

# Design and calibration of Chemcatcher for the monitoring of butyltin compounds in harbour areas.

Antoine Garnier<sup>1,2</sup>, Sylvie Spinelli<sup>1</sup>, Sophie Delpoux<sup>2</sup>, Chrystelle Bancon-Montigny<sup>2</sup>, Catherine Gonzalez<sup>1</sup>

<sup>1</sup>Laboratoire de Génie de l'Environnement Industriel, IMT Mines Alès, Montpellier University, Alès, France

<sup>2</sup>HydroSciences Montpellier, Montpellier University, Montpellier, France

## Introduction

It has so far been shown that tributyltin and its degradation products are present in high concentrations in harbor areas in sediments as well as in the water column (Figure 1) following the intensive use of these compounds in antifouling paints during the second half of the 20th century. Their toxicity is confirmed for aquatic ecosystems and for humans after 1970 resulting in a series of restrictions on their use as well as environmental quality standards set by the Water Framework Directive (maximum authorized concentration of 0.61ng (Sn)/L in fresh and marine water). Monitoring the concentration of these compounds in the environment is therefore a major issue. On the other hand, passive samplers have already shown their effectiveness in detecting various families of pollutants (Aquaref and the CAPTIVEN network). The compounds' concentration in the passive samplers over time follows the model shown Figure 2 below. To determine accumulation rates (Rs), the calibration is performed for the integrating mode (linear domain). However, there are still no effective - tools for the in-situ monitoring of organotin. The aim of this work is to develop a new diagnostic tool (passive sampler) for monitoring water in port areas potentially contaminated by organotin. It will be possible to estimate the quality of marina waters and identify contaminated areas.

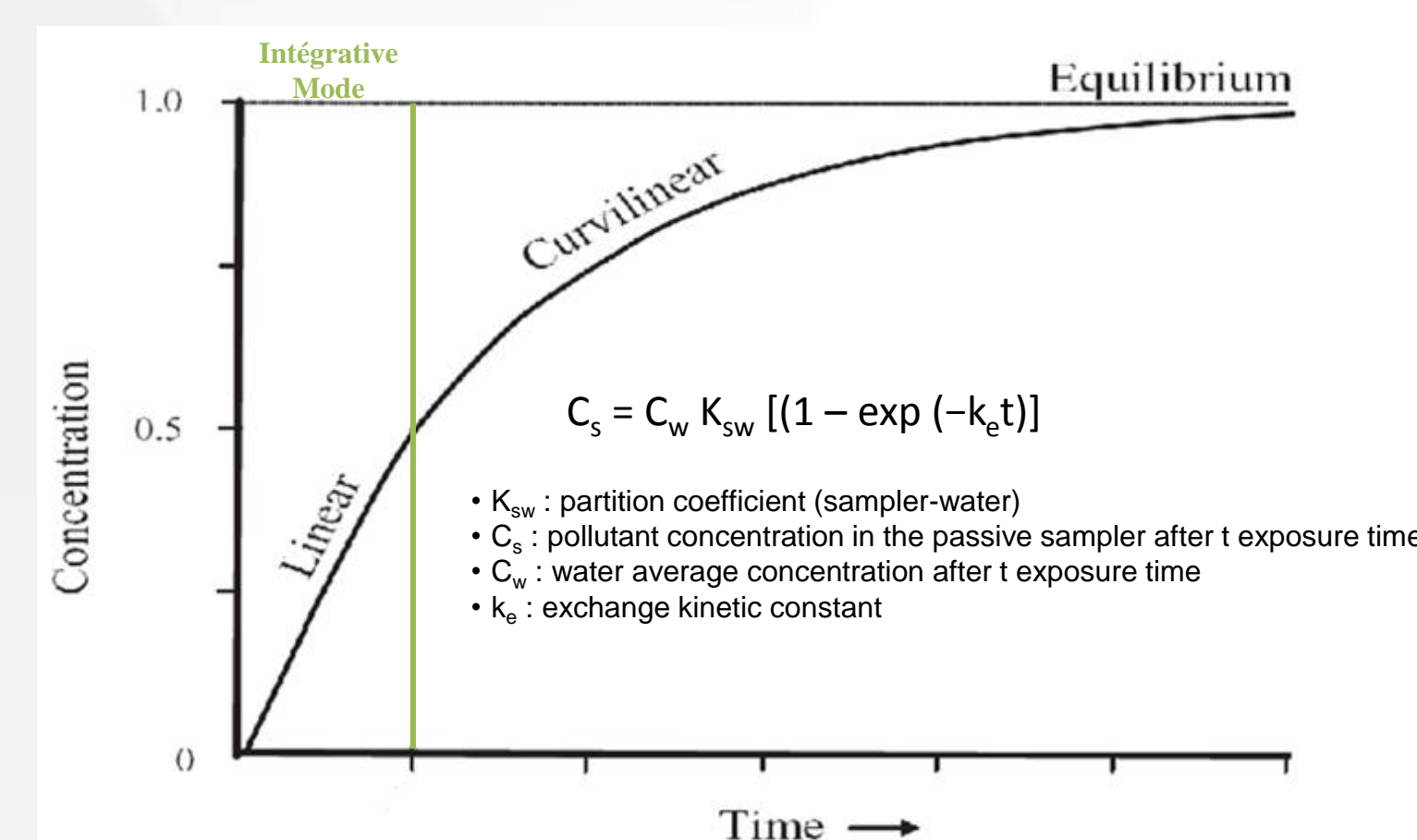


Figure 2 : Diffusion curve through a passive sampler.

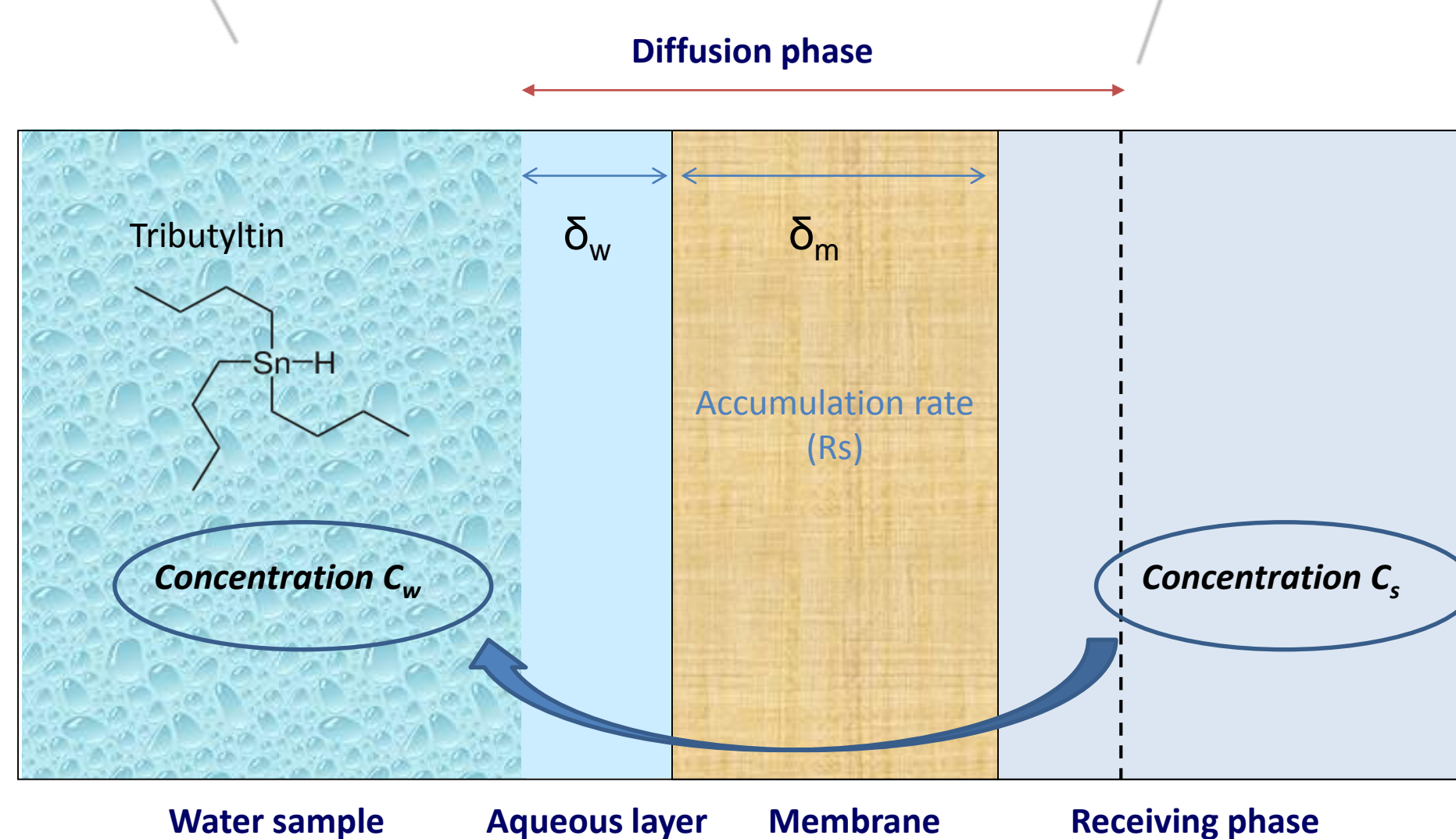


Figure 3 : Passive sampler's diffusive parts description.

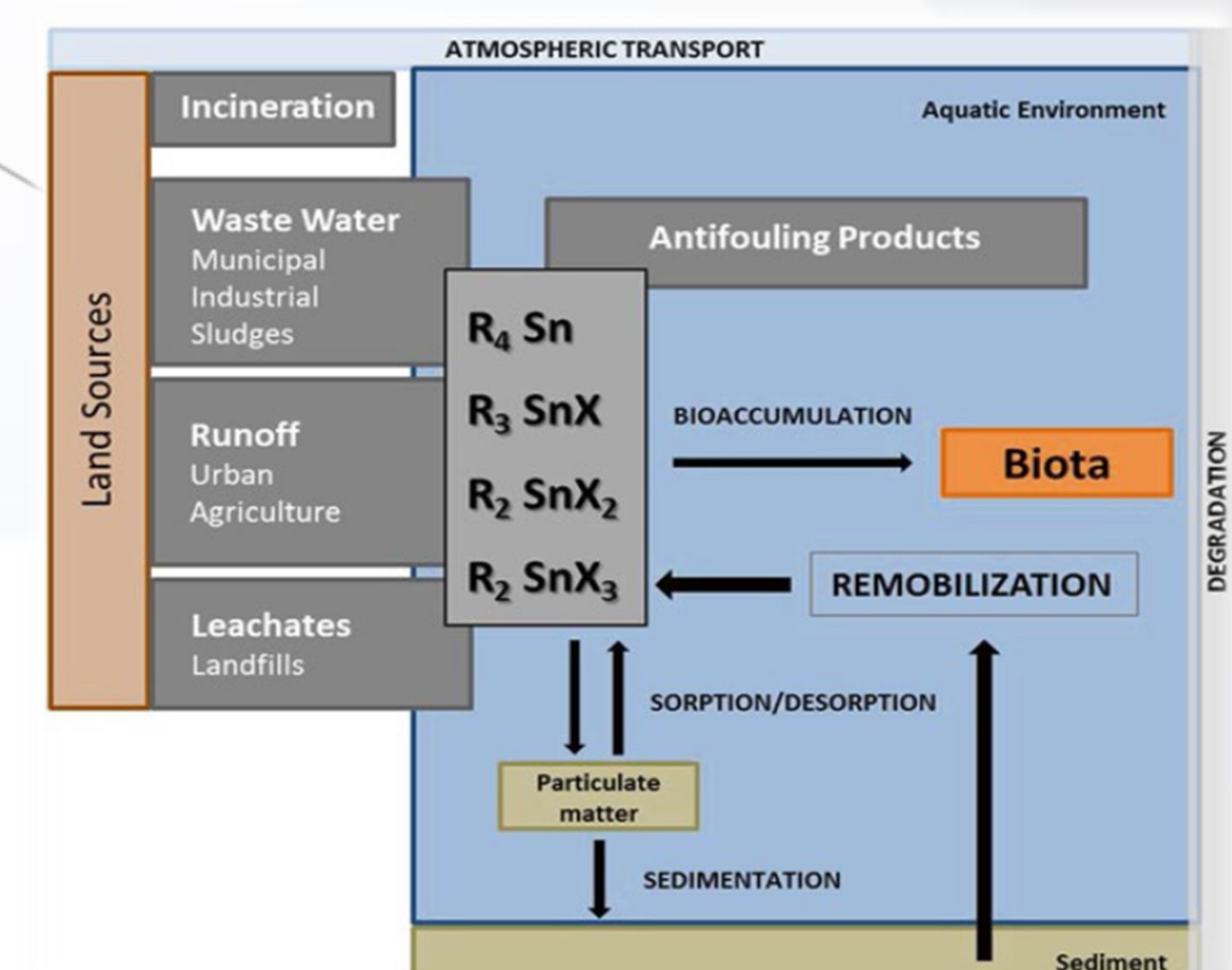


Figure 1 : Pathway of organotins in water (Sousa et al., 2013).

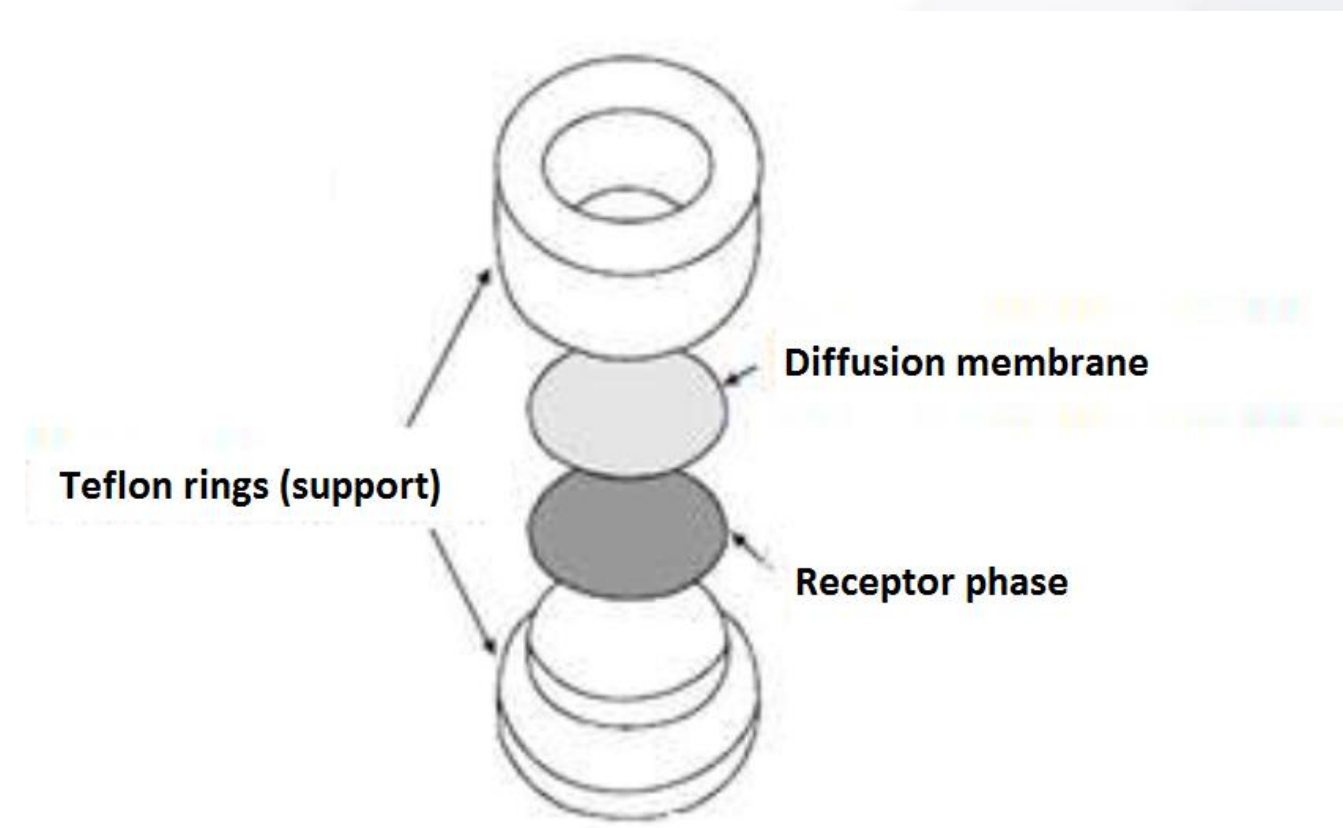


Figure 4 : Chemcatcher's structure.

## Experimental approach

### Adsorption kinetics

Implementation of kinetic studies of organotin adsorption by C18 disks (silica grafted onto a disk-shaped polymeric support used in Chemcatchers®) in order to obtain the kinetic constants of organotin in the receiving phase and their half-life time. Conditioning conditions have been also compared (one night in methanol and one night in methanol followed by 50 mL methanol and 150 mL ultrapure water filtered through the disk). The tests are carried out by contacting the receiving phase with an initial concentration of organotin solution fixed at 100 µg/L and monitored over 24 hours to obtain the kinetics of disappearance (batch system).

### Continuous flow calibration

Implementation of a continuous calibration pilot (Figure) with organotin intake in the passive sampler exposure medium (Chemcatcher®) in order to obtain their respective accumulation rate (Rs).



Figure 5 : Continuous flow calibration pilote.

Passive samplers are used in the integrative mode and are exposed for 15 days (t) to a fixed concentration solution of organotin established by the constant supply of tap water (Q = 30 mL/min) and an organotin solution at 40 µg/L (Q = 0.3 mL/min). The Chemcatcher are rotated at 60 rpm and the room temperature is fixed to 20°C.

The samplers are took of at regular intervals to perform a calibration curve thanks to the mass of compounds retained in the receiving phase function of time (slope = C<sub>w</sub>xR<sub>s</sub>).

## Results

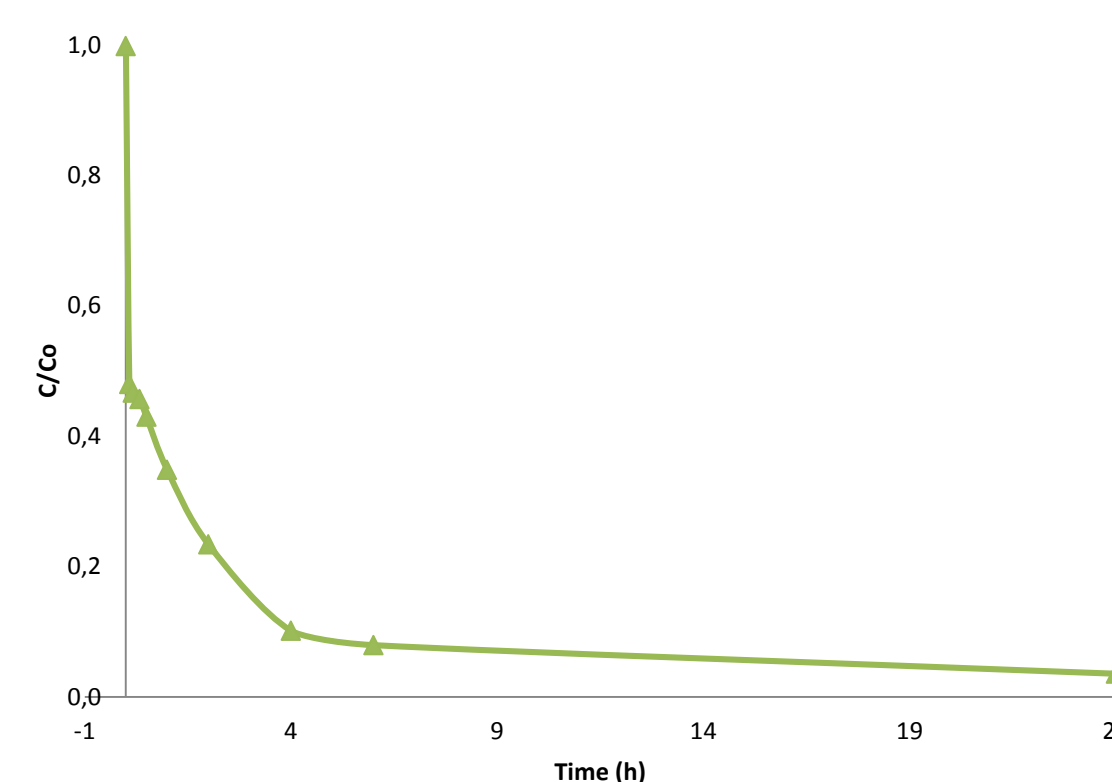


Figure 6 : TBT removal during kinetics essays.

The kinetics essays allowed us to determine kinetic constants 0,0075 ; 0,0022; 0,0012 L.ng<sup>-1</sup>.s<sup>-1</sup> for TBT, DBT and MBT respectively. We can observe a quick removal of compounds at the begining followed by a drop. Studies have also been carried out with separated compounds and showed that there is no debutylatation during the experiment. The sorption percentage have reached 76, 93 and 84% for MBT, DBT and TBT respectively, showing a good efficiency of the chemcatcher for the monitoring of organotins. The conditioning conditions seems havn't got impact on the sorption percentage.

The experiment has been done 2 times and during these experiments the MBT, DBT and TBT concentration were constant. The table above shows the Rs obtained and the respective concentrations for the two experiments done.

	First experiment			Second experiment		
	MBT	DBT	TBT	MBT	DBT	TBT
C <sub>w</sub> (ng/L)	288	489	788	259	527	715
R <sub>s</sub> (mL/day)	245	112	65	254	123	75

Table 1 : Continuous flow calibration results.

## Conclusions and Perspectives

### Reception phase selection

Many solid phases are capable of adsorbing compounds such as organotins : silica (powder / disk), zeolites or molecularly imprinted polymers. The expected results will make it possible to choose the optimum receiving phase (form, adsorption coefficient, extraction, environmental stability, etc.) suitable for sampling organotin compounds in the marine environment in the most reproducible manner possible.

### Design of the new passive sampler

Due to the lipophilic and cationic nature of organotins, these compounds tend to adsorb to a large number of materials, and thus the design of an inert carrier for the passive sampler and resistant to the marine environment is a key point- of this project. A design in the form of Polar Organic Chemicals Integrative Samplers (POCIS) and a material inert to organotin like Teflon seem promising to meet these constraints.

### Environmental use of the new passive sampler

The new passive sampler would be finally used to monitor the harbour area « Port Camargue » quality in France and also to study the diffusion gradient of organotin from the sediments to the water column as studies shown that sediments are a continuing source of TBT for the overlaying waters (Briant et al., 2016). These studies could help collectivities take decisions on the harbour management (dredging for exemple) and help the scientific community to better understand the pathway of organotins in sea water column.

## References

- Aguilar-Martínez, R., et al., *Calibration and use of the Chemcatcher® passive sampler for monitoring organotin compounds in water*. Analytica Chimica Acta, 2008. 618(2): p. 157-167.
- Ibrahim I., *Etude de l'applicabilité des échantillonneurs passifs POCIS et Chemcatcher® pour le suivi des pesticides en milieux aquatiques*, Thèse de science et génie de l'environnement, sous la direction de Catherine Gonzalez, Saint-Etienne, Ecole Nationale Supérieure des Mines Saint-Etienne, 2013.
- Sousa, A.C.A., et al., *Organotin Compounds from Snails to Humans*, in *Pollutant Diseases, Remediation and Recycling*, E. Lichtfouse, J. Schwarzbauer, and D. Robert, Editors. 2013, Springer International Publishing: Cham. p. 215-275.
- Briant N, et al., *Behaviour of butyltin compounds in the sediment pore waters of a contaminated marina (Port Camargue, South of France)*. Chemosphere, 2016. 150 : p. 123-129.