SED.RI.PORT

SEDIMENTI , DRAGAGGI E RISCHI PORTUALI

Livorno 28-29 Novembre 2018

Il campionamento passivo dei composti organici nella valutazione del rischio ambientale legato alla rimobilizzazione dei sedimenti portuali: caratteristiche e potenzialità.

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L’INQUINAMENTO NEI PORTI

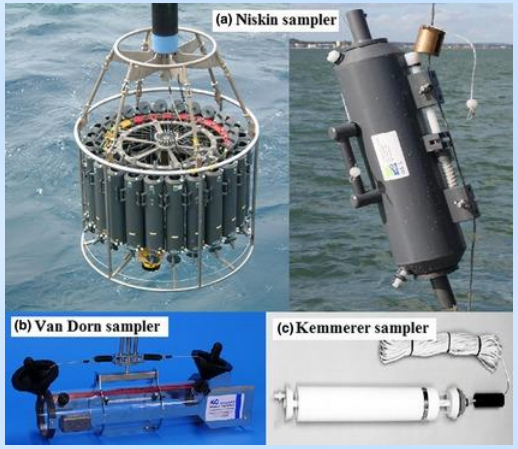
- **I porti sono generalmente punti focali delle attività industriali ed urbane, e sono importanti siti dove I contaminanti si accumulano nei sedimenti.**

Qualunque azione che abbia come conseguenza la risospenzione dei sedimenti presenta aspetti problematici per l'ambiente

La RISOSPENSIONE DI DETRITI rende l'acqua torbida e può causare una ridissoluzione degli inquinanti.

From APAM et al, 2015)

Risospensione dei sedimenti al passaggio delle grandi navi .



CAMPIONAMENTO TRADIZIONALE

ALTI LIMITI DI RILEVABILITA'

RICHIEDE GRANDI VOLUMI

ALTI COSTI

DIFFICOLTA' ANALITICHE

CAMPIONAMENTO ISTANTANEO

SCARSA RAPPRESENTATIVITA'

CAMPIONAMENTO RIPETUTO NEL TEMPO

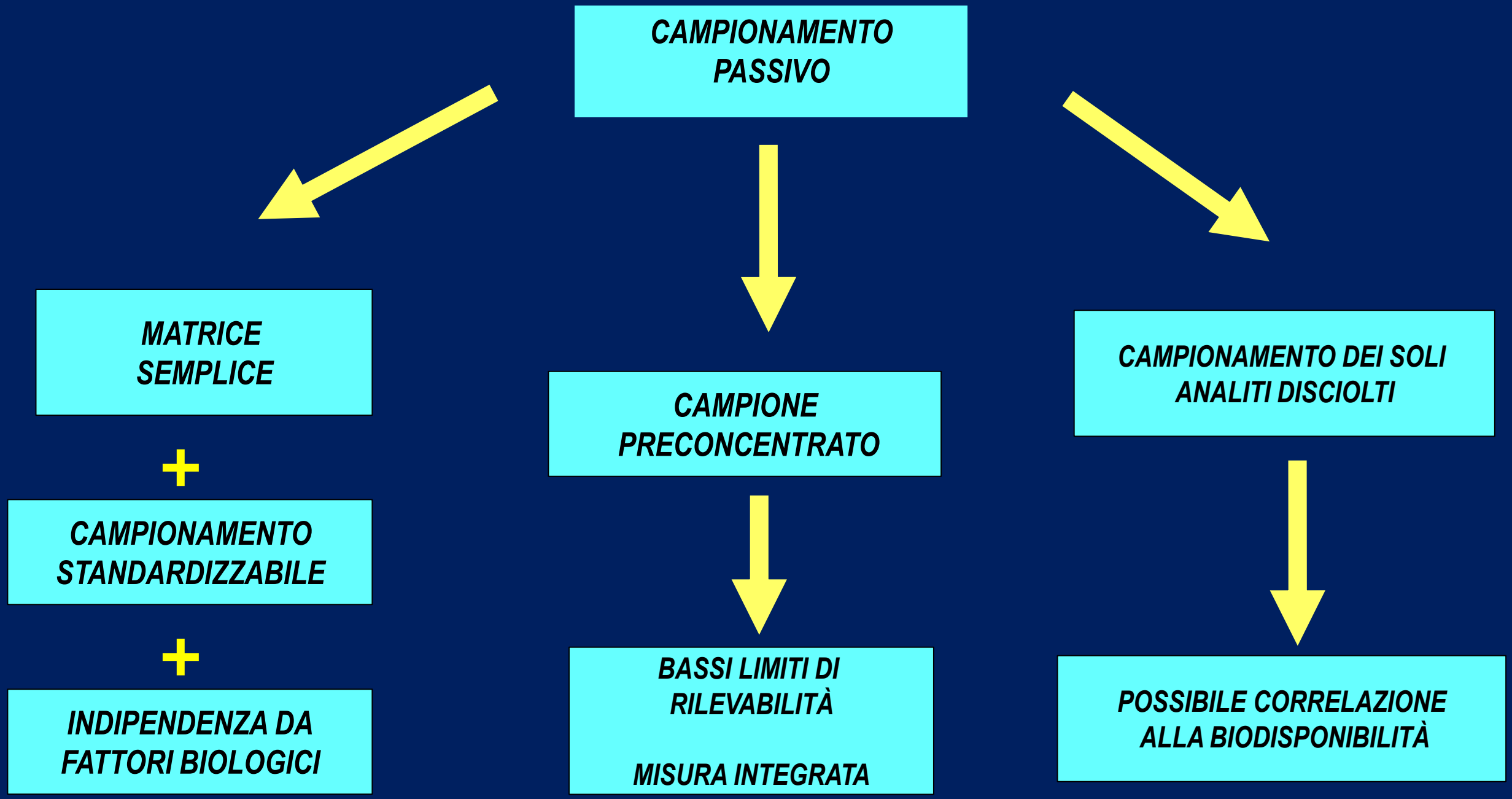
ALTI COSTI

BIOMONITORAGGIO

ASSORBIMENTO CONDIZIONATO DA FATTORI BIOTICI E ABIOTICI

MATRICE COMPLESSA

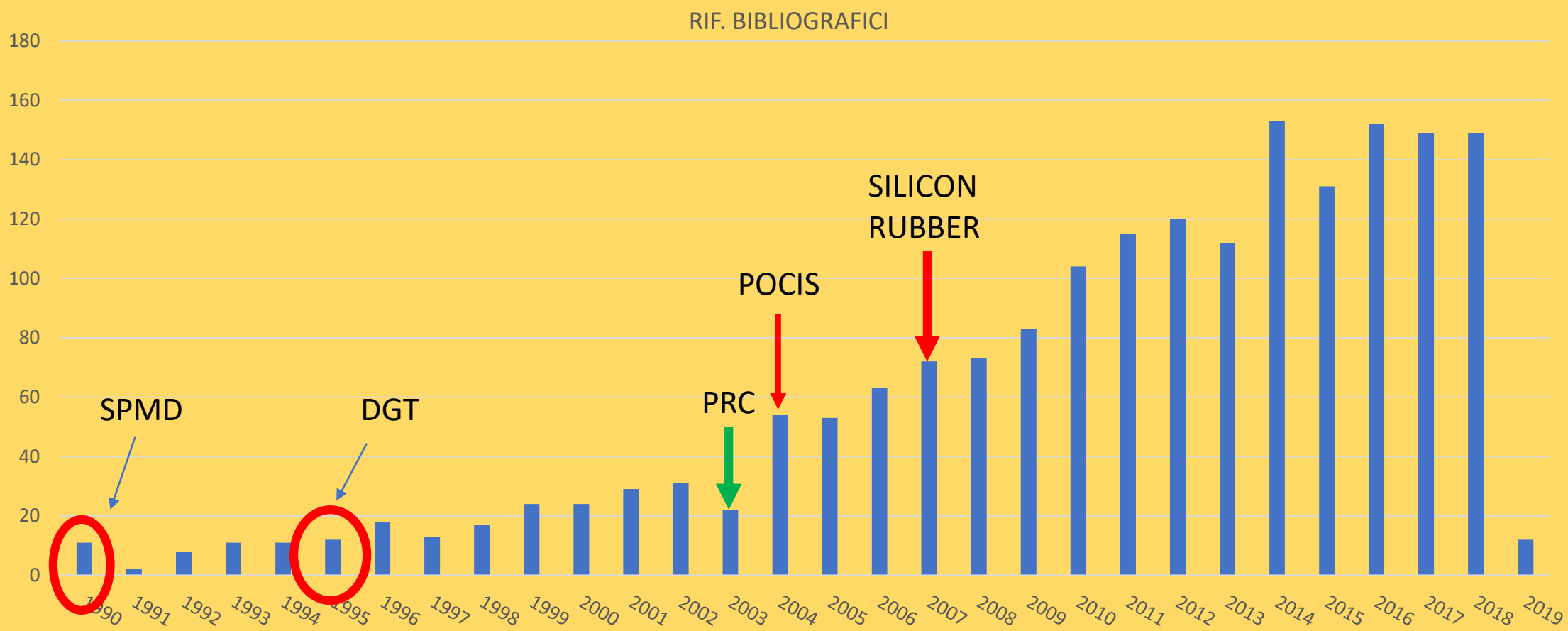
DIFFICILE INTERPRETAZIONE DEI DATI


CAMPIONAMENTO PASSIVO
MATRICE SEMPLICE
+
CAMPIONAMENTO STANDARDIZZABILE
+
INDIPENDENZA DA FATTORI BIOLOGICI
CAMPIONE PRECONCENTRATO
BASSI LIMITI DI RILEVABILITÀ
MISURA INTEGRATA
CAMPIONAMENTO DEI SOLI ANALITI DISCIOLTI
POSSIBILE CORRELAZIONE ALLA BIODISPONIBILITÀ

Passive Sampler Devices

- Nessuna sorgente di energia esterna
- Il flusso molecolare dipende solo dalla differenza di potenziale chimico.
- Il flusso prosegue fino al raggiungimento dell’equilibrio o all’interruzione del campionamento.

PASSIVE SAMPLING WATER

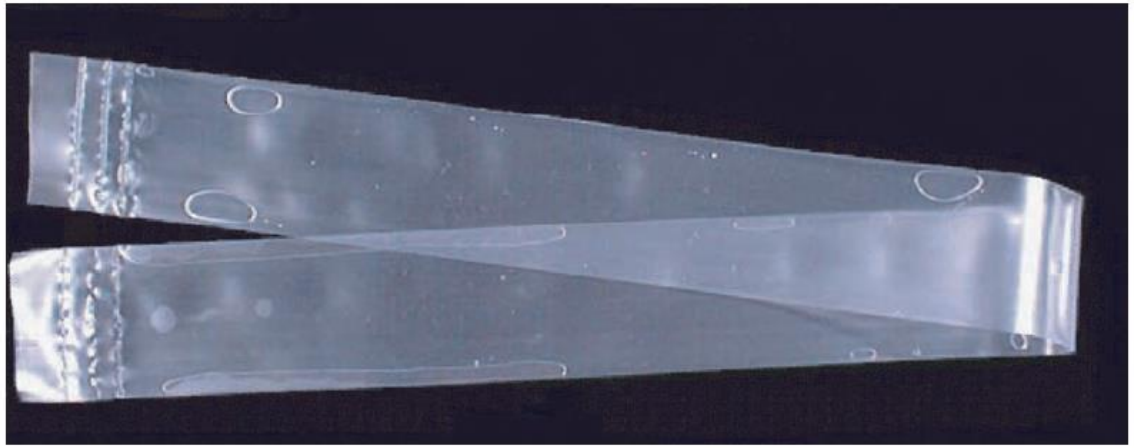


Campionatori Passivi per composti organici

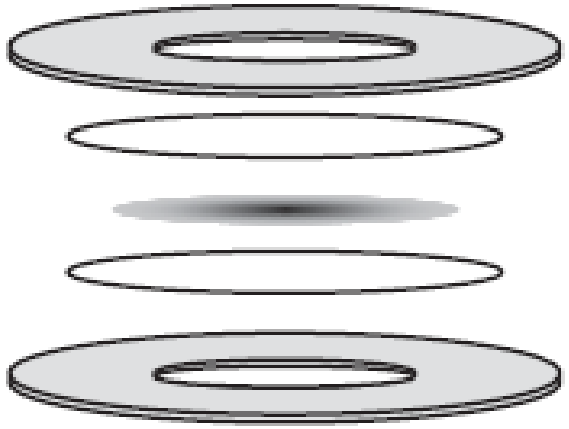
- **SPMD (**SemiPermeable Membrane Devices)
- **POCIS** (Polar Organic Compounds Integrative Sampler)
- **CHEMCATCHER**
- **MESCO** (Membrane-Enclosed Sorptive Coating)
- **SILICONE STRIP SAMPLERS**
- **LDPE** (Low Density PolyEthylene) **STRIP SAMPLERS**

SPMD

SILICON RUBBER



POCIS



Upper Compression Ring

Upper Membrane Disk

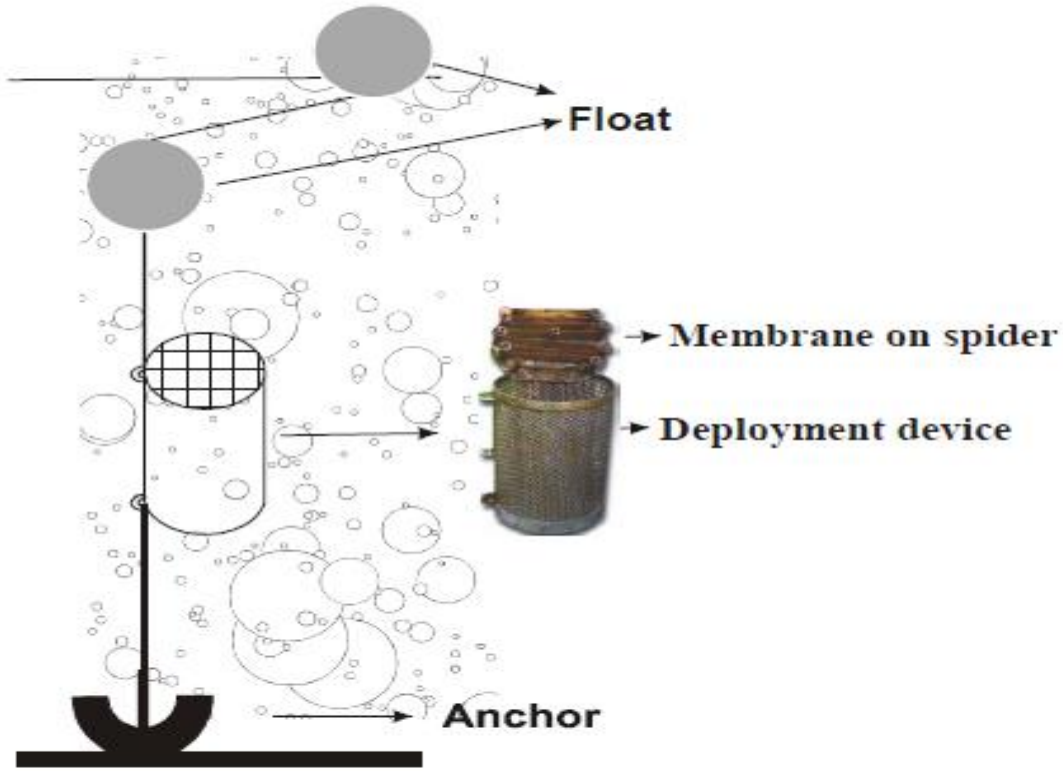
Sorbent Layer

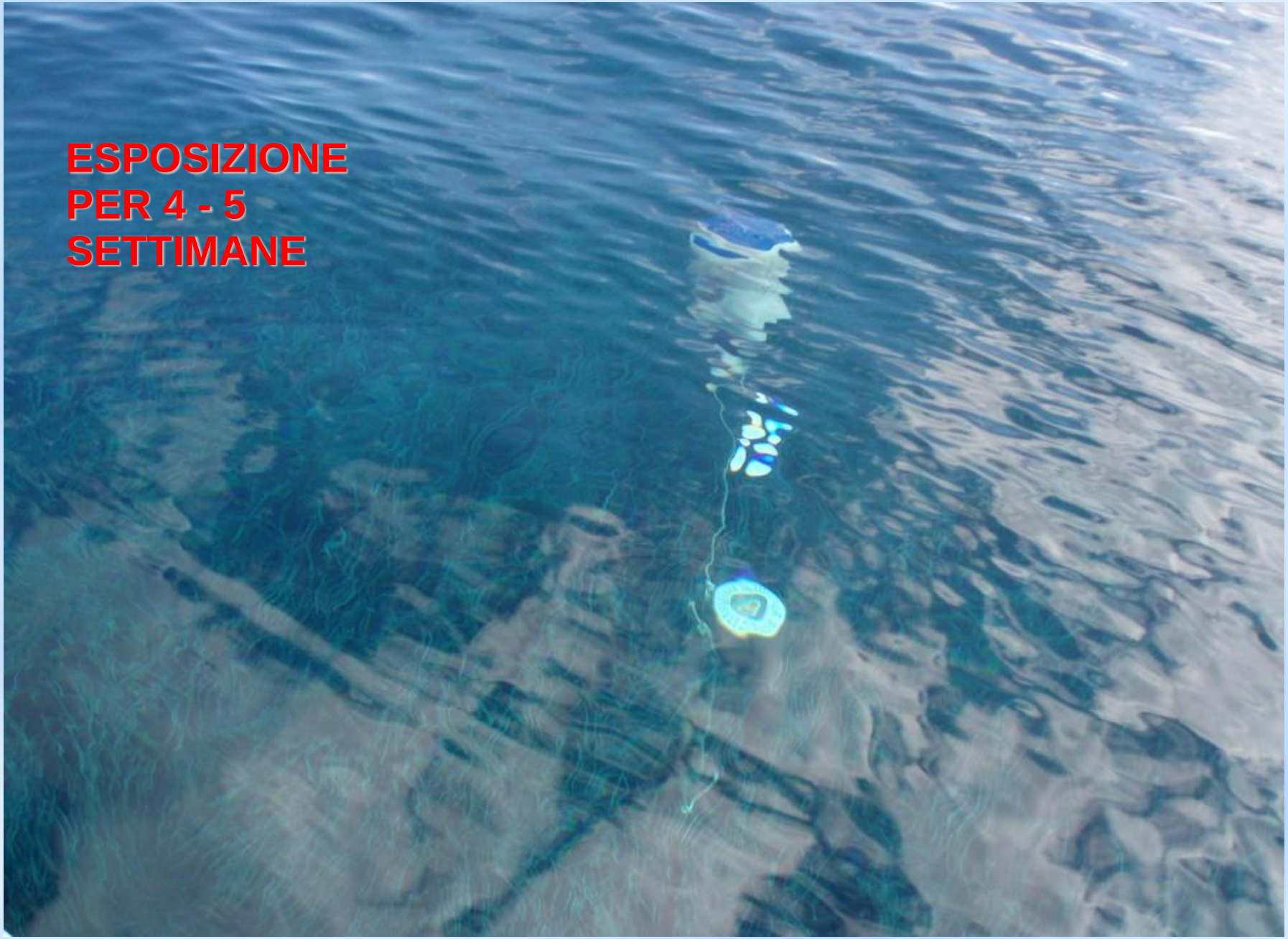
Lower Membrane Disk

Lower Compression Ring

- **Ottimizzato per campionare molecole moderatamente polari (logKow < 4) quali farmaci , pesticidi, surfactanti ecc.**

SILICON RUBBER


Float
Membrane on spider
Deployment device
Anchor


ESPOSIZIONE
PER 4 - 5
SETTIMANE

Contaminanti Determinabili

- **IDROCARBURI POLICICLICI AROMATICI (PAHs)**
- **POLICLOROBIFENILI (PCBs)**
- **PESTICIDI**
- **POLIBROMODIFENILETERI (Ritardanti di fiamma)**
- **COMPOSTI ORGANOSTANNICI**
- **DIOSSINE/FURANI (PCDD/F)**
- **RESIDUI DI FARMACI (Antibiotici, ormoni, antinfiammatori...)**
- **PRODOTTI PER LA CURA PERSONALE**
- **DROGHE D'ABUSO e METABOLITI**
- **……..**

Campionatori Passivi per composti organici

SPMD (SemiPermeable Membrane Devices) e SR (Silicon Rubber)

SOSTANZE APOLARI (idrofobe) con log K_{ow} > 4

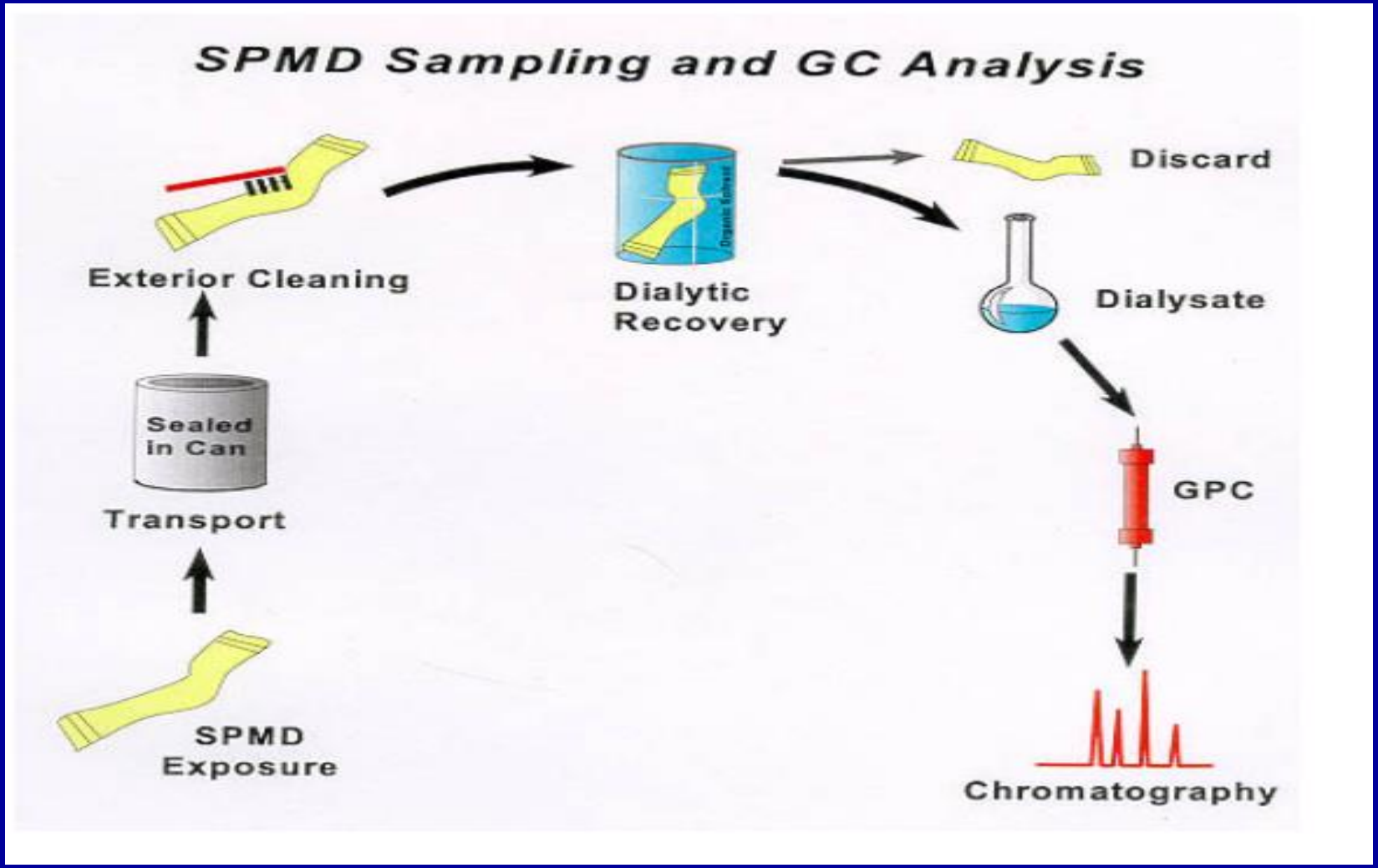
IDROCARBURI POLICICLICI AROMATICI (PAH)
POLICLOROBIFENILI (PCB)
PESTICIDI ORGANOCLORURATI (OCP)
POLIBROMOBIFENILETERI (PBFE)
FILTRI UV
ODORIZZANTI….ecc

POCIS (Polar Organic Compounds Integrative Sampler)

SOSTANZE POLARI (idrofile) con log K_{ow} < 4

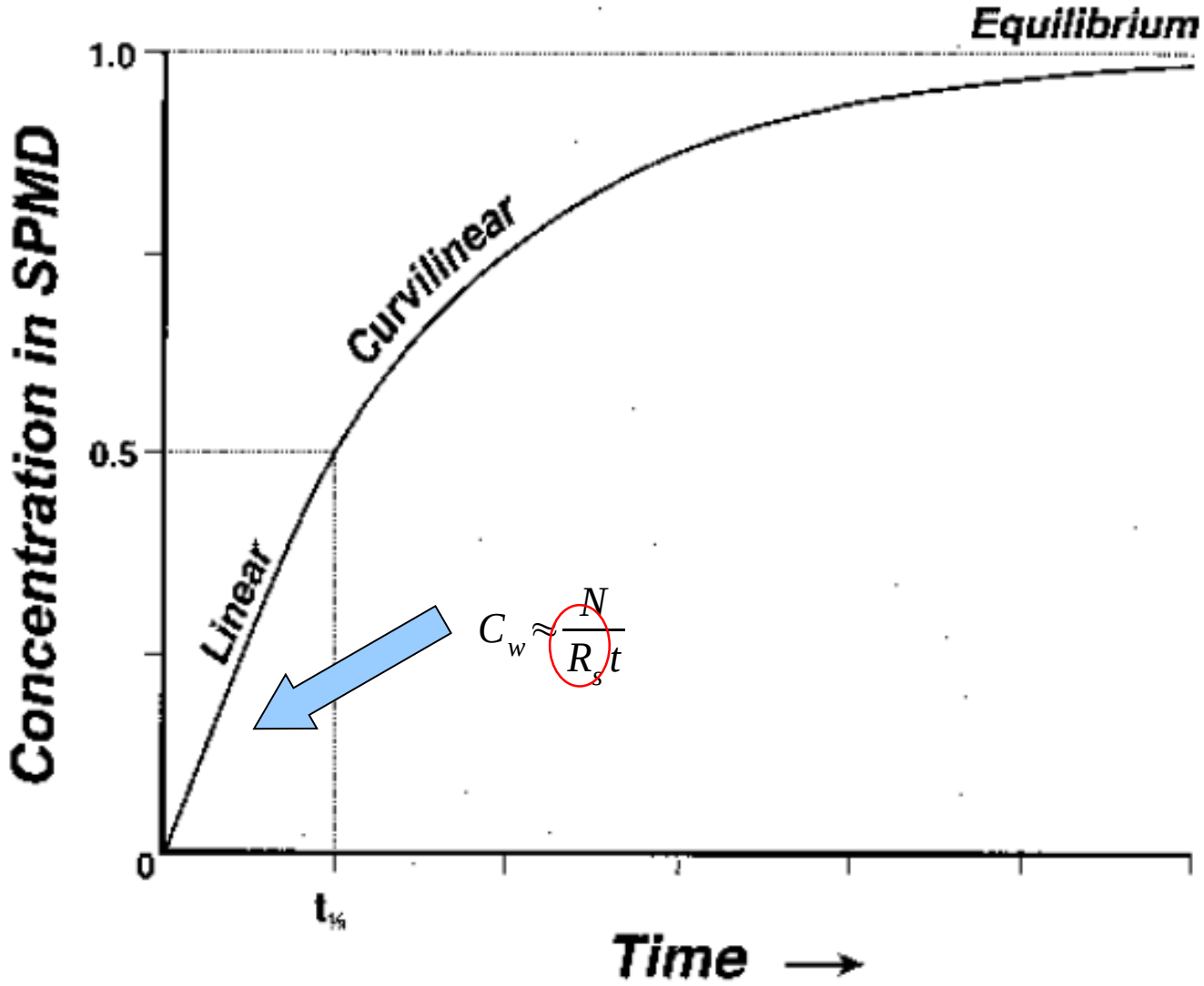
PESTICIDI POLARI
FARMACI
ORMONI
ALCHILFENOLI
ecc.

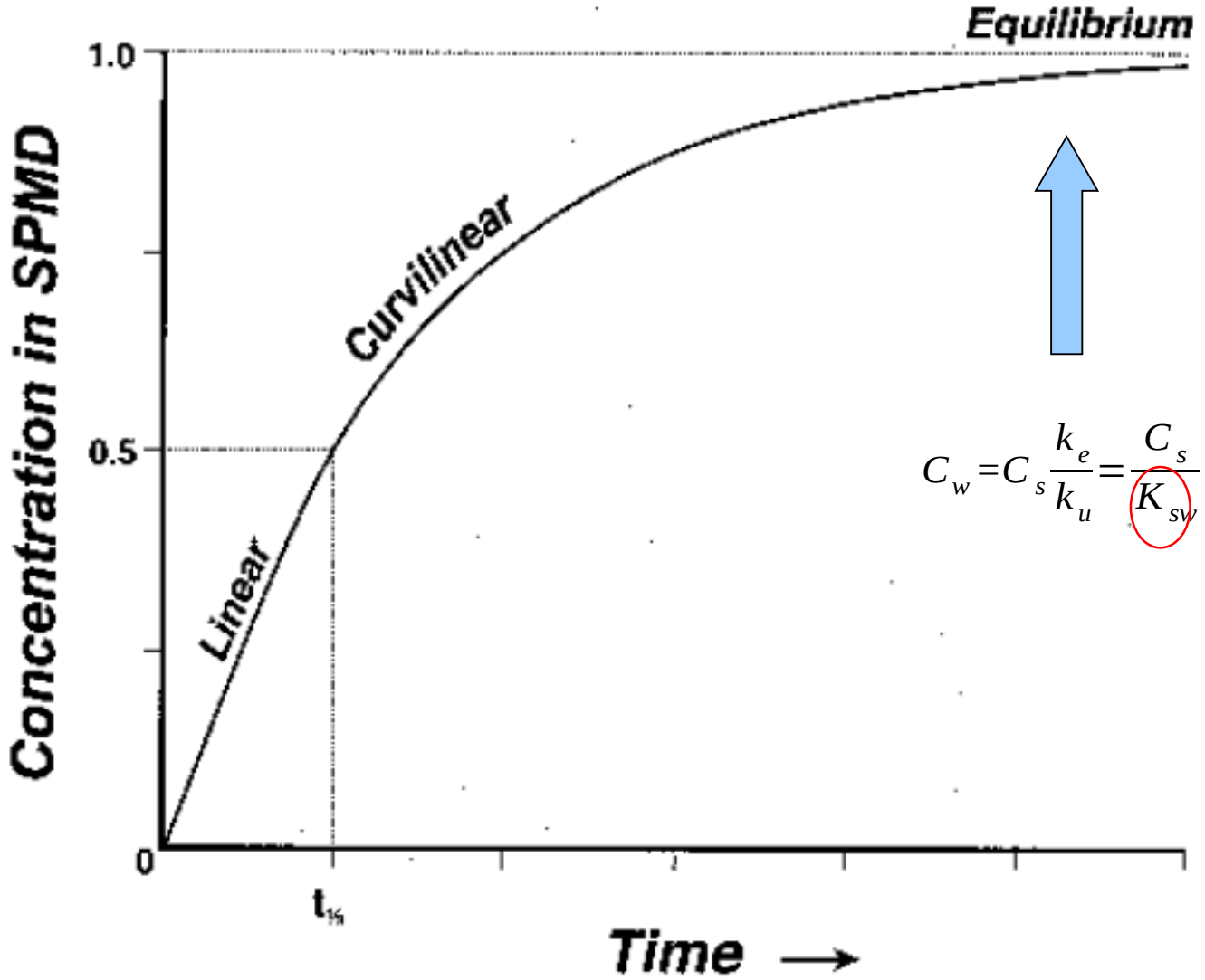
SCHEMA METODOLOGICO

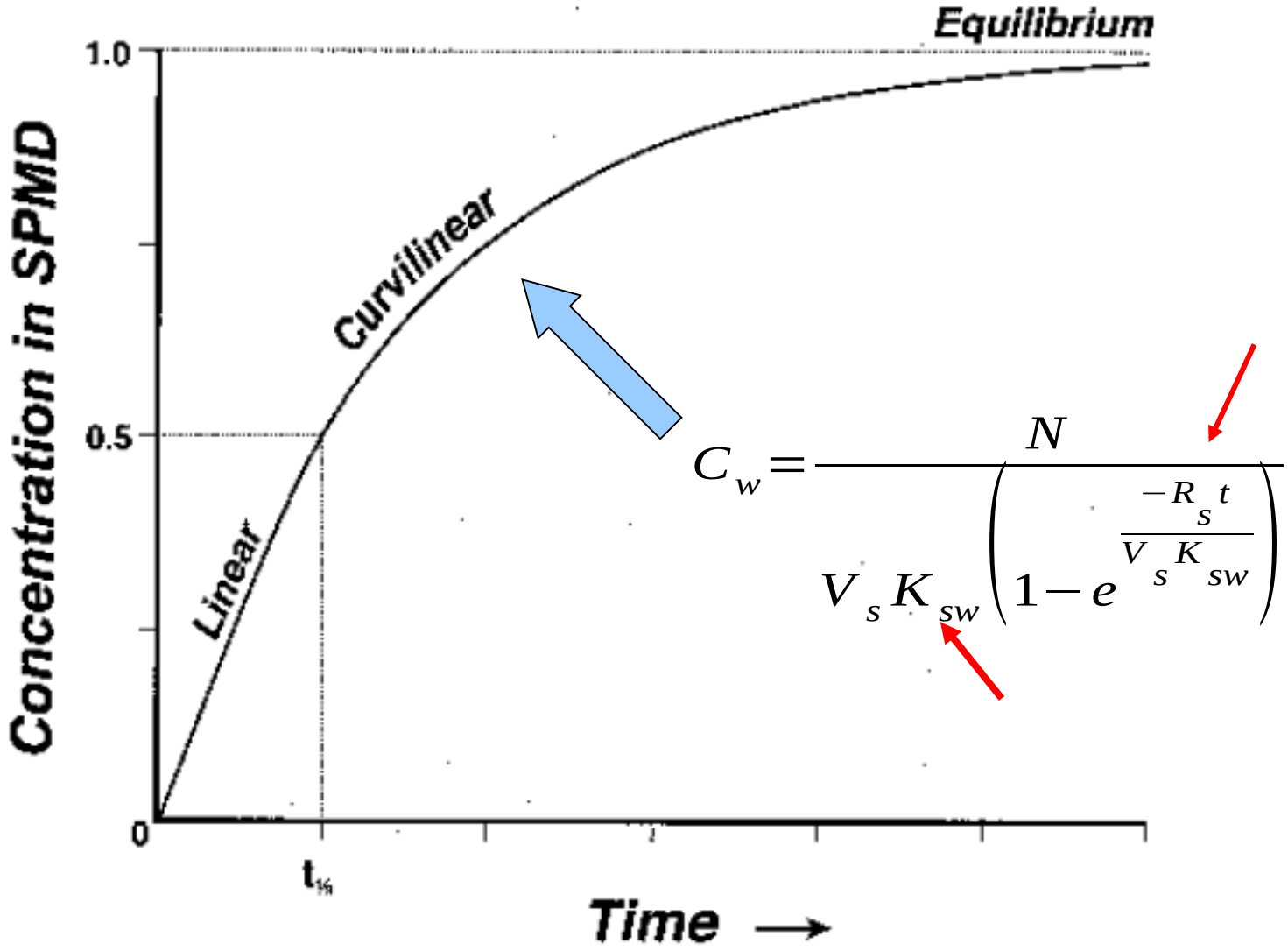


Campionamento passivo

- La concentrazione misurata nel campionatore deve essere proporzionale alla concentrazione ambientale
- Devono essere note le costanti di velocità e d'equilibrio applicabili alla situazione di campionamento per gli analiti
- Le costanti di velocità e d'equilibrio devono essere indipendenti dalla concentrazione ambientale
- Il processo di campionamento non deve ridurre siginificativamente la concentrazione dell'analita nel mezzo campionato


Equilibrium
1.0
0.5
0
Concentration in SPMD
Curvilinear
Linear
$C_w \approx \frac{N}{R_s t}$
$t_{1/2}$
Time


Equilibrium
1.0
0.5
0
Concentration in SPMD
Curvilinear
Linear
$t_{1/2}$
Time
$C_w = C_s \frac{k_e}{k_u} = \frac{C_s}{K_{sw}}$


Equilibrium
1.0
0.5
0
Concentration in SPMD
Curvilinear
Linear
$t_{1/2}$
Time
$C_w = \frac{N}{V_s K_{sw}\left(1 - e^{\frac{-R_s t}{V_s K_{sw}}}\right)}$

VALORI EMPIRICI

Table A.1 SPMD-Water Partition Coefficients (K_{sw}s, mL mL^{-1}) of Mono-Aromatic and Polycyclic Aromatic Hydrocarbons

Compound	M	log K_{ow}[a]	log K_{sw}	°C	ref.[b]
benzene	78.1	2.13	1.78	25	1
toluene	92.1	2.69	2.34	25	1
ethylbenzene	106.2	3.13	2.80	25	1
naphthalene	128.2	3.37	3.20	17	5
naphthalene	128.2	3.37	3.36	24	2
1-methylnaphthalene	142.2	3.87	4.20	17	5
acenaphthylene	152.2	4.00	4.20	17	5

Table A.4 Water Sampling Rates (R_ss) and Uptake Rate Constants (K_us) of 4.5 g, 460 cm^2 SPMDs at a Temperature of 10, 18, and 26 °C, and a Flow Rate of 0.004 cm s^{-1} (Huckins et al., 1999)

Compounds	M (g mol^{-1})	log K_{ow}[a]	V_{Lebas}(cm^3 mol^{-1})	R_s(L d^{-1})	k_u(L g^{-1} d^{-1})
0.004 cm s^{-1}, 10 °C					
naphthalene	128.2	3.45	147.6	1.9	0.42
acenaphthylene	152.2	4.08	165.7	2.3	0.51
acenaphthene	154.2	4.22	173.0	2.7	0.60
fluorene	166.2	4.38	188.0	3.0	0.67

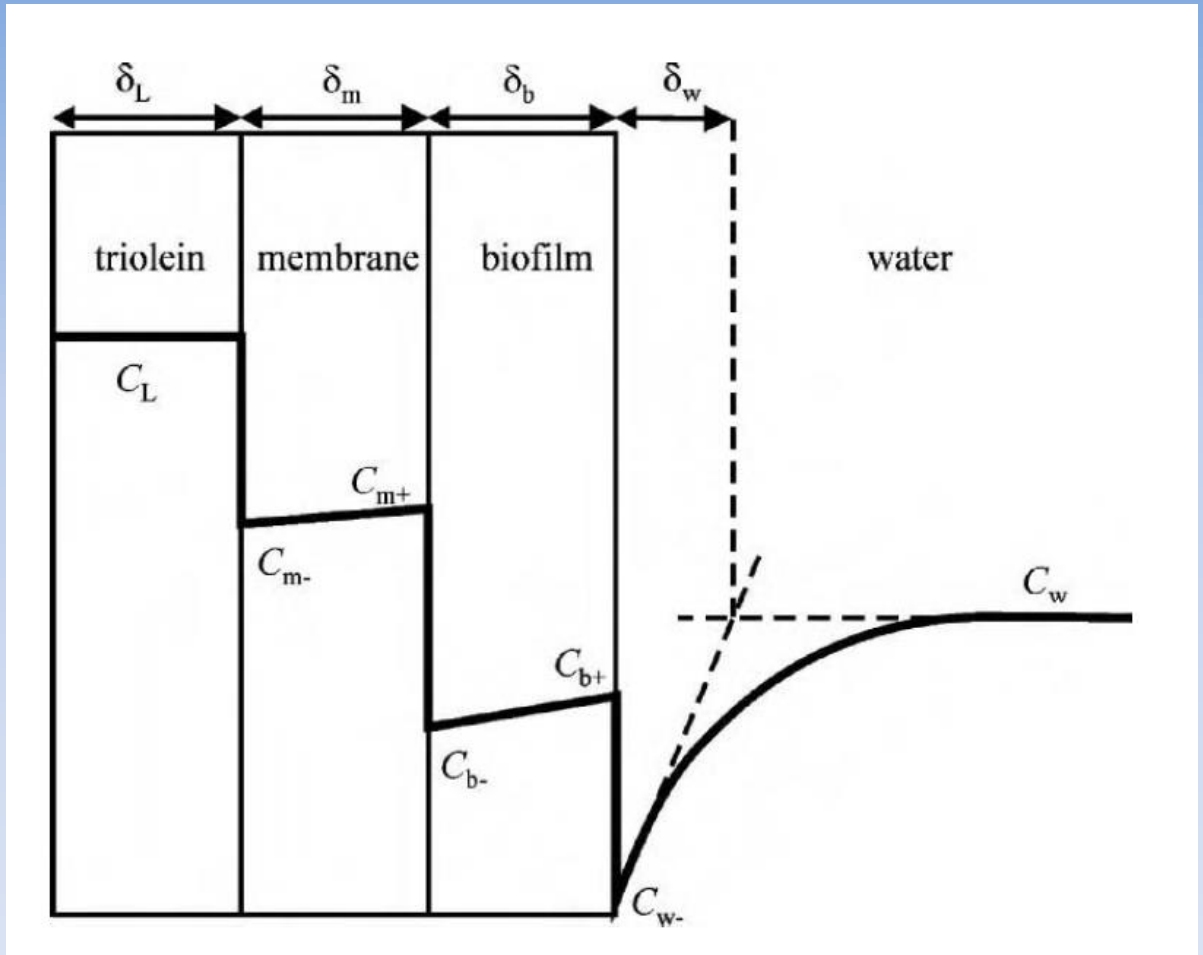
Temperatura = ?

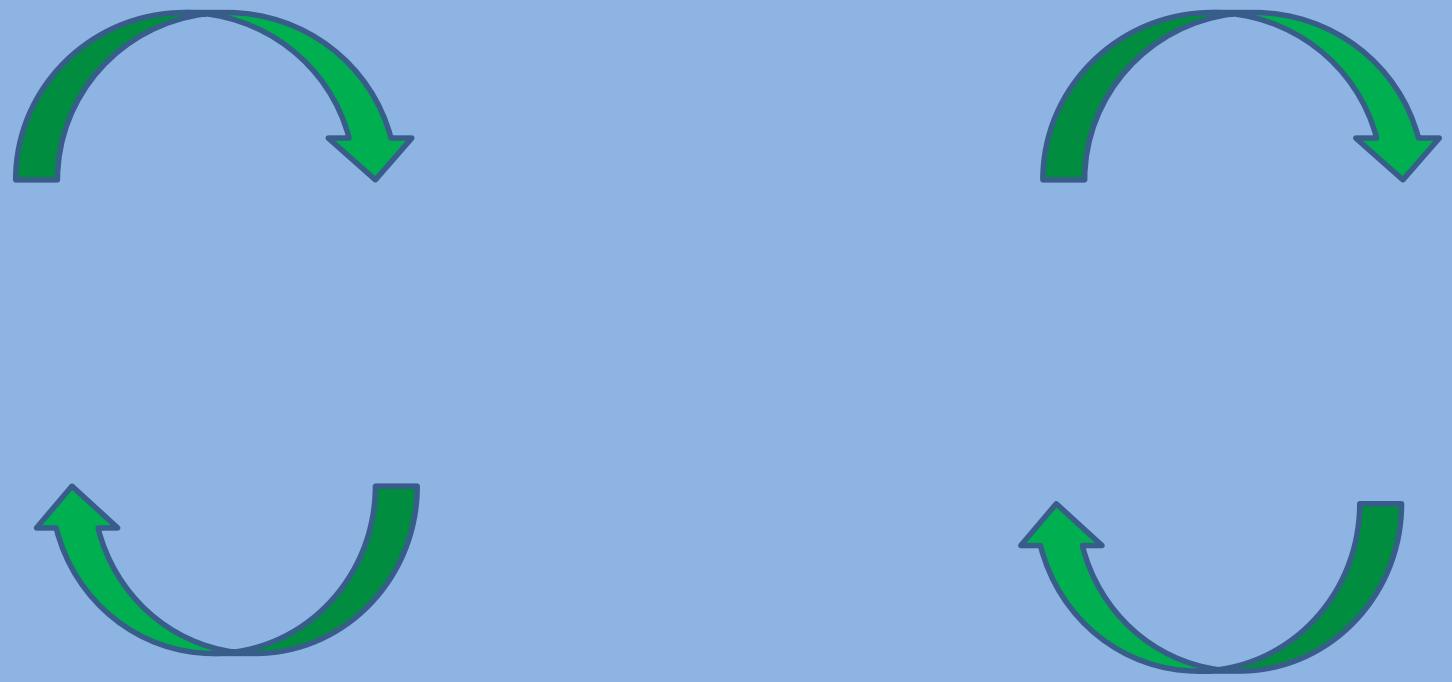
Flusso = ?

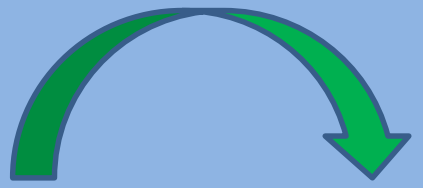
Table A.5 Water Sampling Rates (R_ss) and Uptake Rate Constants (k_us) of 4.5 g, 460 cm^2 SPMDs at a Temperature of 25 °C, and Flow Rates of 0.01 and 50 cm s^{-1} (Luellen and Shea, 2002)

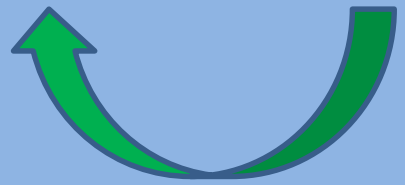
Compound	M(g mol^{-1})	log K_{ow}[a]	V_{Lebas}(cm^3 mol^{-1})	R_s(L d^{-1})	k_u(L g^{-1} d^{-1})
0.01 cm s^{-1}, 25 °C					
naphthalene	128.2	3.37	147.6	3.0	0.68
C1-naphthalenes	142.2	3.86	169.8	5.4	1.20
biphenyl	154.2	3.90	184.6	4.4	0.97
C2-naphthalenes	156.2	4.37	192.0	7.3	1.62
fluorene	166.2	4.18	188.0	5.1	1.14
dibenzofuran	168.2	4.12	184.6	5.2	1.16

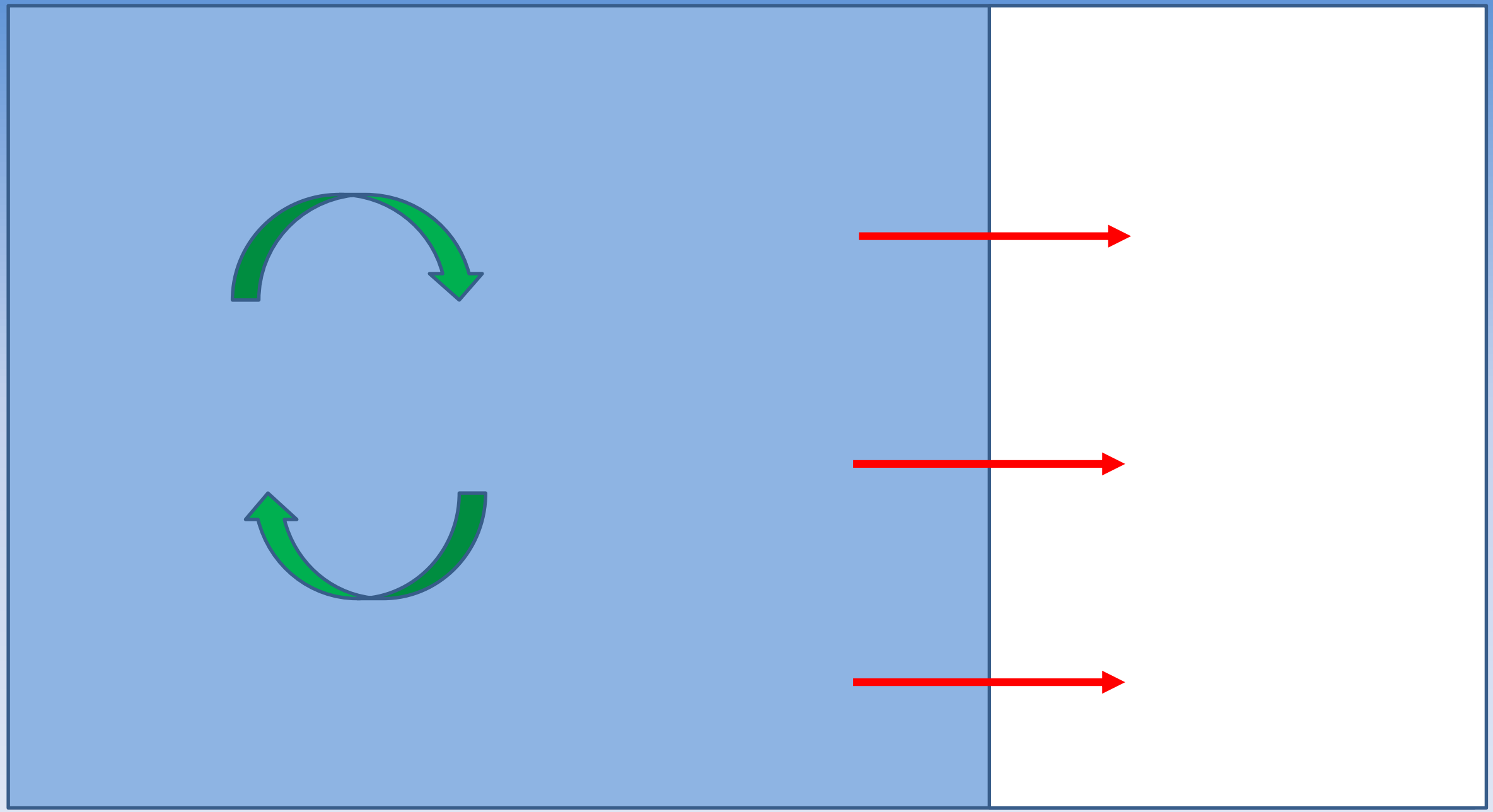
Schema di un SPMD

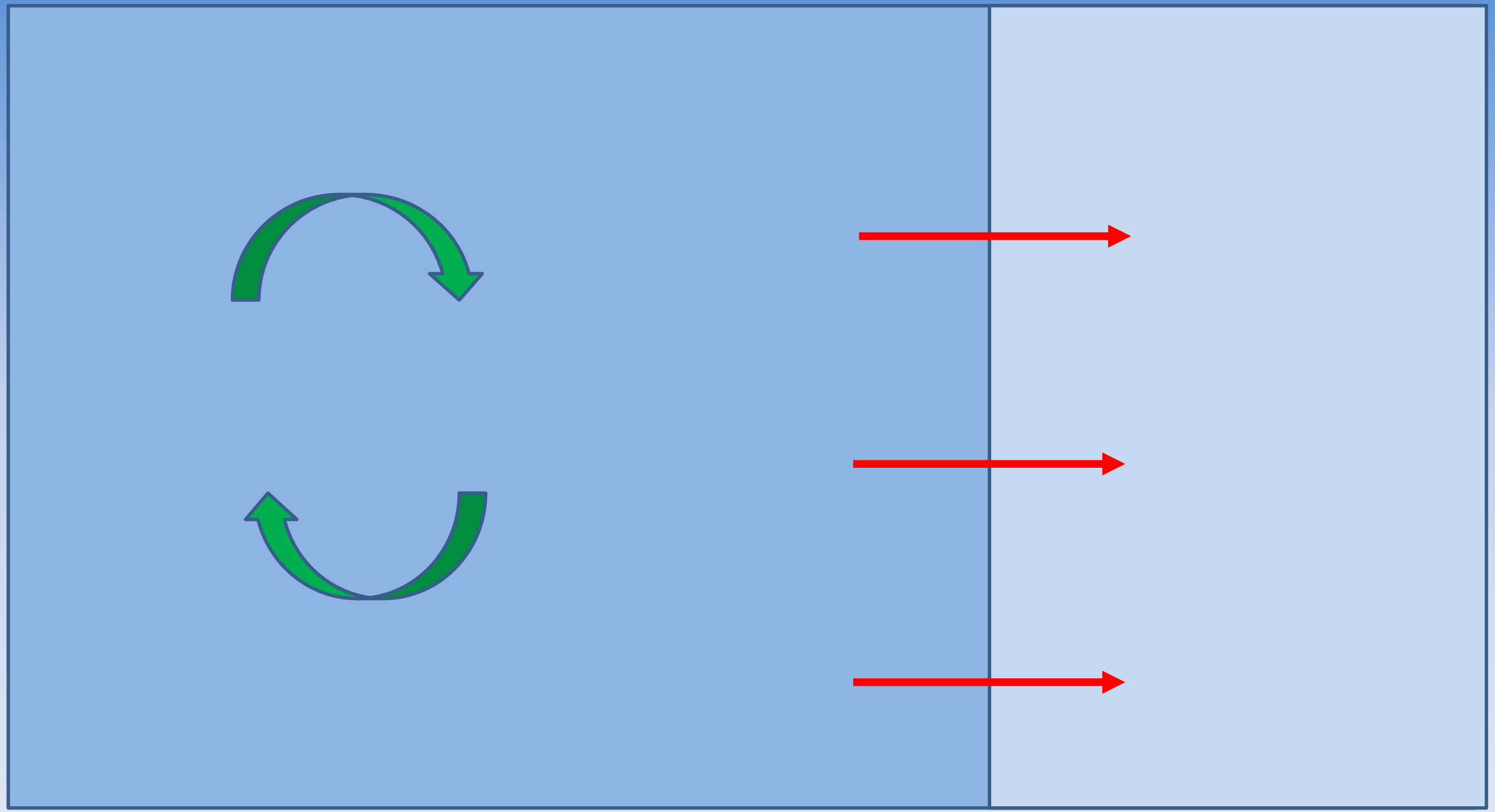


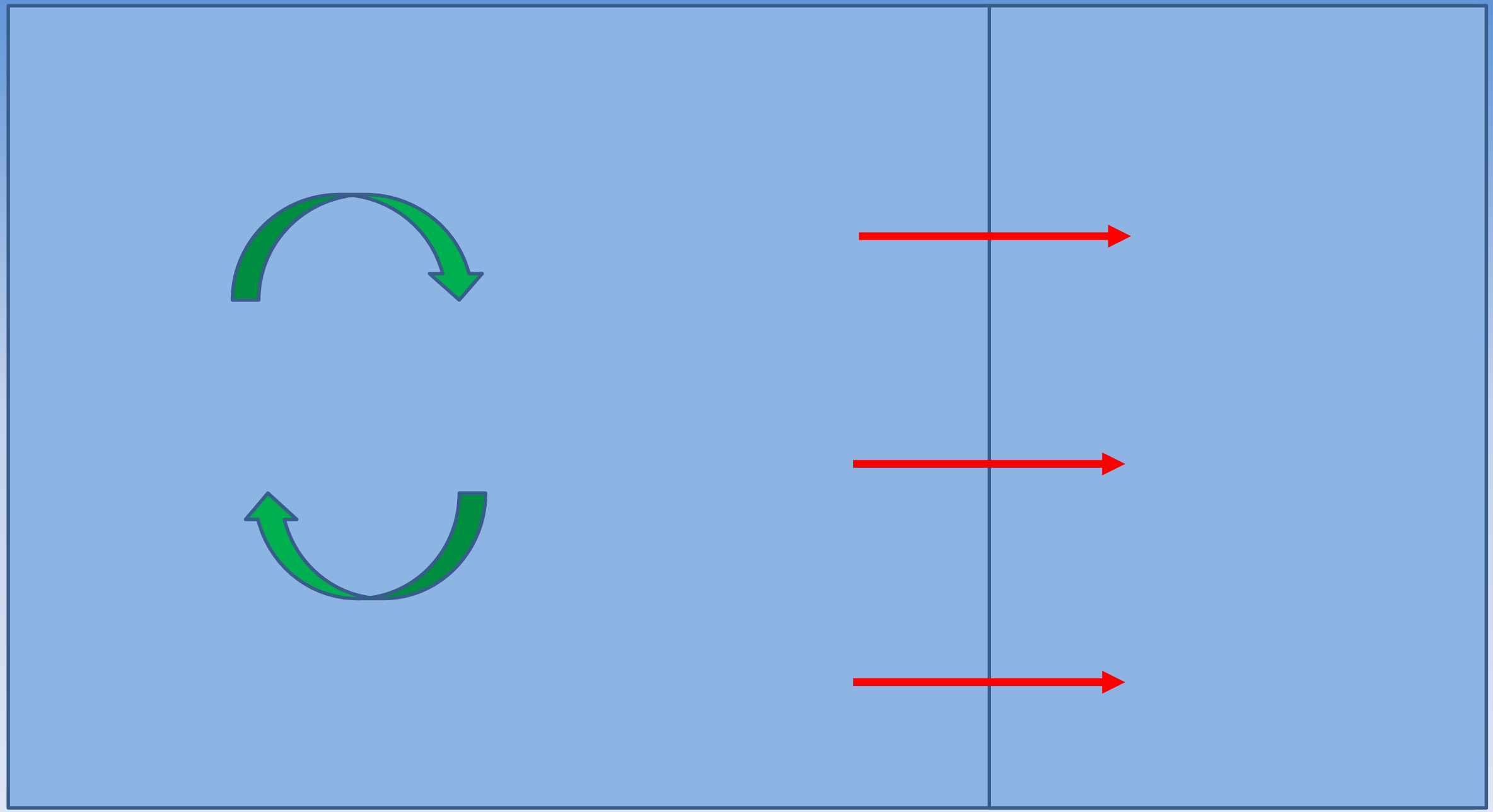


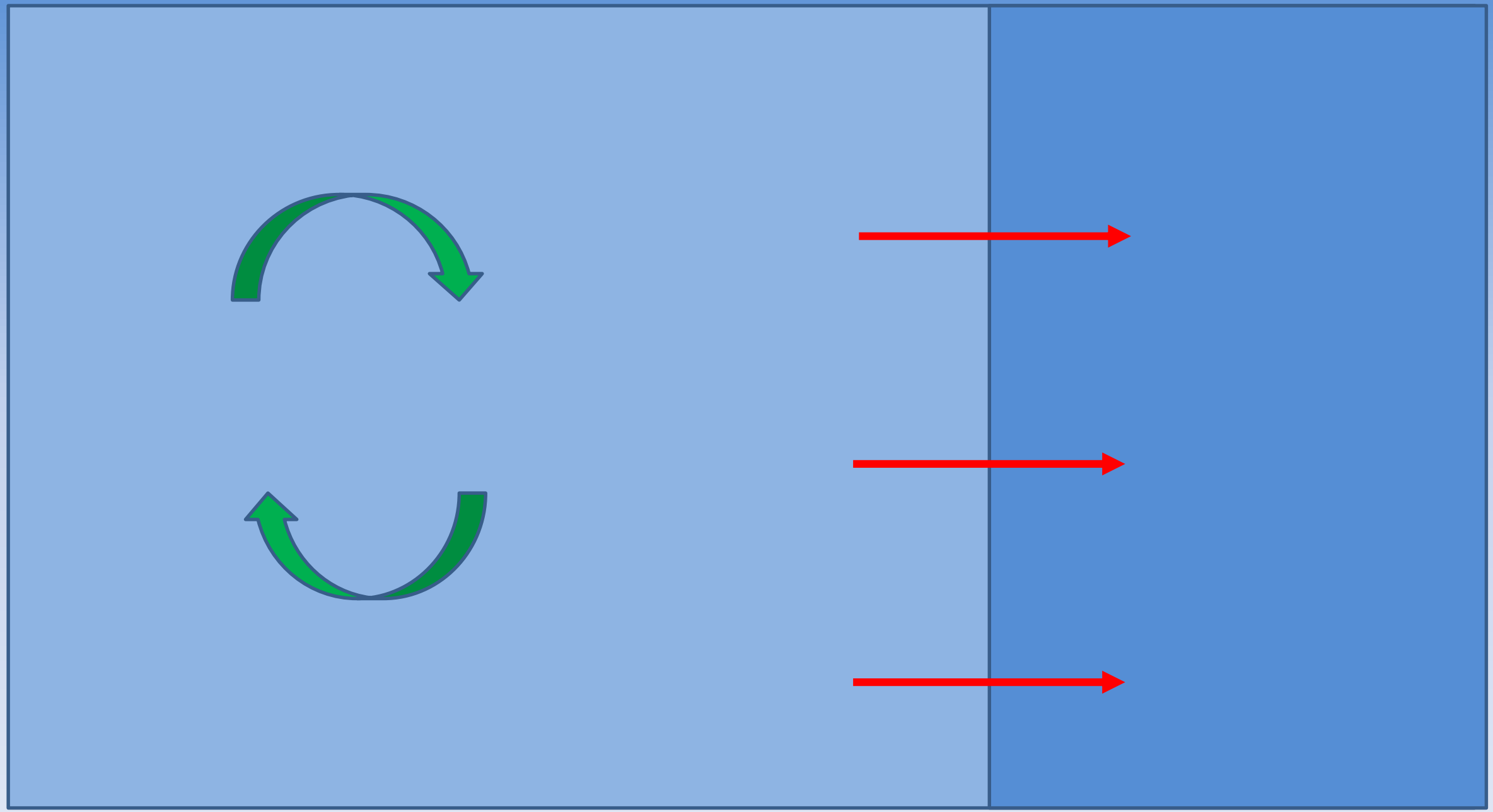


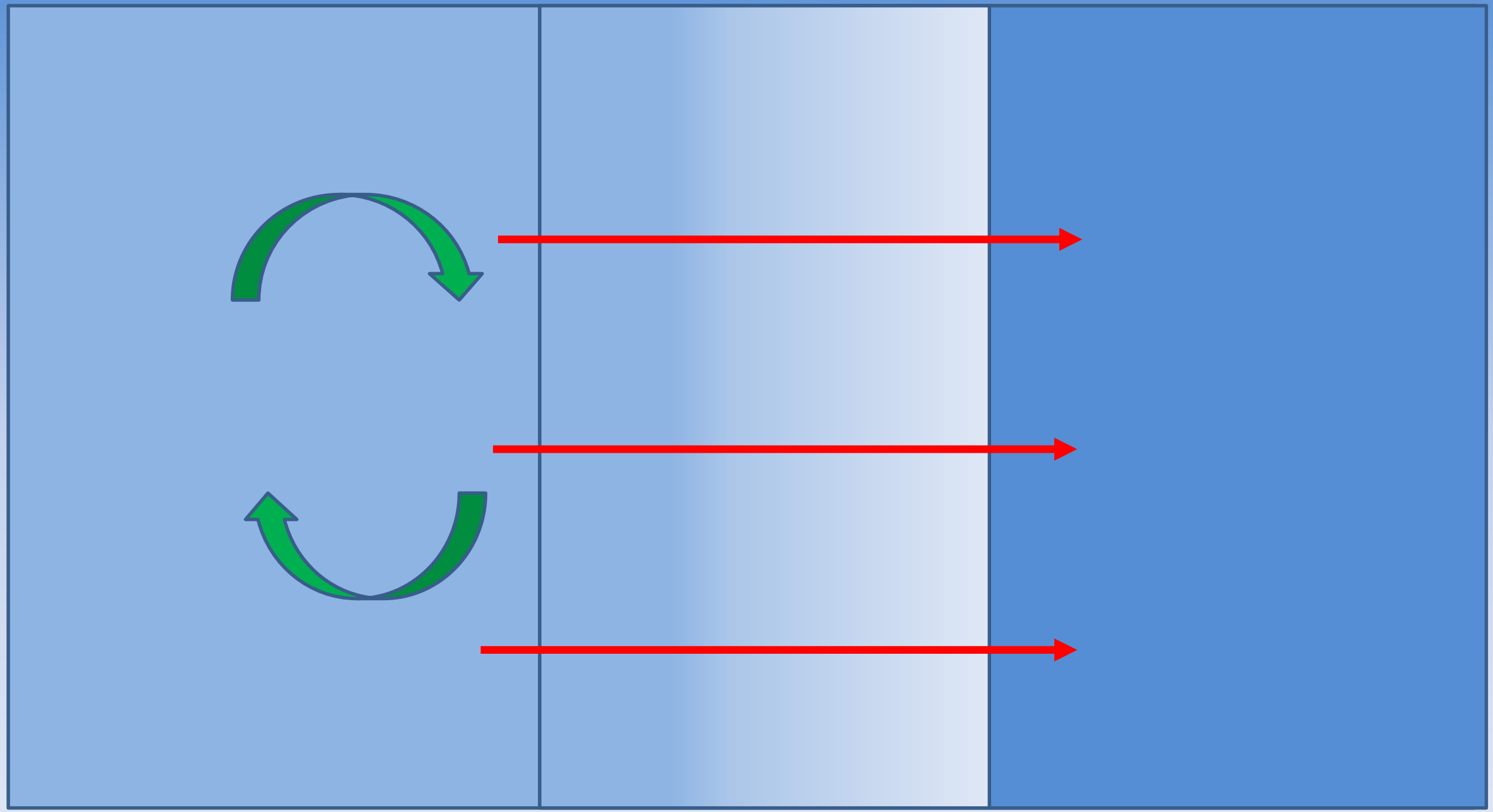


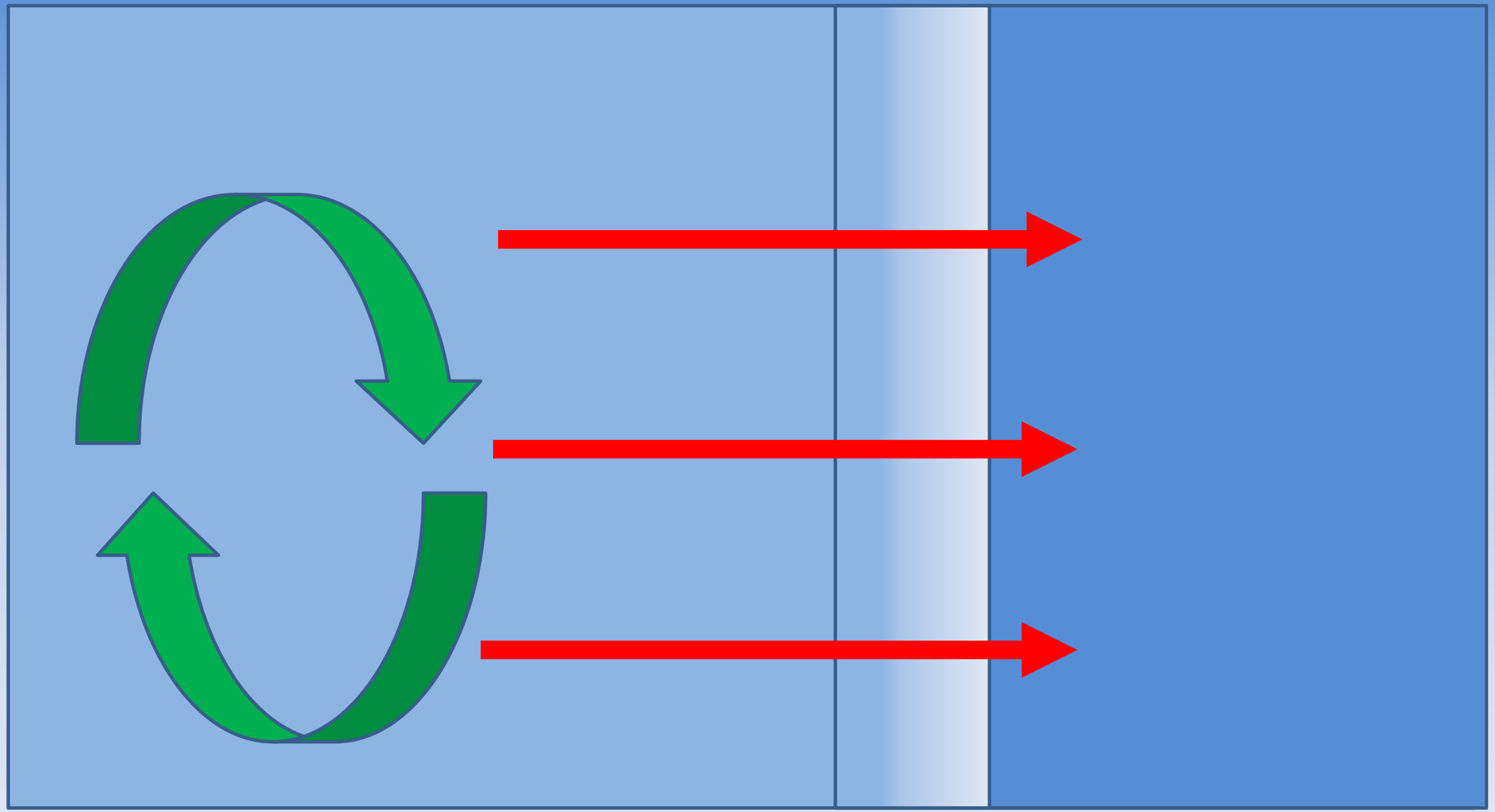












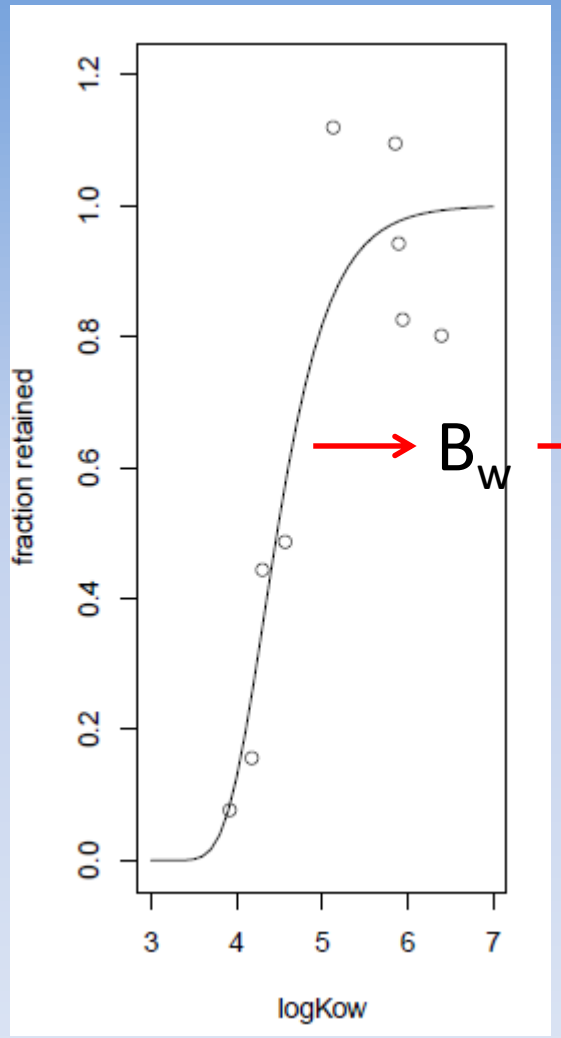
Performance Reference Compounds (PRCs)

Come fare a conoscere la K_e (e quindi la R_s) quando non si conoscono le condizioni ambientali ?

Si usano i PRC.

Sostanza analoga agli analiti (cogenere o marcata con deuterio o C^{13}), non presente nell'ambiente, aggiunta al campionatore prima della esposizione.

GRAFICO



B_w

$$R_s = k_o A = \frac{1}{\frac{1}{A B_m K_{ow}^{0.682}} + \frac{1}{A B_w K_{ow}^{-0.044}}}$$

R_s

In pratica :

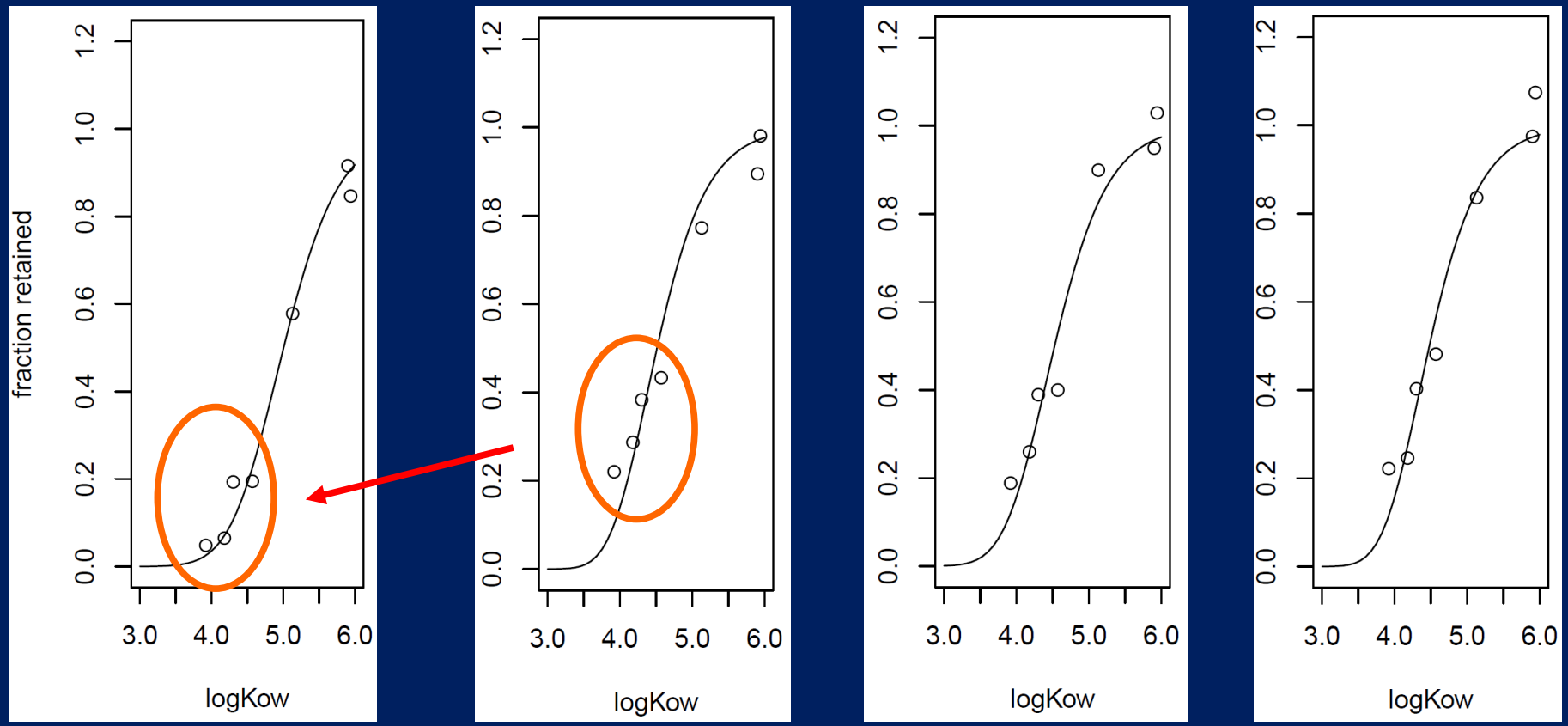
B_w

$$R_s = k_o A = \frac{1}{\frac{1}{A B_m K_{ow}^{0.682}} + \frac{1}{A B_w K_{ow}^{-0.044}}}$$

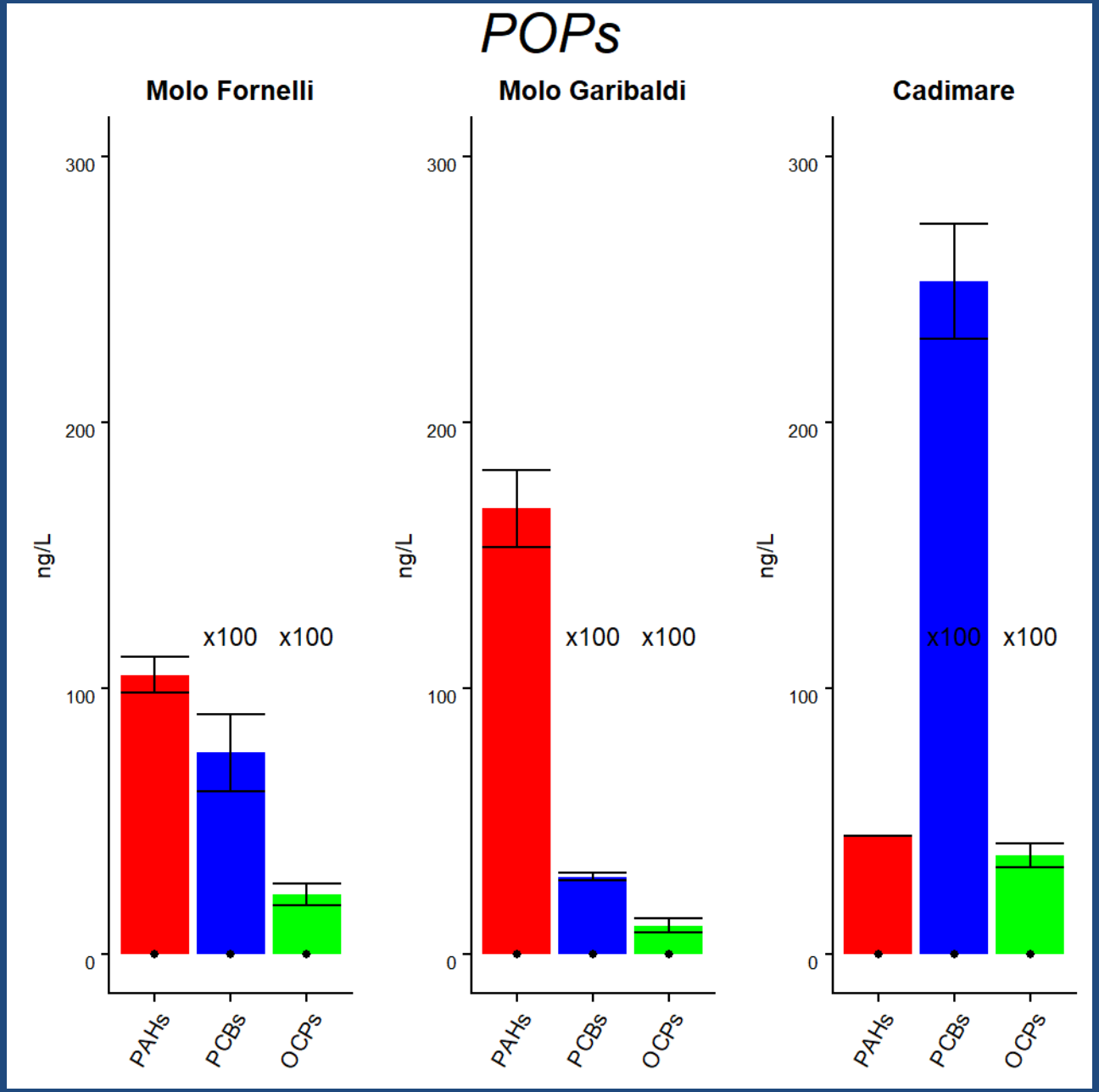
$$C_w = \frac{N}{V_s K_{sw}\left(1 - \exp\left(-\frac{R_s t}{V_s K_{sw}}\right)\right)}$$

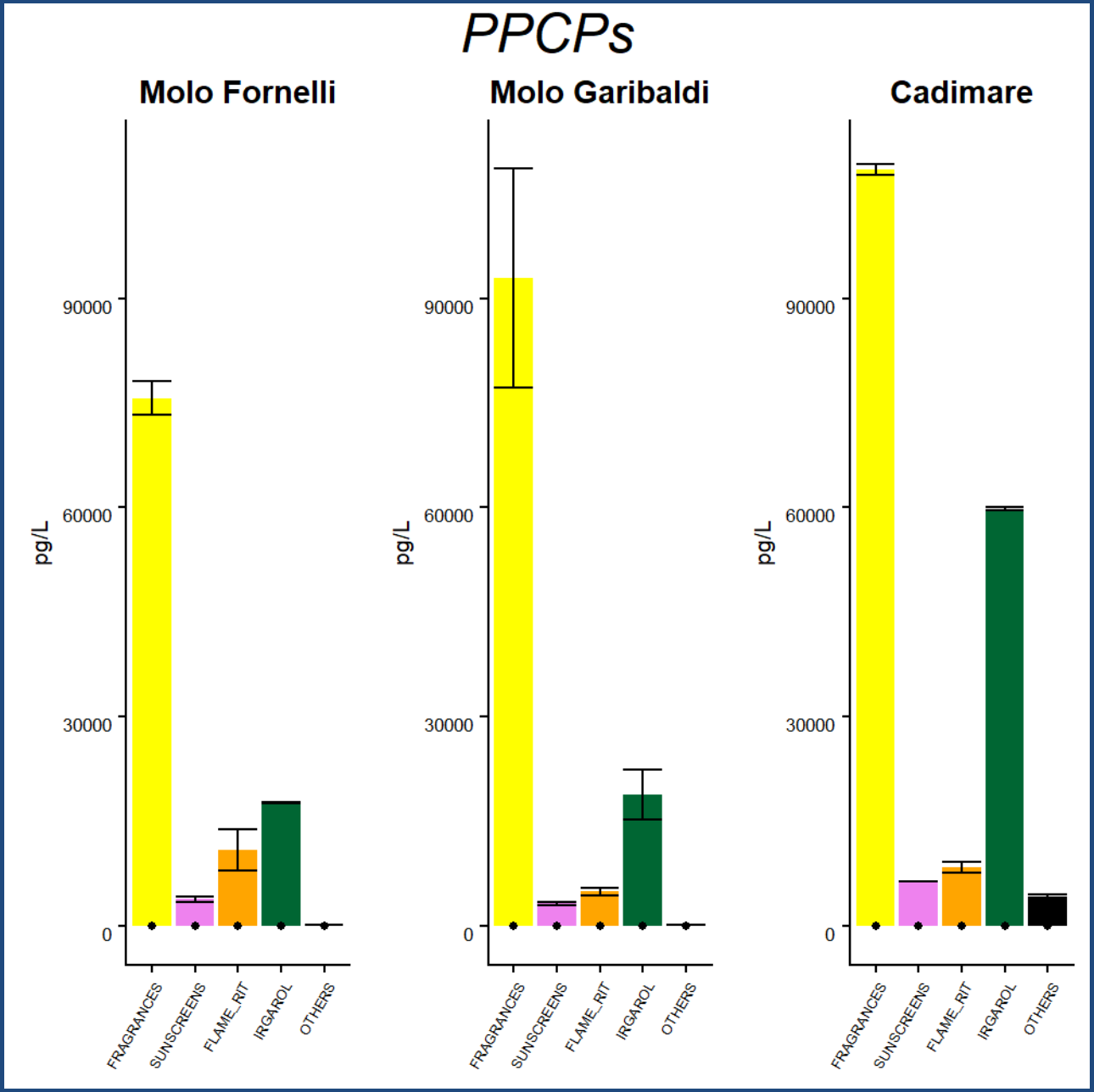
PRCs fractions retained

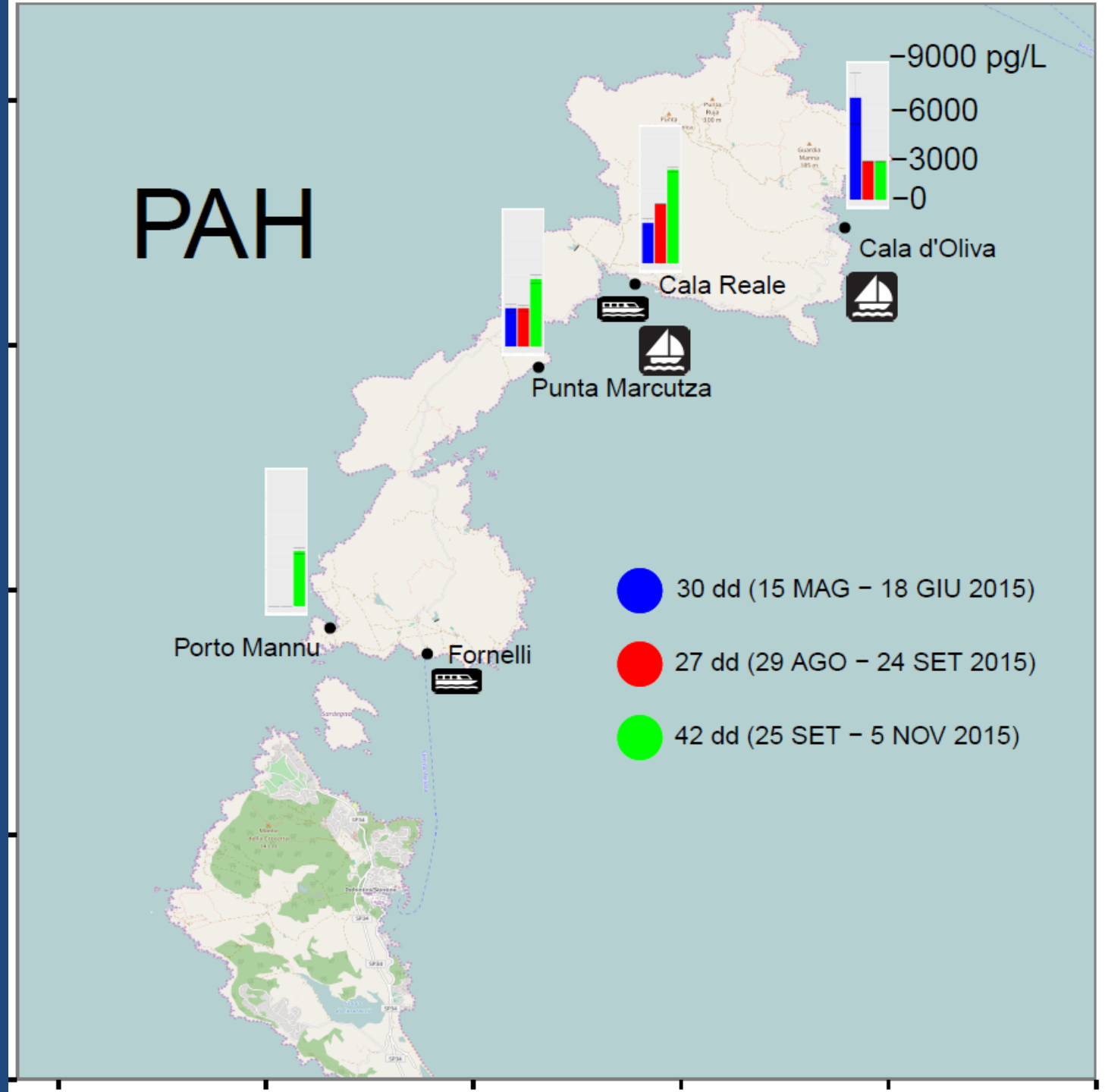
W0 WR WA WL

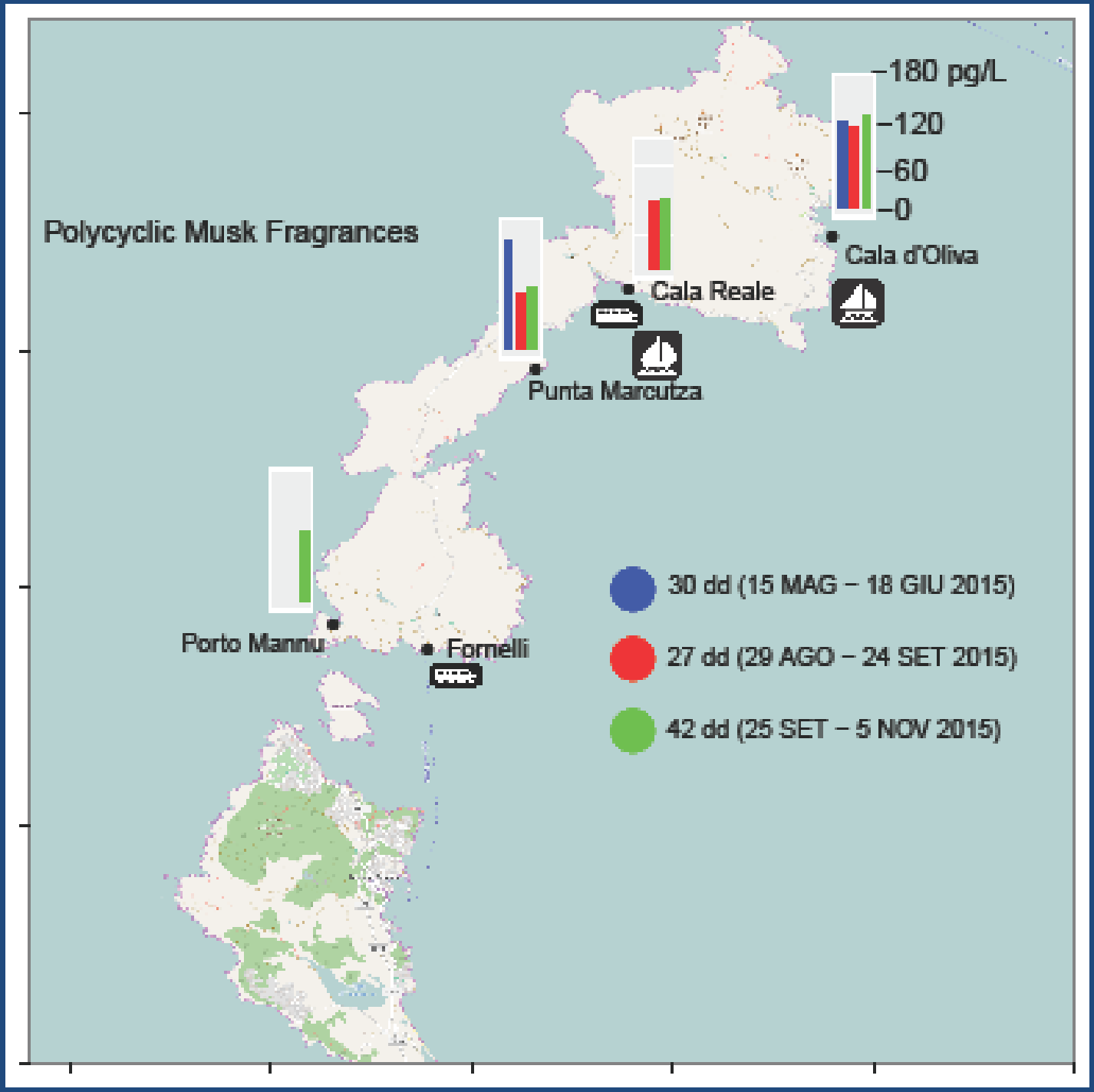


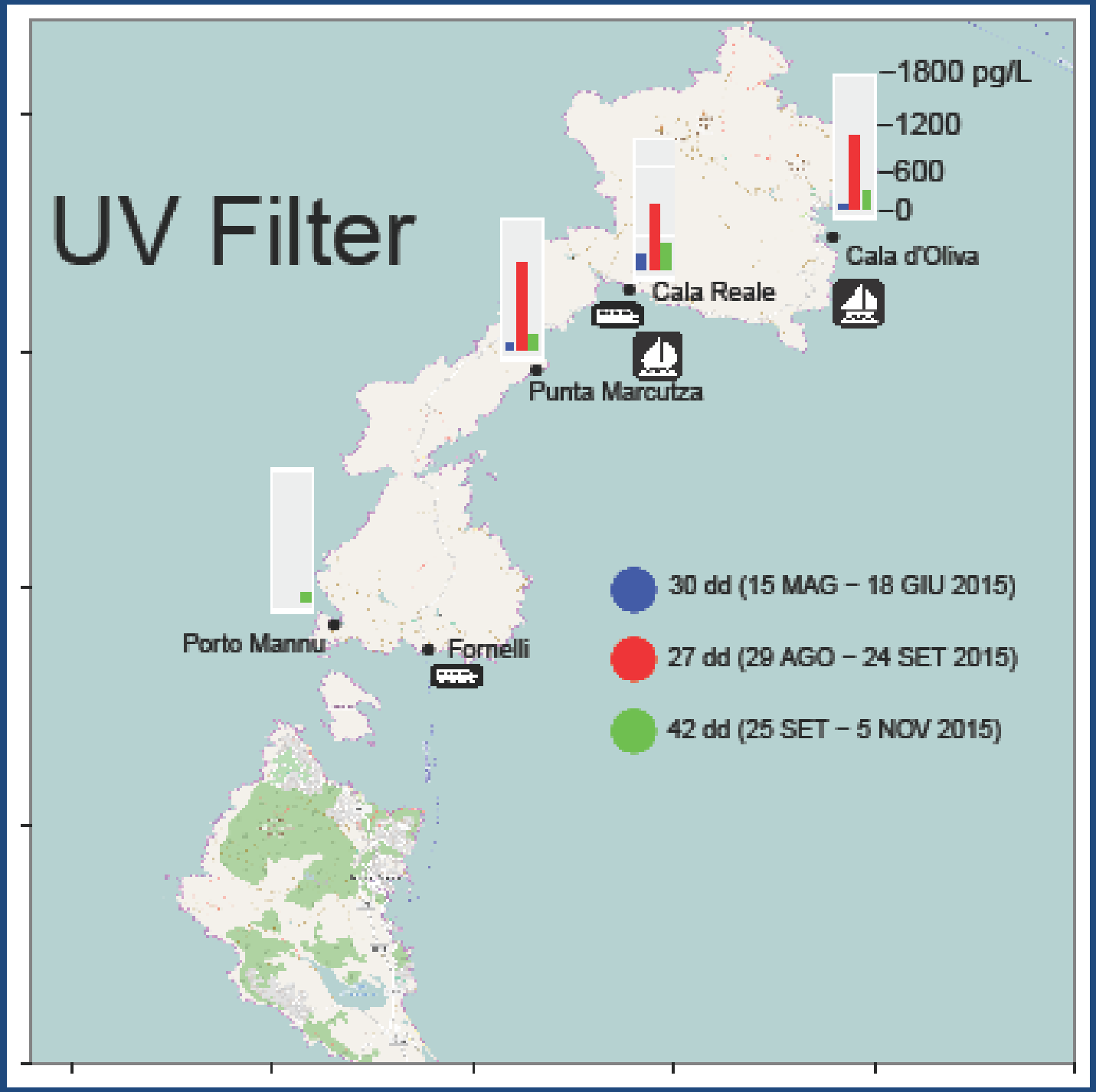
KIDAN COSTA CONCORDIA


POPs
Molo Fornelli
Molo Garibaldi
Cadimare
ng/L
300
200
100
0
x100
x100
PAHs
PCBs
OCPs


PPCPs
Molo Fornelli
Molo Garibaldi
Cadimare
pg/L
90000
60000
30000
0
FRAGRANCES
SUNSCREENS
FLAME_RIT
IRGAROL
OTHERS


PAH
9000 pg/L
6000
3000
0
Cala d'Oliva
Cala Reale
Punta Marcutza
Porto Mannu
Fornelli
30 dd (15 MAG – 18 GIU 2015)
27 dd (29 AGO – 24 SET 2015)
42 dd (25 SET – 5 NOV 2015)


Polycyclic Musk Fragrances
180 pg/L
120
60
0
Cala d'Oliva
Cala Reale
Punta Marcutza
Porto Mannu
Formelli
30 dd (15 MAG – 18 GIU 2015)
27 dd (29 AGO – 24 SET 2015)
42 dd (25 SET – 5 NOV 2015)


UV Filter
1800 pg/L
1200
600
0
Cala d'Oliva
Cala Reale
Punta Marcutza
Porto Mannu
Formelli
30 dd (15 MAG – 18 GIU 2015)
27 dd (29 AGO – 24 SET 2015)
42 dd (25 SET – 5 NOV 2015)

Linee guida

- **ITRC** - *Technology Overview of Passive Sampler Technologies* - 2006
- **UE** - Water quality - Sampling - Part 23*: Guidance on passive sampling in surface waters* (ISO 5667-23:2011)
- **USGS** - *Guidelines for the Use of the Semipermeable Membrane Device (SPMD) and the Polar Organic Chemical Integrative Sampler (POCIS) in Environmental Monitoring Studies* – 2010
- **ICES** - *Guidelines for passive sampling of hydrophobic contaminants in water using silicone rubber samplers* – 2012
- **FOKS** - *Guide for Passive sampling technology for water assessment - A tool for identification of key sources of water contamination* -2010
- **EPA** - *Guidelines for Using Passive Samplers to Monitor Organic Contaminants at Superfund Sediment Sites* - 2012
- **NOAA/AFSC** - *Plastic Membrane Device (PMD) samplers - Placement and Retrieval Methods*