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1           **Assessment of background concentrations of organometallic compounds**  
2           **(methylmercury, ethyllead and butyl- and phenyltin) in French aquatic environments**

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25

26 **ABSTRACT**

27 The aim of this work is to estimate background concentrations of organometallic compounds,  
28 such as tributyltin (TBT), dibutyltin (DBT), monobutyltin (MBT), triphenyltin (TPhT),  
29 diphenyltin (DPhT), monophenyltin (MPhT), methylmercury (MeHg), inorganic mercury  
30 (iHg) and diethyllead (Et<sub>2</sub>Pb) in the aquatic environment at the French national scale.  
31 Both water and sediment samples were collected all over the country, resulting in 152 water  
32 samples and 123 sediment samples collected at 181 sampling points. Three types of surface  
33 water bodies were investigated: rivers (140 sites), lakes (19 sites) and coastal water (42 sites),  
34 spread along the 11 French river basins. The choice of sites was made on the basis of previous  
35 investigation results and the following target criteria: reference, urban sites, agricultural and  
36 industrial areas. The analytical method was properly validated for both matrices prior to  
37 analysis, resulting in low limits of quantification (LOQ), good precision and linearity in  
38 agreement with the Water Framework Directive demands. The results were first evaluated as  
39 a function of their river basins, type of surrounding pressure and water bodies. Later,  
40 background concentrations at the French national scale were established for both water and  
41 sediment matrices, as well as their threshold, i.e., the concentration that distinguishes  
42 background from anomalies or contaminations. Background concentrations in water are  
43 ranging between <0.04 – 0.14 ng Hg. L<sup>-1</sup> for MeHg, <0.14 – 2.10 ng Hg. L<sup>-1</sup> for iHg, <0.1 –  
44 8.43 ng Pb. L<sup>-1</sup> for Et<sub>2</sub>Pb and 0.49 – 151 ng Sn. L<sup>-1</sup>, <0.15 – 3.04 ng Sn. L<sup>-1</sup> and <0.25 ng Sn.  
45 L<sup>-1</sup> for MBT, DBT and TBT, respectively. For sediments, background concentrations were  
46 set as <0.09 – 1.11 ng Hg. g<sup>-1</sup> for MeHg, <0.06 – 24.3 ng Pb. g<sup>-1</sup> for Et<sub>2</sub>Pb and <2.0 – 13.4 ng  
47 Sn. g<sup>-1</sup>, <1.6 – 8.54 ng Sn. g<sup>-1</sup>, <0.6 – 1.16 ng Sn. g<sup>-1</sup> and <0.02 – 0.61 ng Sn. g<sup>-1</sup> for MBT,  
48 DBT, TBT and DPhT, respectively. TBT occurs in higher concentrations than the available  
49 environmental protection values in 24 and 38 sampling sites for both water and sediment  
50 samples, respectively. Other phenyltins (MPhT and TPhT) did not occur above their LOQ and

51 therefore no background was possible to establish. Throughout this work, which is the first  
52 assessment of background concentrations for organometallic compounds at the French  
53 national level ever being published, it was possible to conclude that over the last 10 to 20  
54 years organotin concentrations in French river basins have decreased while MeHg  
55 concentration remained stable.

56

57

58 *Keywords:* organometallic compounds; speciation analysis; screening study; background  
59 concentration; aquatic environment

60

61

## 62 **1. INTRODUCTION**

63 The Water Framework Directive (WFD) requires Member States of the European Union (EU)  
64 to monitor at river basin level an established list of substances. Despite these provisions, it is  
65 widely recognized by the scientific community that several substances of emerging concern  
66 are currently overlooked and as a result they are not adequately monitored by national  
67 authorities (Dulio and Andres, 2012). As part of the implementation of the National Action  
68 Plan on Micropollutants in the Aquatic Environment, the French Ministry of Ecology decided  
69 to implement an innovative and comprehensive approach to improve national monitoring  
70 programs (Dulio and Andres, 2012). This includes the setting up of a watch list of substances  
71 to be investigated at the national level in order to acquire missing information about the level  
72 of exposure of emerging contaminants in the aquatic environment and allow regular updating  
73 of the list of River Basin-Specific Pollutants to be regularly monitored. As part of this action  
74 plan, a large national screening study took place in 2012 in France, where organometallic  
75 compounds, among others, were monitored (ONEMA, 2012).

76 Organotin compounds (OTC) were extensively used as powerful biocides in anti-fouling  
77 paints and pesticide formulations (Graceli et al., 2013; Hoch, 2001) particularly tributyltin  
78 (TBT) and triphenyltin (TPhT), until their complete prohibition in January 1st, 2008  
79 (Comission, 2003; Dafforn et al., 2011). These compounds enter the aquatic ecosystems  
80 through landfill leaching (Pinel-Raffaitin et al., 2008; Yi et al., 2012), the constant leach rate  
81 of the antifouling paint, its scrap off due to ship grounding or ice-breakers activities, or even  
82 due to cleaning activities in shipyards (Du et al., 2014), and therefore most occurrence studies  
83 refer to marine and coastal environments, where concentrations range from non-detected to  
84  $197 \text{ ng Sn.L}^{-1}$  for water samples and from non-detected to  $7673 \text{ ng Sn.g}^{-1} \text{ dw}$  for sediments  
85 from European harbors (Antizar-Ladislao, 2008). Studies about their volatilization and  
86 atmospheric deposition (Amouroux et al., 2000; Huang et al., 2004) suggest that these  
87 compounds should also be monitored upstream, in lakes and rivers, where they are expected  
88 to occur in considerably lower concentrations.

89 Mercury is also widely spread in aquatic ecosystems, not only as a result of anthropogenic  
90 activities, but also by natural earth processes (Hsu-Kim et al., 2013). Inorganic mercury (iHg)  
91 is biomethylated by microorganisms originating methyl mercury (MeHg) which is known to  
92 be extremely toxic and bioaccumulate along the food web to potentially harmful  
93 concentrations, while, on the other hand, the toxicological role of iHg is still under debate  
94 (Clarkson, 2002). When lacking anthropogenic and geological sources, total mercury  
95 concentrations in water samples range from  $0.3$  to  $8 \text{ ng Hg.L}^{-1}$  and, in the presence of  
96 industrial pollution and gold mining activities, concentrations can vary between  $10$  and  $40 \text{ ng}$   
97  $\text{Hg.L}^{-1}$  (Wiener et al., 2003).

98 Organolead compounds (OLC) were introduced in the early 1920s as antiknocking agents for  
99 gasoline engines and remained in use for 55 years before the beginning of their phase-out in  
100 Japan and USA due to their neurotoxic effects (Craig, 2003). Today, and according to data

101 from April 2015 available on the United Nation Environment Programme (UNEP) website,  
102 there are still 6 countries in the world that use leaded gasoline (UNEP, 2015). As the most  
103 important source of lead in urban environments is highway runoff water, due to the gasoline  
104 lead deposited onto roads (Pattee and Pain, 2003), concentrations of triethyllead ( $\text{Et}_3\text{Pb}$ ) ranges  
105 from non-detects to  $400 \text{ ng Pb.L}^{-1}$  in these environments, and its degradation product,  
106 diethyllead ( $\text{Et}_2\text{Pb}$ ), ranges from non-detected to  $1800 \text{ ng Pb.L}^{-1}$  (Craig, 2003), being the two  
107 most frequent organolead species to be detected and quantified in water samples. In  
108 sediments, ethylated species are only sporadically detected in concentrations lower than  $1 \text{ ng}$   
109  $\text{Pb.L}^{-1}$  (Craig, 2003).

110 REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) is the  
111 European Union regulation made to spread awareness about the safe use of chemicals, in  
112 order to protect the environment and human health from risks posed by those chemicals. The  
113 Predicted No Effect Concentration (PNEC) is the international environmental protection  
114 values developed in the context of REACH legislation and can be defined as the concentration  
115 below which a specified percentage of species in an ecosystem is expected to be protected  
116 (Pennington, 2003), usually 95 %. In risk assessment studies, if the measured concentrations  
117 are higher than the environmental protection values, the ecosystem may be classified as at risk  
118 of environmental damage. A completely different approach to assess the environmental  
119 quality of a given area is by comparing with established background concentration levels.  
120 This approach is supported by some authors who claim that the transposition of  
121 ecotoxicological results to regulatory levels is difficult, as it might set these regulatory levels  
122 down to natural background concentrations and consequently lead to unnecessary clean-up to  
123 levels below the natural occurring concentrations, resulting in severe financial and  
124 environmental consequences (Reimann and Garrett, 2005).

125 The term “background” has not yet been defined precisely although this subject is object of  
126 several discussions (Ander et al., 2013; Reimann and Garrett, 2005). The US Environmental  
127 Protection Agency (USEPA) defines background levels as it is interpreted in this study: “the  
128 concentration of a hazardous substance that provides a defensible reference point that can be  
129 used to evaluate whether or not a release from the site has occurred” and which do not have to  
130 reflect pristine conditions (EPA, 1995). Several authors found more useful to present  
131 background levels as a concentration range (minimum, 25<sup>th</sup> percentile, median, 75<sup>th</sup>  
132 percentile, maximum), and not as a single value usually called “baseline” (Reimann et al.,  
133 2005; Vestenius et al., 2011). As important as establishing background concentrations it is to  
134 determine its threshold, i.e., the upper limit which differentiates background variability from  
135 anomalies and defines when action should be taken (Reimann et al., 2005).

136 The aim of this work is to establish background concentrations of several organometallic  
137 substances with a potential risk for the aquatic environment in the French territory and study  
138 the occurrence. For this reason, the substances included in this screening study were  
139 monitored at least at the PNEC (predicted no-effect concentration) levels and the background  
140 concentrations of the occurring target substances were defined, as well as their threshold. It is  
141 also important to highlight that this is the first assessment of organometallic compounds’  
142 occurrence in French watersheds at the national level.

143

144

## 145 **2. EXPERIMENTAL**

### 146 ***2.1. Water and sediment sampling strategy***

147 Three types of water bodies were investigated in Spring of 2012 in order to reflect the  
148 structure of the permanent monitoring network: rivers (140 sites), lakes (20 sites) and coastal  
149 sites (40 sites). However, coastal water samples were not sampled due to unsteady physical-

150 chemical conditions typical in estuaries and coastal environments and related sampling  
151 logistic limitations. The sampling sites, some of which are illustrated on Figure 1, were  
152 selected by French Water Agencies and selection criteria were defined by the INERIS at  
153 national level, not only in metropolitan water basins (Adour-Garonne, Artois-Picardie, Loire-  
154 Bretagne, Rhône-Méditerranée and Corsica, Rhin-Meuse, Seine-Normandie), but also in  
155 overseas territories (Guadeloupe, French Guiana, Mayotte, Martinique and Réunion).  
156 Agricultural, urban and industrial pressures were considered for the selection of the sampling  
157 sites; additionally, reference sites (no anthropogenic pressures) and some sites classified as  
158 “poor ecological status” according to the definitions of the Water Framework Directive, were  
159 also included in the study. The choice of sites was made on the basis of previous investigation  
160 results and the following target criteria: at least 20 % of reference sites and 16 % of sites  
161 where conditions for good ecological status are not achieved. The remaining 64 % were  
162 chosen based on land use: urban sites, sites for agricultural activities or breeding and  
163 industrial areas. The effect of seasonal variability was not addressed and will not be  
164 discussed.

165 Surface river bed sediment samples (1-2 cm) were collected within an area close to the river  
166 bank, pooled in an hermetic glass jar to avoid aeration and stored at 4 °C until further  
167 treatment (see Sample preparation section). The wet river bed sediment samples were sieved  
168 at 2 mm, then freeze-dried and sieved at 250 µm, grinded, homogenized and stored in amber  
169 flasks in a cold room (4 °C).

170 Water sampling was performed directly into 250 mL amber borosilicate bottles (VWR,  
171 Øxh:64x119 mm, Ø int. col: 38) or with the help of a pump or an integrating water-sampler,  
172 and shipped directly for analysis by fast courier within 24 hours (maximum 48 h) in  
173 thermostatic boxes (4 °C). For overseas territories, samples arrived by fast courier all within  
174 48 hours (maximum 96 h). Every water sample was filtered upon arrival at the laboratory and



175 further acidified to 2 % with pure glacial acetic acid and placed in the storage cold room at 4  
176 °C until sample preparation. Filtration was performed under a laminar flow hood (Class 100)  
177 in an acid-cleaned polysulfonate vacuum filtration unit from Sartorius (Aubagne, France) and  
178 under pyrolyzed 0.7 µm GF/F Whatmann filters (from Sigma-Aldrich in Lyon, France). The  
179 250-mL borosilicate bottles were not cleaned prior to sampling because a previous blank  
180 storage test was performed and the obtained blank were similar to regular blank values.

181

## 182 **2.2. Speciation analysis of organometallic compounds**

### 183 2.2.1. Chemicals

184 TBT chloride (96%), DBT dichloride (97%), MBT trichloride (95%) and iHg (II) chloride  
185 ( $\geq 99.5\%$ ) salts were obtained from Sigma-Aldrich, whereas TPhT chloride (98%), DPhT  
186 dichloride (96%), MPhT trichloride (95%) and the MeHg chloride standard (98.4%) were  
187 obtained from Strem Chemicals (Newburyport, MA, USA). Triethyllead chloride ( $\text{Et}_3\text{PbCl}$ ,  
188 82.3%) was purchased from Dr. Ehrenstorfer (LGC Standards, Molheim, France). No other  
189 organolead standards (such as  $\text{Et}_2\text{Pb}$ ) are commercially available, therefore all validation was  
190 performed for  $\text{Et}_3\text{Pb}$  and extrapolated to  $\text{Et}_2\text{Pb}$ . The isotopically enriched species used were  
191 purchased from ISC Science (Oviedo, Spain): iHg enriched in  $^{199}\text{Hg}$  ( $^{199}\text{iHg}$ , 91%) at  $10\ \mu\text{g}\cdot\text{g}^{-1}$   
192  $^1$ , MeHg enriched in  $^{201}\text{Hg}$  ( $^{201}\text{MeHg}$ , 96.5%) at  $5.494\ \mu\text{g}\cdot\text{g}^{-1}$  and a mix of MBT, DBT and  
193 TBT enriched in  $^{119}\text{Sn}$  (82.4%,  $^{119}\text{MBT}$ ,  $^{119}\text{DBT}$ ,  $^{119}\text{TBT}$ ) at 0.110, 0.691 and  $1.046\ \mu\text{g}\cdot\text{g}^{-1}$ ,  
194 respectively.

195 A mixture of MPhT, DPhT and TPhT enriched in  $^{116}\text{Sn}$  ( $^{116}\text{MPhT}$ ,  $^{116}\text{DPhT}$ ,  $^{116}\text{TPhT}$ ) was  
196 synthesized by phenylation of metallic tin obtained from Oak Ridge National Laboratory  
197 (Oak Ridge, TN, USA) according to a method described elsewhere (Kumar et al., 2004).  
198 Purity and concentrations in this methanol solution were the following:  $^{116}\text{MPhT}$  (90.2%) at  
199  $4.2\ \mu\text{g}\cdot\text{L}^{-1}$ ,  $^{116}\text{DPhT}$  (97.4%) at  $48.5\ \mu\text{g}\cdot\text{L}^{-1}$  and  $^{116}\text{TPhT}$  (97.5%) at  $677\ \mu\text{g}\cdot\text{L}^{-1}$ . In order to

200 control any possible degradation or interconversion of species, this solution was kept in the  
201 freezer and its concentration regularly determined by reverse isotope dilution.  
202 Hydrochloric acid (HCl, 33–36%, ultrexII ultrapure reagent) and glacial acetic acid (HOAc,  
203 Instra-analyzed) were purchased from J.T. Baker (Phillipsburg, NJ, USA). Methanol (MeOH,  
204  $\geq 99.9\%$  Chromasolv) and isooctane, or 2,2,4-trimethylpentane (ACS reagent,  $\geq 99.0\%$ ) were  
205 obtained from Sigma-Aldrich (Seelze, Germany). Ammonium hydroxide ( $\text{NH}_4\text{OH}$ ,  $\geq 25\%$  in  
206  $\text{H}_2\text{O}$ , TraceSELECT<sup>®</sup> Ultra, for ultratrace analysis) was purchased from Fluka (Steinheim,  
207 Germany) and sodium acetate trihydrate ( $\text{NaOAc}$ , puriss p.a.) from Riedel-de-Haën (Seelze,  
208 Germany). Sodium tetrapropylborate ( $\text{NaBPr}_4$ ) (98%) was purchased from Merseburger  
209 Spezialchemikalien (Schkopau, Germany).  
210 All stock solutions ( $1000 \mu\text{g}\cdot\text{g}^{-1}$  as Sn, Hg or Pb) were prepared by dissolving the  
211 corresponding salt either in a 3:1 mixture of acetic acid/methanol for OTC, methanol for  
212 MeHg and  $\text{Et}_3\text{Pb}$ , 1% HCl in ultrapure water for iHg and were kept in the dark at  $4^\circ\text{C}$  until  
213 use. Working solutions of the organo-tin, -mercury and -lead compounds were prepared daily  
214 before analysis by dilution of the stock solutions with 1% HCl in ultrapure water.

215

### 216 2.2.2. Water sample preparation

217 Water samples were treated according to Monperrus et al. (Monperrus et al., 2005). Briefly, 5  
218 mL of HOAc/NaOAc buffer ( $\text{pH } 4.8$ ,  $0.1 \text{ mol}\cdot\text{L}^{-1}$ ) was added to a flask containing 100 mL of  
219 water sample as well as 5  $\mu\text{L}$  (gravimetrically controlled) of the isotopically enriched spike  
220 solution ( $102.8 \mu\text{g Hg}\cdot\text{L}^{-1}$  for  $^{199}\text{iHg}$ ,  $92.4 \mu\text{g}\cdot\text{L}^{-1}$  for  $^{201}\text{MeHg}$ ,  $9.3 \mu\text{g Sn}\cdot\text{L}^{-1}$  for  $^{119}\text{MBT}$ ,  $34.6$   
221  $\mu\text{g Sn}\cdot\text{L}^{-1}$  for  $^{119}\text{DBT}$ ,  $35.6 \mu\text{g Sn}\cdot\text{L}^{-1}$  for  $^{119}\text{TBT}$ ,  $4.2 \mu\text{g Sn}\cdot\text{L}^{-1}$  for  $^{116}\text{MPhT}$ ,  $48.5 \mu\text{g Sn}\cdot\text{L}^{-1}$   
222 for  $^{116}\text{DPhT}$  and  $677 \mu\text{g Sn}\cdot\text{L}^{-1}$  for  $^{116}\text{TPhT}$ ) for the simultaneous analysis of organometallic  
223 species. The pH was then re-adjusted with ultrapure  $\text{NH}_4\text{OH}$  to  $\text{pH } 4.8$  and 1 mL of isooctane  
224 and 1 mL of 1% (w/v)  $\text{NaBPr}_4$  were added. Propylation occurred during vigorous shaking of

225 the sample for 5 min and the organic phase was then transferred into a 1.5-mL vial kept at -20  
226 °C until analysis.

227

### 228 2.2.3. Sediment sample preparation

229 The extraction of the organometallic species from the sediments was carried out following the  
230 guidelines in Pacheco-Arjona et al. (Pacheco-Arjona et al., 2008) with a few changes. Briefly,  
231 an Explorer focused microwave system from CEM Corporation (Mathews, NC, USA) was  
232 used to extract the organometallic species from the sediment by adding 5 mL of the mixture  
233 of HOAc: methanol (3:1, v/v) to 0.25 g of sediment and stirring for 3 min at 70 °C. The  
234 extracts were then centrifuged at 2300 rpm for 3 minutes and 1 mL of the extracted solution  
235 was added to 22-mL glass vials containing 5 mL of HOAc/NaOAc buffer (pH 4.8, 0.1 mol.L<sup>-1</sup>  
236 <sup>1</sup>). Ten µL (gravimetrically controlled) of the isotopically enriched spike solution (192.0 µg  
237 Hg.L<sup>-1</sup> for <sup>199</sup>iHg, 0.94 µg.L<sup>-1</sup> for <sup>201</sup>MeHg, 27.4 µg Sn.L<sup>-1</sup> for <sup>119</sup>MBT, 23.5 µg Sn.L<sup>-1</sup> for  
238 <sup>119</sup>DBT, 25.2 µg Sn.L<sup>-1</sup> for <sup>119</sup>TBT, 16.6 µg Sn.L<sup>-1</sup> for <sup>116</sup>MPhT, 77.7 µg Sn.L<sup>-1</sup> for <sup>116</sup>DPhT  
239 and 377.5 µg Sn.L<sup>-1</sup> for <sup>116</sup>TPhT) was added, the pH was re-adjusted with ultrapure NH<sub>4</sub>OH to  
240 pH 4.8 and 1 mL of isooctane and 1 mL of 1% (w/v) NaBPr<sub>4</sub> were added to each vial. The  
241 mixture was then manually and vigorously shaken for 5 min to allow propylation to occur.  
242 The organic phase was retrieved and transferred into a 1.5 mL vial which was kept at -20 °C  
243 until analysis.

244

### 245 **2.3. GC-ICP/MS analysis**

246 A Thermo X Series 2 inductively coupled plasma-mass spectrometer (ICP/MS) coupled to a  
247 gas chromatograph (GC) (Trace GC Ultra, Thermo Fisher, Waltham, MA, USA equipped  
248 with a TriPlus RSH autosampler) was used with a commercial GC-ICP/MS interface  
249 (SilcoSteel, 0.5 m length, outer i.d. 1.0 mm and o.d. 1.6 mm, inner i.d. 0.28 mm and o.d. 0.53

250 mm, Thermo Fisher). A MXT I column (30 m x 0.28  $\mu\text{m}$  i.d., 1  $\mu\text{m}$ , Restek Corporation,  
251 Bellefonte, PA, USA) was used to perform the chromatographic separation and Table S1  
252 (Supplementary Material) lists the operating conditions. The optimization of the instrument's  
253 performance was made with liquid standards and tin (m/z 116, 117, 118, 119, 120), mercury  
254 (m/z 199, 200, 201, 202) and lead (m/z 206, 208) isotopes where measured with a 30ms dwell  
255 time. The isotopes of Tl (m/z 203, 205 during 5 ms) and Sb (m/z 121, 123 during 5 ms) were  
256 measured to check the mass bias in each chromatographic run.

257

#### 258 **2.4. Quantification methods**

259 Diethyllead was determined by interpolation on the external calibration curve of  $\text{Et}_3\text{Pb}$  as no  
260 commercial standard for diethyllead, neither isotopic tracers, are available.

261 The use of a mixed isotopic spike solution containing  $^{199}\text{iHg}$ ,  $^{201}\text{MeHg}$ ,  $^{119}\text{MBT}$ ,  $^{119}\text{DBT}$ ,  
262  $^{119}\text{TBT}$ ,  $^{116}\text{MPhT}$ ,  $^{116}\text{DPhT}$  and  $^{116}\text{TPhT}$  allowed to quantify organotin and organomercury  
263 compounds by speciated isotope dilution mass spectrometry (SIDMS) which takes into  
264 account the cross-species transformations (only for Hg species, in this particular case), the  
265 loss of analytes during sample preparation and the signal drift. The isotopic spike was added  
266 to sediment samples after the microwave extraction, as it is well known that no artifacts are  
267 formed during this procedural step (Rodriguez Martin-Doimeadios et al., 2003; Monperrus et  
268 al., 2003), and method validation through the use of certified reference materials was  
269 performed.

270

#### 271 **2.5. QA/QC for sediment samples**

272 CRM-462 (coastal sediment, certified for DBT and TBT species), the CRM-646 (freshwater  
273 sediment, certified for Butyl-Sn and Phenyl-Sn species) and IAEA 405 (estuarine sediment,  
274 certified for MeHg) were the certified reference materials used for validating the methodology

275 and were purchased from the Institute for Reference Materials and Measurements (IRMM,  
276 Geel, Belgium).

277 For organolead species, no CRM is available; therefore, recovery tests were performed on  
278 both CRM-462 and CRM-646 by adding different concentrations of these species (10xLOQ,  
279 100xLOQ and 1000xLOQ, where LOQ is the limit of quantification) before microwave  
280 extraction. Analyses proceeded as described for sediment samples.

281

## 282 ***2.6. QA/QC for water samples***

283 In what concerns water samples, no CRM is available for organotin, organomercury and  
284 organolead species. In order to verify the accuracy of the water sample analysis and the  
285 stability of the equipment during the whole analytical protocol, several control samples were  
286 regularly prepared. Recoveries were determined for mineral water (Evian<sup>TM</sup> mineral water)  
287 samples spiked with natural compounds at a concentration level equivalent to the LOQ and 10  
288 times the LOQ. Recoveries were also determined for tap water spiked with 10 times the LOQ  
289 during one week of storage without acidification. These quality control samples followed the  
290 same preparation procedure and analysis as water samples.

291

## 292 ***2.7. Data Analysis***

293 For statistical purposes, samples with concentrations between LOQ and LOD were given their  
294 calculated value. For samples with concentrations below LOD, the concentration was set on  
295  $LOD/\sqrt{2}$  as it is advised in Croghan et al. (Croghan and Egeghy, 2003). A significant level  
296 ( $p < 0.05$ ) was employed for all statistical analysis which were performed using R software  
297 from The R Project for Statistical Computing.

298

299

### 300 3. RESULTS AND DISCUSSION

#### 301 *3.1. Analytical Performances and Protocol Validation*

302 The figures of merit of the analytical methods were evaluated and are represented in Table S2  
303 (Supplementary Information). Limits of detection (LOD) and limits of quantification (LOQ)  
304 where calculated as 3 and 10 times the standard deviation of twelve procedural blank  
305 measurements, respectively, and LOQ ranged between 0.03 – 1.0 ng.L<sup>-1</sup> for water samples  
306 and between 0.09 – 16.6 ng.g<sup>-1</sup> for sediments. The European Directive 2009/90/EC requires  
307 that all analytical methods applied in the context of the WFD must present a limit of  
308 quantification equal or below 30 % of the relevant EQS. This analytical technique is highly  
309 sensitive and efficient for the monitoring of organometallic compounds in water and  
310 sediments while complying with the 2009/90/EC Directive requirements (Monperrus et al.,  
311 2005). However, it was found that the plastic cover of the flasks used for this monitoring  
312 caused a slightly higher blanks in particular for MBT and DBT. Additionally, in this work 8  
313 different species are studied and 7 isotopically enriched spike solutions are mixed in order to  
314 quantify all the species simultaneously. As these spike solutions have isotopic abundances  
315 different from 100% (in particular the home-made <sup>116</sup>phenyltin mix solution), this results in  
316 degradation of the method and its analytical performances due to the compromise that a multi-  
317 contaminant analysis requires. Even so, these limits comply with the WFD demands as they  
318 are lower than the established environmental quality standards (1.2 µg.L<sup>-1</sup> as annual average  
319 (AA) value for Pb, 0.07 µg.L<sup>-1</sup> as maximum allowable concentration (MAC) for Hg and  
320 0.0002 µg.L<sup>-1</sup> as AA and 0.0015 µg.L<sup>-1</sup> as MAC for TBT).

321

#### 322 *3.2. Certified Reference Material analysis*

323 Table S3 (Supplementary Information) shows the certified values for organotin species in  
324 CRM-462 and CRM-646 and for MeHg in the CRM 405. The experimental results obtained  
325 for each CRM are also represented in the Table S3.

326 Good agreement was found between certified values and experimentally obtained results for  
327 organotin and organomercury species, except for MBT which usually bonds more strongly  
328 with the matrix and therefore presents lower extraction recoveries in samples with high  
329 organic matter content (Inagaki et al., 2003; Kumar et al., 2003; Ruiz Encinar et al., 2002). In  
330 order to conclude the validation of the sediment analysis, recoveries were also determined for  
331 both these CRM-462 and CRM-646 spiked with 10 times, 100 times and 1000 times the LOQ  
332 for Et<sub>3</sub>Pb because there are no CRMs available for the analysis of OLC in sediment matrices.  
333 Results are showed in Table S4 (Supplementary Information). All recoveries obtained are  
334 between 92 % and 111 %, which assures the quantitative extraction of the organolead species  
335 from the sediment matrix.

336

### 337 ***3.3. Stability tests on water samples***

338 In order to test stability of water samples when stored in cold room, recoveries were  
339 calculated for acidified mineral water (Evian) samples spiked at LOQ concentration level and  
340 10 times the LOQ and results are shown in Tables 1, 2 and 3, as well as the recoveries  
341 obtained for a non acidified tap water sample stored in cold room (4 °C) also spiked with 10  
342 times the LOQ concentration.

343 For all species, a significant decrease in concentration is observed for non-acidified tap water  
344 samples over time and might be due to its adsorption into the walls of the bottle (especially  
345 when the species are ionic), while acidified mineral water samples keep their  
346 representativeness throughout the 7 days of storage.

347 Even if the decreases due to adsorption in non-acidified water are not noteworthy on the first  
348 72 h (which is longer than the maximum delay between sample collection and sample arrival  
349 to the laboratory for metropolitan locations), water samples were filtered, transferred into the  
350 sampling recipient again and then acidified and stored in a cold room (4° C) in order to  
351 recover the maximum amount of analytes possibly adsorbed into the walls of the sampling  
352 recipients.

353

### 354 ***3.4. Occurrence of organo-tin –mercury and –lead compounds: influence of watersheds,*** 355 ***types of pressure and water bodies***

356 The results of water and sediment samples were gathered by watershed, type of surrounding  
357 pressure and type of water body, and were represented as boxplots where the LOQs are also  
358 indicated. Data outside the 1.5 times the interquartile range were considered as outliers and  
359 were removed as recommended by the “Statistical Guidance for Determining Background  
360 Ground Water Quality and Degradation” published by the Idaho Department of  
361 Environmental Quality (Dai and Welhan, 2014) for the establishment of background  
362 concentrations.

363 MeHg occurred (>LOD) in 86% of water samples, iHg in 99%, Et<sub>2</sub>Pb in 79%, MBT in 100%,  
364 DBT in 95%, TBT in 40%, MPhT in 13%, while DPhT and TPhT did not occur in any water  
365 samples. In the case of sediment samples, frequency of occurrence was 90% for MeHg, 99%  
366 for Et<sub>2</sub>Pb, 92% for MBT, 72% for DBT, 67% for TBT, 4% for MPhT, 54% for DPhT and  
367 finally 9% for TPhT.

368

#### 369 3.4.1. Differences in French watersheds

370 The results obtained for water and sediments were displayed according to the watershed they  
371 were collected from (Figure S1, Supplementary Information). Watersheds were labeled from



372 A to K, in which French metropolitan watersheds are represented from A to F and French  
373 overseas departments are labeled from G to K. When observing the boxplot representation on  
374 Figure S2, sediments from the departments overseas seem to be consistently lower than  
375 metropolitan areas. MeHg ranged from  $<0.09 - 7 \text{ ng Hg.g}^{-1}$  in metropolitan areas, while  
376 remained below the LOQ in the overseas samples. A similar trend was registered for  $\text{Et}_2\text{Pb}$   
377 (metropolitan:  $<0.60 - 60 \text{ ng Pb.g}^{-1}$ ; overseas:  $<0.60 \text{ ng Pb.g}^{-1}$ ) and for the butyltin species  
378 (MBT metropolis:  $<2.0 - 50 \text{ ng Sn.g}^{-1}$ , overseas territories:  $<2.0 - 8 \text{ ng Sn.g}^{-1}$ ; DBT  
379 metropolis:  $<1.6 - 60 \text{ ng Sn.g}^{-1}$ , overseas:  $<1.6 - 7 \text{ ng Sn.g}^{-1}$ ; TBT metropolis:  $<0.60 - 1.4 \text{ ng}$   
380  $\text{Sn.g}^{-1}$ , overseas:  $<0.60 \text{ ng Sn.g}^{-1}$ ). The 3 phenyltin species were only present simultaneously  
381 in watershed A. For all the others, MPhT and TPhT were below their LOQ and only DPhT  
382 presented data ranging between  $<0.20 \text{ ng Sn.g}^{-1} - 6.0 \text{ ng Sn.g}^{-1}$ .

383 This tendency is not observed in the corresponding water samples where MeHg and iHg  
384 ranged from  $<0.04 - 0.60 \text{ ng Hg.L}^{-1}$  and  $<0.14 - 2.5 \text{ ng Hg.L}^{-1}$ , respectively,  $\text{Et}_2\text{Pb}$  from  $<1.0$   
385  $- 18 \text{ ng Pb.L}^{-1}$ , MBT from  $<0.14 - 400 \text{ ng Sn.L}^{-1}$ , DBT from  $<0.15 - 5 \text{ ng Sn.L}^{-1}$  and TBT  
386 from  $<0.19 - 0.50 \text{ ng Sn.L}^{-1}$ . These differences were statistically evaluated through a Kruskal-  
387 Wallis Test ( $p < 0.05$ ,  $\alpha = 0.95$ ), because data did not exhibit simultaneously a normal  
388 distribution (Shapiro-Will normality test,  $p < 0.05$ ,  $\alpha = 0.95$ ) neither homogeneity of variances  
389 (Bartlett test,  $p < 0.05$ ,  $\alpha = 0.95$ ), so ANOVA could not be performed. For sediments,  
390 watersheds were significantly different for MeHg, iHg,  $\text{Et}_2\text{Pb}$ , MBT, DPhT and TPhT  
391 ( $p < 0.05$ ), as for water samples only MBT did not show a significant difference ( $p = 0.11$ )  
392 between the watersheds. A Mann-Whitney test for between-groups comparisons with  
393 Bonferroni correction for multiple comparisons (for 11 watersheds,  $\alpha = 0.95/11 = 0.09$  and  $p < 1-$   
394  $0.09$  or  $p < 0.91$ ) was further performed and confirmed significant differences between  
395 metropolitan watersheds and overseas watersheds for mercury species and  $\text{Et}_2\text{Pb}$  ( $p < 0.91$ ).

396 As the higher amount of MBT might be due to the TBT and DBT decay over the years,  
397 correlation was searched between these species. In water, no correlation is observed for MBT  
398 and DBT in relation to TBT ( $r = -0.19$  and  $r = 0.28$ , respectively,  $p < 0.05$ ), suggesting that  
399 organotin species concentration is not influenced by any particular pollution source. In  
400 sediments, however, the correlation between TBT and its degradation products is stronger ( $r =$   
401  $0.42$  and  $r = 0.68$ , respectively,  $p < 0.05$ ) as a record of TBT point sources already decaying.  
402 Older data on butyltins in French watersheds are available for comparison due to the TBT  
403 issue discovered in the Arcachon Bay (France) in the early 80s, which boosted research on  
404 organotin species all over the country, mostly in coastal environments at a local scale.  
405 Unfortunately, national surveys are scarce. A 1998 report from the French National  
406 Observation Network (RNO, today named as ROCCH) discloses butyltins and TPT  
407 concentrations in 237 coastal water samples from 36 different coastal areas (Michel and  
408 Averty, 1998), where concentrations in water ranged between  $<0.2 - 26.9 \text{ ng Sn.L}^{-1}$  for MBT,  
409  $<0.2 - 125.0 \text{ ng Sn.L}^{-1}$  for DBT,  $<0.2 - 114.6 \text{ ng Sn.L}^{-1}$  for TBT and  $<0.32 - 11.1 \text{ ng Sn.L}^{-1}$   
410 for TPT. Between 1998 and today, no other national survey data was found, but the  
411 comparison of both allows to conclude that the concentrations of TBT, DBT and TPT in  
412 French river basins are decreasing.

413 Environmental monitoring programs were also searched in other countries for comparison as  
414 data from ports, shipyards and other coastal environments with high boating activities are  
415 very frequent on the literature, but not adequate to compare with the data from this national  
416 survey. In Canada, a national survey took place in 1994-95 and revealed butyltin  
417 concentrations up to  $27.2 \text{ ng Sn.L}^{-1}$  in fresh and seawater, while phenyltin concentrations  
418 were below their limits of quantification. In Portugal, a national survey in 1999-2000  
419 registered butyltin concentrations from  $<3.0 - 30 \text{ ng.L}^{-1}$  (Díez et al., 2005) and in Slovenia

420 concentrations varied from  $<1.1 - 718 \text{ ng.L}^{-1}$  for butyltins and up to  $16 \text{ ng.L}^{-1}$  for phenyltins,  
421 in the period 2000-2006 (Nemanič et al., 2008).

422 Sediments from Mediterranean ponds were studied by the French National Observation  
423 Network in 1999 and revealed TBT concentrations ranging between  $<0.3 - 52.0 \text{ ng Sn.g}^{-1}$  but  
424 other organotin species were not addressed (RNO, 1999). Two years later, in 2001, eleven  
425 rivers from the Adour-Garonne river basin were studied and concentrations found in  
426 sediments for butyltins ranged from  $<0.03 - 125 \text{ ng Sn.g}^{-1}$ , while phenyltins ranged from  
427  $<0.03 - 40 \text{ ng Sn.g}^{-1}$  (Bancon-Montigny et al., 2004). In 2007/2008 another study in the  
428 Adour estuary and in the Arcachon Bay showed sediment concentrations between  $1.28 - 5.44$   
429  $\text{ng Sn.g}^{-1}$  (Rodriguez-Gonzalez et al., 2012).

430 As for international data, the Canada survey registered butyltin concentrations up to  $2525$   
431  $\text{ng.g}^{-1}$  and phenyltin concentrations up to  $19.6 \text{ ng.g}^{-1}$ . In Portugal, butyltin concentrations  
432 ranged from  $<3.8 - 78 \text{ ng.g}^{-1}$  while in Slovenia sediments registered concentrations up to  
433  $1995 \text{ ng.g}^{-1}$ .

434 The organotins concentrations obtained in the sediments collected in the present study are  
435 consistently lower, supporting the argument that organotins concentrations in the French  
436 aquatic environment are decreasing. The same decreasing trend for TBT and TPT was found  
437 by the German Environmental Specimen Bank in biological samples collected during 21  
438 years, from 1985 to 2006 (Rüdel et al., 2009, 2007).

439

440 There are several French local data available which report MeHg concentration in water and  
441 sediments. MeHg in the Adour estuary ranged from  $0.02$  to  $0.95 \text{ ng Hg.L}^{-1}$  between 2004  
442 (Stoichev et al., 2004) and 2010 (Sharif et al., 2014), the industrialized Seine estuary  
443 presented MeHg concentrations between  $0.012 - 0.021 \text{ ng Hg.L}^{-1}$  in 2007 while the adjacent

444 coastal waters ranged between 0.010 – 0.014 ng Hg.L<sup>-1</sup> (Laurier et al., 2007). These are in the  
445 same range of concentrations found in this national survey.

446 There are some international data available, although surveys are mostly carried out in  
447 seafood and fish. Lakes and rivers in California in 1988/1989 exhibited MeHg concentrations  
448 between 0.04 – 97 ng.L<sup>-1</sup> and 0.17 – 3.0 ng.L<sup>-1</sup>, respectively (Gill and Bruland, 1990). In 1994  
449 the average MeHg concentration was 0.013 ng.L<sup>-1</sup> in Lake Michigan (Mason and Sullivan,  
450 1997) and later in 2010 was up to 0.66 ng.L<sup>-1</sup> on Indiana watersheds (Risch et al., 2010),  
451 which are – again – in the same range of concentrations found in this national survey.

452 Concerning sediments, Coquery found average MeHg concentrations of 0.18 ng Hg.g<sup>-1</sup> in  
453 sediments from the Loire river in 1994 (Coquery et al., 1997). Ten years later, sediments from  
454 the Adour estuary exhibited MeHg concentrations between 0.1 – 1.6 ng Hg.g<sup>-1</sup> (Stoichev et  
455 al., 2004). There are also different studies about Seine river sediments from 1999 to 2011 in  
456 which the MeHg concentrations varied from 0.1 – 6 ng Hg.g<sup>-1</sup> in 1999 (Mikac et al., 1999),  
457 0.37 – 1.08 ng Hg.g<sup>-1</sup> in 2002 (Foucher, 2002), 0.6 – 3 ng Hg.g<sup>-1</sup> in 2008 (Ouddane et al.,  
458 2008) and finally 0.862 – 2.55 ng Hg.g<sup>-1</sup> in 2011 (Ramond et al., 2011). Today, and similarly  
459 to what was observed for water concentrations, MeHg levels in France stand in the same  
460 range of concentration, although seasonal variations are known to occur (Rodriguez-Gonzalez  
461 et al., 2012; Sharif et al., 2014; Stoichev et al., 2004).

462 Data from other countries are available at a local scale, sometimes due to known Hg pollution  
463 sources, and present great variability making it difficult to compare with the present study.

464

465 The Et<sub>2</sub>Pb is a result of the natural degradation of the tetraethyllead additives used in gasoline  
466 until its phase-out in France during the 90s. Taking into account the short time of half-life of  
467 the organolead species (between 0.6h – 8h for Et<sub>4</sub>Pb and 1.5 days for Et<sub>3</sub>Pb (Harrison and  
468 Allen, 1989)) the occurrence of Et<sub>2</sub>Pb was expected to be very low. Unfortunately, the

469 presence of Et<sub>2</sub>Pb in environmental matrices is not well documented. Most studies on  
470 organolead compounds, published between 1984 – 2000, focus on the evaluation of the ratio  
471 between the sum of organolead species and total lead (probably due to the performances of  
472 the analytical techniques used at the time), which means no data on the occurrence of Et<sub>2</sub>Pb  
473 alone is available. However, the results obtained in this survey are far below the WFD-EQS  
474 which establish an annual average concentration of 1.3 µg.L<sup>-1</sup> for lead and its compounds.

475

#### 476 3.4.2. No significant influence of anthropogenic pressures

477 The influence of types of pressure was evaluated and data was represented as boxplots for  
478 each compound as a function of their surrounding pressure: agricultural, bad ecological status  
479 (BES), industry, mixed, reference and urban (Figure S2, Supplementary Information). The  
480 label “mixed” for surrounding pressure includes sites with urban and agricultural pressure, as  
481 well as both industrial and agricultural activities or even urban and industrial areas.

482 MeHg in sediments exhibit significant lower concentration for mixed surrounding pressure  
483 and significant higher concentration for sites labeled as reference (for 6 types of surrounding  
484 pressure,  $\alpha = 0.95/6 = 0.16$  and  $p < 1 - 0.16$  or  $p < 0.84$ ), ranging between  $< 0.09$  and  $1.5 \text{ ng Hg.g}^{-1}$ ,  
485 but no data on grain size is available to further interpret these results. The corresponding  
486 water samples do not follow the same tendency for the Hg species, neither for organotin  
487 species. All results for MPhT and TPhT for sediments and water samples were below LOQ,  
488 while for DPhT values were below LOQ only in water samples.

489

490 For sediments, Kruskal-Wallis Test ( $p < 0.05$ ) and Mann-Whitney test for multiple groups ( $\alpha$   
491  $= 0.16$  and  $p < 0.84$ ) showed that mixed surrounding pressure was significantly lower than other  
492 pressures for MeHg and Et<sub>2</sub>Pb in sediments ( $p < 0.84$ ) and water ( $p < 0.84$ ). Higher  
493 concentrations of phenyltins were expected for agricultural pressures as a result of the use of

494 fungicides (Donard et al., 2001), but MPhT and TPhT were below LOQs for both sediments  
495 and water samples and only DPhT occurred more frequently although with concentrations  
496 between  $<0.2 - 0.6 \text{ ng Sn.g}^{-1}$ , very close to LOQ. The lack of information on the occurrence  
497 of these compounds in others aquatic environments rather than coastal areas is quite important  
498 because the marine impact of organotins was so deep that community was distracted and  
499 uninterested in other possible sources of these compounds in the environment (Donard et al.,  
500 2001).

501

### 502 3.4.3. Butyltin species consistently higher in coastal water bodies

503 When categorized by type of water body (Figure S3, Supplementary Information) – coastal  
504 water, lakes and rivers – river concentrations found for DBT and  $\text{Et}_2\text{Pb}$  were significantly  
505 higher ( $p<0.05$ ) than lakes. In sediments, however, Kruskal-Wallis Test ( $p<0.05$ ) and Mann-  
506 Whitney test (for 3 types of water bodies,  $\alpha = 0.95/3 = 0.32$  and  $p<1-0.32$  or  $p<0.68$ ) showed  
507 that MeHg concentration is significantly lower ( $p<0.68$ ) for samples collected in lakes (almost  
508 below the related LOQ), while costal sediments had a concentration range between  $<0.09$  and  
509  $3 \text{ ng Hg.g}^{-1}$  and river sediments ranged from  $<0.09$  to  $1.3 \text{ ng Hg.g}^{-1}$ .

510 As expected, butyltin species showed higher concentrations in sediments from coastal waters  
511 and lower concentrations in sediments from rivers: DBT concentrations in coastal sediments  
512 are significantly higher ( $p<0.68$ ) and TBT concentrations are significantly lower ( $p<0.68$ ) in  
513 rivers (Figure 2). TBT in costal sediments ranged from  $<0.6 - 55 \text{ ng Sn.g}^{-1}$ , while in lakes and  
514 rivers was no higher than  $3 \text{ ng Sn.g}^{-1}$ .

515

### 516 ***3.5. Background concentrations and thresholds of organometallic compounds in water and*** 517 ***sediment samples***

518 In order to define background concentrations, all data were gathered in Figure S4  
519 (Supplementary Information) where the results are represented as boxplots. Table 4a and 4b  
520 are a brief summary of the results presented, such as the range of concentrations obtained  
521 (minimum and maximal concentration), the median concentration, the 25<sup>th</sup> and 75<sup>th</sup>  
522 percentiles, the number of samples below the LOD and the calculated threshold, i.e., upper  
523 limit which differentiates background from anomalies. According to the guidelines from the  
524 Idaho Geological Survey (Dai and Welhan, 2014) for non-normal distributed data, which do  
525 not meet the steady state condition and for which possible seasonal effects were not corrected,  
526 this threshold should be calculated as the (median + 1.65 x (interquartile range)) but the  
527 compounds must have a valid median, or, on other words, at least 50 % of the occurrence data  
528 for these compounds must be above LOQ.

529 Background concentrations for iHg in water at the French national level are between <0.14  
530 and 2.1 ng Hg. L<sup>-1</sup>, and for MeHg are between <0.04 and 0.14 ng Hg. L<sup>-1</sup>, which is much  
531 lower than the estimated environmental protection values. Et<sub>2</sub>Pb background concentration  
532 ranged from <0.1 to 8.43 ng Pb. L<sup>-1</sup> but no environmental protection values for this specie in  
533 particular is established. MBT and DBT estimated background concentrations are 0.49 – 151  
534 ng Sn. L<sup>-1</sup> and <0.15 – 3.04 ng Sn. L<sup>-1</sup>, respectively. It is not possible to estimate background  
535 range of concentrations for TBT and phenyltin species due to the high number of samples  
536 below the LOQ.

537 In what concerns sediments, background concentration was set as <0.09 – 1.11 ng Hg. g<sup>-1</sup> for  
538 MeHg and <0.06 – 24.3 ng Pb. g<sup>-1</sup> for Et<sub>2</sub>Pb, while MBT, DBT and TBT backgrounds are  
539 <2.0 – 13.4 ng Sn. g<sup>-1</sup>, <1.6 – 8.54 ng Sn. g<sup>-1</sup> and <0.6 – 1.16 ng Sn. g<sup>-1</sup>, respectively. Again,  
540 phenyltins did not occur above their LOQ, except DPhT, for which it is possible to establish a  
541 background concentrations in the <0.02 – 0.61 ng Sn. g<sup>-1</sup> range. When compared with the  
542 environmental protection values s available (EQS and PNEC), background concentrations

543 reveal that only TBT occurs at higher concentrations in both water and sediment samples  
544 (EQS:  $0.2 \text{ ng.L}^{-1}$  and PNEC:  $0.024 \text{ ng.g}^{-1}$ ), reinforcing the need to monitor this substance and  
545 the correspondent decay products in order to assure its decreasing occurrence.

546

#### 547 **4. CONCLUSIONS**

548 The analytical method for the determination of organotin (MBT, DBT, TBT, MPhT, DPhT  
549 and TPhT), organomercury (MeHg and iHg) and organolead ( $\text{Et}_2\text{Pb}$ ) compounds was properly  
550 validated before analysis and data treatment. LOQs ranged from  $0.03 - 1.0 \text{ ng.L}^{-1}$  for water  
551 samples and from  $0.09 - 16.6 \text{ ng.g}^{-1}$  for sediment samples, which are below EQS and  
552 therefore in agreement to the quality demands of the EU WFD. Additionally, linearity was  
553 higher than 0.985 at the concentration range LOQ –  $6 \text{ ng.L}^{-1}$  (water) and LOQ –  $30 \text{ ng.g}^{-1}$   
554 (sediments), and precision below 10%.

555 This sampling campaign, with 152 water samples and 123 sediment samples, allowed the  
556 assessment of the organometallic concentrations of as a function of the watersheds, types of  
557 surrounding pressure and water bodies. Results obtained for sediments from the overseas  
558 departments seemed to be consistently lower than those obtained for metropolitan areas, but  
559 significant differences were only found for  $\text{Et}_2\text{Pb}$ , generally correlated with urban  
560 environments. When types of pressure were compared, only the samples label as “mixed”  
561 pressure showed significantly lower concentrations for water and sediment samples. Finally,  
562 coastal water sediments presented the highest concentrations of butyltin species and river  
563 sediments presented the lowest. These results reveal an overall decreasing on organotin  
564 concentrations in French river basins, when compared to data from the French National  
565 Observation Network in 1998, while concentrations for mercury species remain stable over  
566 time.



567 Updated background concentrations at the French national level were subsequently calculated  
568 for the target organometallic compounds in both matrices except phenyltins, which occurred  
569 below their LOQ. These data also revealed that TBT background concentration is higher than  
570 the available quality standards in both sediments and water samples.

571 The results of this 2012 monitoring campaign will contribute to the regular update of the list  
572 of substances to be integrated in the monitoring programs of the Water Agencies in the  
573 various river basins.

574

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584

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Table 1. Recoveries (%) obtained for butyltin and phenyltin species in acidified mineral water samples spiked with 1xLOQ concentration, 10xLOQ and for a non acidified tap water sample spiked with 10xLOQ

days	MBT			DBT			TBT		
	Mineral water (1xLOQ)	Mineral water (10xLOQ)	Tap water (10xLOQ)	Mineral water (1xLOQ)	Mineral water (10xLOQ)	Tap water (10xLOQ)	Mineral water (1xLOQ)	Mineral water (10xLOQ)	Tap water (10xLOQ)
t = 0	100	85	101	96	95	116	103	105	93
t = 3	-	101	48	-	96	97	-	108	80
t = 5	-	89	49	-	97	83	-	94	93
t = 7	-	88	20	-	95	64	-	103	60

days	MPhT			DPhT			TPhT		
	Mineral water (1xLOQ)	Mineral water (10xLOQ)	Tap water (10xLOQ)	Mineral water (1xLOQ)	Mineral water (10xLOQ)	Tap water (10xLOQ)	Mineral water (1xLOQ)	Mineral water (10xLOQ)	Tap water (10xLOQ)
t = 0	99	102	85	101	107	85	93	98	81
t = 3	-	79	67	-	96	17	-	105	75
t = 5	-	94	4	-	108	2	-	84	83
t = 7	-	77	3	-	70	1	-	102	55

Table 2. Recoveries (%) obtained for Et<sub>3</sub>Pb in acidified mineral water samples spiked with 1xLOQ concentration, 10xLOQ and for a non acidified tap water sample spiked with 10xLOQ

days	Et <sub>3</sub> Pb		
	Mineral water	Mineral water	Tap water
	(1xLOQ)	(10xLOQ)	(10xLOQ)
t = 0	137	108	127
t = 3	-	89	109
t = 7	-	105	47

Table 3. Recoveries (%) obtained for organomercury species in acidified mineral water samples spiked with 1xLOQ concentration, 10xLOQ and for a non acidified tap water sample spiked with 10xLOQ

days	<b>MeHg</b>			<b>iHg</b>		
	Mineral water (1xLOQ)	Mineral water (10xLOQ)	Tap water (10xLOQ)	Mineral water (1xLOQ)	Mineral water (10xLOQ)	Tap water (10xLOQ)
t = 0	98	110	114	96	117	81
t = 3	-	n.d.	126	-	n.d.	83
t = 5	-	n.d.	122	-	n.d.	81
t = 7	-	n.d.	70	-	n.d.	40

n.d. not determined

Table 4a. Background concentrations for water matrices (expressed as metal concentration) defined as minimum, 25<sup>th</sup> percentile, median, 75<sup>th</sup> percentile and maximum concentration, as well as the calculated threshold and the Environmental Quality Standard (EQS) regulated for each substance (n = 152 samples)

	MeHg	iHg	Et <sub>2</sub> Pb	MBT	DBT	TBT	MPhT	DPhT	TPhT
Min Concentration (ng.L <sup>-1</sup> )	< 0.04	<0.14	<1.0	0.49	<0.08	<0.08	-	-	-
25 <sup>th</sup> percentile (ng.L <sup>-1</sup> )	< 0.04	0.30	<1.0	7.89	0.26	<0.08	-	-	-
Median Concentration (ng.L <sup>-1</sup> )	0.04	0.50	2.16	16.1	0.57	<0.08	17.6*	-	-
75 <sup>th</sup> percentile (ng.L <sup>-1</sup> )	0.06	0.83	4.52	46.0	1.33	0.09	-	-	-
Max Concentration (ng.L <sup>-1</sup> )	0.14	2.10	8.43	151	3.04	0.25	-	-	-
Nr of samples below LD	21	2	32	0	7	91	132	152	152
Calculated threshold (ng.L <sup>-1</sup> )	0.10	1.38	8.60	79.0	2.33	n.c.	n.c.	n.c.	n.c.
Quality Standards (ng.L <sup>-1</sup> )	50 <sup>c</sup> ; 10 <sup>d</sup>	636 – 3180 <sup>a</sup>	n.a.	n.a.	n.a.	0.08 <sup>c</sup>	n.a.	n.a.	0.64 <sup>b</sup>

\*only one sample was quantified. <sup>a</sup> PNEC from (Rodrigues et al., 2013) <sup>b</sup> PNEC from (Yi et al., 2012) <sup>c</sup> EU-WFD

<sup>d</sup> PNEC from (Vincent et al., 2010) n.c. not calculated n.a. not attributed

Table 4b. Background concentrations for sediments (expressed as metal concentration) defined as minimum, 25<sup>th</sup> percentile, median, 75<sup>th</sup> percentile and maximum concentration, as well as the calculated threshold and the Environmental Quality Standard (EQS) regulated for each substance (n = 123 samples)

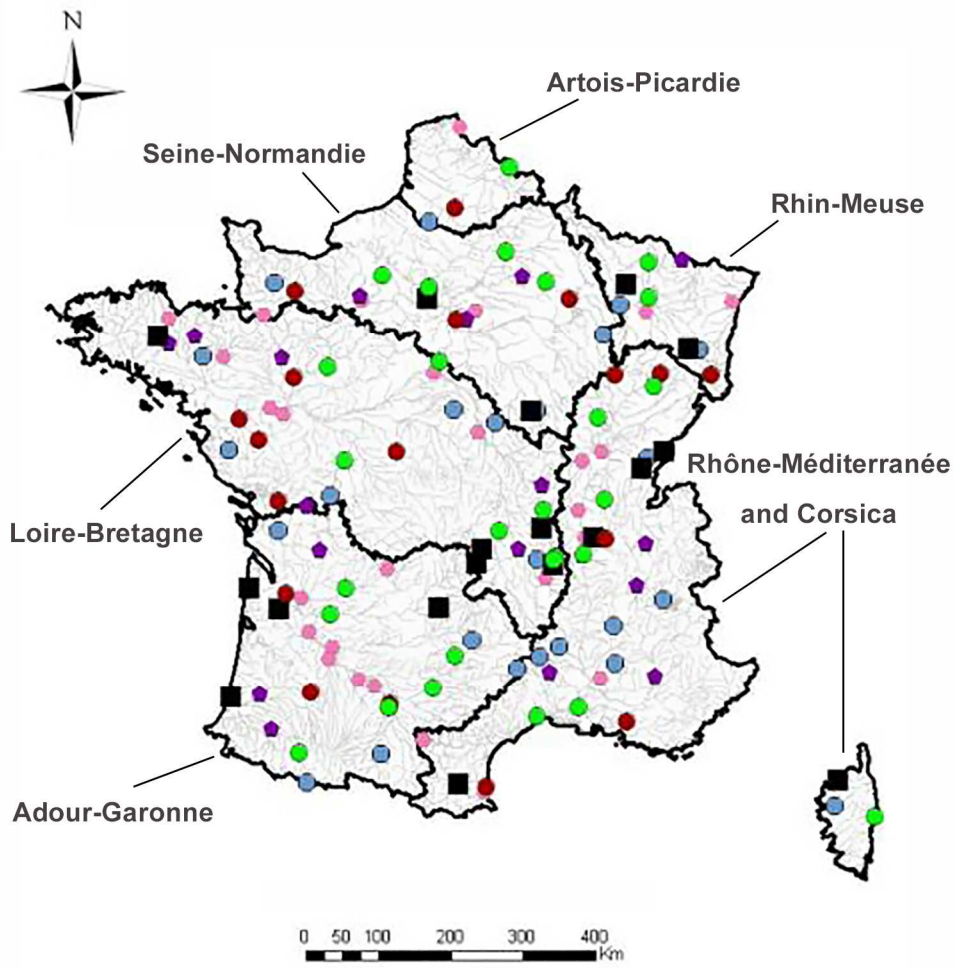
	MeHg	Et <sub>2</sub> Pb	MBT	DBT	TBT	MPhT	DPhT	TPhT
Min Concentration (ng.g <sup>-1</sup> )	< 0.09	<0.6	<1.4	<0.82	<0.25	<0.93	<0.08	-
25 <sup>th</sup> percentile (ng.g <sup>-1</sup> )	< 0.09	<0.6	<1.4	<0.82	<0.25	<0.93	<0.08	-
Median Concentration (ng.g <sup>-1</sup> )	< 0.09	1.66	2.80	1.84	0.25	<0.93	<0.08	3.2*
75 <sup>th</sup> percentile (ng.g <sup>-1</sup> )	0.29	5.79	5.11	3.20	0.52	<0.93	0.21	-
Max Concentration (ng.g <sup>-1</sup> )	1.11	24.3	13.4	8.54	1.16	6.1†	0.61	-
Nr of samples below LD	12	1	10	35	40	118	57	112
Calculated threshold (ng.g <sup>-1</sup> )	n.c.	10.9	9.96	6.54	0.90	n.c.	n.c.	n.c.
Quality Standards (ng.g <sup>-1</sup> )	1100 <sup>b</sup>	n.a.	n.a.	n.a.	0.024 <sup>a</sup>	n.a.	n.a.	n.a.

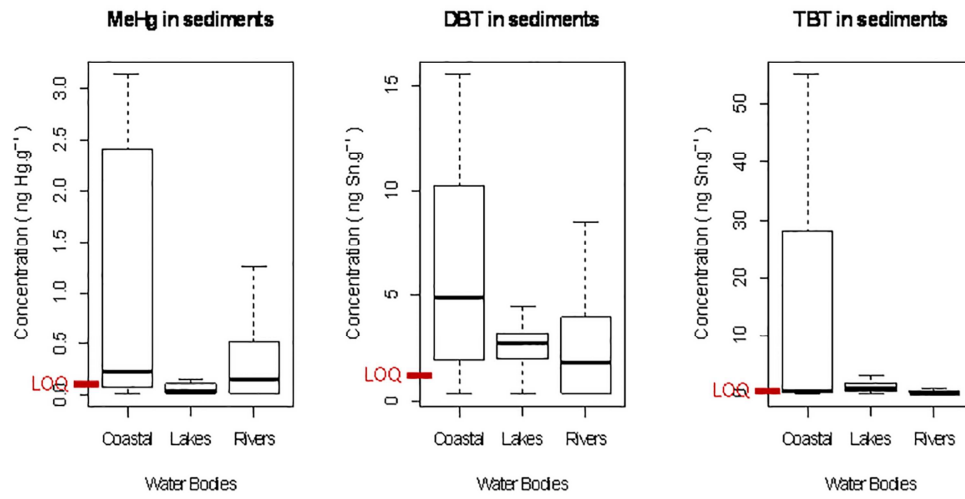
\*only one sample was quantified. †only two samples were quantified. <sup>a</sup>PNEC from (Silva et al., 2014)

<sup>d</sup> PNEC from (Vincent et al., 2010) n.c. not calculated n.a. not attributed

Figure 1. Illustration of the sampling sites in the French metropolitan area, in which green, pink, blue, purple and dark red color dots represent watercourses from urban, agricultural, reference, industrial and “poor ecological status”, respectively, and black squares refer to water bodies.

Figure 2. Boxplot representations of MeHg, DBT and TBT concentrations in sediments from different water bodies







**HIGHLIGHTS**

First assessment of background concentrations for organometallic compounds in France;

Water (152 samples) and sediment samples (123) were collected all over the country;

The analytical method was properly validated for both matrices prior to analysis;

The results reveal an overall decreasing on organotin concentrations in French river basins;

Concentrations for mercury species remain stable over time.