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Continuous Flow Integrative Sampler (CFIS). An innovative device for time weighted average monitoring.

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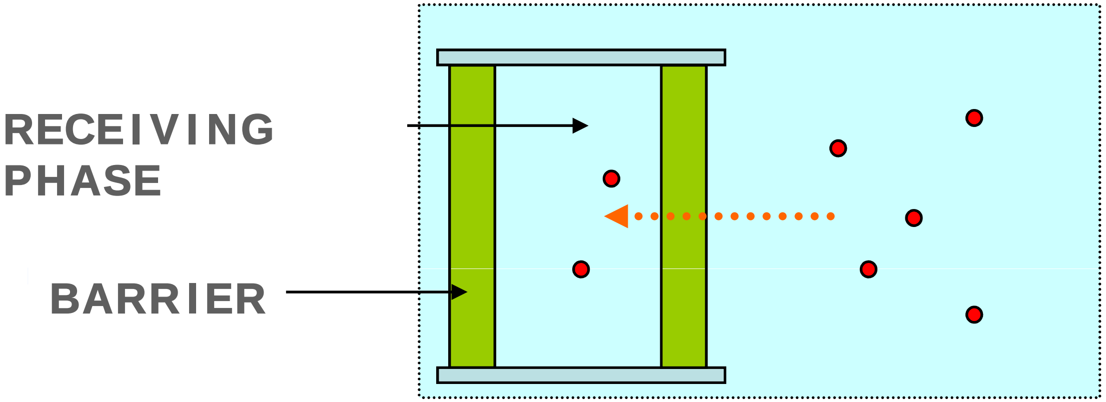
- Description of the device
- Testing and results
- Conclusions

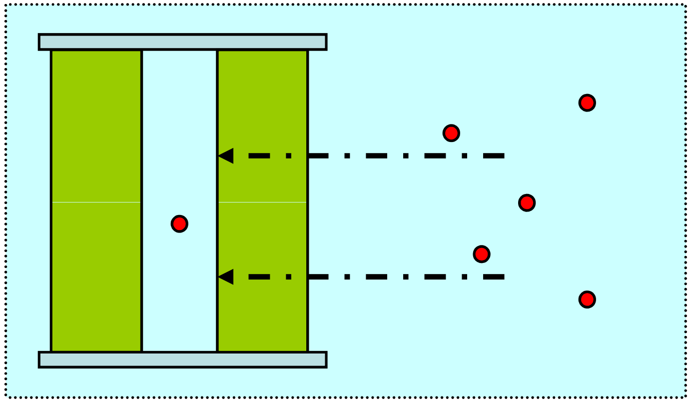
BASIC CONSIDERATIONS



- ✓ **Sampling rate, Rs :** "amount of contaminant accumulated per unit time". Rs (D, geometry, turbulence, temperature, biofilm)
- ✓ **Lag time:** Time in which contaminants reach the steady state along the different barriers.
- ✓ **t ½ :** Linear integrative period
- ✓ **Practical and economical aspects:** biofilm, analitycal method, cost per sampler, etc.

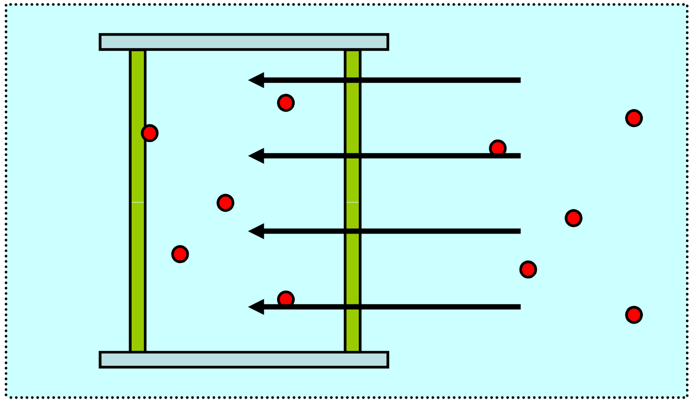
MORE IN DEPTH CONSIDERATIONS

SLOW SAMPLER



- ✓ LOW influence with turbulence
- ✓ LOW Rs
- ✓ HIGH Lag time

FAST SAMPLER

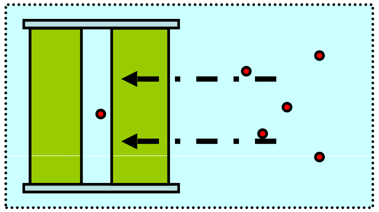


- ✓ HIGH Rs
- ✓ LOW Lag time
- ✓ HIGH influence with turbulence
- ✓ t ½ !!!!!!

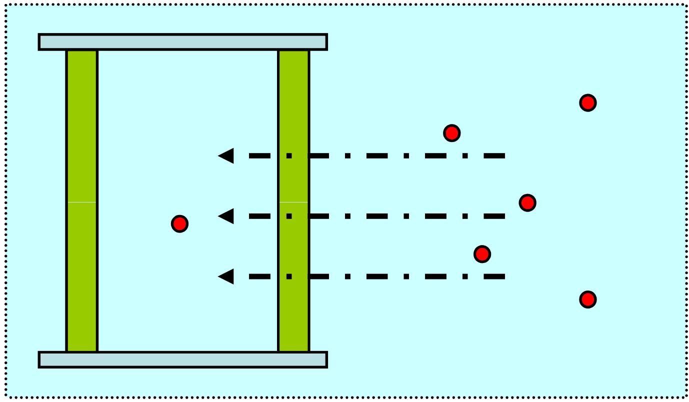
MORE IN DEPTH CONSIDERATIONS

COMPROMISE

SLOW SAMPLER



- ✓ LOW influence with turbulence
- ✓ LOW Rs
- ✓ HIGH Lag time

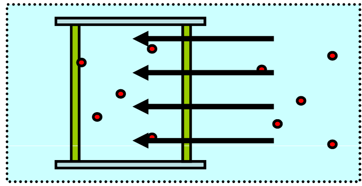


- ✓ MEDIUM Rs

- ✓ MEDIUM Lag time

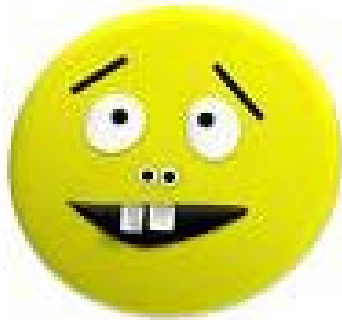
- ✓ MEDIUM influence with turbulence

FAST SAMPLER



- ✓ HIGH influence with turbulence
- ✓ HIGH Rs
- ✓ LOW Lag time
- ✓ t ½ !!!!!!

PRC



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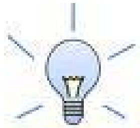
THOUGTHS FOR DISCUSSION



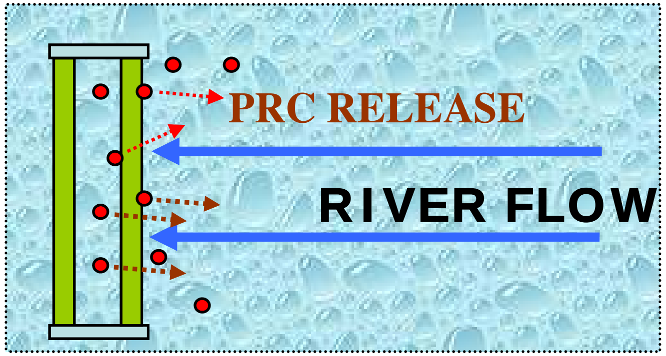
PRC

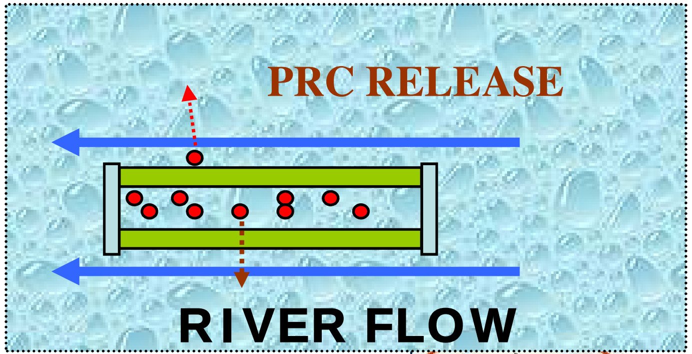
~~TIME WEIGHTED AVERAGE CONCENTRATION~~

FLOW WEIGHTED AVERAGE CONCENTRATION

TWA *vs* FWA

Are we measuring the "REAL" flow?





THE OBJECTIVE

DEVELOPMENT OF A NEW SAMPLING DEVICE (APOLAR COMPOUNDS):

1.-TIME WEIGHTED AVERAGE (TWA) VALUES

2.-SAMPLING RATES (Rs) INDEPENDENT FROM THE IN-FIELD TURBULENCES.

3.-LOW OR NEGLIGIBLE LAG TIME.

4.-t ½ > 5 days

5.-"COMPETITIVE" PRICE.

THE TEAM

THE MONEY

FUNDED PROJECTS ON PASSIVE SAMPLING

DURATION	ORGANISM	FUNDED AMOUNT €
2006-2007	MINISTERIO DE INDUSTRIA, TURISNMO Y COMERCIO (MITYC)	**62,450**
2007-2008	MINISTERIO DE MEDIO AMBIENTE	**26,919**
2007-2008	IMPIVA	**15,906**
2007-2008	Applus	**22,118**
2007-2011	CDTI	**125,000**
2009-2010	MINISTERIO DE MEDIO AMBIENTE Y MEDIO RURAL Y MARINO	**40,440**
2008-2010	MINISTERIO DE CIENCIA E INNOVACIÓN (INSTITUTO ESPAÑOL DE OCEANOGRAFÍA)	**16,000**

TOTAL FUNDED **308,833 €**

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FIRST APROACHES

✓ **LITERATURE REVIEW AND LEARNING PROCESS:**

B.Vrana: theoretical and practical aspects on PS.

R. Greenwood: Chemcatcher.

Audrone Zaliauskiene: SPMD.

A.Paschke: MESCO.

✓ **SELECTION OF THE RECEIVING PHASE :** PDMS

✓ **Experiments with MESCO and some variations around this device.**

FIRST APROACHES

TWA, Rs not affected by turbulences, low Lag time

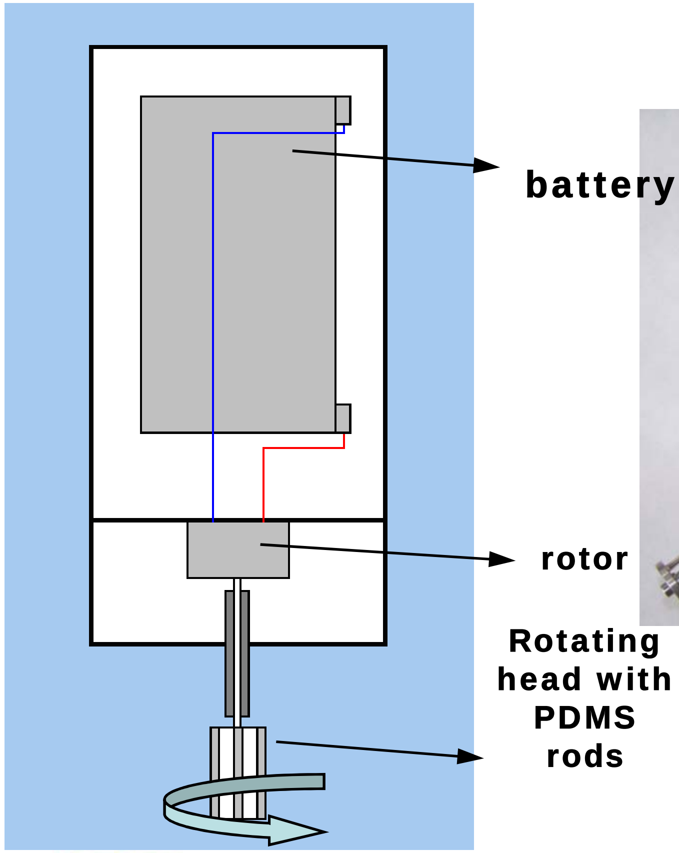
COMPROMISE

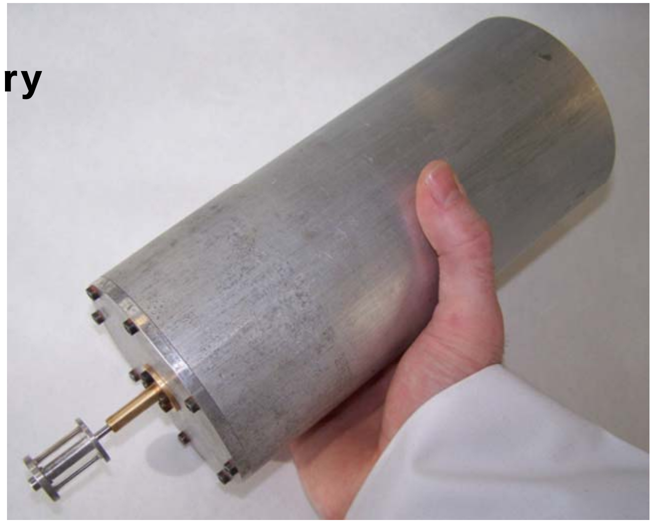
ABANDON PASSIVE SYSTEMS

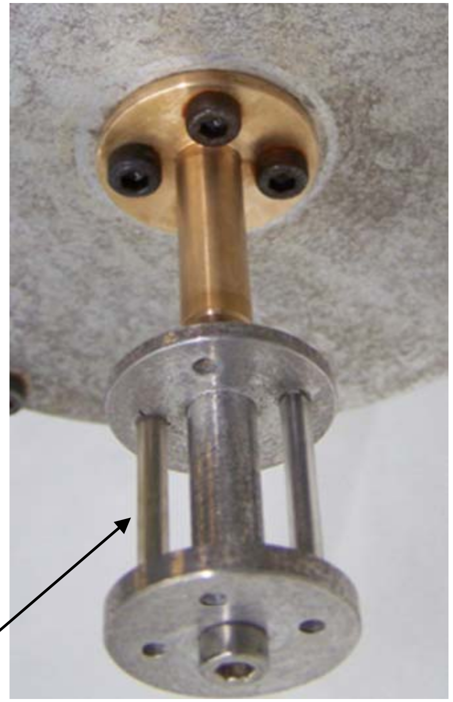
Introduce some "small energy" to control turbulence

Previous prototypes

CSS: Constantly Stirred Sorbent



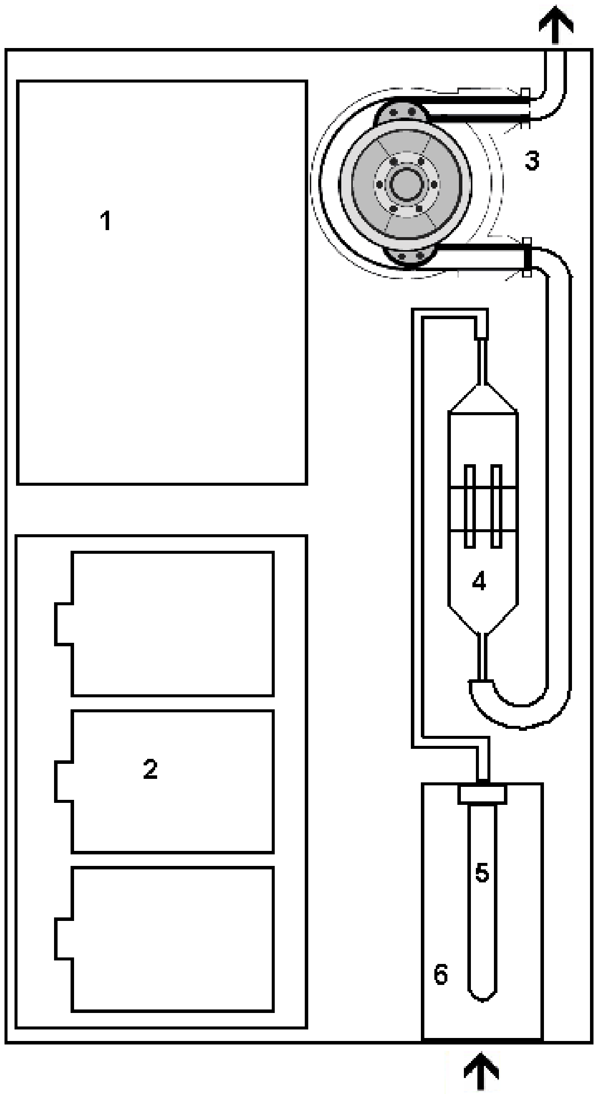




Twister™

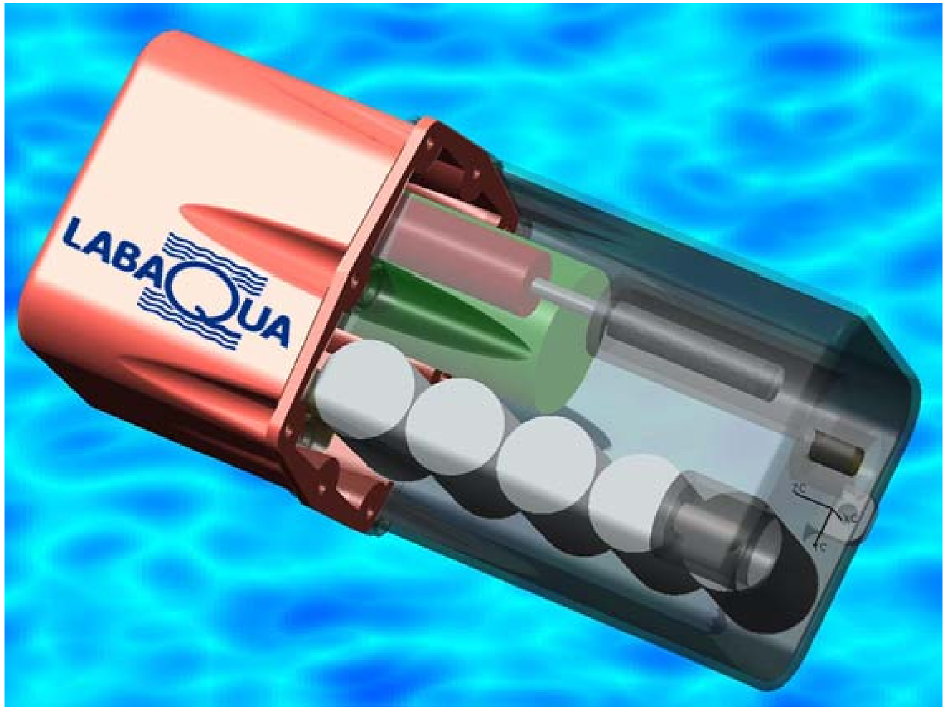
Continuous Flow Integrative Sampler (CFIS)

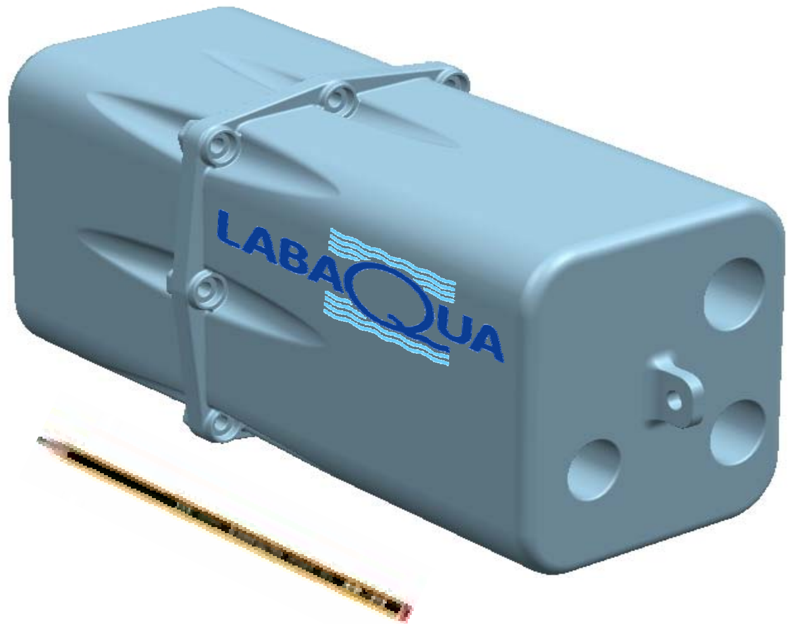
Basic scheme

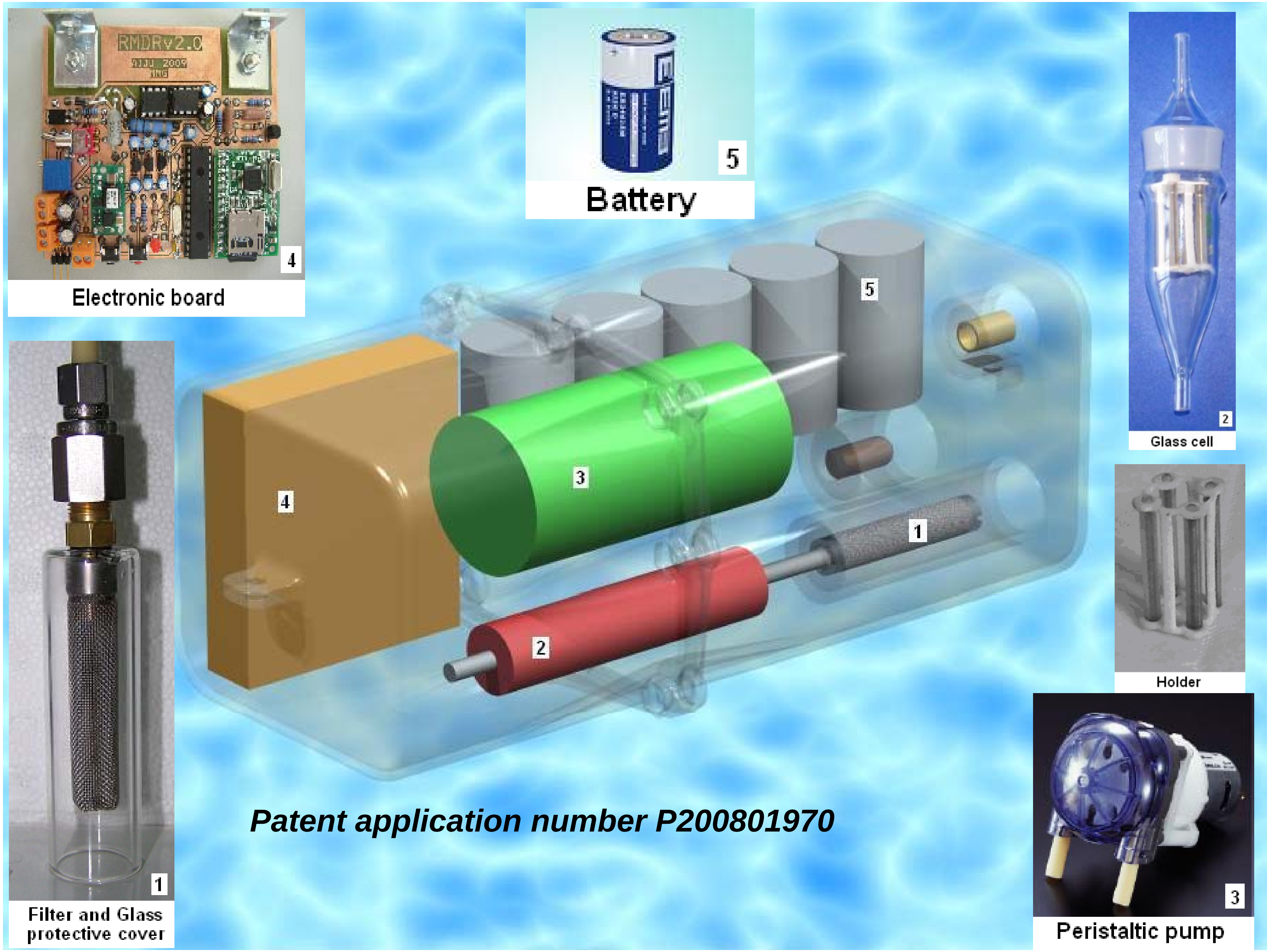


1.- Electronic board .
2.- Lithium batteries.
3.- Mini-peristaltic pump.
4.- Glass cell with sorbent.
5.- Stainless steel filter
6.- Glass sleeve.

Continuous Flow Integrative Sampler (CFIS)

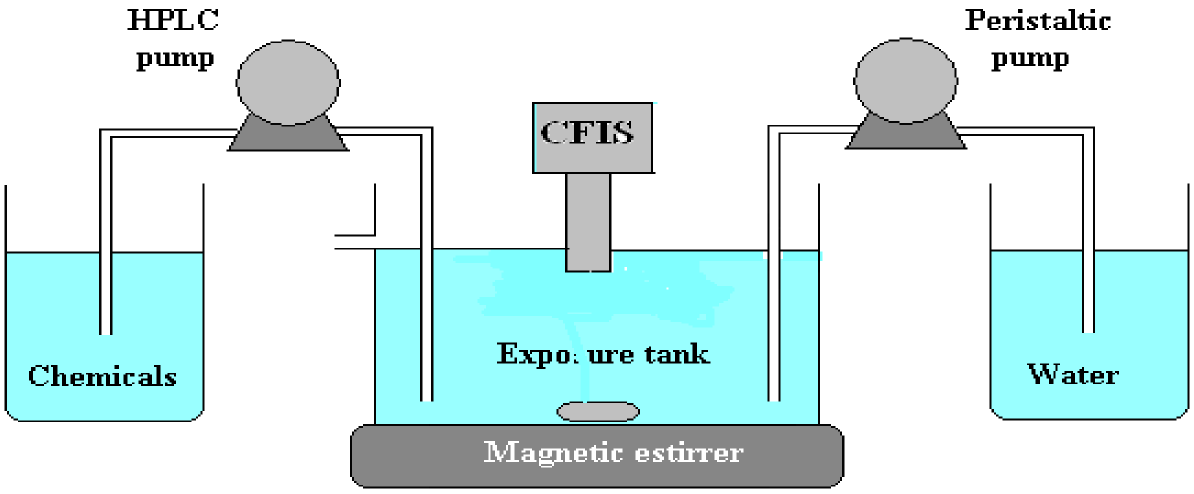





RMDRv2.0
4
Electronic board
5
Battery
5
3
4
1
2
2
Glass cell
Holder
1
Filter and Glass protective cover
Patent application number P200801970
3
Peristaltic pump

Materials and methods

Scheme of the flow through exposure system.



Materials and methods

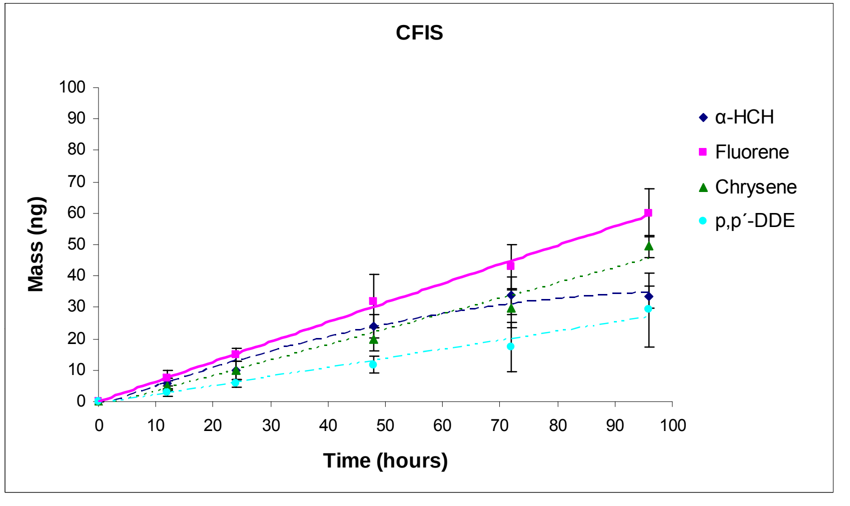
Selected physicochemical properties of test analytes. (Dw : Diffusion coefficients in water).

Compound	MW	log K_{ow}	log K_{PDMSW} [c]	D_w [d]
Lindane	290.8	3.8[b]	3.36	5.4×10^{-10}
α-HCH	290.8	3.9[b]	3.44	5.4×10^{-10}
Fluorene	166.2	4.2[a]	3.68	6.8×10^{-10}
Phenanthrene	178.2	4.5[a]	3.93	6.6×10^{-10}
Fluoranthene	202.3	5.1[a]	4.42	6.3×10^{-10}
Chrysene	228.3	5.7[a]	4.91	5.8×10^{-10}
p,p´-DDE	318.0	6.1[b]	5.24	5.1×10^{-10}
Benzo[a]pyrene	252.3	6.2[a]	5.32	5.5×10^{-10}
Benzo[ghi]perylene	276.3	6.9[a]	5.90	5.3×10^{-10}

a: D. Mackay, W.Y. Shiu, K.C. Ma, *Illustrated Handbook of Physicalechemical Properties of Environmental Fate of Organic Chemicals*, 1-2, Lewis Publishers, MI, USA (1992).
b: A. Paschke, P. Popp, *J. Chromaogr. A*, 999 (2003) 35.
c: R.A. Doong, S.M. Chang, *Anal. Chem*., 72 (2000) 3647.
d: Diffusion coefficient in water (m2s-1) from Hayduk-Laudie equation. Compound molar volume estimated from Schroeder equation.

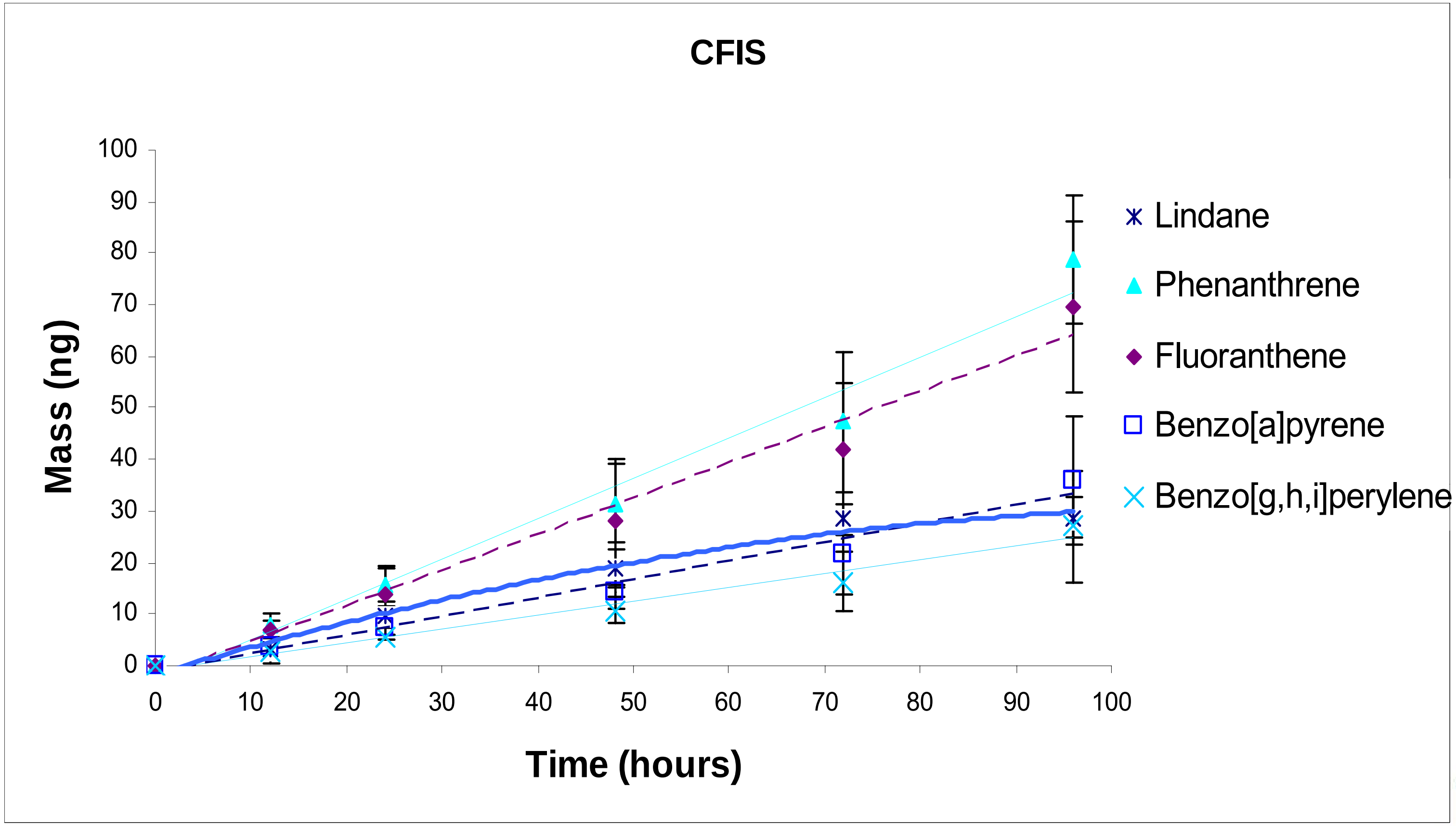
Results and discussion

Accumulation time profiles with CFIS



Results and discussion

Accumulation time profiles with CFIS



Results and discussion

Main performance parameters obtained with CFIS

Compound	t_{50} (h)	R_s (L/day)	Equation	R^2
Lindane	51	0.032	y=0.41x-0.69	0.982[a]
α-HCH	49	0.038	y=0.49x-0.55	0.980[a]
Fluorene	80	0.050	y=0.64x-0.07	0.979[b]
Phenanthrene	**120**	0.053	y=0.48x-0.99	0.982[c]
Fluoranthene	**519**	0.047	y=0.43x-0.79	0.976[c]
Chrysene	**2494**	0.033	y=0.303x-0.59	0.972[c]
p,p´ -DDE	**7723**	0.020	y=0.13x-0.45	0.976[c]
Benzo[a]pyrene	**12859**	0.024	y=0.21x-0.69	0.976[c]
Benzo[g,h,i]perylene	**21506**	0.018	y=0.15x-0.49	0.976[c]

a calculated for t : 0, 12, 24 and 48 h.
b calculated for t: 0, 12, 24, 48 and 72 h.
c calculated for t : 0, 12, 24, 48, 72 y 96 h.
n = 3 repetitions and 4 twisters each one.

Results and discussion

LOD calculated for CFIS

Compound	CFIS (pg/L) [a]
Lindane	63
α-HCH	91
Fluorene	20
Phenanthrene	15
Fluoranthene	4.0
Chrysene	12
p,p´-DDE	144
Benzo[a]pyrene	200
Benzo[ghi]perylene	544

[a] LOD calculated for 5 days sampling period

Results and discussion

In field evaluation

Effluent from secondary BOD_5= 12 mg/L, SS= 15 mg/L

VERSUS

Sampling conditions

- ✓ 5 days sampling period
- ✓ Autosampler collected 100 mL samples every 15 min. At the end of each day, sample filtration, integration and storage at 4ºC.
- ✓ Analysis by SBSE-GC-MS.

Results and discussion

Results obtained for the In Field evaluation of the prototype in the effluent of the WWTP.

Compound	CFIS (ng /L) [a]	Autosampler (ng /L) [a]
Lindane	2.0 ±13	3.1±17
Phenanthrene	2.5 ±12	2.2±16
Fluorene	0.9 ±17	0.8±18
Fluoranthene	1.1 ±16	0.9±14
Chrysene	2.5 ±12	1.5±16
***p,p´*-DDE**	0.8 ±19	≤1
Benzo [a] pyrene	2.1 ±13	2.4 ±18
Benzo [g,h,i] perylene	0.9 ±15	1.0 ±17

[a] mean values ± RSD (%) for n=4 (4 twisters with CFIS and 4 sample analysis with autosampler)

Accuracy considerations

- ✓ **Three analysis are involved in a measurement carried out by means of a sampler using PRC.**

  1.-PRC concentration spiked in the sampler

  2.-PRC concentration after the exposure period.

  3.-Analyte concentration.

$$U = \sqrt{20^2 + 20^2 + 20^2} = 36\ \%$$

- ✓ **Only one analysis with no PRC**

$$U = 20\ \%$$

CONCLUSIONS

1.-An innovative sampler for the TWA monitoring with Rs independent from in-field turbulences has been developed.

2.-Because no membrane is present, lag time values can be considered as negligible.

3.-PDMS in the twisterTM format has been used, nevertheless many other formats can be used. This makes it possible to choose the desired Rs (sensitivity) and/or t ½ values.

4.-The fact that no PRC is needed makes the TWA calculation very easy and accurate because a single chromatographic analysis is needed

5.-Different sorbents can be installed inside the cell increasing the range of applications to polar compounds or metals.

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