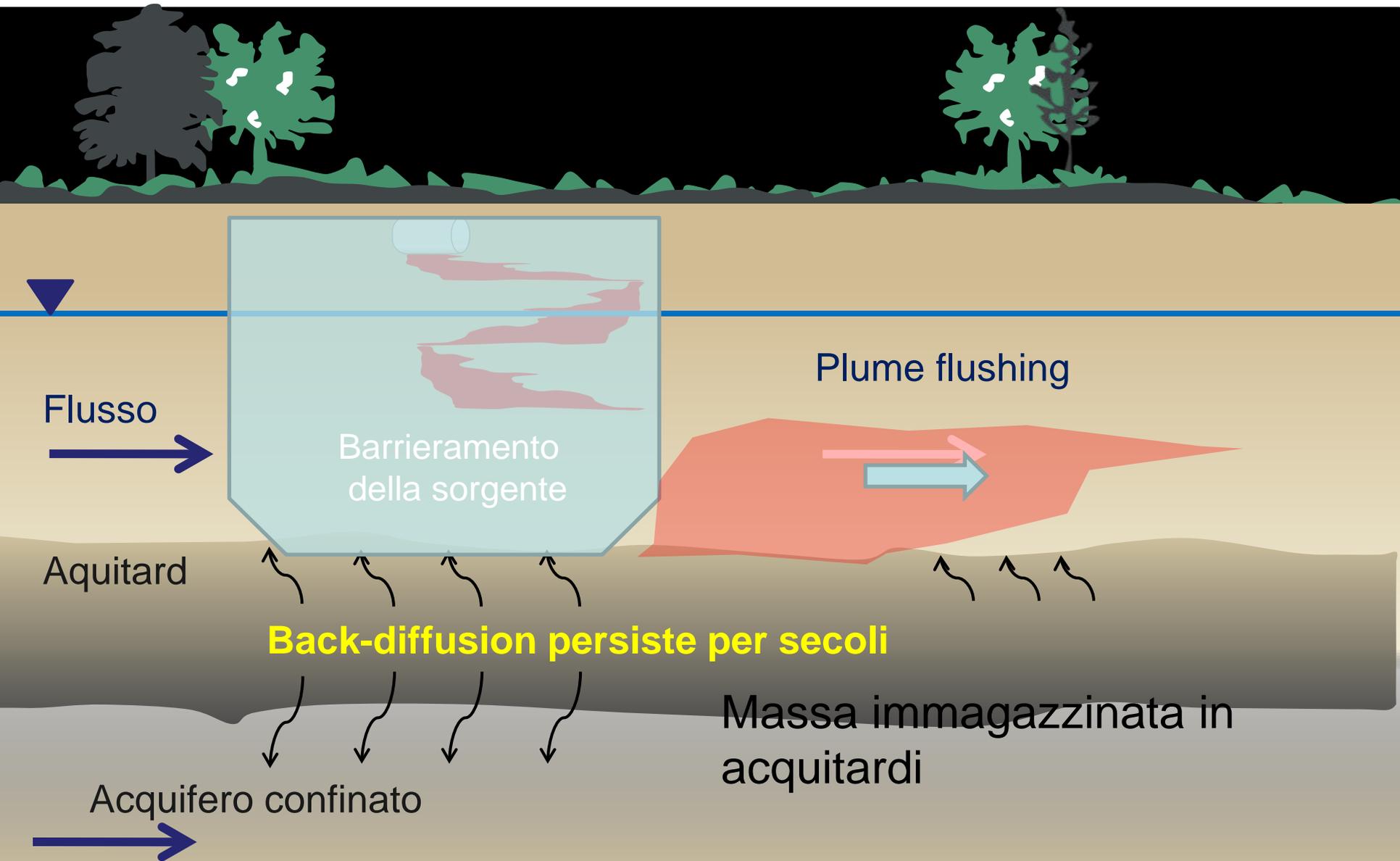




Acquitardi non sono barriere per i DNAPL

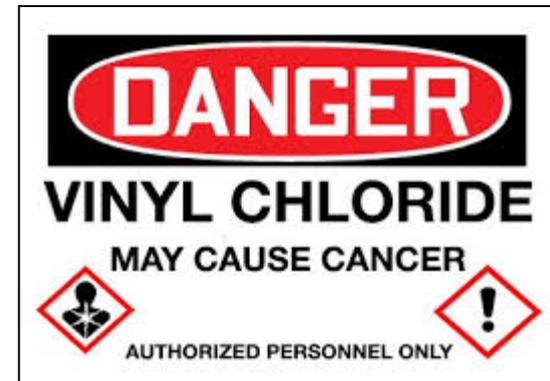
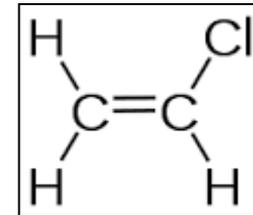
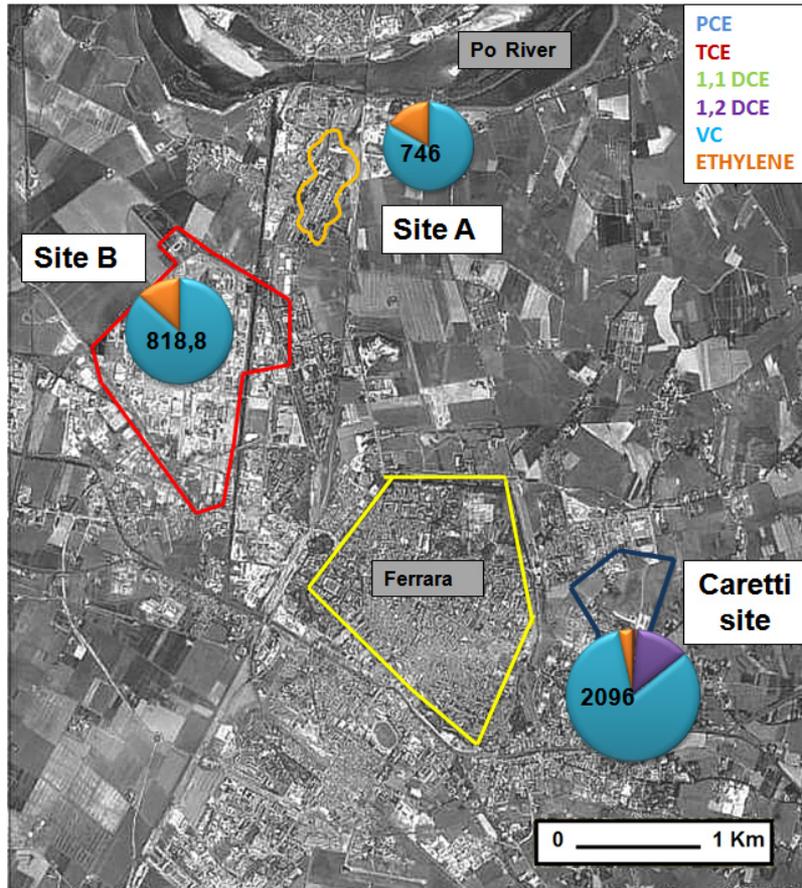
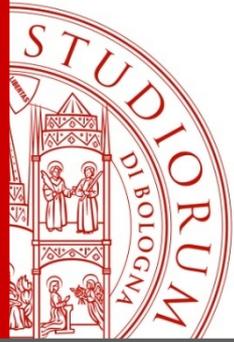


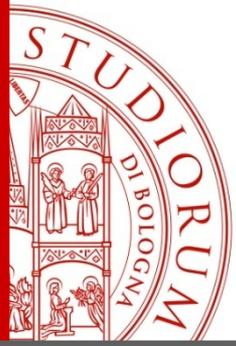
Persistenza del plume per back-diffusion dall'acquitrardo



Condizioni di formazione del Cloruro di Vinile

Peculiarità del sito di Ferrara





Le sfide

1 - Approccio multilivello della caratterizzazione

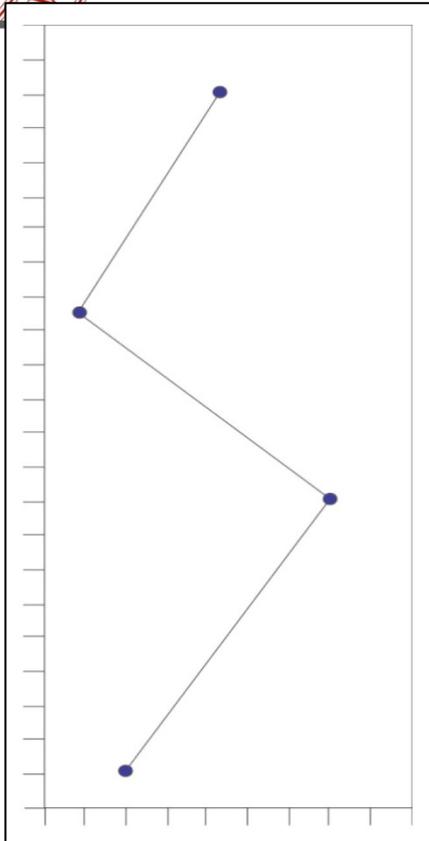
“To exploit at the most one single borehole is better than use several simple boreholes”

J.A. Cherry and B.L. Parker

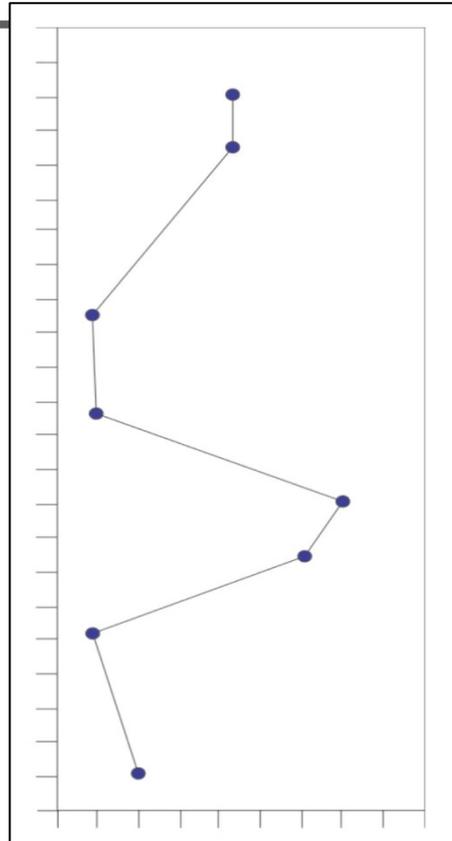
Profili verticali di dati

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

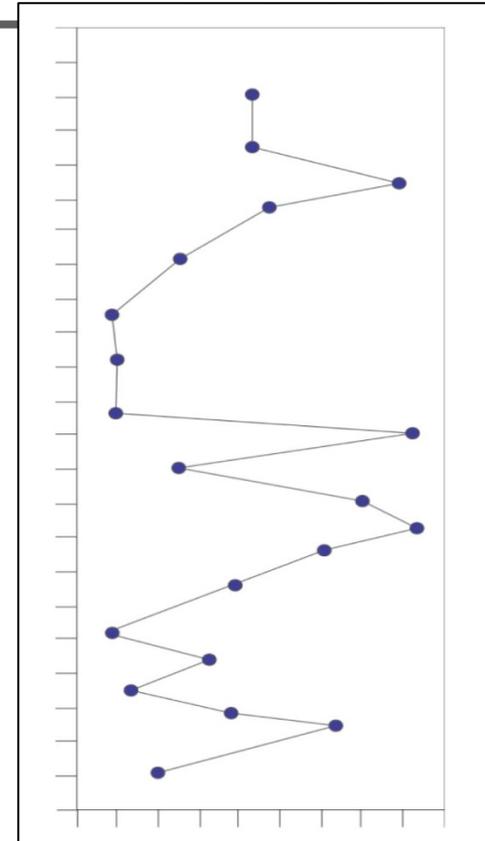
4 livelli



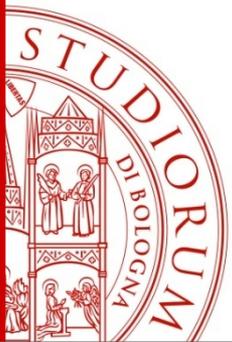
8 livelli



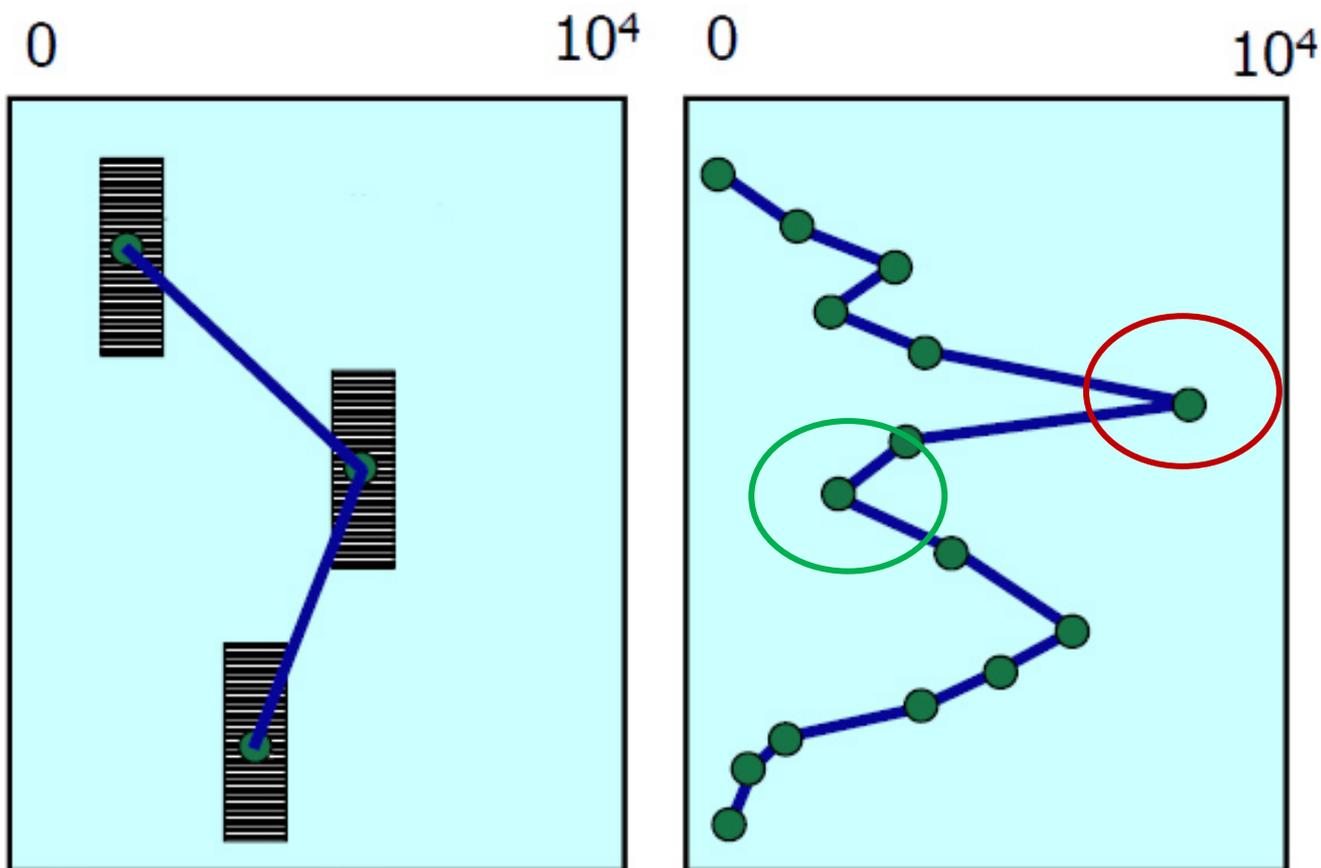
20 livelli

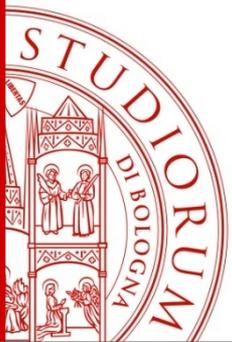


Profondità



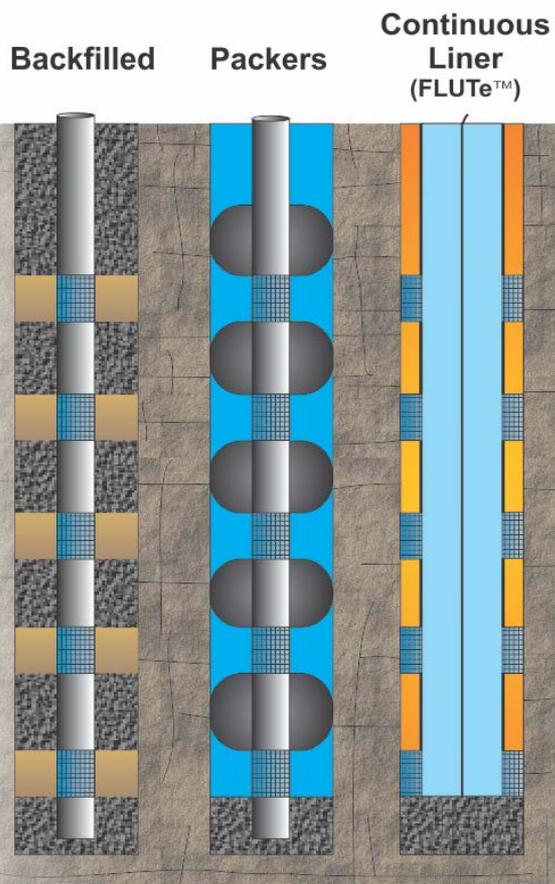
Evidente inadeguatezza dei piezometri "classici"





Monitoraggio multilivello a profondità discreta (MLS)

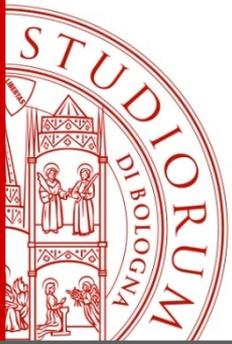
Cherry, 2000



Sistema multilivello

(MLS)

Partizione di un
singolo foro in porte
discrete per il
campionamento



MLS commerciali disponibili sul mercato

Westbay



Water
FLUTE[™]

Flexible Liner Underground Technologies, Ltd. Co.

A medley of innovative designs



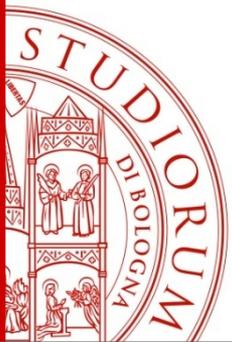
Waterloo
Solinst[®]



CMT
Solinst[®]



UNIVERSITÀ DI BOLOGNA

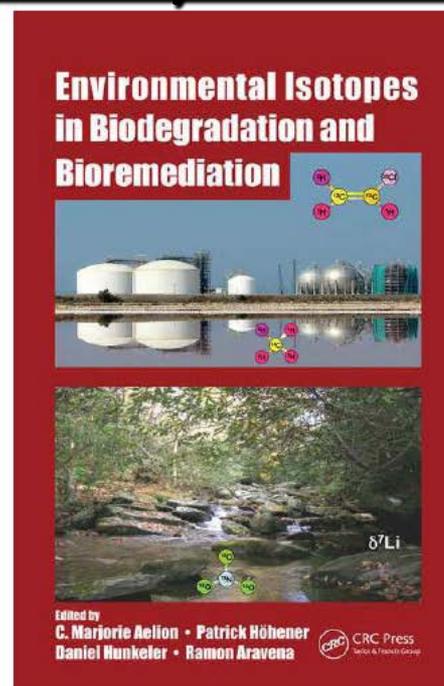
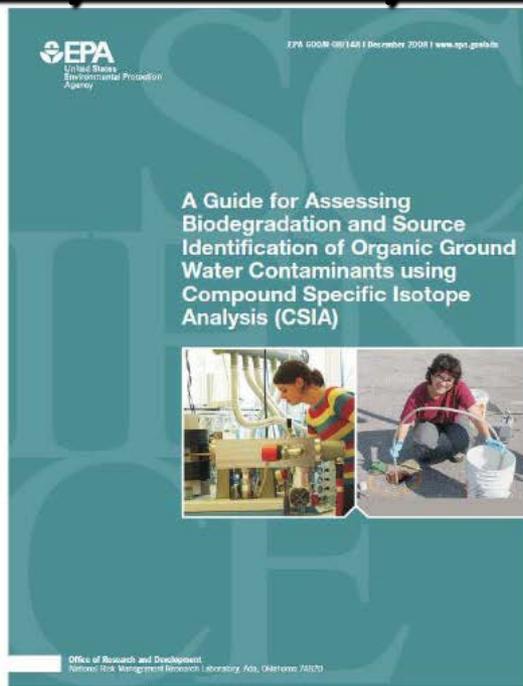


Le sfide

2- "Pays polluter principe"

CSIA

Compound Specific Isotope Analysis

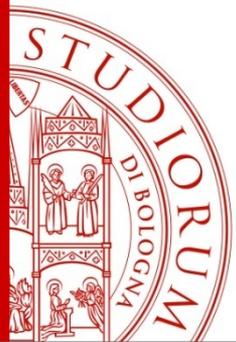


<http://nepis.epa.gov/Exe/ZyPDF.cgi?Dockey=P1002VAI.PDF>

RAPPORTO ISOTOPICO MEDIO DI COMPOSTI NATURALI DEL CARBONIO

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

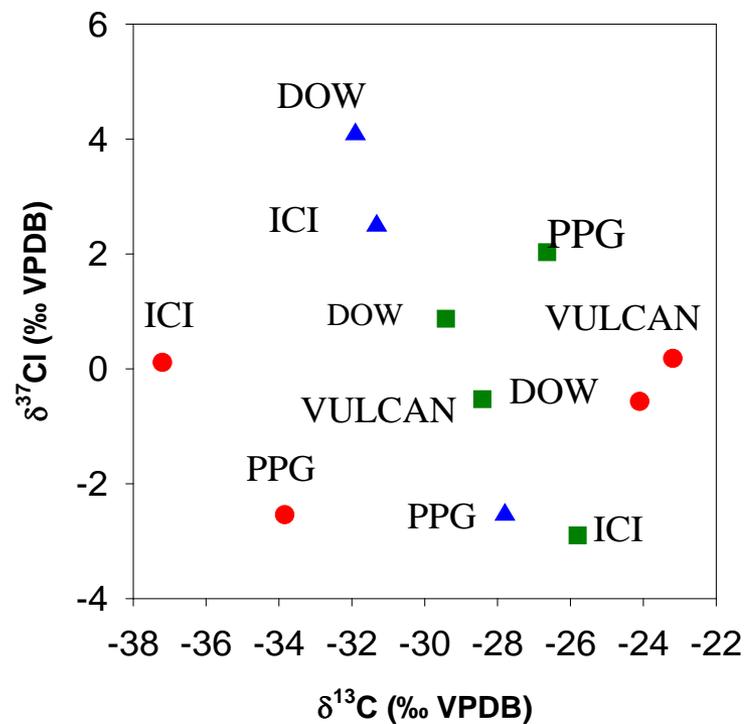
	${}^{13}\text{C}/{}^{12}\text{C}$	$\delta^{13}\text{C}$	
Carbonati	0.01124	0	↑ Più PESANTE ${}^{13}\text{C}$
CO ₂ atmosferica	0.01116	-7	
Biomassa	0.01096	-25	
Metano biogenico	0.01045	-70	



Firma isotopica di solventi in commercio



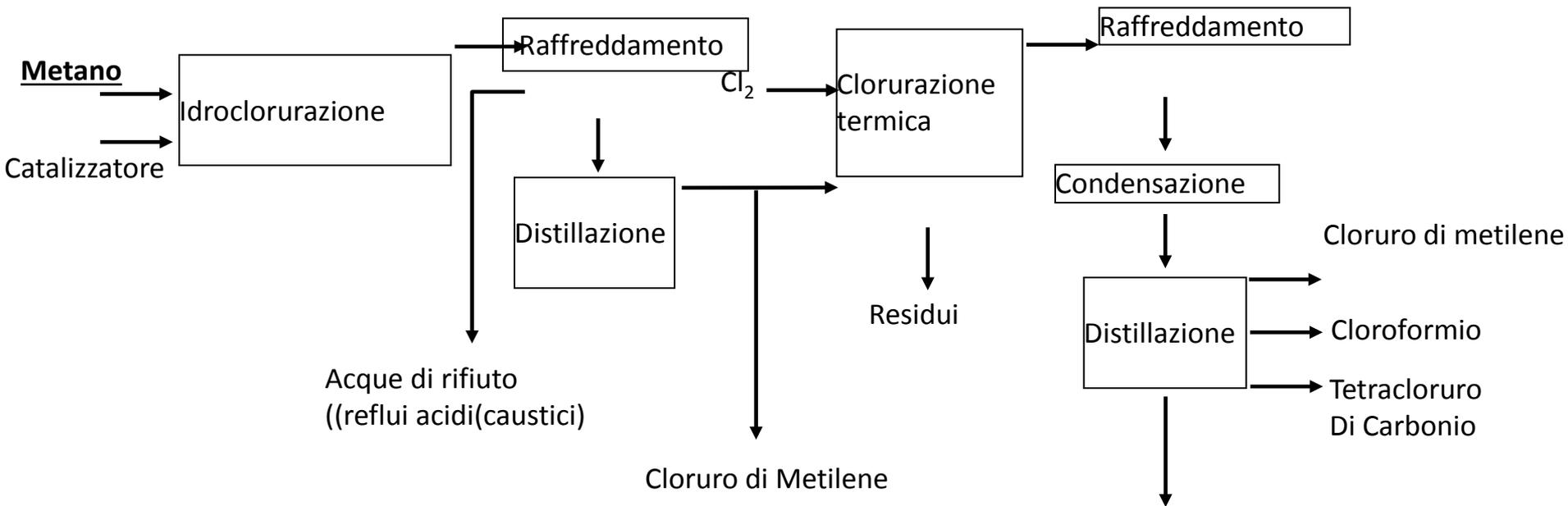
- Tetrachloroethene (PCE)
- ▲ Trichloroethene (TCE)
- 1,1,1-Trichloroethane (TCA)



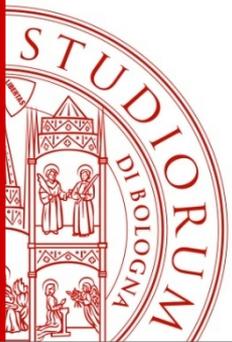
Van Warmerdam et al., 1995

PROCESSO PRODUTTIVO TIPICO DI UNO STABILIMENTO DI CLORO-METANI

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

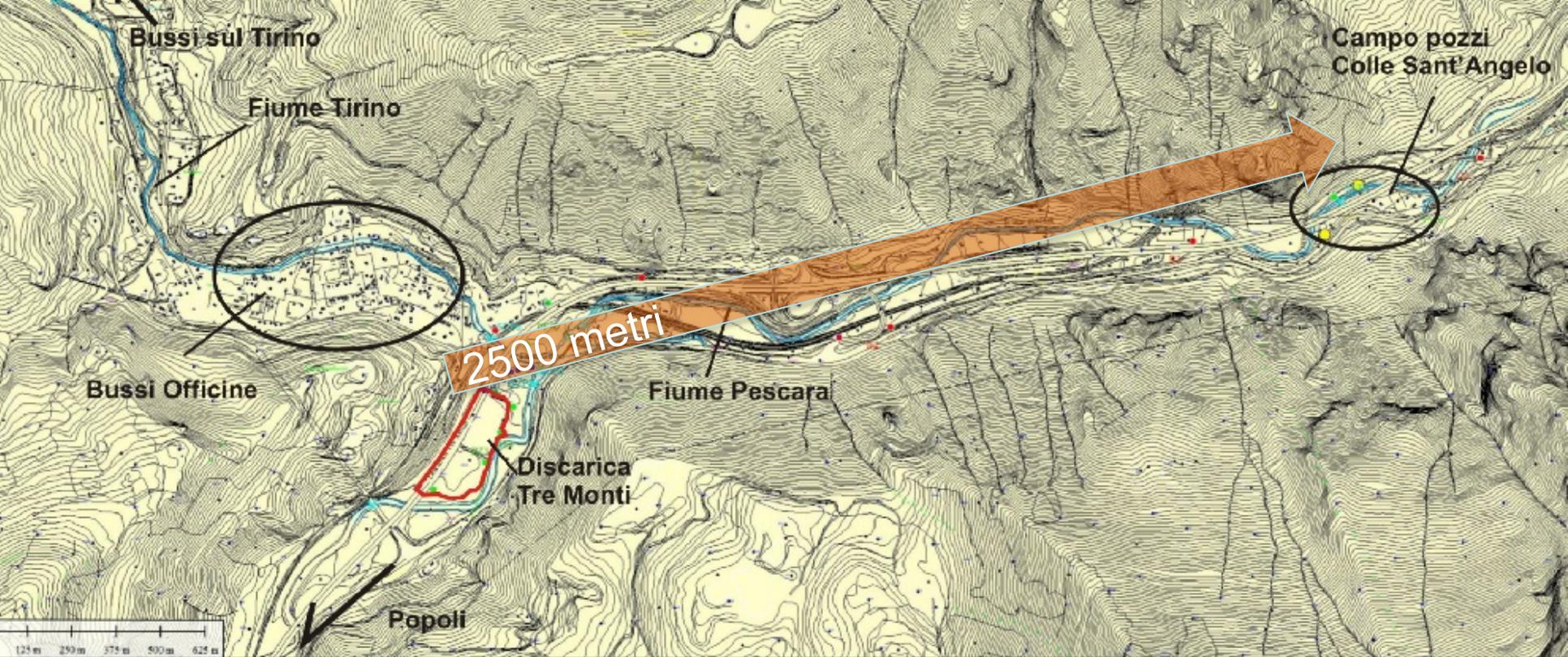


**RIFIUTI: PECCI CLORURATE
MORCHIE LIQUIDO/OLEOSE RICCHE DI
PCE, TCE, ESACLOROETANO,
TETRACLORURO DI CARBONIO
Etc..**



Sito "Caretti" (Ferrara) Sito "I Tre Monti" (Bussi sul Tirino)

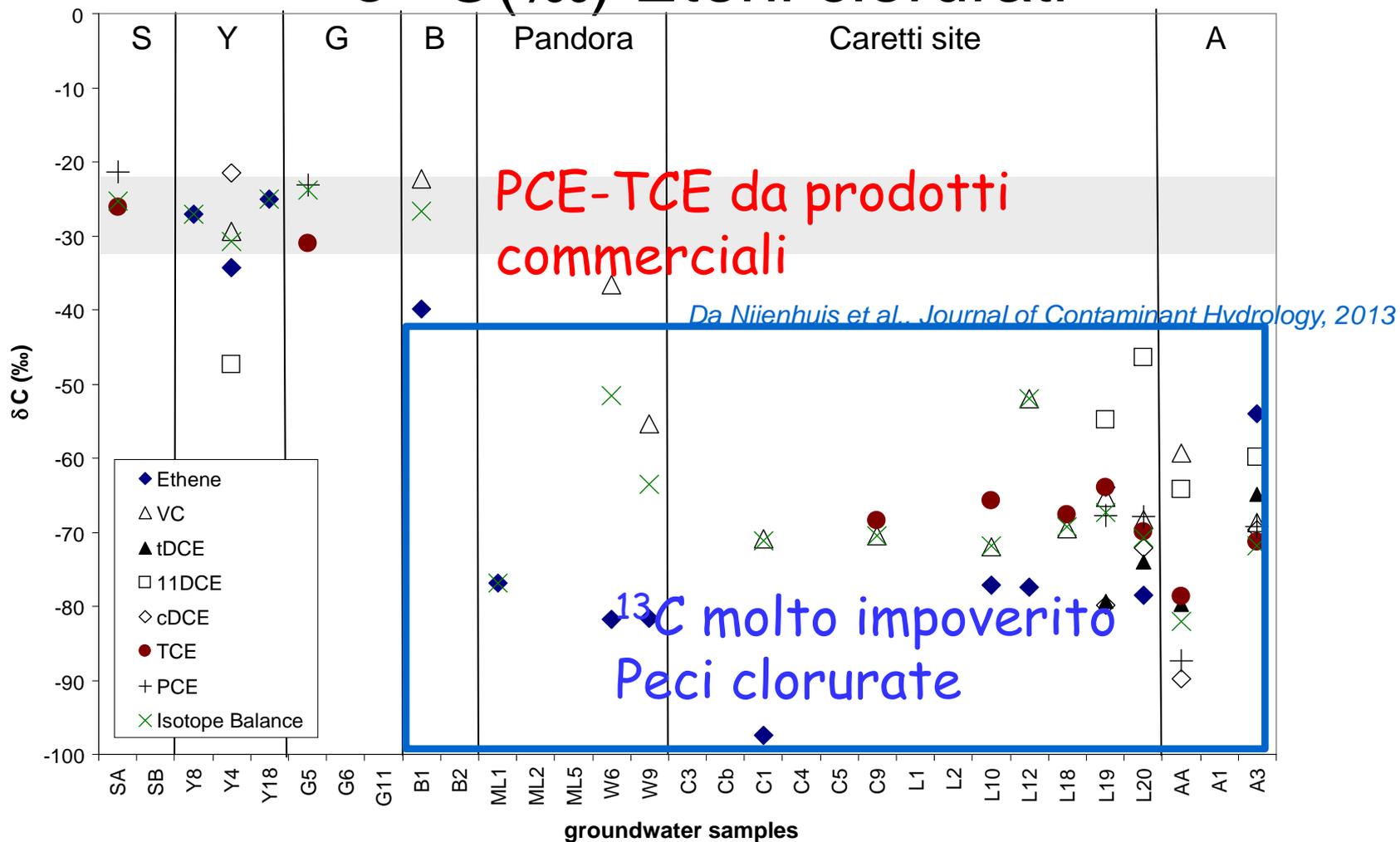


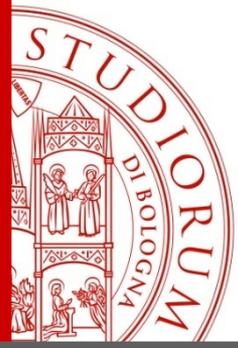


Sito di Bussi sul Tirino (Pescara)

Fingerprinting isotopico siti di Ferrara

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



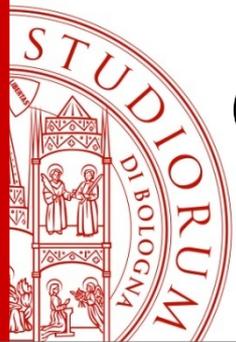


Le sfide

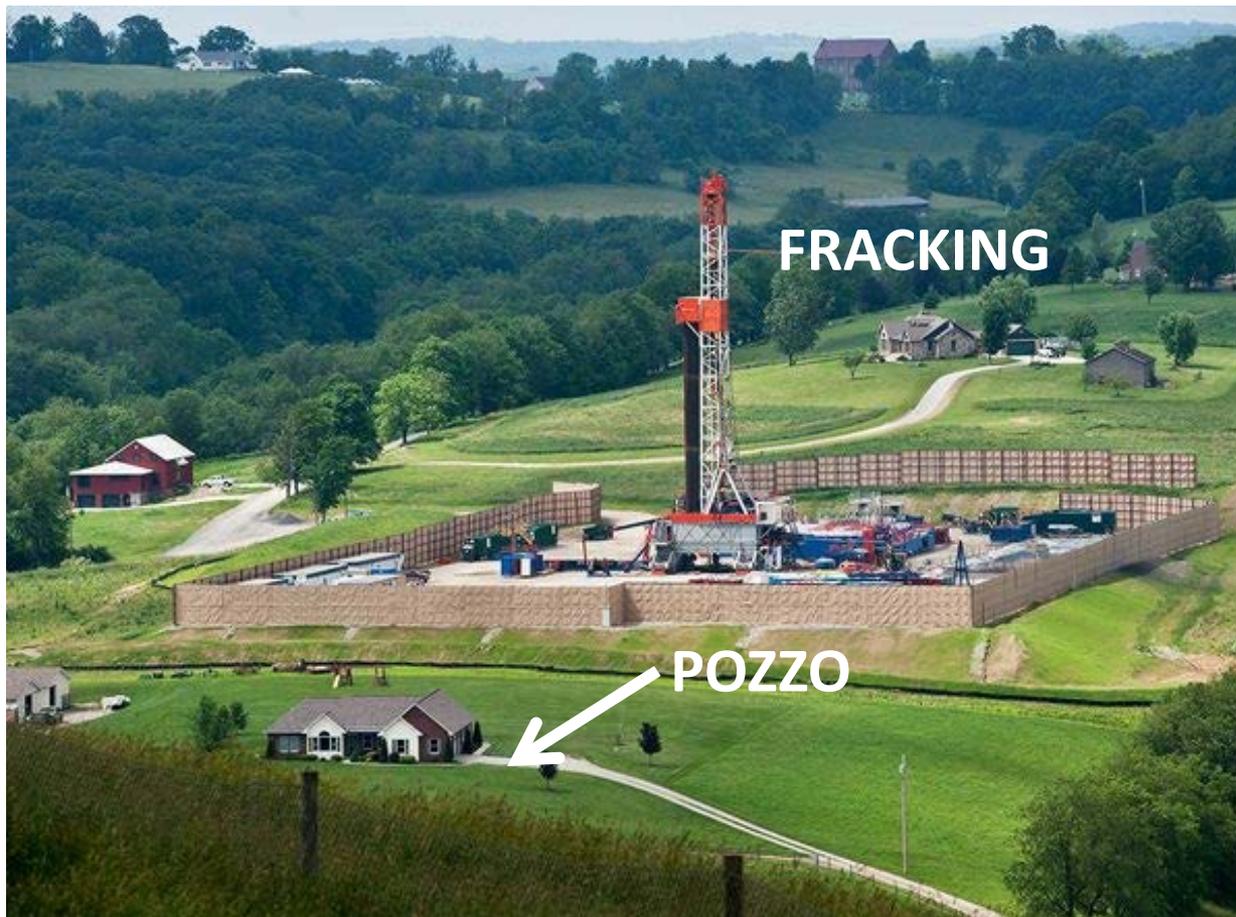
3-Assimilation Capacity (Capacità di assimilazione)

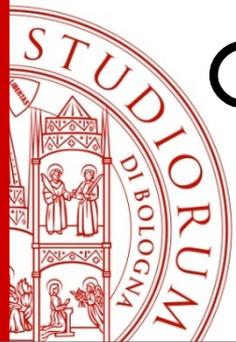
Definizione: la capacità di un recettore idrico (lago, fiume, mare, acquifero, groundwater dependent ecosystem) di assimilare acque di rifiuto o sostanze tossiche **senza effetti dannosi per la biocenosi e gli esseri umani che consumano l'acqua**

Cherry (2014)



Quale è la distanza di sicurezza?

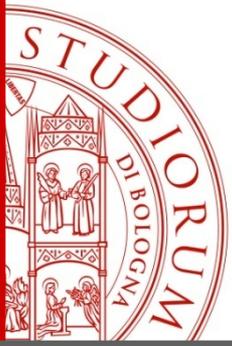




Quale concentrazione posso dichiarare "sostenibile/assimilabile" in falda

- Dispersione
- Diffusione
- Adsorbimento (reversibile)
- Reazioni chimiche (alcune reversibili)
- Degradazione biologica
- Volatilizzazione

I processi sono sito specifici e legati al sistema idrogeologico



CONSIDERAZIONI CONCLUSIVE

- 1) L'idrogeologia dei solventi clorurati riflette situazioni di estrema complessità che richiedono modelli concettuali ed approcci del tutto innovativi*
- 2) Oltre che strumenti innovativi (MLS, isotopi) la caratterizzazione accurata della geologia e idrogeologia del sito diventa essenziale*
- 3) NON POSSIAMO PENSARE DI AVERE LE RISORSE PER BONIFICARE TUTTI GLI ACQUIFERI CONTAMINATI DA SOLVENTI. URGE UNA RIFLESSIONE SUL CONCETTO DI PUNTO DI CONFORMITA' ALLA CSC AL LIMITE DI PROPRIETA' ED UN INCANALARE LE RISORSE SECONDO UN A CLASSIFICA DI PRIORITA' CONDIVISA DA TAVOLI TECNICI DECISORI*

Ringraziamenti

Alessandro Amorosi

UNIVERSITÀ DI BOLOGNA

Ramon Aravena

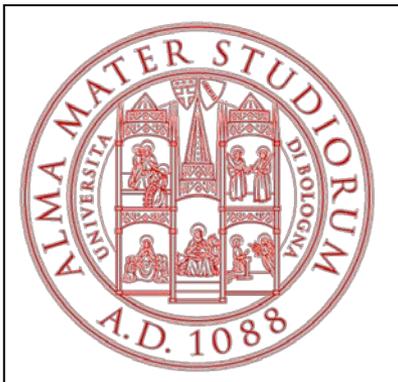
UNIVERSITÀ DI WATERLOO

Hans Richnow, Ivonne Nijenhuis

UFZ LEIPZIG

Beth Parker

Università di Guelph



University of Guelph, Ontario



The Centre for Applied
Groundwater Research

INTERNATIONAL ASSOCIATION
OF HYDROGEOLOGISTS
42ND CONGRESS



ROME, ITALY
SEPTEMBER 13th-18th, 2015
ANGELICUM CONGRESS CENTRE

www.iah2015.org



AQUA 2015

HYDROGEOLOGY: BACK TO THE FUTURE!

MAIN TOPICS

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

in scientific partnership with



Food and Agriculture Organization
of the United Nations



United Nations
Educational, Scientific and
Cultural Organization



International
Hydrological
Programme

with the high patronage of



PRESIDENZA DELLA
REPUBBLICA ITALIANA

President of the Italian Republic



MINISTERO DELL'AMBIENTE
E DELLA TUTELA DEL TERRITORIO E DEL MARE
Minister of the Environment
and Protection of Land and Sea