# Campionatori passivi nel controllo e monitoraggio di acque sotterranee: stato dell'arte e prospettive applicative

S. Chiavarini, P. Massanisso, C. Ubaldi

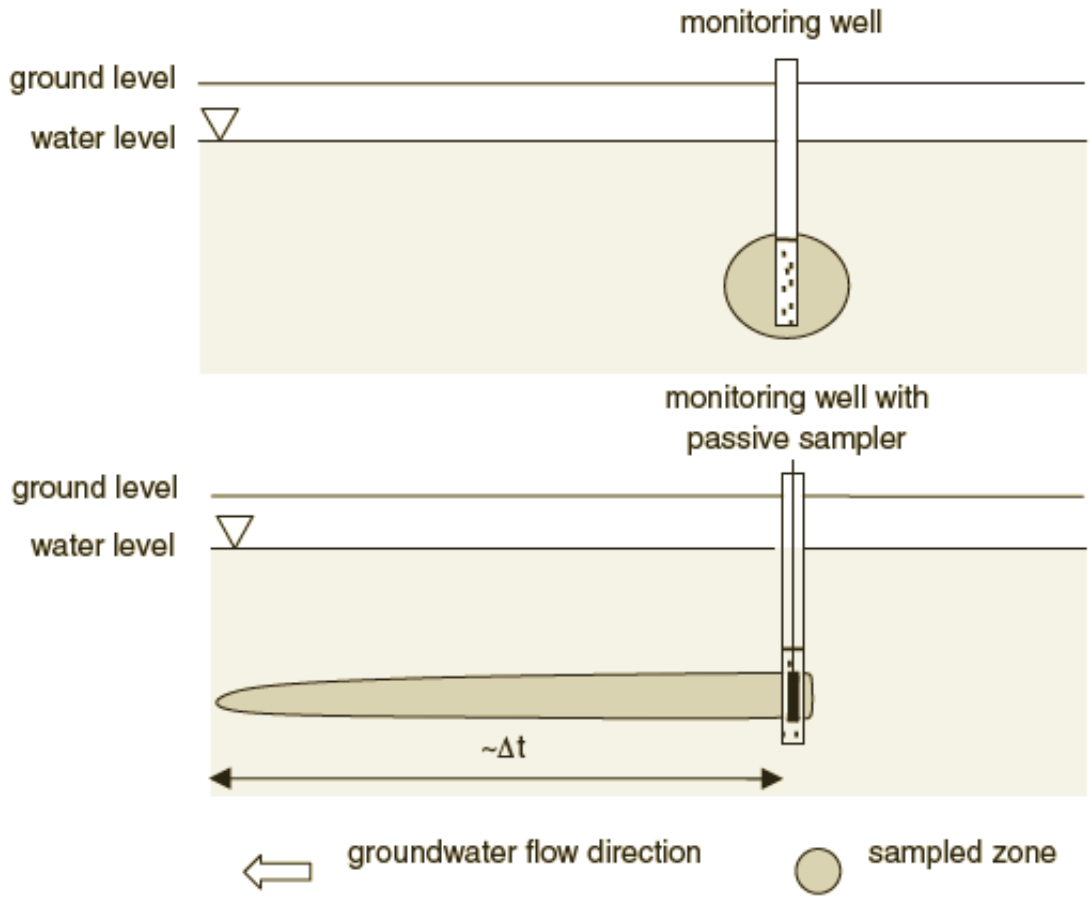
ENEA *UTPRA*

# Campionamento passivo - pro

- Indipendenza da sorgenti di energia (es. pompe)
- Dato integrato nel tempo
- Bassi limiti di concentrazione apprezzabili
- Semplicità operativa e di implementazione
- Minor costo globale (?)

# Campionamento passivo - contro

- Difficile valutazione delle variabili al contorno
- Dati quantitativi non sempre possibili (calibrazione)
- Scelta del tipo di campionatore non banale
- Metodologie non normate o esplicitamente previste (es. per WFD)




**active** sampling

-

- snapshot
- in combination with Darcy water flux measurement
- higher costs

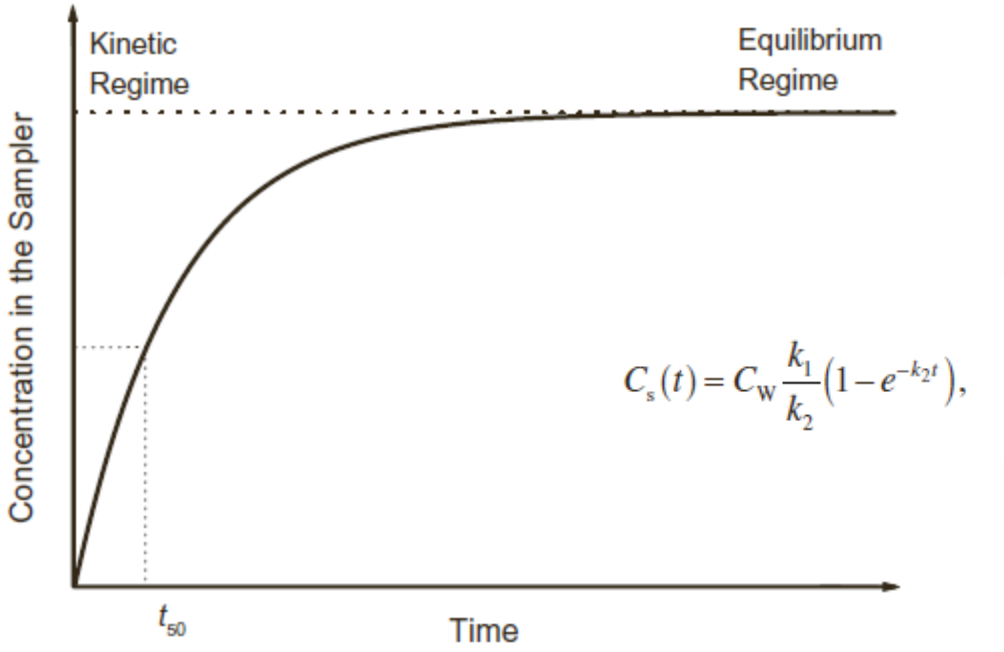
**passive** sampling

+

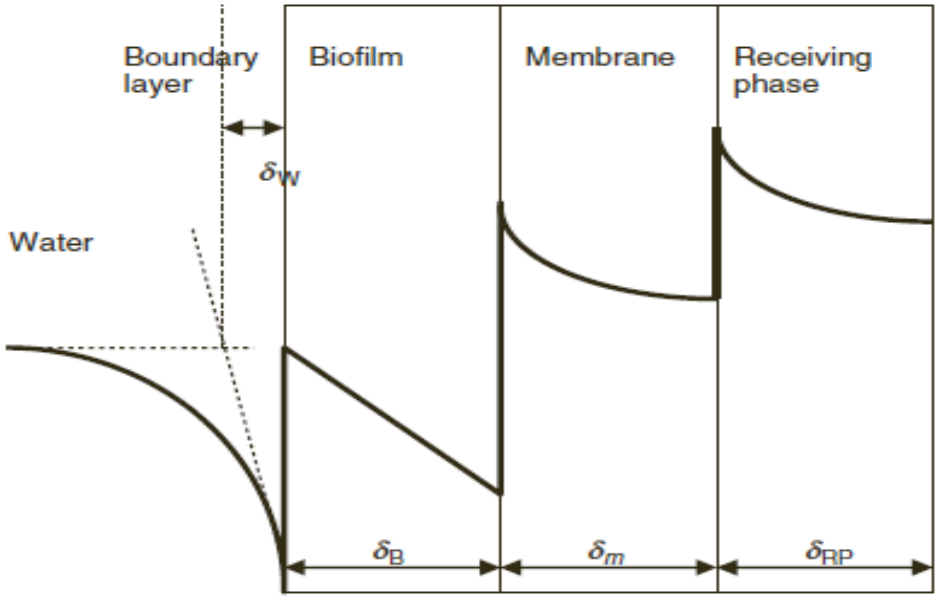
- more representative
- long-term monitoring
- lower costs

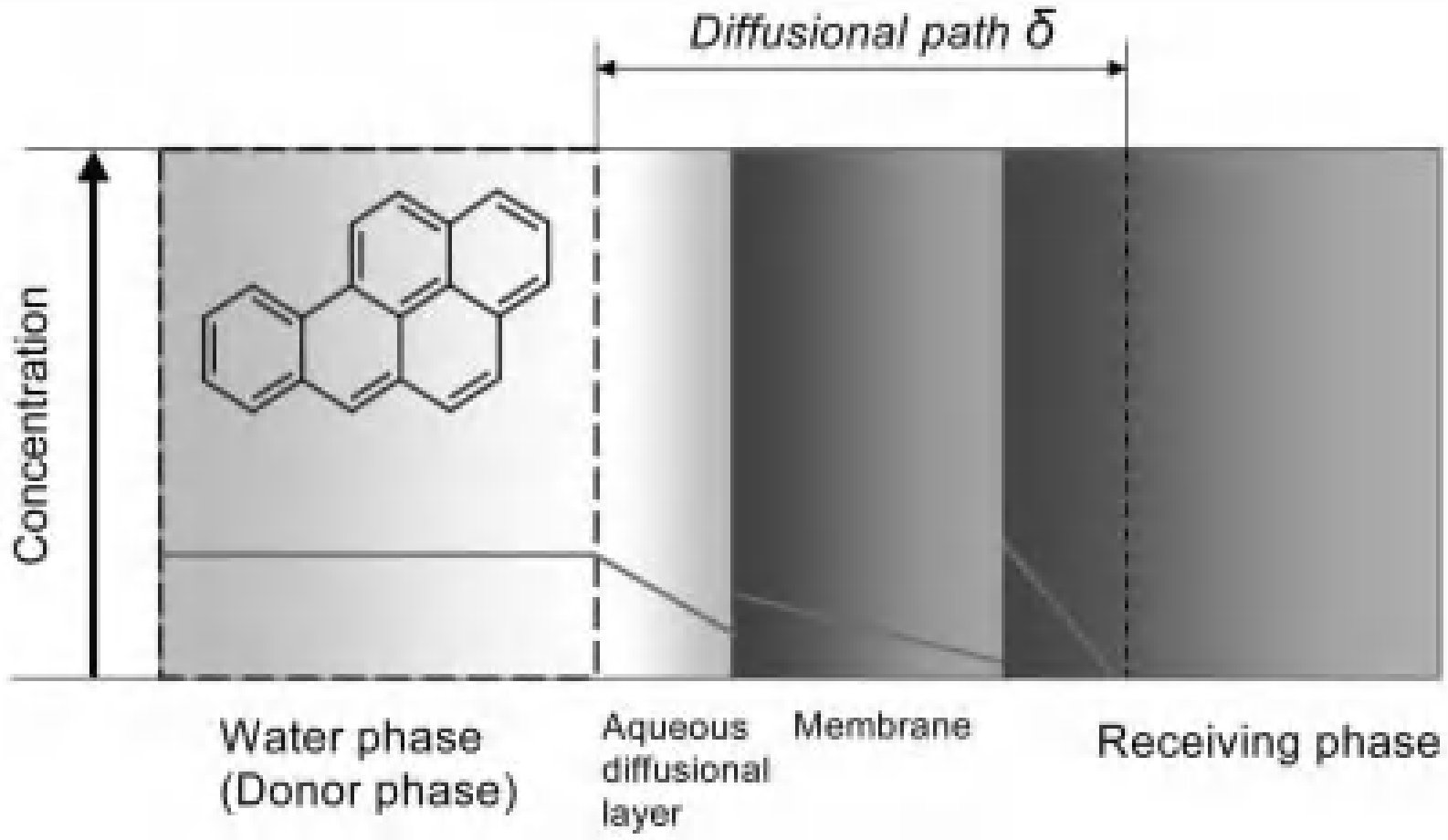
Diffusion/permeation barriers and receiving phases employed in various passive samplers for the application in water

| | Sampler | Barrier type | Sorbent/receiving phase | Operating region | Analyte |
|---|---|---|---|---|---|
| 1 | Regenerated cellulose dialysis membrane samplers | Cellulose dialysis membrane (approximately 18 Å pore size) | Deionized water | Equilibrium | Organic and inorganic constituents |
| 2 | Nylon screen passive diffusion samplers | Nylon screen with approx 125 μm pore size nylon mesh | Deionized water | Equilibrium | Organic and inorganic constituents |
| 3 | Passive vapor diffusion (PVD) samplers | Low density polyethylene | Clean air | Equilibrium | VOCs |
| 4 | Peeper samplers | Polysulfone membrane | Deionized water | Equilibrium | Organic and inorganic compounds |
| 5 | Polyethylene diffusion bag (PDB) samplers | Low density polyethylene | Deionized water | Equilibrium | Dissolved VOCs |
| 6 | Rigid porous polyethylene samplers (RPPS) | Porous polyethylene (6–15 μm pore size) | Deionized water | Kinetic, equilibrium | Organic and inorganic compounds |
| 7 | Zhang and Hardy sampler | Polycarbonate | XAD-7, Tenax | Kinetic | Phenolic compounds |
| 8 | Trimethylpentane-containing passive sampler (TRIMPS) | Polyethylene membrane | 2,2,3-Trimethyl pentane | Kinetic | Pesticides |
| 9 | Semi-permeable membrane devices (SPMD) | Low density polyethylene. Historically, silicone, polypropylene and polyvinyl chloride have also been tried | Triolein | Linear, non linear, equilibrium | Non-polar hydrophobic compounds |
| 10 | Gore sampler | Gore-Tex membrane (expanded PTFE) | Various sorbents depending on the analyte of interest | Kinetic | VOCs and SVOCs |
| 11 | Polar organic chemical integrative sampler (POCIS) | Polyethersulfone membrane | Generic – three types of sorbent; pharmaceutical – single sorbent (Oasis HLB) | Kinetic | Polar organic compounds (pesticides, pharmaceuticals, etc.) |
| 12 | Passive in-situ concentration extraction sampler (PISCES) | Low density polyethylene | Hexane or *iso*-octane | Kinetic | Non-polar hydrophobic compounds |
| 13 | Kot et al. sampler | Polypropylene or PTFE | Hexane or *iso*-octane | Kinetic, equilibrium | Organic compounds |
| 14 | Solid phase microextraction (SPME) | None | Various sorbents coated on the SPME fiber | Kinetic, equilibrium | Various depending on the sorbent |
| 15 | Ceramic dosimeter | Diffusion through porous ceramic membrane | Various – ion-exchange resin, Tenax | Kinetic | Organic and inorganic compounds |
| 16 | Chemcatcher | Various – cellulose acetate, polysulfone, polyethylene, etc. | Various – immobilized chelating acceptor resin coated on PTFE, $C_{18}$ Empore Disk | Kinetic | Polar and non-polar organic compounds |
| 17 | MESCO sampler | Cellulose or low-density polyethylene | PDMS coated on a stir bar | Kinetic | PAHs, PCBs and organochlorine pesticides |
| 18 | Lee and Hardy passive sampler | Silicone polycarbonate | Porapak-Q and Tenax-TA | Kinetic | Monocyclic aromatic hydrocarbons |
| 19 | Solid phase adsorption toxin tracking (SPATT) bags | 95 μm polyester mesh | Porous, hydrated adsorption resin | Kinetic | Biotoxin |
| 20 | Solvent-filled dialysis membrane sampler | Dialysis membrane | Hexane or heptane | Kinetic | Lipophilic compounds |
| 21 | Stabilized liquid membrane device (SLMD) | Low-density polyethylene lay-flat tube | Solution of acidic compounds like oleic acid | Kinetic | Doubly charged metal ions |
| 22 | Passive integrative mercury sampler (PIMS) | Low-density polyethylene lay-flat tube | PIMS reagent | Kinetic | Mercury vapor |
| 23 | Permeation liquid membrane (PLM) sampler | Membrane made of 1,10-didecyldiaza-18-crown-6 (22DD) and lauric acid (1:1 ratio) in 1:1 (v/v) toluene/phenylhexane | 1,2-Cyclohexylene-aminotetraacetic acid (CDTA) or pyrophosphate solution | Kinetic | Cu, Pb, Ni |
| 24 | Diffusion gradient in thin-film (DGT) | Acrylamide gel | Metal-binding resin incorporated into acrylamide gel | Kinetic | Metals |
| 25 | Empore disk | Without and with polysulfone and polyethylene membrane | $C_{18}$ resin | Equilibrium | Organic compounds |
| 26 | DiGiano et al. sampler | Diffusion through holes drilled into polyacrylate | Activated carbon | Kinetic | Organic compounds |


Kinetic
Regime
Equilibrium
Regime
Concentration in the Sampler
$t_{50}$
Time
$C_s(t) = C_W \frac{k_1}{k_2}\left(1 - e^{-k_2 t}\right),$

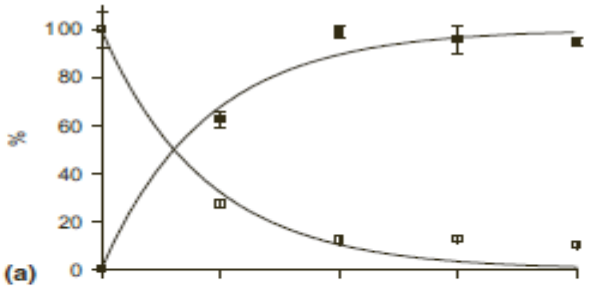
$$\frac{1}{k_o} = \frac{1}{k_w} + \frac{1}{K_{bw} k_b} + \frac{1}{K_{mw} k_m}$$

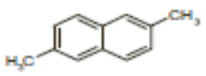



Diffusional path δ
Concentration
Water phase
(Donor phase)
Aqueous
diffusional
layer
Membrane
Receiving phase

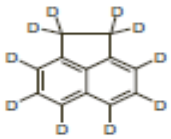
# Calibrazione

- Esposizione statica
- Batch renewal
- Esposizione in flusso
- Calibrazione *in situ* (uso di PRC – Performance Reference Compounds)

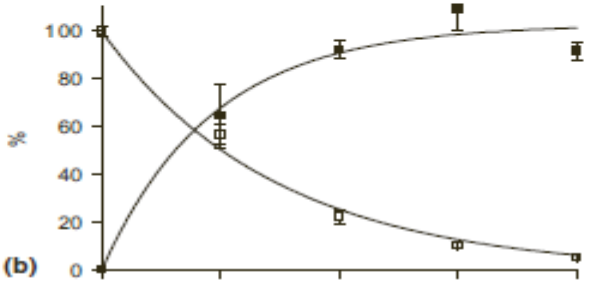


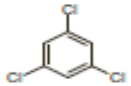




2,6-Dimethylnaphthalene
(4.3)

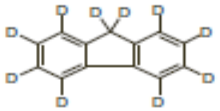


Acenaphthene-D10
(4.2)

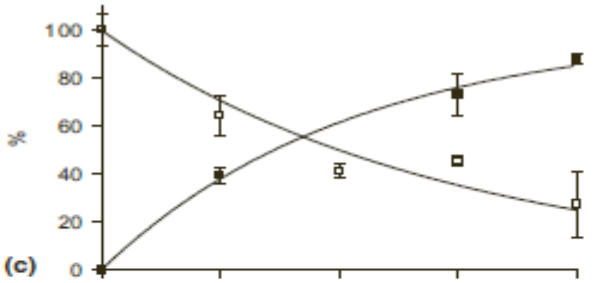


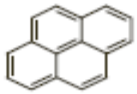




1,3,5-Trichlorobenzene
(4.2)

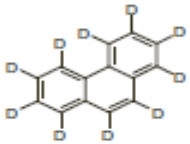


Fluorene-D10
(4.4)

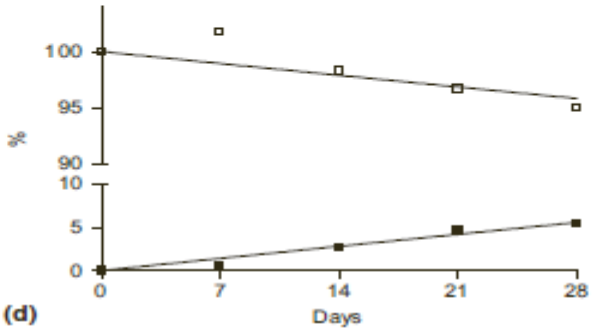


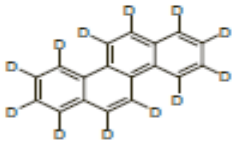



Pyrene
(5.3)

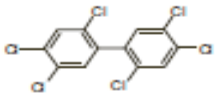


Phenanthrene-D10
(4.5)



Chrysene-D12
(5.8)

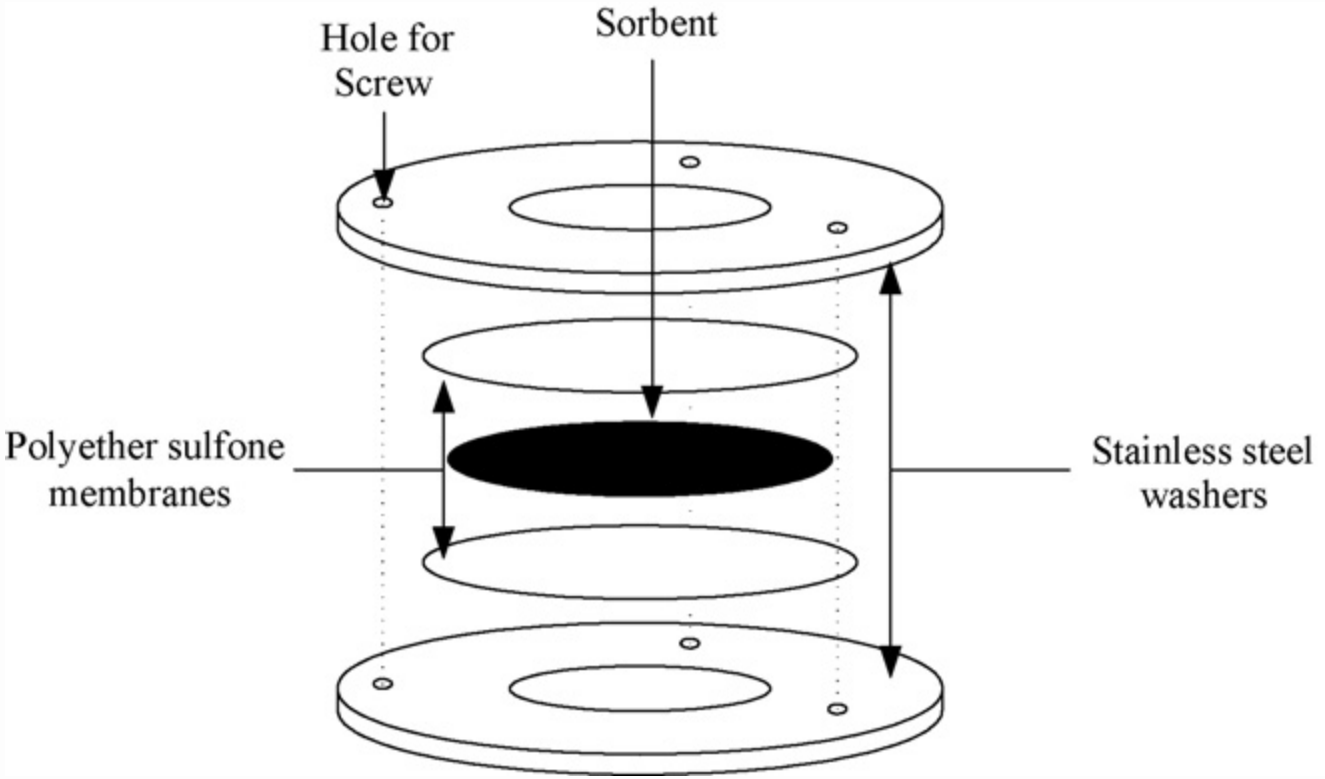



2,2',4,4',5,5'-Hexachlorobiphenyl
(6.9)

ISPRA

# *Semi-permeable membrane device*
# SPMD

# *Polar Organic Chemical Integrative Sampler* - POCIS

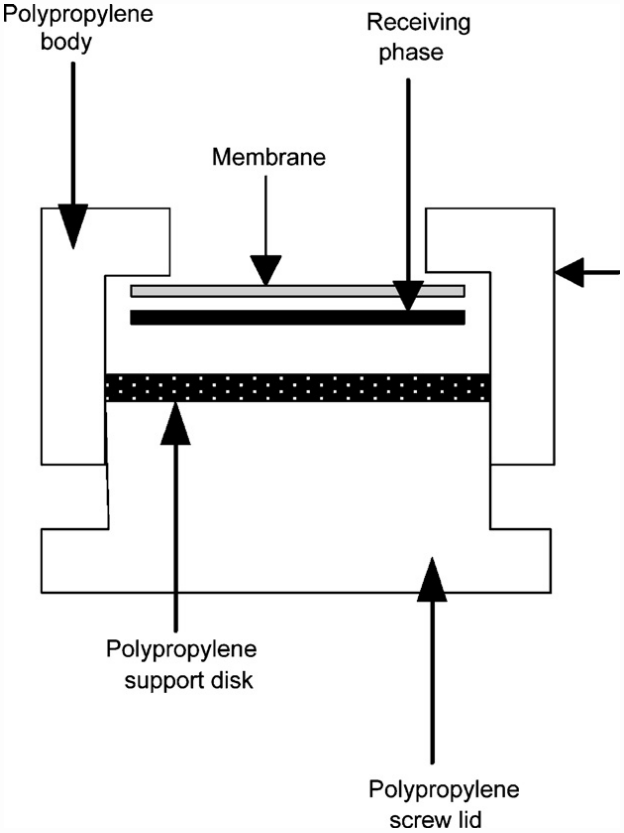

Hole for
Screw
Sorbent
Polyether sulfone
membranes
Stainless steel
washers

Sampling rates ($R_s$ values) of POCIS (L day$^{-1}$; 41 cm$^2$ POCIS) under quiescent (non-stirred) and turbulent (stirred) conditions

| Analyte | $R_s$ from quiescent renewals (L day$^{-1}$) | $R_s$ from turbulent renewals (L day$^{-1}$) |
|---|---|---|
| *Herbicides* | | |
| Diuron[a] | 0.011 | 0.100 |
| Isoproturon[a] | 0.034 | 0.200 |
| *Prescription pharmaceuticals* | | |
| Azithromycin[a] | 0.048 | 0.270 |
| Fluoxetine[a] | 0.027 | 0.200 |
| Levothyroxine[a] | 0.021 | 0.120 |
| Omeprazole[a] | 0.016 | 0.068 |
| *Illicit drugs* | | |
| Methamphetamine | N/A[b] | 0.089 |
| MDMA | N/A[b] | 0.170 |

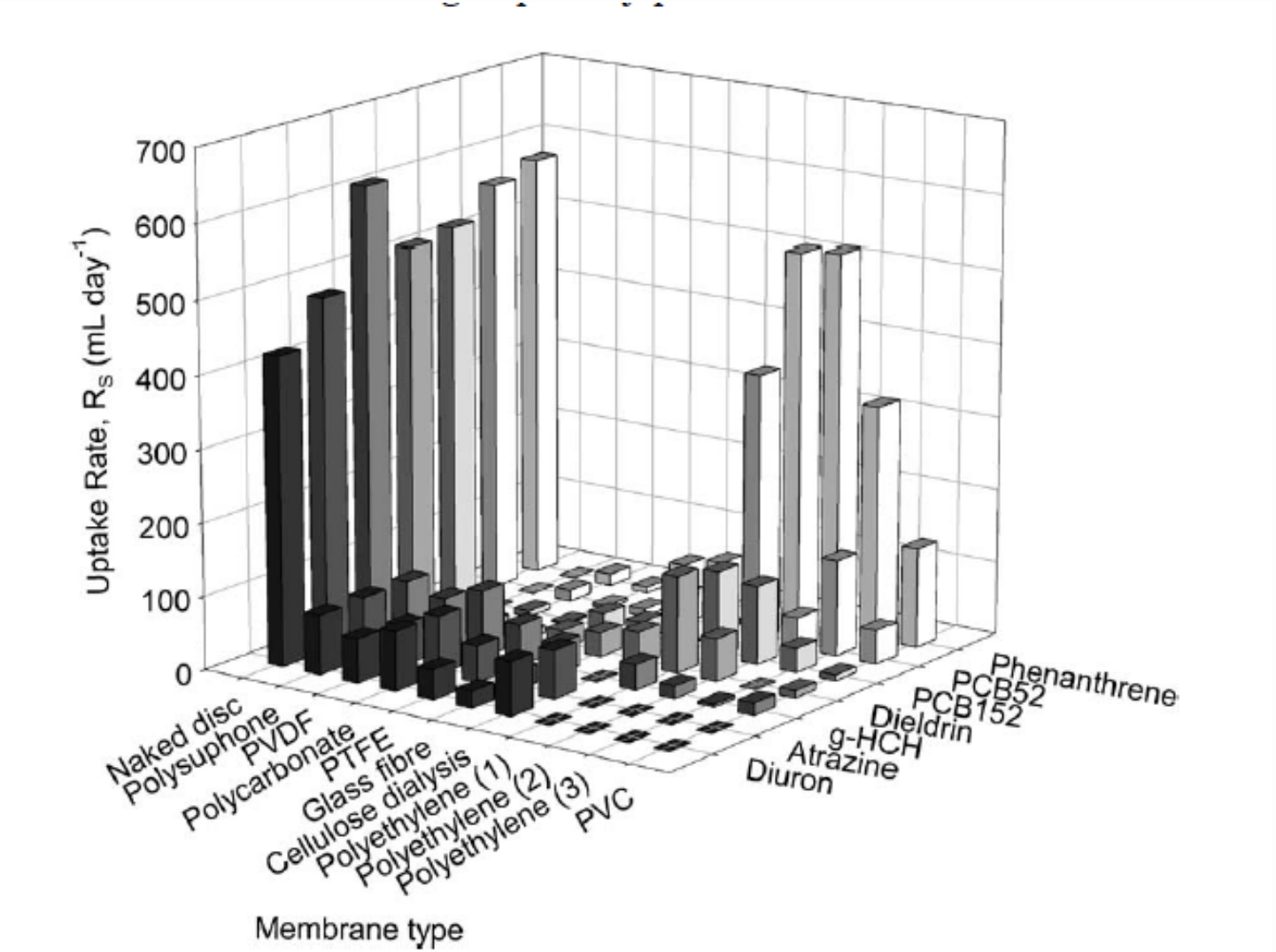
Values reported are means ($n = 3$).

# Chemcatcher

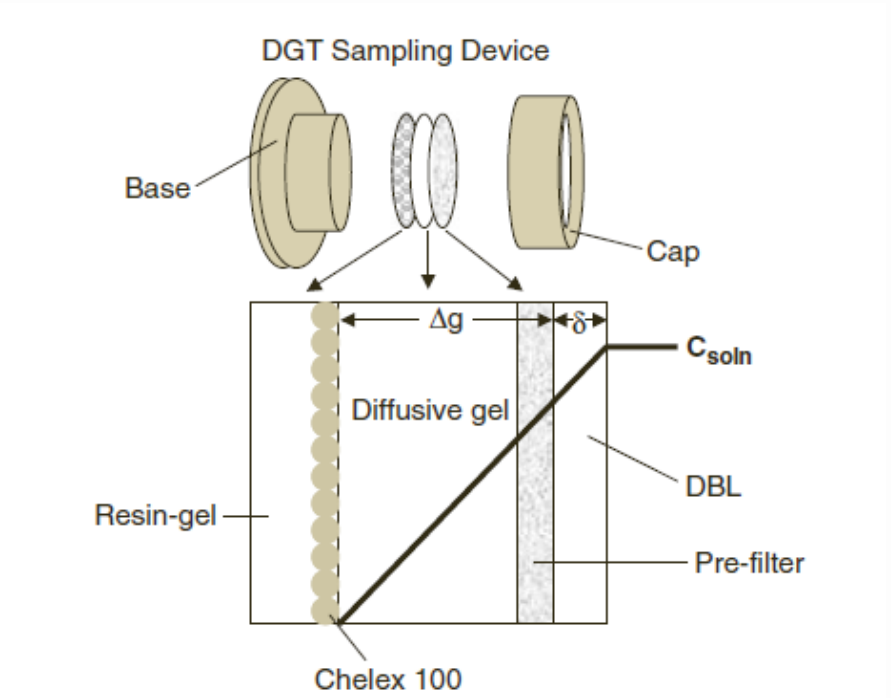


Chemcatcher configurations for integrative sampling of various pollutant classes

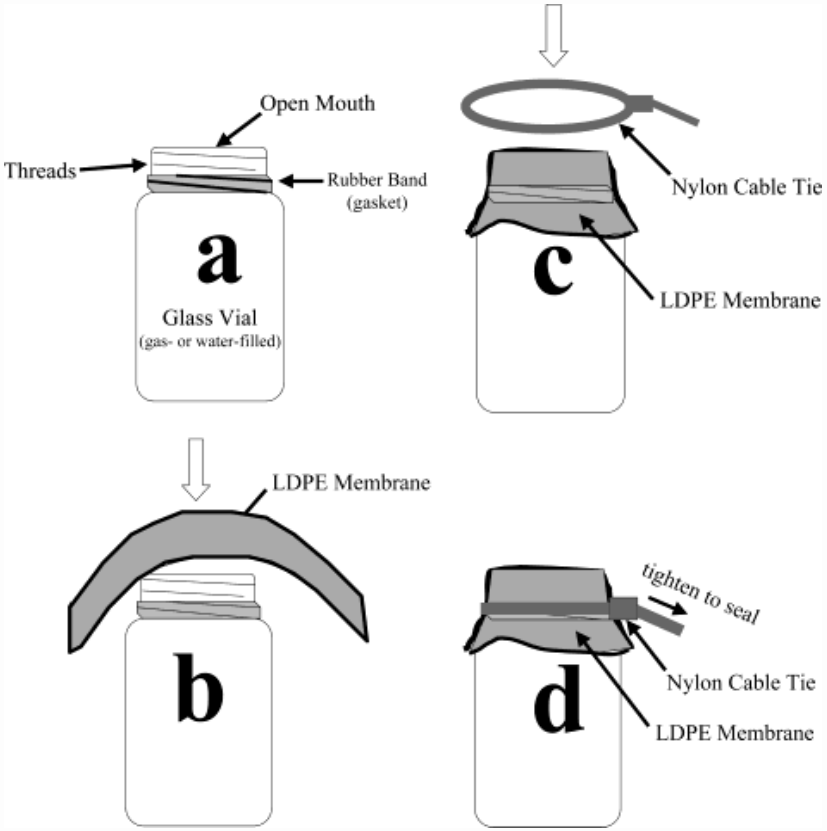
| Pollutant class | Receiving phase | Diffusion membrane |
|---|---|---|
| Hydrophobic organic compounds (log $K_{OW} > 3$) | $C_{18}$ Empore™ disk | Non-porous low-density polyethylene (LDPE) |
| Hydrophilic organic compounds (log $K_{OW} < 3$) | $C_{18}$ Empore™ disk | Microporous polysulfone (PS) |
| | SDB-RPS Empore™ disk | Microporous polyethersulfone (PES) |
| Metals | Chelating Empore™ disk | Microporous cellulose acetate (CA) |
| Mercury | Chelating Empore™ disk | Microporous polyethersulfone (PES) |
| Organotin compounds | $C_{18}$ Empore™ disk | Microporous cellulose acetate (CA) |


Uptake Rate, $R_S$ (mL day$^{-1}$)
700
600
500
400
300
200
100
0
Naked disc
Polysuphone
PVDF
Polycarbonate
PTFE
Glass fibre
Cellulose dialysis
Polyethylene (1)
Polyethylene (2)
Polyethylene (3)
PVC
Membrane type
Diuron
Atrazine
g-HCH
Dieldrin
PCB152
PCB52
Phenanthrene

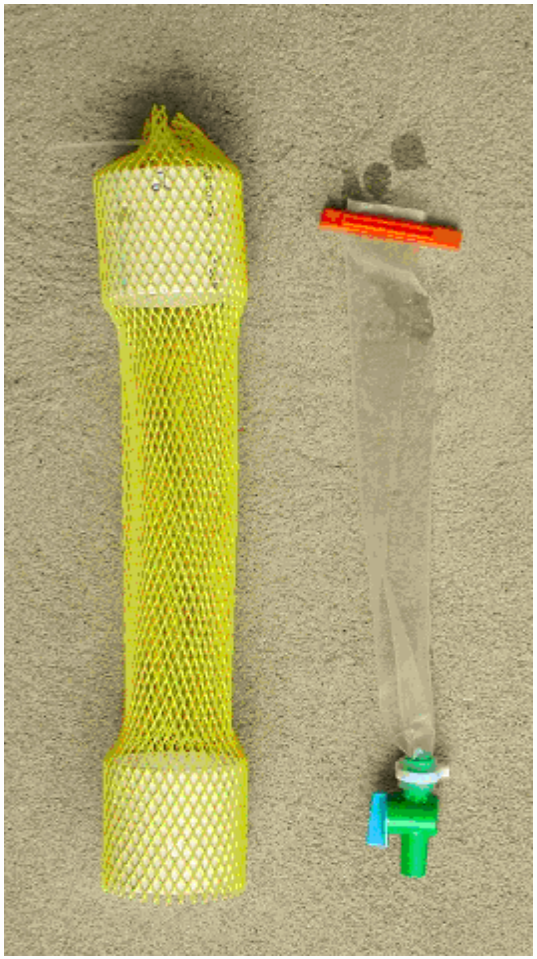
# *Diffusive Gradients in Thin-films* - DGT

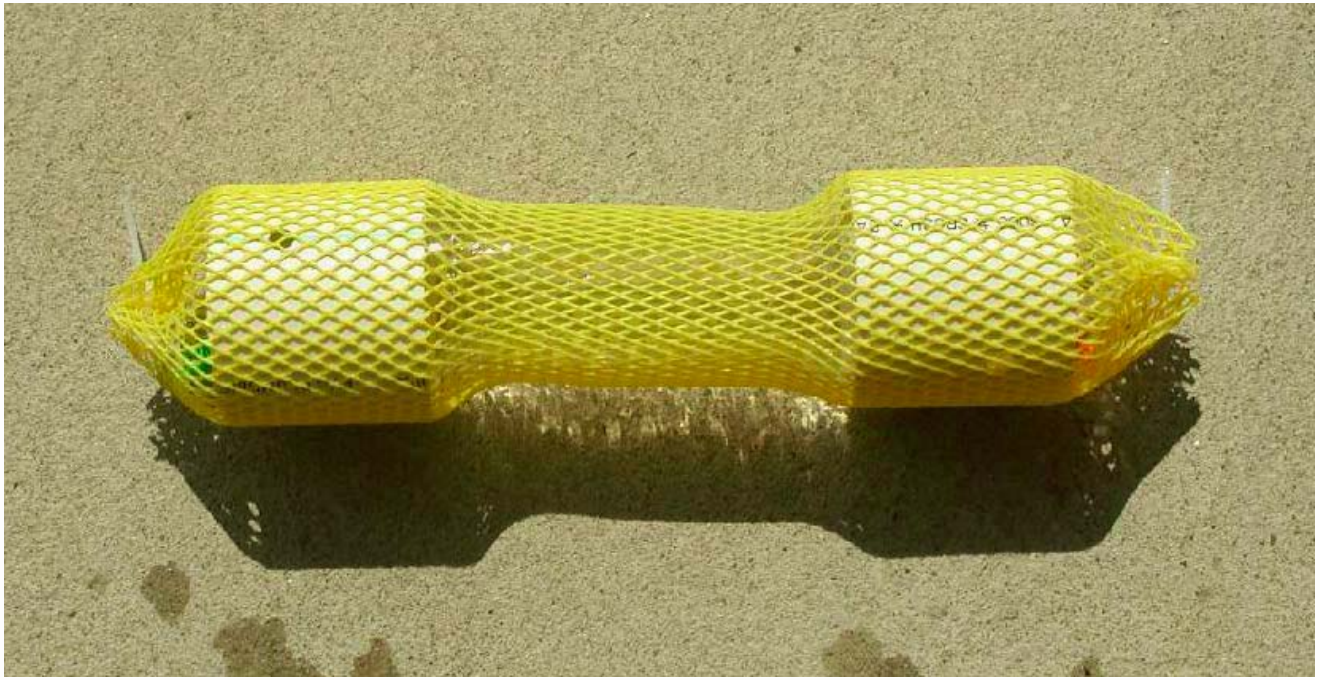


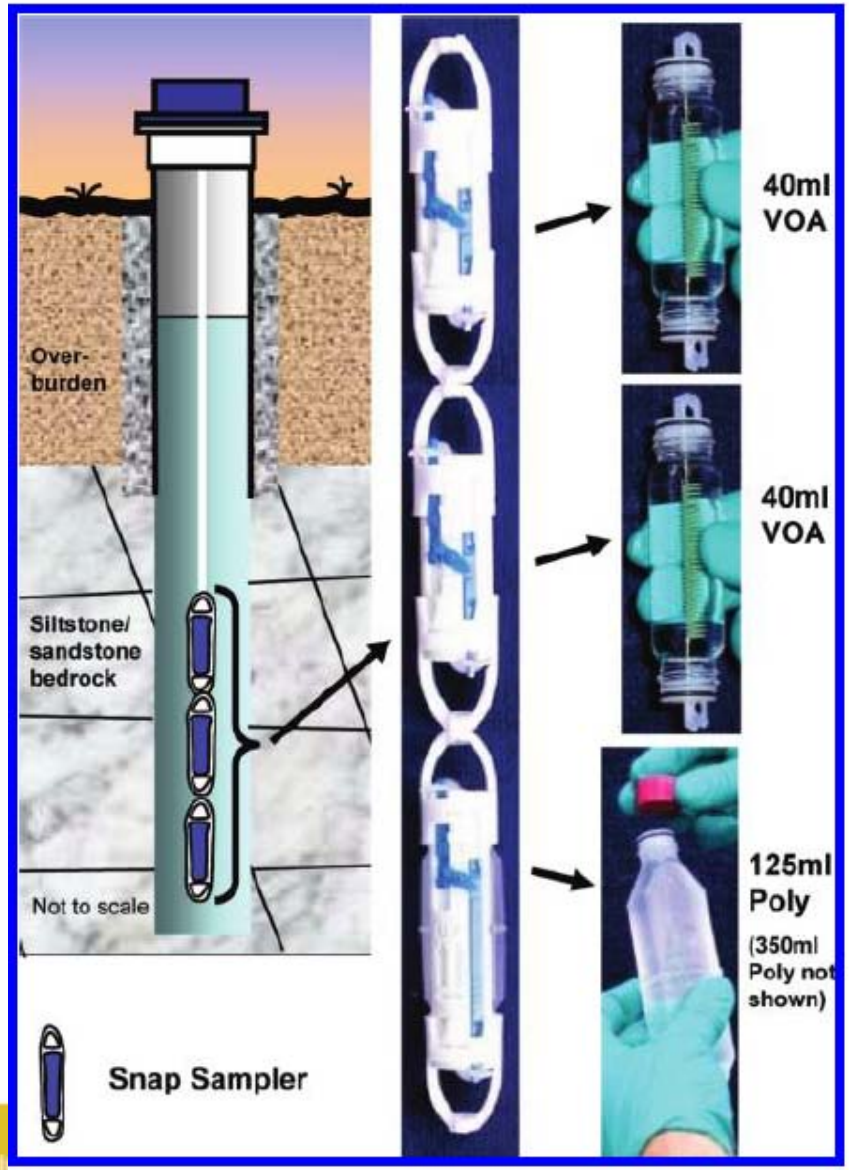
# Passive diffusion (PD) sampler



# Membrana da dialisi

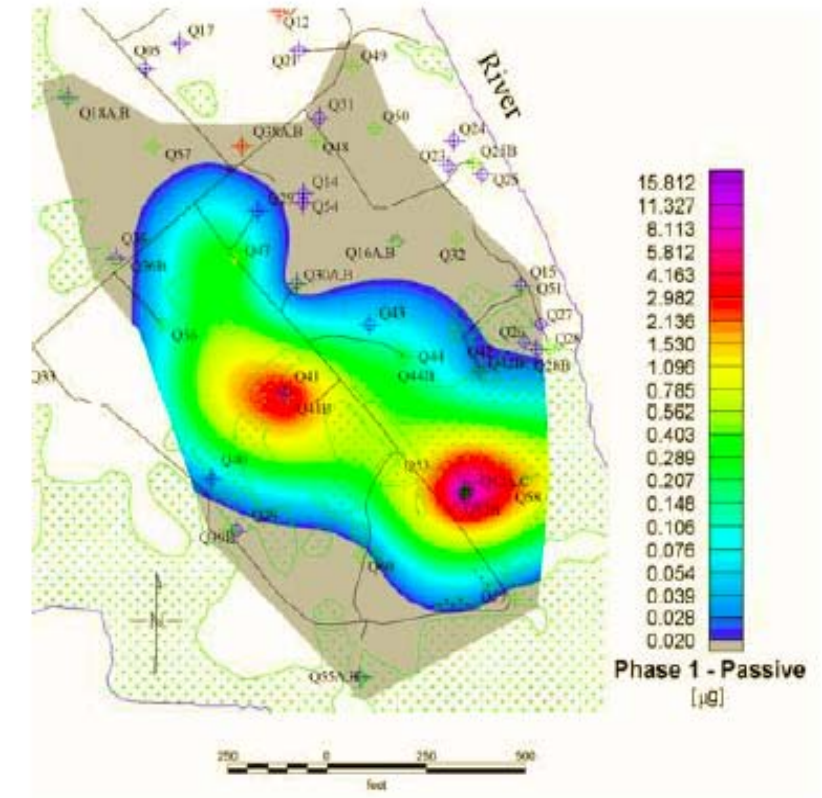


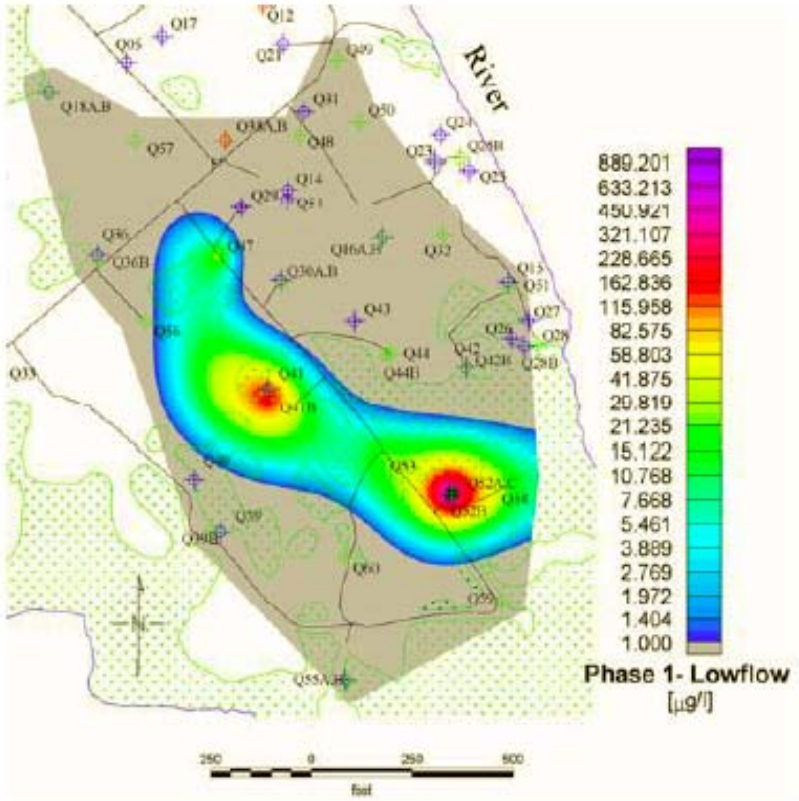



Over-
burden
Siltstone/
sandstone
bedrock
Not to scale
Snap Sampler
40ml
VOA
40ml
VOA
125ml
Poly
(350ml
Poly not
shown)

# Modulo GORE


GORE-SORBER
MODULE
W.L. Gore & Associates
Phone: (410)
Fax: (410)
Accuracy Counts
418807
GORE-SORBER™ MODULE
418807


River
15.812
11.327
8.113
5.812
4.163
2.982
2.136
1.530
1.096
0.785
0.562
0.403
0.289
0.207
0.148
0.106
0.076
0.054
0.039
0.028
0.020
Phase 1 - Passive
[µg]
250
0
250
500
feet


River
889.201
633.213
450.921
321.107
228.665
162.836
115.958
82.575
58.803
41.875
29.819
21.235
15.122
10.768
7.668
5.461
3.889
2.769
1.972
1.404
1.000
Phase 1- Lowflow
[µg/l]
250
0
250
500
feet

# Come scegliere? - Attivo

- Trasporto attivo di acqua indotto dal pompaggio e dallo spurgo
- Frequente prelievo di campione da zone adiacenti alla posizione di prelievo
- Campione dipendente dal flusso
  - Criticità dei volumi di spurgo e di campionamento
  - Scambi gassosi e mixing
- Può aumentare la torbidità del campione
  - Mobilizzazione di colloidi e sedimenti
  - Mobilizzazione di fasi stratificate
- Metodologia aderente alle esigenze normative

# Come scegliere? - Passivo

- Nessun trasporto attivo e advezione artificiosa di acqua
- Semplice campionamento multilivello
- Fortemente dipendente da condizioni di equilibrio del pozzo relativamente all'acquifero
- Ridotto disturbo degli equilibri idrodinamici
- Bassa torbidità
  - Rappresenta meglio le "condizioni naturali
- Non è normato