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

**J. Cavaleiro^a, C. Sola^{a,b}, J. Baldanza^a, E. Tessier^a, F. Lestremat^c, F. Botta^c, H.
Preudhomme^{a,d}, M. Monperrus^a, D. Amouroux^{a*}**

^a *Laboratoire de Chimie Analytique Bio-inorganique et Environnement (LCABIE), Institut
Pluridisciplinaire de Recherche sur l'Environnement et les Matériaux (IPREM), CNRS UMR
5254, Université de Pau et des Pays de l'Adour, Hélioparc Pau Pyrénées, 2, av. P. Angot,
64053 Pau cedex 9, France*

^b *Departamento de Química y Edafología, Facultad de Ciencias, Universidad de Navarra,
Pamplona, Spain*

^c *Institut National de l'Environnement Industriel et des Risques (INERIS); Parc
Technologique ALATA, BP 2, 60550 Verneuil-en-Halatte, France*

*Corresponding author: david.amouroux@univ-pau.fr

^d *(present address) Qatar Environment and Energy Research Institute (QEERI), Member of
the Qatar Foundation, P.O.Box 5825, Doha, QATAR*

ABSTRACT

The aim of this work is to estimate background concentrations of organometallic compounds, such as tributyltin (TBT), dibutyltin (DBT), monobutyltin (MBT), triphenyltin (TPhT), diphenyltin (DPhT), monophenyltin (MPhT), methylmercury (MeHg), inorganic mercury (iHg) and diethyllead (Et₂Pb) in the aquatic environment at the French national scale.

Both water and sediment samples were collected all over the country, resulting in 152 water samples and 123 sediment samples collected at 181 sampling points. Three types of surface water bodies were investigated: rivers (140 sites), lakes (19 sites) and coastal water (42 sites), spread along the 11 French river basins. The choice of sites was made on the basis of previous investigation results and the following target criteria: reference, urban sites, agricultural and industrial areas. The analytical method was properly validated for both matrices prior to analysis, resulting in low limits of quantification (LOQ), good precision and linearity in agreement with the Water Framework Directive demands. The results were first evaluated as a function of their river basins, type of surrounding pressure and water bodies. Later, background concentrations at the French national scale were established for both water and sediment matrices, as well as their threshold, i.e., the concentration that distinguishes background from anomalies or contaminations. Background concentrations in water are ranging between <0.04 – 0.14 ng Hg. L⁻¹ for MeHg, <0.14 – 2.10 ng Hg. L⁻¹ for iHg, <0.1 – 8.43 ng Pb. L⁻¹ for Et₂Pb and 0.49 – 151 ng Sn. L⁻¹, <0.15 – 3.04 ng Sn. L⁻¹ and <0.25 ng Sn. L⁻¹ for MBT, DBT and TBT, respectively. For sediments, background concentrations were set as <0.09 – 1.11 ng Hg. g⁻¹ for MeHg, <0.06 – 24.3 ng Pb. g⁻¹ for Et₂Pb and <2.0 – 13.4 ng Sn. g⁻¹, <1.6 – 8.54 ng Sn. g⁻¹, <0.6 – 1.16 ng Sn. g⁻¹ and <0.02 – 0.61 ng Sn. g⁻¹ for MBT, DBT, TBT and DPhT, respectively. TBT occurs in higher concentrations than the available environmental protection values in 24 and 38 sampling sites for both water and sediment samples, respectively. Other phenyltins (MPhT and TPhT) did not occur above their LOQ and

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

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

1. INTRODUCTION

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

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

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

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

from April 2015 available on the United Nation Environment Programme (UNEP) website, there are still 6 countries in the world that use leaded gasoline (UNEP, 2015). As the most important source of lead in urban environments is highway runoff water, due to the gasoline lead deposited onto roads (Pattee and Pain, 2003), concentrations of triethyllead (Et_3Pb) ranges from non-detects to 400 ng Pb.L^{-1} in these environments, and its degradation product, diethyllead (Et_2Pb), ranges from non-detected to $1800 \text{ ng Pb.L}^{-1}$ (Craig, 2003), being the two most frequent organolead species to be detected and quantified in water samples. In sediments, ethylated species are only sporadically detected in concentrations lower than 1 ng Pb.L^{-1} (Craig, 2003).

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

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

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

2. EXPERIMENTAL

2.1. Water and sediment sampling strategy

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

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

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

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

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

2.2. Speciation analysis of organometallic compounds

2.2.1. Chemicals

TBT chloride (96%), DBT dichloride (97%), MBT trichloride (95%) and iHg (II) chloride ($\geq 99.5\%$) salts were obtained from Sigma-Aldrich, whereas TPhT chloride (98%), DPhT dichloride (96%), MPhT trichloride (95%) and the MeHg chloride standard (98.4%) were obtained from Strem Chemicals (Newburyport, MA, USA). Triethyllead chloride (Et_3PbCl , 82.3%) was purchased from Dr. Ehrenstorfer (LGC Standards, Molheim, France). No other organolead standards (such as Et_2Pb) are commercially available, therefore all validation was performed for Et_3Pb and extrapolated to Et_2Pb . The isotopically enriched species used were purchased from ISC Science (Oviedo, Spain): iHg enriched in ^{199}Hg (^{199}iHg , 91%) at $10\text{ }\mu\text{g.g}^{-1}$, MeHg enriched in ^{201}Hg ($^{201}\text{MeHg}$, 96.5%) at $5.494\text{ }\mu\text{g.g}^{-1}$ and a mix of MBT, DBT and TBT enriched in ^{119}Sn (82.4%, ^{119}MBT , ^{119}DBT , ^{119}TBT) at 0.110, 0.691 and $1.046\text{ }\mu\text{g.g}^{-1}$, respectively.

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

control any possible degradation or interconversion of species, this solution was kept in the freezer and its concentration regularly determined by reverse isotope dilution.

Hydrochloric acid (HCl, 33–36%, ultrexII ultrapure reagent) and glacial acetic acid (HOAc, Instra-analyzed) were purchased from J.T. Baker (Phillipsburg, NJ, USA). Methanol (MeOH, $\geq 99.9\%$ Chromasolv) and isooctane, or 2,2,4-trimethylpentane (ACS reagent, $\geq 99.0\%$) were obtained from Sigma-Aldrich (Seelze, Germany). Ammonium hydroxide (NH_4OH , $\geq 25\%$ in H_2O , TraceSELECT® Ultra, for ultratrace analysis) was purchased from Fluka (Steinheim, Germany) and sodium acetate trihydrate (NaOAc , puriss p.a.) from Riedel-de-Haën (Seelze, Germany). Sodium tetrapropylborate (NaBPr_4) (98%) was purchased from Merseburger Spezialchemikalien (Schkopau, Germany).

All stock solutions ($1000 \mu\text{g}\cdot\text{g}^{-1}$ as Sn, Hg or Pb) were prepared by dissolving the corresponding salt either in a 3:1 mixture of acetic acid/methanol for OTC, methanol for MeHg and Et_3Pb , 1% HCl in ultrapure water for iHg and were kept in the dark at 4°C until use. Working solutions of the organo-tin, -mercury and -lead compounds were prepared daily before analysis by dilution of the stock solutions with 1% HCl in ultrapure water.

2.2.2. Water sample preparation

Water samples were treated according to Monperrus et al. (Monperrus et al., 2005). Briefly, 5 mL of HOAc/NaOAc buffer (pH 4.8, $0.1 \text{ mol}\cdot\text{L}^{-1}$) was added to a flask containing 100 mL of water sample as well as 5 μL (gravimetrically controlled) of the isotopically enriched spike solution ($102.8 \mu\text{g Hg}\cdot\text{L}^{-1}$ for ^{199}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}MBT , $34.6 \mu\text{g Sn}\cdot\text{L}^{-1}$ for ^{119}DBT , $35.6 \mu\text{g Sn}\cdot\text{L}^{-1}$ for ^{119}TBT , $4.2 \mu\text{g Sn}\cdot\text{L}^{-1}$ for $^{116}\text{MPhT}$, $48.5 \mu\text{g Sn}\cdot\text{L}^{-1}$ for $^{116}\text{DPhT}$ and $677 \mu\text{g Sn}\cdot\text{L}^{-1}$ for $^{116}\text{TPhT}$) for the simultaneous analysis of organometallic species. The pH was then re-adjusted with ultrapure NH_4OH to pH 4.8 and 1 mL of isooctane and 1 mL of 1% (w/v) NaBPr_4 were added. Propylation occurred during vigorous shaking of

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

2.2.3. Sediment sample preparation

The extraction of the organometallic species from the sediments was carried out following the guidelines in Pacheco-Arjona et al. (Pacheco-Arjona et al., 2008) with a few changes. Briefly, an Explorer focused microwave system from CEM Corporation (Mathews, NC, USA) was used to extract the organometallic species from the sediment by adding 5 mL of the mixture of HOAc: methanol (3:1, v/v) to 0.25 g of sediment and stirring for 3 min at 70 °C. The extracts were then centrifuged at 2300 rpm for 3 minutes and 1 mL of the extracted solution was added to 22-mL glass vials containing 5 mL of HOAc/NaOAc buffer (pH 4.8, 0.1 mol.L⁻¹). Ten µL (gravimetrically controlled) of the isotopically enriched spike solution (192.0 µg Hg.L⁻¹ for ¹⁹⁹iHg, 0.94 µg.L⁻¹ for ²⁰¹MeHg, 27.4 µg Sn.L⁻¹ for ¹¹⁹MBT, 23.5 µg Sn.L⁻¹ for ¹¹⁹DBT, 25.2 µg Sn.L⁻¹ for ¹¹⁹TBT, 16.6 µg Sn.L⁻¹ for ¹¹⁶MPhT, 77.7 µg Sn.L⁻¹ for ¹¹⁶DPhT and 377.5 µg Sn.L⁻¹ for ¹¹⁶TPhT) was added, the pH was re-adjusted with ultrapure NH₄OH to pH 4.8 and 1 mL of isooctane and 1 mL of 1% (w/v) NaBPr₄ were added to each vial. The mixture was then manually and vigorously shaken for 5 min to allow propylation to occur. The organic phase was retrieved and transferred into a 1.5 mL vial which was kept at -20 °C until analysis.

2.3. GC-ICP/MS analysis

A Thermo X Series 2 inductively coupled plasma-mass spectrometer (ICP/MS) coupled to a gas chromatograph (GC) (Trace GC Ultra, Thermo Fisher, Waltham, MA, USA equipped with a TriPlus RSH autosampler) was used with a commercial GC-ICP/MS interface (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

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

2.4. Quantification methods

Diethyllead was determined by interpolation on the external calibration curve of Et_3Pb as no commercial standard for diethyllead, neither isotopic tracers, are available.

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

2.5. QA/QC for sediment samples

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

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

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

2.6. QA/QC for water samples

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

2.7. Data Analysis

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

3. RESULTS AND DISCUSSION

3.1. Analytical Performances and Protocol Validation

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

3.2. Certified Reference Material analysis

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

Good agreement was found between certified values and experimentally obtained results for organotin and organomercury species, except for MBT which usually bonds more strongly with the matrix and therefore presents lower extraction recoveries in samples with high organic matter content (Inagaki et al., 2003; Kumar et al., 2003; Ruiz Encinar et al., 2002). In order to conclude the validation of the sediment analysis, recoveries were also determined for both these CRM-462 and CRM-646 spiked with 10 times, 100 times and 1000 times the LOQ for Et₃Pb because there are no CRMs available for the analysis of OLC in sediment matrices. Results are showed in Table S4 (Supplementary Information). All recoveries obtained are between 92 % and 111 %, which assures the quantitative extraction of the organolead species from the sediment matrix.

3.3. Stability tests on water samples

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

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

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

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

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

MeHg occurred (>LOD) in 86% of water samples, iHg in 99%, Et₂Pb in 79%, MBT in 100%, DBT in 95%, TBT in 40%, MPhT in 13%, while DPhT and TPhT did not occur in any water samples. In the case of sediment samples, frequency of occurrence was 90% for MeHg, 99% for Et₂Pb, 92% for MBT, 72% for DBT, 67% for TBT, 4% for MPhT, 54% for DPhT and finally 9% for TPhT.

3.4.1. Differences in French watersheds

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

A to K, in which French metropolitan watersheds are represented from A to F and French overseas departments are labeled from G to K. When observing the boxplot representation on Figure S2, sediments from the departments overseas seem to be consistently lower than metropolitan areas. MeHg ranged from $<0.09 - 7 \text{ ng Hg.g}^{-1}$ in metropolitan areas, while remained below the LOQ in the overseas samples. A similar trend was registered for Et_2Pb (metropolitan: $<0.60 - 60 \text{ ng Pb.g}^{-1}$; overseas: $<0.60 \text{ ng Pb.g}^{-1}$) and for the butyltin species (MBT metropolis: $<2.0 - 50 \text{ ng Sn.g}^{-1}$, overseas territories: $<2.0 - 8 \text{ ng Sn.g}^{-1}$; DBT metropolis: $<1.6 - 60 \text{ ng Sn.g}^{-1}$, overseas: $<1.6 - 7 \text{ ng Sn.g}^{-1}$; TBT metropolis: $<0.60 - 1.4 \text{ ng Sn.g}^{-1}$, overseas: $<0.60 \text{ ng Sn.g}^{-1}$). The 3 phenyltin species were only present simultaneously in watershed A. For all the others, MPhT and TPhT were below their LOQ and only DPhT presented data ranging between $<0.20 \text{ ng Sn.g}^{-1} - 6.0 \text{ ng Sn.g}^{-1}$.

This tendency is not observed in the corresponding water samples where MeHg and iHg ranged from $<0.04 - 0.60 \text{ ng Hg.L}^{-1}$ and $<0.14 - 2.5 \text{ ng Hg.L}^{-1}$, respectively, Et_2Pb from $<1.0 - 18 \text{ ng Pb.L}^{-1}$, MBT from $<0.14 - 400 \text{ ng Sn.L}^{-1}$, DBT from $<0.15 - 5 \text{ ng Sn.L}^{-1}$ and TBT from $<0.19 - 0.50 \text{ ng Sn.L}^{-1}$. These differences were statistically evaluated through a Kruskal-Wallis Test ($p < 0.05$, $\alpha = 0.95$), because data did not exhibit simultaneously a normal distribution (Shapiro-Will normality test, $p < 0.05$, $\alpha = 0.95$) neither homogeneity of variances (Bartlett test, $p < 0.05$, $\alpha = 0.95$), so ANOVA could not be performed. For sediments, watersheds were significantly different for MeHg, iHg, Et_2Pb , MBT, DPhT and TPhT ($p < 0.05$), as for water samples only MBT did not show a significant difference ($p = 0.11$) between the watersheds. A Mann-Whitney test for between-groups comparisons with Bonferroni correction for multiple comparisons (for 11 watersheds, $\alpha = 0.95/11 = 0.09$ and $p < 1 - 0.09$ or $p < 0.91$) was further performed and confirmed significant differences between metropolitan watersheds and overseas watersheds for mercury species and Et_2Pb ($p < 0.91$).

As the higher amount of MBT might be due to the TBT and DBT decay over the years, correlation was searched between these species. In water, no correlation is observed for MBT and DBT in relation to TBT ($r = -0.19$ and $r = 0.28$, respectively, $p < 0.05$), suggesting that organotin species concentration is not influenced by any particular pollution source. In sediments, however, the correlation between TBT and its degradation products is stronger ($r = 0.42$ and $r = 0.68$, respectively, $p < 0.05$) as a record of TBT point sources already decaying. Older data on butyltins in French watersheds are available for comparison due to the TBT issue discovered in the Arcachon Bay (France) in the early 80s, which boosted research on organotin species all over the country, mostly in coastal environments at a local scale. Unfortunately, national surveys are scarce. A 1998 report from the French National Observation Network (RNO, today named as ROCCH) discloses butyltins and TPT concentrations in 237 coastal water samples from 36 different coastal areas (Michel and Averty, 1998), where concentrations in water ranged between $<0.2 - 26.9 \text{ ng Sn.L}^{-1}$ for MBT, $<0.2 - 125.0 \text{ ng Sn.L}^{-1}$ for DBT, $<0.2 - 114.6 \text{ ng Sn.L}^{-1}$ for TBT and $<0.32 - 11.1 \text{ ng Sn.L}^{-1}$ for TPT. Between 1998 and today, no other national survey data was found, but the comparison of both allows to conclude that the concentrations of TBT, DBT and TPT in French river basins are decreasing. Environmental monitoring programs were also searched in other countries for comparison as data from ports, shipyards and other coastal environments with high boating activities are very frequent on the literature, but not adequate to compare with the data from this national survey. In Canada, a national survey took place in 1994-95 and revealed butyltin concentrations up to $27.2 \text{ ng Sn.L}^{-1}$ in fresh and seawater, while phenyltin concentrations were below their limits of quantification. In Portugal, a national survey in 1999-2000 registered butyltin concentrations from $<3.0 - 30 \text{ ng.L}^{-1}$ (Díez et al., 2005) and in Slovenia

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

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

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

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

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

coastal waters ranged between 0.010 – 0.014 ng Hg.L⁻¹ (Laurier et al., 2007). These are in the same range of concentrations found in this national survey.

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

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

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

The Et₂Pb is a result of the natural degradation of the tetraethyllead additives used in gasoline until its phase-out in France during the 90s. Taking into account the short time of half-life of the organolead species (between 0.6h – 8h for Et₄Pb and 1.5 days for Et₃Pb (Harrison and Allen, 1989)) the occurrence of Et₂Pb was expected to be very low. Unfortunately, the

presence of Et₂Pb in environmental matrices is not well documented. Most studies on organolead compounds, published between 1984 – 2000, focus on the evaluation of the ratio between the sum of organolead species and total lead (probably due to the performances of the analytical techniques used at the time), which means no data on the occurrence of Et₂Pb alone is available. However, the results obtained in this survey are far below the WFD-EQS which establish an annual average concentration of 1.3 µg.L⁻¹ for lead and its compounds.

3.4.2. No significant influence of anthropogenic pressures

The influence of types of pressure was evaluated and data was represented as boxplots for each compound as a function of their surrounding pressure: agricultural, bad ecological status (BES), industry, mixed, reference and urban (Figure S2, Supplementary Information). The label “mixed” for surrounding pressure includes sites with urban and agricultural pressure, as well as both industrial and agricultural activities or even urban and industrial areas. MeHg in sediments exhibit significant lower concentration for mixed surrounding pressure and significant higher concentration for sites labeled as reference (for 6 types of surrounding pressure, $\alpha = 0.95/6 = 0.16$ and $p < 1 - 0.16$ or $p < 0.84$), ranging between < 0.09 and 1.5 ng Hg.g^{-1} , but no data on grain size is available to further interpret these results. The corresponding water samples do not follow the same tendency for the Hg species, neither for organotin species. All results for MPhT and TPhT for sediments and water samples were below LOQ, while for DPhT values were below LOQ only in water samples.

For sediments, Kruskal-Wallis Test ($p < 0.05$) and Mann-Whitney test for multiple groups ($\alpha = 0.16$ and $p < 0.84$) showed that mixed surrounding pressure was significantly lower than other pressures for MeHg and Et₂Pb in sediments ($p < 0.84$) and water ($p < 0.84$). Higher concentrations of phenyltins were expected for agricultural pressures as a result of the use of

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

3.4.3. Butyltin species consistently higher in coastal water bodies

When categorized by type of water body (Figure S3, Supplementary Information) – coastal water, lakes and rivers – river concentrations found for DBT and Et_2Pb were significantly higher ($p<0.05$) than lakes. In sediments, however, Kruskal-Wallis Test ($p<0.05$) and Mann-Whitney test (for 3 types of water bodies, $\alpha = 0.95/3 = 0.32$ and $p<1-0.32$ or $p<0.68$) showed that MeHg concentration is significantly lower ($p<0.68$) for samples collected in lakes (almost below the related LOQ), while costal sediments had a concentration range between <0.09 and 3 ng Hg.g^{-1} and river sediments ranged from <0.09 to 1.3 ng Hg.g^{-1} .

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

3.5. Background concentrations and thresholds of organometallic compounds in water and sediment samples

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

Background concentrations for iHg in water at the French national level are between <0.14 and 2.1 ng Hg. L⁻¹, and for MeHg are between <0.04 and 0.14 ng Hg. L⁻¹, which is much lower than the estimated environmental protection values. Et₂Pb background concentration ranged from <0.1 to 8.43 ng Pb. L⁻¹ but no environmental protection values for this specie in particular is established. MBT and DBT estimated background concentrations are 0.49 – 151 ng Sn. L⁻¹ and <0.15 – 3.04 ng Sn. L⁻¹, respectively. It is not possible to estimate background range of concentrations for TBT and phenyltin species due to the high number of samples below the LOQ.

In what concerns sediments, background concentration was set as <0.09 – 1.11 ng Hg. g⁻¹ for MeHg and <0.06 – 24.3 ng Pb. g⁻¹ for Et₂Pb, while MBT, DBT and TBT backgrounds are <2.0 – 13.4 ng Sn. g⁻¹, <1.6 – 8.54 ng Sn. g⁻¹ and <0.6 – 1.16 ng Sn. g⁻¹, respectively. Again, phenyltins did not occur above their LOQ, except DPhT, for which it is possible to establish a background concentrations in the <0.02 – 0.61 ng Sn. g⁻¹ range. When compared with the environmental protection values s available (EQS and PNEC), background concentrations

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

4. CONCLUSIONS

The analytical method for the determination of organotin (MBT, DBT, TBT, MPhT, DPhT and TPhT), organomercury (MeHg and iHg) and organolead (Et_2Pb) compounds was properly validated before analysis and data treatment. LOQs ranged from $0.03 - 1.0 \text{ ng.L}^{-1}$ for water samples and from $0.09 - 16.6 \text{ ng.g}^{-1}$ for sediment samples, which are below EQS and therefore in agreement to the quality demands of the EU WFD. Additionally, linearity was higher than 0.985 at the concentration range LOQ – 6 ng.L^{-1} (water) and LOQ – 30 ng.g^{-1} (sediments), and precision below 10%.

This sampling campaign, with 152 water samples and 123 sediment samples, allowed the assessment of the organometallic concentrations of as a function of the watersheds, types of surrounding pressure and water bodies. Results obtained for sediments from the overseas departments seemed to be consistently lower than those obtained for metropolitan areas, but significant differences were only found for Et_2Pb , generally correlated with urban environments. When types of pressure were compared, only the samples label as “mixed” pressure showed significantly lower concentrations for water and sediment samples. Finally, coastal water sediments presented the highest concentrations of butyltin species and river sediments presented the lowest. These results reveal an overall decreasing on organotin concentrations in French river basins, when compared to data from the French National Observation Network in 1998, while concentrations for mercury species remain stable over time.

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

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

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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	Mineral water	Tap water	Mineral water	Mineral water	Tap water	Mineral water	Mineral water	Tap water
	(1xLOQ)	(10xLOQ)	(10xLOQ)	(1xLOQ)	(10xLOQ)	(10xLOQ)	(1xLOQ)	(10xLOQ)	(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	Mineral water	Tap water	Mineral water	Mineral water	Tap water	Mineral water	Mineral water	Tap water
	(1xLOQ)	(10xLOQ)	(10xLOQ)	(1xLOQ)	(10xLOQ)	(10xLOQ)	(1xLOQ)	(10xLOQ)	(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 Et₃Pb in acidified mineral water samples spiked with 1xLOQ concentration, 10xLOQ and for a non acidified tap water sample spiked with 10xLOQ

days	Et ₃ 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	MeHg			iHg		
	Mineral water	Mineral water	Tap water	Mineral water	Mineral water	Tap water
	(1xLOQ)	(10xLOQ)	(10xLOQ)	(1xLOQ)	(10xLOQ)	(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						

n.d. not determined

Table 4a. Background concentrations for water matrices (expressed as metal concentration) defined as minimum, 25th percentile, median, 75th 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 ₂ Pb	MBT	DBT	TBT	MPhT	DPhT	TPhT
Min Concentration (ng.L ⁻¹)	< 0.04	<0.14	<1.0	0.49	<0.08	<0.08	-	-	-
25 th percentile (ng.L ⁻¹)	< 0.04	0.30	<1.0	7.89	0.26	<0.08	-	-	-
Median Concentration (ng.L ⁻¹)	0.04	0.50	2.16	16.1	0.57	<0.08	17.6*	-	-
75 th percentile (ng.L ⁻¹)	0.06	0.83	4.52	46.0	1.33	0.09	-	-	-
Max Concentration (ng.L ⁻¹)	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 ⁻¹)	0.10	1.38	8.60	79.0	2.33	n.c.	n.c.	n.c.	n.c.
Quality Standards (ng.L ⁻¹)	50 ^c ; 10 ^d	636 – 3180 ^a	n.a.	n.a.	n.a.	0.08 ^c	n.a.	n.a.	0.64 ^b

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

^d 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, 25th percentile, median, 75th 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 ₂ Pb	MBT	DBT	TBT	MPhT	DPhT	TPhT
Min Concentration (ng.g ⁻¹)	< 0.09	<0.6	<1.4	<0.82	<0.25	<0.93	<0.08	-
25 th percentile (ng.g ⁻¹)	< 0.09	<0.6	<1.4	<0.82	<0.25	<0.93	<0.08	-
Median Concentration (ng.g ⁻¹)	< 0.09	1.66	2.80	1.84	0.25	<0.93	<0.08	3.2*
75 th percentile (ng.g ⁻¹)	0.29	5.79	5.11	3.20	0.52	<0.93	0.21	-
Max Concentration (ng.g ⁻¹)	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 ⁻¹)	n.c.	10.9	9.96	6.54	0.90	n.c.	n.c.	n.c.
Quality Standards (ng.g ⁻¹)	1100 ^b	n.a.	n.a.	n.a.	0.024 ^a	n.a.	n.a.	n.a.

*only one sample was quantified. †only two samples were quantified. ^a PNEC from (Silva et al., 2014)

^d 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.