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Article

Synthesis of an Organotin Specific Molecularly Imprinted Polymer for Organotin Passive Sampling in Seawater

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Abstract: Environmental contaminations can sometimes be difficult to measure, particularly in complex matrices such as seawater. This is the case of organotin compounds (OSn) such as the monobutyltin (MBT), dibutyltin (DBT), and tributyltin (TBT), whose range of polarity is wide. These compounds, mostly coming from antifouling paints used on ship shell, can be found in water and sediments where they are stable and can persist for years. Passive sampling is gaining in interest to offer solutions to monitor these kinds of compounds even in low concentrations. However, due to the diversity of pollutants present in the environment nowadays, it is important to propose solutions that allow a specific sampling. This work aims to highlight the usability of molecularly imprinted polymers (MIPs) in passive sampling for the monitoring of OSn. MIPs were synthesized using three synthesis ways (bulk, suspension, and mini-emulsion processes) and kinetics were realized in order to estimate the retention of OSn by the solid MIP phase. Results highlighted a good retention of OSn with mean retention kinetic constants near 10^{-5} , 10^{-6} and 10^{-7} L·ng·s⁻¹ for DBT, TBT and MBT respectively. The synthesis mode showed no impact on retention kinetics, therefore, bulk synthesis is recommended because of its simplicity. If the elimination of OSn from MIPs is to be optimized, the retention of OSn on MIPs has been demonstrated, and is very promising for their use in specific passive samplers.

Keywords: molecularly imprinted polymers; MIP; organotin; marina water; passive sampling



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1. Introduction

Butyltin compounds such as monobutyltin (MBT), dibutyltin (DBT), and tributyltin (TBT) are known to be among the most hazardous compounds for both humans and aquatic ecosystems. Consistent effects of these compounds in the aquatic environment have already been observed at concentrations under 1 ng L^{-1} [1,2]. Huge amounts of OSn have been used for years in several activity sectors as antifouling paints for boats, namely a biocide to protect the hull. OSn have also been used as stabilizers in PVC, as well as pesticides and bactericides [3–5]. In 1999, the United States Environmental Protection Agency (US-EPA) [6] recommended a maximum of 10 ng L^{-1} of TBT (as a cation) in seawater and 63 ng L^{-1} in freshwater. Meanwhile the European Environmental Quality Standard (EQS) of TBT for all types of waters covered by the Water Framework Directive (WFD) have been set at 0.2 ng L^{-1} for annual average concentration, and a maximum allowed concentration set at 1.5 ng L^{-1} in unfiltered water samples [7]. However, despite these regulations, OSn are used (heat stabilizer, catalytic agents, and biocidal) and are still present in the

environment [8]. Indeed, sediments are both a sink and a source of butyltin in which their stability has been evaluated at about ten years [9]. The measurement of the concentration of these pollutants in the water column is therefore important for assessing their potential long-term biological impact.

The use of passive sampling techniques for monitoring water quality has been gaining interest in recent years [10–15]. Passive sampling devices allow the measurement of compounds in water and can provide more efficiency in storage (between sampling and analysis), deployment, and sensibility. A lot of passive sampling devices are available depending on the pollutant of interest and the matrix sampled. The Semi-Permeable Membrane Devices (SPMD) can be used for non-polar ($\log K_{ow} > 3$) organic compounds sampling such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and pesticides [16,17].

Inorganic compounds including cationic (Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn) and oxyanionic (As, V) can be sampled using Diffusion Gradient Thin films (DGT) using a chelating resin [18–20]. The DGT is composed of an inert body and a receiving phase composed of agarose gel. Recent studies show an interest in using o-DGT passive sampler to sample organic chemicals. The receiving phase of these samplers is composed of resin and different types of particles.

The Polar Organic Chemical Integrative Sampler (POCIS) [21–23] is used to monitor polar ($\log K_{ow} < 3$) hydrophilic organic compounds (pharmaceutical residues, herbicides). This sampler is composed of two semi-permeable membranes between which the sampling phase is sequestered under silica powder form. However, the nature of the powder can be changed to obtain POCIS-like samplers allowing the sampling of other compounds such as less polar organic compounds or non-polar compounds.

The Chemcatcher[®] passive sampler device, by contrast, can be deployed to evaluate the time-weighted average concentration (TWAC) of both organic [24,25] and inorganic (heavy metal) compounds [26] in the aquatic environment ($1.5 < \log K_{ow} < 6$). This sampler is composed of an inert body, a membrane, and a receiving phase under disc form. Different types of discs exist according to the chemicals targeted.

Passive samplers can be used for short-term (few days) and long-term exposures (several weeks). They are used in environmental monitoring to obtain an insight into pollution and they are more representative than spot sampling.

A lot of solutions exist in passive sampling for a huge amount of chemicals; however, sampling sometimes needs to be more specific of one chemical, particularly in a heavily contaminated environment such as seawater. In fact, depending on the type of sampler and compounds studied, several receiving phases already exist to sample a wide range of compounds (organic solvent, C18 disks, hydrogels). However, the sampling of a determined compound in a complex matrix with these non-specific receiving phases could be complicated. For OSn, as an example, the usual analysis is achieved by gas or liquid chromatography, and some research has shown difficulties in limit detection and quantification in complexes matrices [27,28]. In order to solve this problem, studies such as the one conducted by Gallegos-Gallegos and his team recommend using molecularly imprinted polymers (MIPs) for the preconcentrating phase during solid phase extractions (SPE) for environmental analysis [29–32]. This kind of solid phase extraction allows the specific separation of compounds thanks to its structure holding functionalized cavities [33]. Indeed, molecular imprinting of polymers is a process in which a functional monomer and a cross-linking agent are copolymerized in the presence of a target analyte (the imprint molecule) that acts as a molecular template to imitate natural molecular recognition [34]. The imprint molecule is then removed to form binding sites whose sizes and structure are complementary to the template. The molecular imprinted polymer and its target relationship is like the one observed between an enzyme and its substrate. Therefore, MIPs are functionalized materials capable of recognizing a specific molecule in a complex matrix.

Several syntheses of molecularly imprinted polymers exist [27,29,32,35]. Among them, the bulk polymerization is widely used because it is easy to implement. However, the

shape and size of the particles cannot be controlled, and it needs a crush and sieving step to achieve the wanted size of particles. In order to obtain size-controlled spherical particles, suspension and mini-emulsion synthesis can be applied. These syntheses are more complex because they require more reagents and solvents, an emulsification step, and more complicated purifications. Indeed, organic droplets are created in aqueous solution, and the synthesis takes place in those droplets that allow for the control of shape and size of the obtained particles. The particles obtained with this synthesis can reach μm to nm sizes, which improve specific surface area, and consequently, the retention efficiency.

Thanks to this specificity, MIPs are used in many areas such as separation techniques for environmental application such as seawater preconcentrating and analysis [34], and agricultural sample analysis [36–38], biological [37] and in organic synthesis as a catalyzer to stabilize the reactions [33,39,40]. MIPs have been recently used in chemical sensors for bisphenol A [41] and OSn detection [42], and in the passive sampler POCIS for the glyphosate sampling [43]. Concerning the study of Zamora, regarding sensors for tributyltin, detection did not allow to reach the EQS required for the WFD, and was only tested and validated for filtered seawater matrices.

The presence of OSn is still a problem, especially in port areas where they can be resuspended during dredging operations [44]. In view of the extremely low environmental quality standards adopted and the complexity of the seawater matrix (presence of salts, ionic species, and biota), it is necessary to develop alternatives to spot samples that are not representative of the contamination of the environment. Successfully used as a preconcentration technique (solid phase for selective extraction (SPE)), the objective of the present study is to synthesize an OSn-specific molecularly imprinted polymer in order to provide a new application as a receptor phase for an OSn-specific passive sampler. In this study, bulk, suspension, and mini-emulsion polymerizations have been tested to obtain the MIP particles and accumulation kinetics of MBT and DBT, and TBT by MIPs have been performed in tap water.

2. Materials and Methods

2.1. Chemicals and Reagents

All solvents and reagents were of analytical grade, or higher purity. Tributyltin chloride (96%), dibutyltin dichloride (97%), and monobutyltin trichloride (95%) were obtained from Sigma-Aldrich Chimie SARL (Saint-Quentin-Fallavier, France) and LGC Promochem (Molsheim, France), and the tripropyltin chloride (98%) from Strem Chemicals (Bisheim, France). Tripropyltin was used as a chromatographic internal standard because it is easily derivatized, and normally absent in polluted water. Standards and working solution were prepared similarly to those done by Garnier et al. [45]. For analysis, an aqueous solution of 2% NaBEt_4 (97%, Sigma Aldrich Chimie S.a.r.l, Saint-Quentin-Fallavier, France) in ultrapure water was used as a derivatizing agent, and an acetic–acetate buffer (2 mol L^{-1} , pH 4.8) was used to control the derivatization. This was prepared using sodium acetate (Saint-Quentin-Fallavier, France) and acetic acid (Carlo Ebra reagents, Val-de-Reuil, France). Ethylated derivatives were simultaneously extracted either by isooctane (analysis grade, Carlo Ebra, Val-de-Reuil, France) for liquid–liquid extraction, or by SPME for liquid–solid extraction, immediately prior to GC-ICP-MS analysis.

MIPs were synthesized using methacrylic acid (MAA, Acros Organics 99.5%), ethylene glycol methacrylate (EGDMA, Acros Organics 98%), azobisisobutyronitrile (AIBN, Fluka, Sigma Aldrich Chimie S.a.r.l, Saint-Quentin-Fallavier, France), acetonitrile (CAN, Fisher Scientifics, Illkirch, France), polyvinyl alcohol (PVA, Celanese, grade Erkol 26/88), chloroform (CH_3Cl_3 , Sigma Aldrich, Saint-Quentin-Fallavier, France), hexadecane (Sigma Aldrich 99%), and Sodium dodecyl sulfate (SDS, Sigma Aldrich, Saint-Quentin-Fallavier, France).

2.2. Synthesis of MIPs

As explained in the Introduction, the MIP synthesis consists of a polymerization of monomers and monomer chains around a template in order to create functionalized

cavities. In this study, three kinds of synthesis were performed. Figure 1 is a schematic representation of these syntheses. The reaction mechanisms remain the same in each synthesis, the differences reside in the volume of the organic phase where these reactions take place.

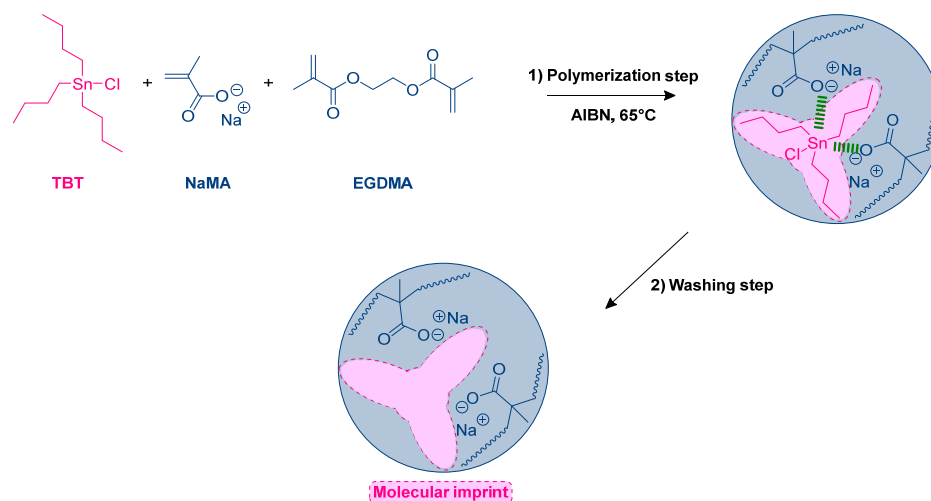


Figure 1. Schematic representation of the MIP synthesis.

2.2.1. Bulk Synthesis

The bulk synthesis of the adsorbent was carried out following the procedure used by Gallegos-Gallegos [30]. Into a 50 mL flask equipped with a condenser, 150 mg of TBT was mixed with 200 μ L of methacrylic acid (MAA). The mixture was left for 5 min under stirring in order to form the complex template-monomer, origin of the functionalized sites. Then, 2 mL of ethylene glycol dimethacrylate (EGDMA), 20 mg of azobisisobutyronitrile (AIBN), and 5 mL of acetonitrile were added. The mixture was kept under stirring at 65 $^{\circ}$ C for 24 h in order to complete the polymerization process. After the reaction, the solvent was evaporated. The polymer was crushed in a porcelain mortar, and then purified by Soxhlet extraction using a solution of hydrochloric acid in methanol (0.1 M) for 8 h. In order to evaluate the impact of the initial amount of TBTCl during polymerization, another polymerization with 15 mg of TBTCl was performed in the same polymerization conditions.

2.2.2. Suspension Synthesis

A suspension synthesis of molecularly imprinted polymers was performed in order to obtain more regular particles than those obtained in bulk polymerization. The protocol utilized is inspired by the one used by Gallegos-Gallegos [31]. The template molecule (TBTCl, 150 mg) and functional monomer (MAA, 169 μ L) were dissolved in 8 mL of chloroform (CH_3Cl). The cross-linker (EGDMA, 2 g) and the initiator (AIBN, 20 mg) were then added to this mixture and sonicated until dissolution. This mixture is identified as the organic part of the emulsion in which the polymerization takes place. Polyvinyl alcohol (PVA, 6 g) was dissolved in 150 mL of hot ultrapure water in a 250 mL flask under stirring. After cooling to room temperature, the organic mixture was added to the aqueous solution drop by drop with a syringe. Then, the obtained solution was kept at 65 $^{\circ}$ C under stirring for 15 h. The obtained product was washed with hot water to remove PVA and dried. The polymer particles were finally purified by Soxhlet extraction using a mixture of hydrochloric acid in methanol (0.1 M) for 8 h. The same protocol was used with a lower concentration of PVA in order to evaluate the impact of the aqueous phase viscosity on the shape and size of MIP particles.

2.2.3. Mini-Emulsion Synthesis

In order to obtain smaller particles, a synthesis of MIP was performed by using a mini-emulsion process. The protocol used was inspired by a protocol applied for the synthesis of a MIP for the detection of bisphenol A [46]. First, a mixture containing the template molecule (TBTCl, 150 mg) and functional monomer (MAA, 169 μL) was prepared and stirred for 5 min in order to rearrange the molecules to improve the non-covalent interactions. The crosslinker (EGDMA, 2 mL), the initiator (AIBN 20 mg), and the co-stabilizer (Hexadecane, 0.5 g) were then added to this mixture. The solution obtained was stirred for 5 min and added to 50 mL of a solution of deionized water and sodium dodecylsulfate (SDS, 0.001 mol L⁻¹). The mixture was finally stirred for 10 min and placed under sonication for 10 min (DIGITAL SONIFIER 450 from BRANSON ULTRASONICS at 30% of power). The polymerization was then performed in a 250 mL flask at 65 °C for 15 h. The reaction mixture obtained was lyophilized, washed two times with cyclohexane, and then purified by Soxhlet extraction using a mixture of hydrochloric acid in methanol (0.1 M). The resume of these synthesis conditions can be found in Table 1.

Table 1. Amount of chemical reagents used during polymerization.

	TBT (g)	MAA (μL)	EGDMA (mL)	AIBN (g)	ACN (mL)	PVA (g)	CH ₃ Cl (mL)	Eau (mL)	SDS (g)	Hexadecane (g)	MIP Mass (g)
Bulk 1	0.15	200	2	0.02	5						~2
Bulk 2	0.015	200	2	0.02	5						~2
Suspension 1	0.15	169	2	0.02		6	8	150			~2
Suspension 2	0.15	169	2	0.02		0.6	8	150			~2
Mini-emulsion	0.15	169	2	0.02				50	0.015	0.5	~2

2.3. Washing Steps

The Soxhlet purification was not efficient in removing the OSn residues from the MIPs [32] intended to be used in environmental compartments where concentrations are generally in the ng L⁻¹ range. In fact, residues of TBT, MBT, and DBT were still found after Soxhlet extraction. In our study, several solvents were tested to wash the first bulk MIP synthesized (with 150 mg of TBTCl). The cleaning was performed in 50 mL polyethylene tubes. The MIP was synthesized with the bulk protocol (with 150 mg of TBT) and mixed with 40 mL of different solvents. The solvents tested were: methanol, a methanol/HCl (0.1 M) mixture, and dichloromethane (CH₂Cl₂) as suggested by Gallegos-Gallegos [30], and a methanol/CH₂Cl₂ (4:1) mixture also tested by this team [31]. When the solvent was added to the polymer to clean, the tubes were shaken manually for a few seconds and placed under sonication for 30 min. Solvent and MIP were separated by centrifugation (4500 rpm, 10 min). Then, MIP was extracted with 10 mL of a methanol/acetic acid (3:1) mixture under sonication for 15 min. Extract was then recovered after centrifugation (4500 rpm, 10 min) to be analyzed by GC-ICP-MS. This analysis allows for the determination of the amount of TBT extractible with each extracting solvent (generally used in sediments and receiving phase extraction). It should be noted that several molecules are trapped inside the cross-linked structure of the MIP particles. These molecules cannot be removed by the solvent washings and are theoretically non-desorbable from MIP and therefore will not be a problem in the environment.

Cleaning the suspension synthesized MIP was then performed similarly to the protocol above with the methanol/HCl (0.1 M) mixture, dichloromethane (CH₂Cl₂), and methanol/CH₂Cl₂ (4:1) mixture, and the extractant methanol/acetic acid (3:1) solution as washing solvent before extraction steps.

2.4. Kinetics Experiments

In order to evaluate the OSn accumulation potential by MIPs, accumulation kinetic tests were performed on the bulk synthesized MIPs. The polymer was washed 5 times with a mixture of acetic acid/methanol and dried in a proofer before use. The experiments

were conducted in 30 mL polyethylene vials. For each kinetic test, eight vials were used containing 100 mg of MIPs and 20 mL of ultrapure water spiked to 100 ng L⁻¹ with MBT, DBT, and TBT. All the vials were stirred at 300 rpm during the experiment at 18 °C. Every hour, a vial was eliminated, and the solution was filtered with 0.2 µm filters in order to determine the OSn concentration and evaluate the amount adsorbed by the MIP. The evolution of OSn concentration allows for the determination of accumulation kinetics rates. Second order reaction was obtained. Kinetic constants *k* (expressed in L·ng⁻¹·s⁻¹) have been calculated using reversed concentration linearization of the considered compound (1/[OSn]) (Equation (1))

$$\frac{1}{[\text{OSn}]} = k.t + \frac{1}{[\text{OSn}^{\circ}]} \quad (1)$$

2.5. Butyltin Species Analysis

Butyltin extraction from molecularly synthesized imprinted polymers was performed similarly to the OSn extraction from receiving disks in the Aguilar experiment [11] and Garnier's study [44]. The extract was then prepared for analysis. The butyltin species (MBT, DBT, and TBT) were determined using a gas chromatograph (TRACE 1300, GC Thermo Fisher Scientific®, Waltham, MA, USA), along with an inductively coupled plasma mass spectrometer (ICP-MS X Series II, Thermo Fisher Scientific®, Waltham, MA, USA) [47]. This analysis method requires an OSn derivatization step done with NaBEt₄, which exchanges butyl groups with analytes to make them more volatile. Liquid injection was used for the analysis of extracted OSn and a liquid-liquid extraction was performed in accordance with Garnier [44]. Concentrations were obtained using the standard addition method. This method was validated using certified reference material analysis (CRM PACS-2 and PACS-3). Detection and quantification limits obtained with this method are presented in Table 2.

Table 2. Detection and quantification limits of the organotin analysis method.

	MBT	DBT	TBT
LOD ngSn·L ⁻¹	0.1	0.2	0.09
LOQ ngSn·L ⁻¹	0.6	0.3	0.2

3. Results

3.1. Synthesized MIP Comparisons

Different methods for the synthesis of molecularly imprinted polymers have been carried out in this work. Methods in bulk, in suspension, and in mini-emulsion have been used to compare each one with the others and with the literature.

3.1.1. Bulk

The bulk polymerization is simple to set up, as all of the reagents are melted in the reactor together in one homogeneous phase. The obtained MIP particles using the bulk procedure are similar to the particles obtained by Gallegos-Gallegos and his collaborators [31] (Figure 2). The synthesis, thanks to its simple set-up, can be reiterated by different researchers and provide similar results. However, this synthesis results in a solid block of MIP which needs to be grinded. As shown in Figure 2, the particles obtained are irregular and their size can range from a few nanometers to several micrometers. Scanning electron microscopy also shows that the surface of the particles is nonporous. The retention mechanisms of compounds with this kind of material would consequently occur at the surface of particles, specifically. According to Gallegos-Gallegos [31], the amount of porogen solvent added to the mixture could affect the porosity of particles; an increase of porogen solvent could provide a more porous material in order to optimize the retention of compounds [48].

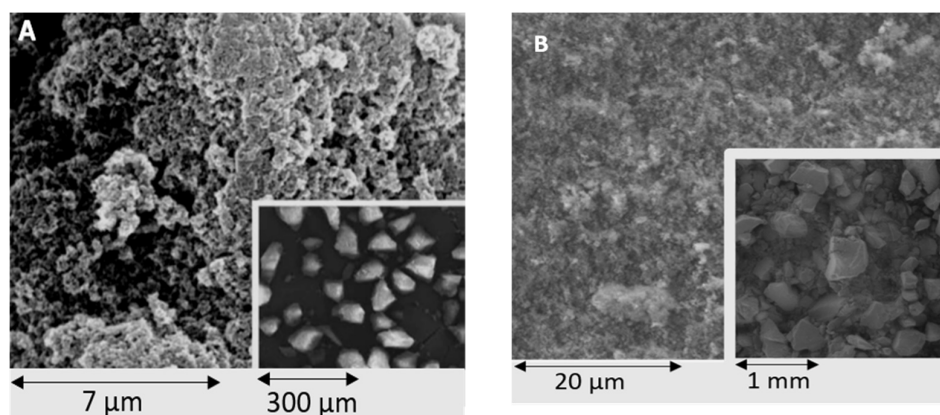


Figure 2. Scanning electron microscopy pictures of Bulk synthesized MIP by Gallegos-Gallegos [28] (A) and in this study (B).

3.1.2. Suspension

The suspension polymerization is more difficult to set up because of the use of two solvents to create an emulsion. However, the result obtained (Figure 3) shows that the particles synthesized are perfectly spherical and the particles range in size from approximately 10 μm to 40 μm . The size differences between particles can be due to turbulences in the reactor during the emulsion and polymerization. For these polymer particles, they also appear to have a non-porous surface; the compounds' retention will be then carried out to the surface of particles homogeneously thanks to their spherical fate. However, the particle size obtained allows for the increasing of specific surface area and should improve the quantity of butyltin compounds trapped at the surface of MIPs. The particles obtained in this experiment are similar to those synthesized by Gallegos-Gallegos [31]. A suspension synthesis has also been found with the same procedure but with 10 times less polyvinyl alcohol, to evaluate the impact of aqueous phase viscosity on particles synthesized. The particles obtained (Figure 4) present bigger sizes ranging from 30 μm to 100 μm , which may be due to bigger droplets formed during emulsion. Furthermore, close to the totality of particles seem to be broken, a phenomenon that can occur during solvent vaporization while breaking a particle's structure.

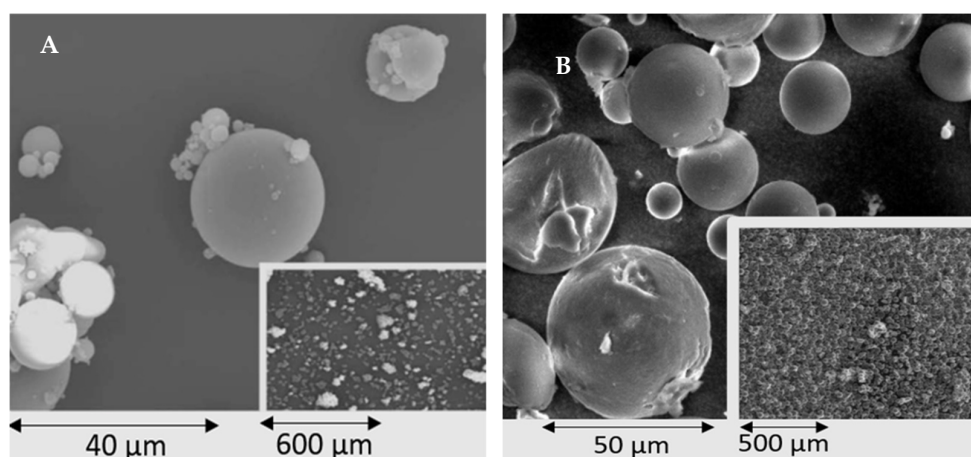


Figure 3. Scanning electron microscopy pictures of Suspension synthesized MIP by Gallegos-Gallegos [31] (A) and in this study (B).

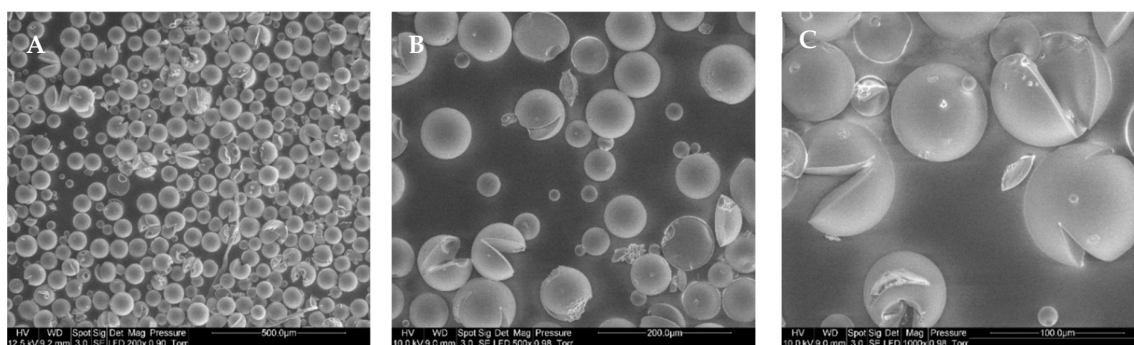


Figure 4. Scanning electron microscopy pictures of Suspension synthesized MIP with $2024 \text{ g}\cdot\text{L}^{-1}$ of polyvinyl alcohol. The pictures have been zoomed in 200 times (A), 500 times (B), and 1000 times (C).

3.1.3. Mini-Emulsion

The mini-emulsion synthesis is more complex to carry out because of stirring/sonication and mixing steps before performing the polymerization. These steps are important in order to form the smallest droplets as possible. However, the results obtained with this synthesis are encouraging. In fact, as shown in Figure 5, the particles obtained are spherical and their size ranges from 200 nm to 2 µm. The specific surface area should be much larger with these sizes of MIP particles. However, the particles seem to agglomerate together which could finally reduce the available specific surface and cause troubles during retention steps.

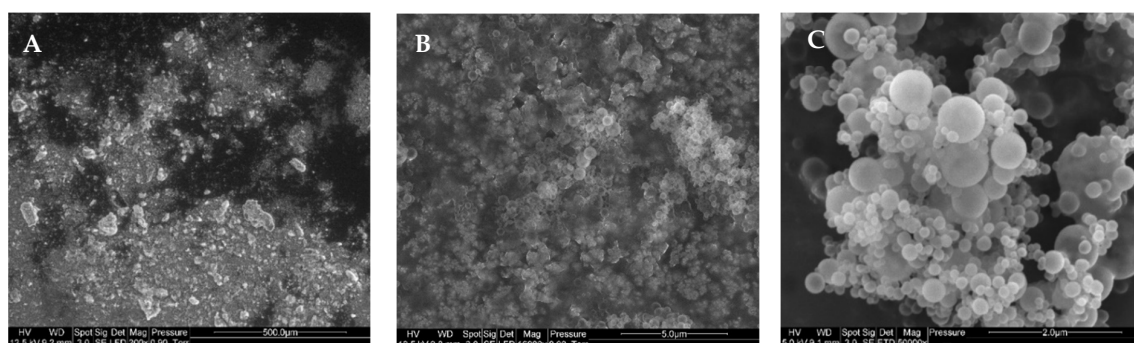


Figure 5. Scanning electron microscopy pictures of mini-emulsion synthesized MIPs zoomed in 200 times (A), 1600 times (B), and 50,000 times (C).

3.2. Template Molecule Removal

In order to use these MIPs in environmental conditions (low concentrations in water), it is necessary to remove the totality of butyltins present in the MIPs' structure. In fact, the theoretical concentration of TBT present in the MIP after synthesis is around 75 mg g^{-1} (7.5 mg g^{-1} when the procedure "bulk 2" MIP was used). Furthermore, during the polymerization and purification process (in Soxhlet), where the temperature is high, it appears that TBT is degraded into MBT and DBT. This reaction of debutylation can occur by photodegradation of TBT [49], and this photodegradation kinetic may have been increased at high temperature. Removal experiments have been carried out considering the total amount of Sn in the polymer. The initial concentration of Sn in the polymer has been theoretically set at the amount of TBT introduced during the synthesis per mass of polymer obtained at the end of the synthesis.

3.2.1. Purification of Bulk Polymers

The results obtained during the washing steps of bulk synthesized polymers are shown in Figure 6. In this part, the Soxhlet and solvent washing steps have not been differentiated. These results highlighted the removal efficiency of OSn with different solvents, particularly with dichloromethane (CH_2Cl_2) and the methanol/dichloromethane (3:1) mixture with

removal efficiencies close to 94% (around 4 mg g^{-1} to 5 mg g^{-1} remaining in volume and surface). This is in accordance with the results of Gallegos [32]. However, despite more than 90% removal efficiency, this result remained too high for environmental uses where concentrations found were very low, around 1 ng L^{-1} (European Water Framework Directive, fixed an annual average to $0.2 \text{ ng Sn} \cdot \text{L}^{-1}$). Further studies are needed to improve these results and leave MIPs fully free of OSn. Other washing solvents could be tested with stronger bindings with OSn or different washing set-ups such as cascade washes or higher contact time between the solvent and the MIP. Furthermore, as the surfaces of MIPs are non-porous, the solvent cannot reach the enclosed TBT within the particles. This could lead to leakages if particles break during uses.

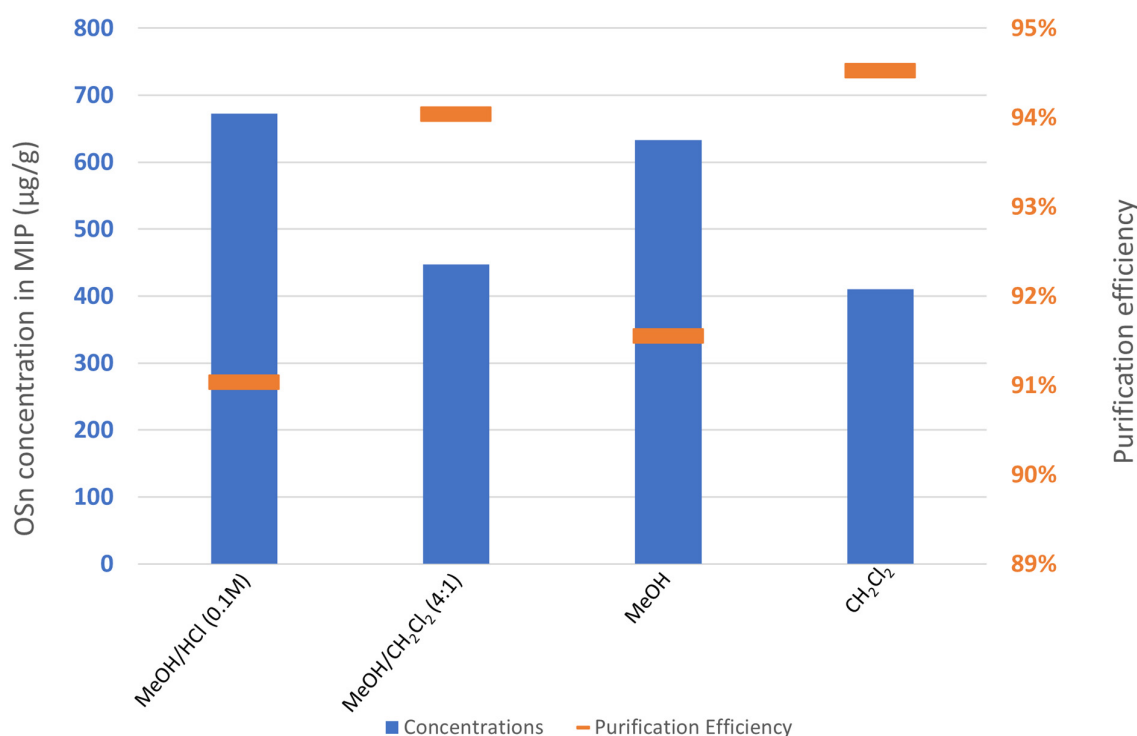


Figure 6. OSn concentrations remaining in the extracts of bulk synthesized MIP after washing steps and its respective removal efficiencies.

3.2.2. Suspension and Mini-Emulsion Polymer Purification

In this study, other types of solvents have been used during suspension MIP washes. The removal efficiency after the Soxhlet step is also presented here for the suspension and mini-emulsion of MIPs. As we can see in Figure 7, the removal efficiencies after the Soxhlet steps are already more than 90%. The Soxhlet allows for the removal of polymerization residues and the butyltin present in the polymer. Furthermore, the washes performed after the Soxhlet allows it to reach more than 99% with a mixture of acetic acid (CH_3COOH)/methanol (3:1), as well as being used for the OSn extraction before GC-ICP-MS analysis, and almost 100% with a mixture methanol/hydrochloric acid (HCl) (0.1 M). Contrary to the bulk synthesized MIP, the suspension MIP seems to be better washed with these two solvents but not with CH_2Cl_2 or the MeOH/ CH_2Cl_2 (4:1) mixture, which allowed for reaching the removal efficiencies of 94% and 90%, respectively.

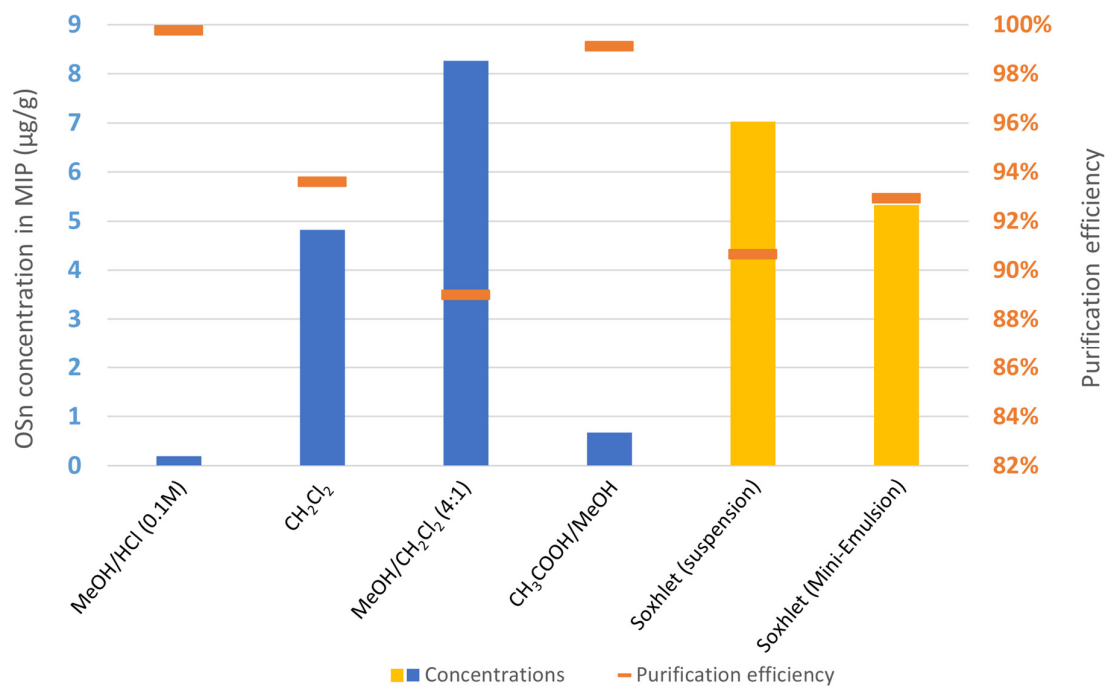


Figure 7. OSn concentrations remaining in the extracts of suspension synthesized MIP after washing steps and its respective removal efficiencies. OSn concentrations and efficiencies after Soxhlet steps and before washing steps.

3.3. Retention Kinetics

Kinetic essays have been carried out to evaluate the OSn retention efficiency of the bulk synthesized MIP. No swelling was observed during the experiment which lasted up to 8 h. Unfortunately, the MIP was not totally free of OSn before use, as exposed in Figure 8.

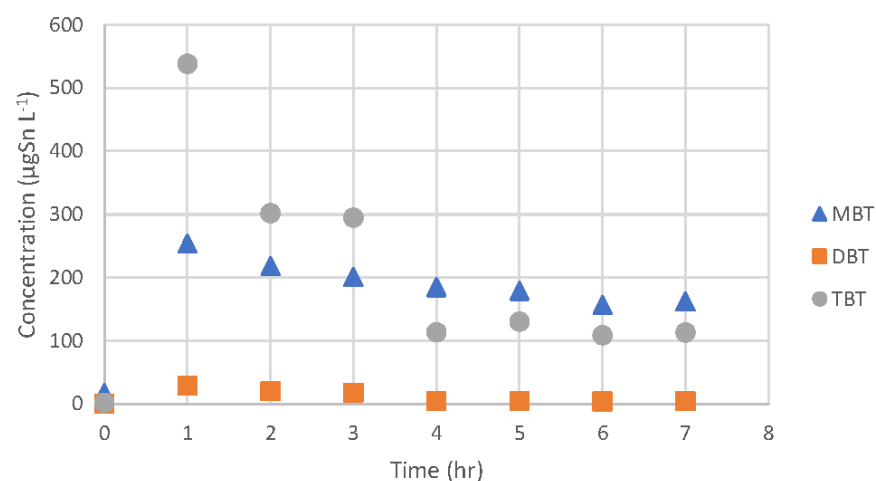


Figure 8. Example of OSn concentration in water during retention kinetic essay with bulk synthesized MIP.

Despite the initial introduction of 100 ngSn L^{-1} of OSn in the water, this concentration reached 550 µgSn L^{-1} for TBT, 250 µgSn L^{-1} for MBT, and 30 µgSn L^{-1} for DBT, respectively. This highlights the necessity to improve the washing step for an environmental use of these MIPs. However, it appears that the water concentration decreases during the experiment. As no degradation or adsorption of OSn on reactors' surfaces have been observed during the 8 h experiment, this decrease is certainly due to the re-absorption of

OSn in the MIP. Retention of kinetic constants was calculated considering a second order removal in water and considering all components were adsorbed by MIPs (no degradation in 8 h, no adsorption on reactor surfaces, etc.). The results are listed in Table 3 and are expressed as $L \cdot ng^{-1} \cdot s^{-1}$. The higher these constants are, the faster the accumulation is in MIPs. As shown in Table 3, the results obtained for the bulk synthesized MIP with 150 mg of TBT during the synthesis and the one with 15 mg of TBT both show comparable results. This result highlights the fact that even if less TBT is used during the synthesis, the number of activated sites seems to be comparable for both MIPs. It could be more interesting to reduce the amount of TBT during the synthesis to avoid washing problems and remaining TBT. The kinetic constant obtained with the suspension synthesis are like those obtained with the bulk polymer. It seems that the suspension MIP, despite a smaller particle size than the bulk, do not provide better performance for the OSn retention. Furthermore, it appears that mini-emulsion MIP provides lower kinetic constants than the bulk MIP due to the agglomerate formation during the synthesis. In fact, as shown in Figure 5, mini-emulsion MIP agglomerates form bigger particles that could reduce the specific area, which then reduces the retention of compounds.

Table 3. Accumulation kinetic constants of OSn by MIPs synthesized in bulk, suspension, and mini-emulsion expressed in $L \cdot ng^{-1} \cdot s^{-1}$.

Synthesis Mode	MBT ($L \cdot ng^{-1} \cdot s^{-1}$)	DBT ($L \cdot ng^{-1} \cdot s^{-1}$)	TBT ($L \cdot ng^{-1} \cdot s^{-1}$)
Mass (150 mg)	$3.9 \cdot 10^{-7}$	$4.3 \cdot 10^{-5}$	$1.3 \cdot 10^{-6}$
Mass (15 mg)	$7 \cdot 10^{-7}$	$3.2 \cdot 10^{-5}$	$1.3 \cdot 10^{-6}$
Suspension	$2.2 \cdot 10^{-7}$	$8.1 \cdot 10^{-5}$	$2.7 \cdot 10^{-6}$
Mini-emulsion	$6.2 \cdot 10^{-8}$	$4.3 \cdot 10^{-7}$	$9.6 \cdot 10^{-9}$

4. Conclusions

The results obtained during this study highlight the potential of MIPs for OSn retention and therefore, in passive sampling of these compounds.

Comparison of the three syntheses of MIPs highlighted a good retention of OSn with a mean retention kinetic. Retention efficiency of MIPs did not seem to depend on the type of synthesis chosen, consequently, bulk polymerization is recommended because of its simplicity in achievement. Our study demonstrates the possibility of synthesizing MIPs for use in the fabrication of specific phases for passive sampling of organotin compounds. Tests were performed for the first time with these MIPs in powder form and not in cartridge form, and were used to preconcentrate organotin compounds before an analytical technique. The kinetics achieved using powder form under conditions close to those could be implemented in natural ecosystems and testify to the promising character of the use of MIPs.

The template removal after the synthesis is not optimal and would deserve some supplementary assays to achieve a good MIP purification in order to use it in environmental conditions for very low concentration sampling. Some research could be done using less TBT during the MIP synthesis, improvement of washing methods (i.e., cascade wash, ultrasonic bath, stronger solvents, etc.), or by using another template molecule with a similar structure as the tributyltin such as the tributyl lead. This study stands for the first step toward the creation of a new passive sampler based on MIPs for environmental OSn sampling. Once MIPs are totally cleaned from the template, studies on phase formatting such as electrospinning or gel casting can be performed, as well as new kinetic experiments in seawater environments.

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References

1. Meador, J.P.; Krone, C.A.; Dyer, D.W.; Varanasi, U. Toxicity of sediment-associated tributyltin to infaunal invertebrates: Species comparison and the role of organic carbon. *Mar. Environ. Res.* **1997**, *43*, 219–241. [CrossRef]
2. Alzieu, C. Environmental impact of TBT: The French experience. *Sci. Total Env.* **2000**, *258*, 99–102. [CrossRef]
3. Hoch, M. Organotin compounds in the environment—An overview. *Appl. Geochem.* **2001**, *16*, 719–743. [CrossRef]
4. Dobson, S.; Howe, P.; Floyd, P. *Mono- and Disubstituted Methyltin, Butyltin, and Octyltin Compounds*; World Health Organization: Geneva, Switzerland, 2006.
5. Sousa, A.C.A.; Tanabe, S.; Pastorinho, M.R. Organotins: Sources and impacts on health and environment A2-Dellasala, Dominick A. In *Encyclopedia of the Anthropocene*; Goldstein, Elsevier: Oxford, UK, 2017; pp. 133–139.
6. EPA 822-Z-99-001; Agency, U.S.E.P. National Recommended Water Quality Criteria. Office of Water 4304; 1999. Available online: <https://nepis.epa.gov/Exe/ZyPDF.cgi/20003OLV.PDF?DockKey=20003OLV.PDF> (accessed on 25 January 2022).
7. Directive 2008/105/EC of the European Parliament and of the Council (16 December 2008) on Environmental Quality Standards in the Field of Water Policy. *Off. J. Eur. Union* **2008**, *348*, 84–97. Available online: <https://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=LEGISSUM:l28180> (accessed on 20 February 2022).
8. Okoro, H.K.; Fatoki, O.S.; Adekola, F.A.; Ximba, B.J.; Snyman, R.G. Sources, Environmental Levels and Toxicity of Organotin in Marine Environment—A Review. *Asian J. Chem.* **2011**, *23*, 473–482.
9. Langston, W.J.; Pope, N.D.; Davey, M.; Langston, K.M.; O' Hara, S.C.M.; Gibbs, P.E.; Pascoe, P.L. Recovery from TBT pollution in English Channel environments: A problem solved? *Mar. Pollut. Bull.* **2015**, *95*, 551–564. [CrossRef] [PubMed]
10. Cole, R.F.; Mills, G.A.; Parker, R.; Bolam, T.; Birchenough, A.; Kröger, S.; Fones, G.R. Trends in the analysis and monitoring of organotins in the aquatic environment. *Trends Environ. Anal. Chem.* **2015**, *8*, 1–11. [CrossRef]
11. Aguilar-Martínez, R.; Palacios-Corvillo, M.A.; Greenwood, R.; Mills, G.A.; Vrana, B.; Gómez-Gómez, M.M. Calibration and use of the Chemcatcher[®] passive sampler for monitoring organotin compounds in water. *Anal. Chim. Acta* **2008**, *618*, 157–167. [CrossRef] [PubMed]
12. Greenwood, R.; Mills, G.A.; Vrana, B.; Allan, I.; Aguilar-Martínez, R.; Morrison, G. Chapter 9 Monitoring of priority pollutants in water using chemcatcher passive sampling devices. In *Comprehensive Analytical Chemistry*; Elsevier: Amsterdam, The Netherlands, 2007; Volume 48, pp. 199–229.
13. Charriau, A.; Lissalde, S.; Poulhier, G.; Mazzella, N.; Buzier, R.; Guibaud, G. Overview of the Chemcatcher(R) for the passive sampling of various pollutants in aquatic environments Part A: Principles, calibration, preparation and analysis of the sampler. *Talanta* **2016**, *148*, 556–571. [CrossRef] [PubMed]
14. Godlewska, K.; Stepnowski, P.; Paszkiewicz, M. Pollutant analysis using passive samplers: Principles, sorbents, calibration and applications. A review. *Environ. Chem. Lett.* **2021**, *19*, 465–520. [CrossRef]
15. MacKeown, H.; Benedetti, B.; Di Carro, M.; Magi, E. The study of polar emerging contaminants in seawater by passive sampling: A review. *Chemosphere* **2022**, *299*, 134448. [CrossRef] [PubMed]
16. Folsvik, N.; Brevik, E.M.; Berge, J.A. Organotin compounds in a Norwegian fjord. A comparison of concentration levels in semipermeable membrane devices (SPMDs), blue mussels (*Mytilus edulis*) and water samples. *J. Environ. Monit.* **2002**, *4*, 280–283. [CrossRef] [PubMed]
17. Huckins, J.N.; Manuweera, G.K.; Petty, J.D.; Mackay, D.; Lebo, J.A. Lipid-containing semipermeable membrane devices for monitoring organic contaminants in water. *Environ. Sci. Technol.* **1993**, *27*, 2489–2496. [CrossRef]
18. Guibal, R.; Buzier, R.; Charriau, A.; Lissalde, S.; Guibaud, G. Passive sampling of anionic pesticides using the Diffusive Gradients in Thin films technique (DGT). *Anal. Chim. Acta* **2017**, *966*, 1–10. [CrossRef]
19. Casiot, C.; Egal, M.; Elbaz-Poulichet, F.; Bruneel, O.; Bancon-Montigny, C.; Cordier, M.-A.; Gomez, E.; Aliaume, C. Hydrological and geochemical control of metals and arsenic in a Mediterranean river contaminated by acid mine drainage (the Amous River, France); preliminary assessment of impacts on fish (*Leuciscus cephalus*). *Appl. Geochem.* **2009**, *24*, 787–799. [CrossRef]
20. Davison, W.; Zhang, H.; Warnken, K.W. Chapter 16 Theory and applications of DGT measurements in soils and sediments. In *Comprehensive Analytical Chemistry*; Elsevier: Amsterdam, The Netherlands, 2007; Volume 48, pp. 353–378.
21. Branchet, P.; Cadot, E.; Sebag, D.; Fenet, H.; Ngatcha, B.N.; Gonzalez, C. POCIS evidence Yaoundé's rivers pesticides contamination. In *Goldschmidt 2017*; European Association of Geochemistry: Aubièrre, France, 2017.

22. Ibrahim, I. Study of the Applicability of Passive Samplers POCIS and Chemcatcher for Monitoring Pesticides in Aquatic Systems. Ecole Nationale Supérieure des Mines de Saint-Etienne. Available online: <https://tel.archives-ouvertes.fr/tel-00864198/document> (accessed on 10 January 2022).
23. Alvarez, D.A.; Petty, J.D.; Huckins, J.N.; Jones-Lepp, T.L.; Getting, D.T.; Goddard, J.P.; Manahan, S.E. Development of a passive, in situ, integrative sampler for hydrophilic organic contaminants in aquatic environments. *Environ. Toxicol. Chem.* **2004**, *23*, 1640–1648. [[CrossRef](#)] [[PubMed](#)]
24. Vrana, B.; Mills, G.A.; Dominiak, E.; Greenwood, R. Calibration of the Chemcatcher passive sampler for the monitoring of priority organic pollutants in water. *Environ. Pollut.* **2006**, *142*, 333–343. [[CrossRef](#)] [[PubMed](#)]
25. Kingston, J.K.; Greenwood, R.; Mills, G.A.; Morrison, G.M.; Persson, L.B. Development of a novel passive sampling system for the time-averaged measurement of a range of organic pollutants in aquatic environments. *J. Environ. Monit.* **2000**, *2*, 487–495. [[CrossRef](#)] [[PubMed](#)]
26. Persson, L.B.; Morrison, G.M.; Friemann, J.-U.; Kingston, J.; Mills, G.; Greenwood, R. Diffusional behaviour of metals in a passive sampling system for monitoring aquatic pollution. *J. Environ. Monit.* **2001**, *3*, 639–645. [[CrossRef](#)]
27. Zhu, S.; Hu, F.; Yang, T.; Gan, N.; Pan, D.; Cao, Y.; Wu, D. Synthesis and characterization of a molecularly imprinted polymer for the determination of trace tributyltin in seawater and seafood by liquid chromatography–tandem mass spectroscopy. *J. Chromatogr. B* **2013**, *921–922*, 21–26. [[CrossRef](#)] [[PubMed](#)]
28. Puri, B.K.; Muñoz-Olivas, R.; Cámara, C. A new polymeric adsorbent for screening and pre-concentration of organotin compounds in sediments and seawater samples. *Spectrochim. Acta Part B At. Spectrosc.* **2004**, *59*, 209–214. [[CrossRef](#)]
29. Gallego-Gallegos, M.; Garrido, M.L.; Olivas, R.M.; Baravalle, P.; Baggiani, C.; Cámara, C. A new application of imprinted polymers: Speciation of organotin compounds. *J. Chromatogr. A* **2010**, *1217*, 3400–3407. [[CrossRef](#)] [[PubMed](#)]
30. Gallego-Gallegos, M.; Liva, M.; Olivas, R.M.; Cámara, C. Focused ultrasound and molecularly imprinted polymers: A new approach to organotin analysis in environmental samples. *J. Chromatogr. A* **2006**, *1114*, 82–88. [[CrossRef](#)]
31. Gallego-Gallegos, M.; Muñoz-Olivas, R.; Cámara, C. Different formats of imprinted polymers for determining organotin compounds in environmental samples. *J. Environ. Manag.* **2009**, *90*, S69–S76. [[CrossRef](#)] [[PubMed](#)]
32. Gallego-Gallegos, M.; Muñoz-Olivas, R.; Martín-Esteban, A.; Cámara, C. Synthesis and evaluation of molecularly imprinted polymers for organotin compounds: A screening method for tributyltin detection in seawater. *Anal. Chim. Acta* **2005**, *531*, 33–39. [[CrossRef](#)]
33. Ramström, O.; Mosbach, K. Synthesis and catalysis by molecularly imprinted materials. *Curr. Opin. Chem. Biol.* **1999**, *3*, 759–764. [[CrossRef](#)]
34. Turiel, E.; Martín-Esteban, A. Molecularly imprinted polymers for sample preparation: A review. *Anal. Chim. Acta* **2010**, *668*, 87–99. [[CrossRef](#)] [[PubMed](#)]
35. Puzio, K.; Claude, B.; Amalric, L.; Berho, C.; Grellet, E.; Bayouhdh, S.; Nehmé, R.; Morin, P. Molecularly imprinted polymer dedicated to the extraction of glyphosate in natural waters. *J. Chromatogr. A* **2014**, *1361*, 1–8. [[CrossRef](#)]
36. Li, X.; Cao, X.; Zhang, Z.; Zhang, Z.; Jiang, Z.; Yin, J. Synthesis of molecularly imprinted polymer adsorbents for solid-phase extraction of strobilurin fungicides from agricultural products. *J. Sep. Sci.* **2020**, *43*, 2133–2141. [[CrossRef](#)]
37. Haginaka, J. Monodispersed, molecularly imprinted polymers as affinity-based chromatography media. *J. Chromatogr. B* **2008**, *866*, 3–13. [[CrossRef](#)] [[PubMed](#)]
38. Pichon, V.; Chapuis-Hugon, F. Role of molecularly imprinted polymers for selective determination of environmental pollutants—A review. *Anal. Chim. Acta* **2008**, *622*, 48–61. [[CrossRef](#)] [[PubMed](#)]
39. Wulff, G. Enzyme-like Catalysis by Molecularly Imprinted Polymers. *Chem. Rev.* **2002**, *102*, 1–28. [[CrossRef](#)] [[PubMed](#)]
40. Visnjeviski, A.; Schomäcker, R.; Yilmaz, E.; Brüggemann, O. Catalysis of a Diels-Alder cycloaddition with differently fabricated molecularly imprinted polymers. *Catal. Commun.* **2005**, *6*, 601–606. [[CrossRef](#)]
41. Mba Ekomo, V. *From Electrochemical Molecularly Imprinted Polymer to Sensor: Feasibility Study for the Detection of Bisphenol A*; Université de Toulon: Toulon, France, 2018. Available online: <https://tel.archives-ouvertes.fr/tel-02273266/document> (accessed on 10 January 2022).
42. Zamora-Gálvez, A.; Mayorga-Matinez, C.C.; Parolo, C.; Pons, J.; Merkoçi, A. Magnetic nanoparticle-molecular imprinted polymer: A new impedimetric sensor for tributyltin detection. *Electrochem. Commun.* **2017**, *82*, 6–11. [[CrossRef](#)]
43. Duda De Oliveira, D.; Rojas, E.G.; António, M.; Fernandez, S. Should TBT continue to be considered an issue in dredging port areas? A brief review of the global evidence. *Ocean. Coast. Manag.* **2020**, *197*, 105303. [[CrossRef](#)]
44. Berho, C.; Claude, B.; Coisy, E.; Togola, A.; Bayouhdh, S.; Morin, P.; Amalric, L. Laboratory calibration of a POCIS-like sampler based on molecularly imprinted polymers for glyphosate and AMPA sampling in water. *Anal. Bioanal. Chem.* **2017**, *409*, 2029–2035. [[CrossRef](#)]
45. Garnier, A.; Bancon-Montigny, C.; Delpoux, S.; Spinelli, S.; Avezac, M.; Gonzalez, C. Study of passive sampler calibration (Chemcatcher®) for environmental monitoring of organotin compounds: Matrix effect, concentration levels and laboratory vs in situ calibration. *Talanta* **2020**, *219*, 121316. [[CrossRef](#)] [[PubMed](#)]
46. Wang, Z.; Qiu, T.; Guo, L.; Ye, J.; He, L.; Li, X. The synthesis of molecular recognition polymer particles via miniemulsion polymerization. *React. Funct. Polym.* **2018**, *126*, 1–8. [[CrossRef](#)]
47. Briant, N.; Bancon-Montigny, C.; Freydier, R.; Delpoux, S.; Elbaz-Poulichet, F. Behaviour of butyltin compounds in the sediment pore waters of a contaminated marina (Port Camargue, South of France). *Chemosphere* **2016**, *150*, 123–129. [[CrossRef](#)]

-
48. Farrington, K.; Magner, E.; Regan, F. Predicting the performance of molecularly imprinted polymers: Selective extraction of caffeine by molecularly imprinted solid phase extraction. *Anal. Chim. Acta* **2006**, *566*, 60–68. [[CrossRef](#)]
 49. Navio, J.A.; Marchena, F.J.; Cerrillos, C.; Pablos, F. UV photolytic degradation of butyltin chlorides in water. *J. Photochem. Photobiol. A Chem.* **1993**, *71*, 97–102. [[CrossRef](#)]