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Abstract

Mercury (Hg) and methyl mercury (MeHg) concentrations have never been measured in sediments of coastal lakes of Aquitaine, although high concentrations of Hg have been measured in fish. Our objective was to characterize benthic biogeochemical processes and the distribution of Hg in lake sediments and to connect these results with fish contamination. For this, we mapped and characterized sediments. We measured sediment Hg and MeHg content, and biogeochemical parameters. We identified organic deposits in deep areas, and sandy sediments in shallow areas. Sediments were anoxic below the sediment–water interface. The average Hg concentration in organic

sediment was 213 µg kg^{-1} dry weight. Sandy sediments had an average Hg concentration of 4 µg kg^{-1} dw. We measured concentrations below 6 µg kg^{-1} dw in sediments from streams that drain the catchment. Similar concentrations in the four lakes suggest that the source of total Hg was not a point source in a given lake. The highest MeHg concentrations were found in the upper centimetres of organic sediments, where sulphate reduction occurred. MeHg represented 2.53% of total Hg for Lake Carcans-Hourtin, less in other lakes. The proportion of MeHg in sediment followed lake water sulphate concentrations. High sulphate concentrations resulted from agricultural activity in the Lake Carcans-Hourtin catchment. Our results corroborate the hypothesis that Hg methylation is linked to sulphate-reducing activity. High fluxes of sulphate from a drainage basin may induce large proportions of potentially bioavailable MeHg in lake sediment, even in non-polluted areas. The Hg methylation activity in the sediment reflected the exposure of predatory fish to MeHg.

Keywords : Mercury methylation, fish contamination, aquatic sediment, sulphate, freshwater lake

1. Introduction

Technological, industrial, and agricultural progress triggered both the exploitation of natural resources and the dispersion of anthropogenic contaminants. Since the 19th century, mercury (Hg) fluxes in the environment have increased at a global scale. Typical concentrations of Hg range from 50 to 150 µg kg^{-1} in the continental crust (Wedepohl, 1995), from 0.1 to 2 ng L^{-1} in continental and ocean waters (Mason et al., 1994), and from 1 to 3 ng m^{-3} in the atmosphere (Schroeder and Munthe, 1998).

Mercury dynamics is characterizes by properties, such as volatility at ambient temperature, stability of its bonds with carbon and sulphur, and very high bioconcentration and toxicity (Cossa and Ficht, 1999). Methyl mercury (MeHg) is the most toxic chemical form of Hg. It is a neurotoxin for vertebrates, which leads to damage in central nervous system (Allen et al., 2002). Methyl mercury passes easily through biological barriers and can bioaccumulate and biomagnify along the food chain. Although it is present at very low concentrations in water, it can concentrate up to 10 million times in aquatic organisms such as predators (Cossa and Ficht, 1999). Human exposure to MeHg compounds

occurs often through the consumption of fish and fish products (Driscoll et al., 2013). High trophic level species of fish can present very high MeHg concentrations. The maximum tolerable level for the sale of carnivorous fish is 1 mg kg^{-1} wet weight according to the European Commission directive 93/351/EEC.

Mercury is naturally emitted in the environment through degassing of the Earth's crust, volcanoes, and erosion of soils and rocks. Human-related Hg emissions dominate the Hg cycle such that most of the Hg in the atmosphere is anthropogenic (Mason et al., 1994). Natural Hg emission and re-emission mainly occurs as elemental mercury vapours (Hg^0). The main mercury source in aquatic environments comes from wet and dry atmospheric deposition, and via runoff from the drainage basin (Mason and Fitzgerald, 1996). Globally, the main anthropogenic Hg emissions into the atmosphere originate from artisanal gold production, the combustion of coal, and solid wastes (Pirrone et al., 2010; UNEP, 2013; Streets et al. 2017). These emissions, coupled with long-distance transport of elemental Hg, result in a worldwide distribution of Hg deposition with a global average of 5.6 µg m^{-2} yr^{-1} (Lamborg et al., 2002).

In 2015, a large-scale sampling of piscivorous fish was conducted in order to study fish contamination by mercury in the four main lakes in Aquitaine, specifically from the north to the south, lakes Carcans-Hourtin, Lacanau, Cazaux-Sanguinet, and Parentis-Biscarrosse (Fig. 1). The results showed an increasing Hg contamination gradient from Lake Parentis-Biscarrosse to Lake Carcans-Hourtin (south–north gradient), with values in the top predator zander (*Sander lucioperca*) from 2000 µg kg^{-1} dw in the southernmost lake to 7400 µg kg^{-1} dw in the Lake Carcans-Hourtin (Gentès et al., submitted). This latter study showed that trophic transfer efficiency does not explain this Hg latitudinal gradient in biota. The mercury concentration in fish suggested that the lakes underwent variable contamination pressure. However, the four lakes are located in the same geological context, they are subject to identical climate, and they do not have known local Hg sources, suggesting that different fish contamination in each lake results from distinct methylation efficiency of a background Hg flux. Therefore, these lakes represent a natural laboratory, in which the study of biogeochemical parameters allows us to determine the impact of the main factors that control methylation of Hg. Methylation

81 occurs through the action of sulphate-reducing bacteria (Gilmour et al., 1992) and, to a lesser extent,
82 iron-reducing and methanogenic microorganisms (Alpers et al., 2013; Hamelin et al. 2011; Kerin et
83 al., 2006; Parks et al., 2013), which are common in organic-rich sediments. Consequently, methylation
84 is localized in the anoxic zone of aquatic environments such as biofilms, sediment, or water column.
85 As Aquitaine lakes are shallow, between 7 and 23 m maximum depth, the water column is generally
86 well mixed and oxygenated. Therefore, it was expected that anoxic conditions favourable to Hg
87 methylation occurred in anoxic sediments instead of the water column. Indeed, it has been observed
88 recently that the bottom of the deepest parts of Aquitaine lakes are blanketed with anoxic organic
89 muds (Buquet et al., 2017).

90 The present study focuses on the relationship between the biogeochemistry of lakes and the
91 distribution of mercury and MeHg in sediments. The aim was to (i) perform a mapping of lake
92 sediments in order to link Hg concentrations and the nature of the substrate, (ii) measure
93 concentrations of total mercury and methyl mercury in several representative sediment samples, (iii)
94 analyse the redox compounds influencing Hg speciation in sediments, (iv) attempt to explain the
95 differences in sediment mercury speciation between the four lakes studied, and finally (v) determine
96 the relationship of Hg in sediments and Hg in fish.

97

98

99 ## *2. Materials and Methods*

100 ### 2.1.Study site

101 Large lakes in Aquitaine are located close to the French Atlantic coast in the south-western
102 part of France. They are separated from the ocean by a 5-km-wide forested coastal dune system (Fig.
103 1), which represents a physical barrier to streams draining the lowland of Landes de Gascogne. Most
104 of the drainage basin of the lakes is located on the eastern side. The surface areas of the catchments are
105 similar, between 200 and 310 km^2 (Table 1), which is relatively small. The relief of the drainage
106 basins is very flat with an westward slope lower than 0.2%. The geology is homogeneous and consists

of podzols established on Quaternary siliceous aeolian deposits (Jolivet et al., 2007). Soil occupation has been determined by remote sensing using maps of the French national institute of geography (IGN), and aerial photographs analysed with the Geographic Information System (GIS) ArcGIS (Canton et al., 2012). Pine (*Pinus pinaster*) forests dominate the land use and occupy more than 80% of the total surface (Fig. 1). Intensive farming covers between 5% and 20% of lake drainage basins. Housing is confined to the coastal zone.

Lakes are fed by direct rainfall on the lake surface and by low-discharge rivers. River systems are artificial ditches dug to dry up marshes. Water level of lakes is controlled by locks in channels that connect lakes. Locks also determine the water residence time (Table 1). Lake Lacanau is located downstream from Lake Carcans-Hourtin. The lakes are connected by the 7.5-km-long Etang channel. Waters of Lake Lacanau flow to the Arcachon Lagoon through the 18.5-km-long Porge channel. Lake Parentis-Biscarrosse is downstream from Lake Cazaux-Sanguinet. All of these lakes are shallow (less than 23 m) (Table 1). The deepest part is located on the western side of the lakes, at the base of the dunes. Only the southern lakes are deep enough to have a marked summer thermocline at about 12 m depth. The hypolimion does not become totally anoxic in the oligotrophic Lake Cazaux-Sanguinet. Cyanobacteria blooms occur frequently in Lake Parentis-Biscarrosse due to eutrophication caused by the legacy of large amounts of phosphorus stored in lake sediment. This lake experiences short periods of bottom-water anoxia for a few weeks during summer water stratification. Less than 10% of the water volume becomes anoxic during these episodes. Dense stands of invasive aquatic plants (*Egeria densa* and *Lagarosiphon major*) are found in Lake Parentis-Biscarrosse and Lake Lacanau. They are developed in shallow-sheltered or deep-exposed areas and represent about 10% of lake surface area (Bertrin et al., 2017). Only restricted vegetated areas occurs in the other two lakes. The highest biomass is present in Lake Parentis-Biscarrosse, with an estimated amount of 2800 tons (Bertrin et al., 2017).

2.2.Sampling

Fish were collected from the four lakes by fishing associations and federations and by a professional fisherman during autumn 2015. Three well-represented piscivorous species in the four

lakes were selected: zander (*Sander lucioperca*), pike (*Esox Lucius*) and perch (*Perca fluviatilis*). They were placed in zip-locked bags and immediately cooled at 4°C. Sampling of lake sediment was carried out using cores and grabs. The sediment mapping of lakes was obtained from sediment grabs that were deployed along high spatial resolution N–S and E–W transects (Fig. 2). This strategy allowed us to collect samples from the different bathymetric levels. We collected the top 10 cm of sediment. We obtained 70, 55, 59, and 60 homogenized sediment samples from Lakes Carcans-Hourtin, Lacanau, Cazaux-Sanguinet, and Parentis-Biscarrosse, respectively. For Lake Cazaux-Sanguinet the sampling location was constrained by the security perimeter of the Cazaux military base. Maps of the distribution of sediment properties, such as organic carbon or Hg content, were obtained from interpolation between grab and core samples, and bathymetry was used for extrapolation to map whole lakes. Additional grabs have been collected to validate the sediment mapping based on bathymetry.

In addition, sediment cores allowed us to define the vertical distribution of reactive compounds at the water–sediment interface. Sediment cores were collected at three to nine stations for each lake. Stations were selected according to the sedimentary map established with sediment grabs. Cores were collected in organic deposits and sandy sediments from each lake, and also in the vegetated sediment of Lake Parentis-Biscarrosse. Some stations were sampled twice in two different seasons; in April 2014 and in January 2015 for the two northern lakes, and in spring and summer 2016 for the two southern lakes. Bottom water in contact with sediment cores was always oxic. Core sampling was carried out by scuba divers using 10-cm-diameter polycarbonate tubes. Sealed cores were immediately brought to the shore and cut horizontally into several subsamples for pore water extraction. Vertical subsampling and pore water extraction from lake sediment required specific approaches. We distinguished broadly two kinds of sediment: sandy permeable sediments and very fluid organic-rich muds. This latter sediment type was subsampled with a vertical resolution of 2 cm using Tygon tubing connected to a 100-mL syringe. Sandy permeable sediment was collected using a PVC tube pre-cut in the vertical dimension. The core was laid horizontally on its side and immediately halved into two similar parts. The sediment was cut rapidly into 1- to 2-cm-thick slices. This technique prevented the percolation of pore waters in the vertical dimension during subsampling. For each level of sandy and muddy sediment, a subsample was immediately sealed in a pre-weighed clean vial and

frozen under an N_2-atmosphere for further analysis of the solid fraction and determination of water content. Another subsample was put into a centrifuge vial.

Pore waters were extracted by centrifugation at 2100 *g* for 20 min under an inert N_2-atmosphere. For muddy sediments, the supernatant was immediately filtered (0.2-µm cellulose acetate syringe filter). For sandy sediments, we used 0.2-µm VivaSpin20 centrifuge vials (Anschutz and Deborde, 2016). The possibility that traces of oxygen had affected the pore water concentrations of reduced elements during the slicing and filtration could not be excluded. Our strategy to prevent oxidation of reduced compounds was to handle the samples in less than 30 min from slicing to conditioning. One part of filtered interstitial water was frozen at –18°C, and another part was acidified with HCl at a pH close to 2 to measure dissolved manganese and iron. Soils of the Landes de Gascogne forest were sampled to estimate the geochemical mercury background levels of the area. Soils were collected every 5 cm from the surface to a depth of 1 m at three stations in young to mature forests of the Lake Cazaux-Sanguinet watershed.

Lake water and stream waters of the drainage area were collected to measure dissolved sulphate, Fe, and Mn (Buquet et al., 2017). A total of 13 streams were sampled every month in 2014 and 2015. Sampling locations were along roads parallel to the lakes at about 1 km from the east shore. Samples were also collected in headwaters close to agricultural areas. Sediment from the beds of rivers feeding the northernmost lakes was collected manually using 50-mL centrifuge tubes in order to measure total mercury concentrations. Surface lake waters were sampled every month at several stations using a 2-L Niskin bottle. Bottom waters were also sampled at deep stations, where cores were collected on the western side of the lakes. More than 50 samples were collected for each lake. For determination of dissolved sulphate, Fe, and Mn concentration, water was filtered in situ with 0.20-µm cellulose acetate syringe filters. Filtered samples were stored in polypropylene tubes in a fridge after acidification with HCl. Solutes were analysed within 3 weeks.

2.3. Analyses

2.3.1. Fish

188 Fish dissection was performed within 48 h in laboratory conditions. Dorsal muscle tissue free
189 of skin was dissected and frozen then freeze-dried and crushed. Based on the fact that size is correlated
190 with the age of the individuals, only zander between 50 and 70 cm (standard length), pike between 50
191 and 70 cm and perch between 18 and 23 cm were considered to compare Hg concentrations between
192 lakes.

193 *2.3.2. Solid fraction*

194 The grain-size distribution was measured using a Malvern laser diffraction particle size
195 analyser. For organic sediments, granulometry was carried out after organic matter removal with H_2O_2
196 to recover only the mineral particulate fraction. The bulk mineralogy was determined for this fraction
197 by X-ray diffraction using a Siemens D500 X-ray diffractometer with CuKα radiation (1.5405-Å
198 wavelength). Scans were done from 5° to 80° 2θ at 0.02° s^{-1}, using a 40-kV accelerating voltage and
199 30-mA current. Peak identification and relative abundance estimates of minerals were determined
200 using EVA interpretation software and the DIFFRAC software package.

201 Particulate carbon and total sulphur were measured on freeze-dried samples by infrared
202 spectroscopy (LECO 200 C-S analyser). Organic carbon was measured after removal of carbonates
203 with 2 M HCl from 50 mg of powdered sample (Etcheber et al., 1999). The detection limit was 0.2‰
204 for carbon and 0.1‰ for sulphur. The precision of measurement was better than 5%. Ascorbate
205 solution was used to obtain the most reactive particulate Fe(III) and Mn(III,IV) fractions (Fe-asc, Mn-
206 asc) (Kostka and Luther, 1994). Iron and manganese content was analysed colorimetrically according
207 to standardized techniques (Anschutz and Deborde 2016) with ± 5% precision.

208 Total mercury concentration was determined in 100 mg dry and crushed sediment and in fish
209 muscle by cold vapour atomic absorption spectrometry after incineration and amalgamation, using an
210 Advanced Mercury Analyser (Altec AMA 254). The Teflon grinding bowls for fish and the mortar for
211 sediments were washed with HCl 3% and rinsed with milli-Q water between each sample. The
212 analytical results were quality-checked by analysing international certified reference materials (IAEA
213 407 for fish and PACS-2 and MESS-3 for sediment) after each set of 10 samples. For this method,
214 precision was ± 5% and the detection limit was 0.1 ng Hg.

Methyl mercury content in solid sediment was determined in samples of eight chosen cores collected in winter or early spring, one organic sediment and one sandy sediment for each lake. Measurements were performed by gas chromatography coupled to inductively coupled plasma mass spectrometry (Trace Ultra GC-XII Series ICPMS, Thermofisher). Sample preparation and analytical protocol were adapted from Bouchet et al. (2013) and Renedo et al. (2017). Mercury species were extracted from 0.25 g of dry and crushed sediment in 5 mL of 6N ultrapure grade HNO_3 solution using a microwave system (Discover SP-D, CEM). Digestion was achieved in CEM Pyrex vessels by 1 min of warming up to 75 °C and 3 min at 75 °C with magnetic agitation to homogenize the samples. Prior to GC injection, sample extracts were ethylated at pH 4 ($NaBEt_4$, 5% v:v, Merseburger Spezialchemikalien), in order to produce volatile ethylated forms of Hg, then extracted in isooctane by mechanical shaking (elliptic table, 20 min) and readily separated by gas chromatography. Quantification was performed by species-specific isotope dilution by spiking known amounts and concentrations of isotopically enriched standard solutions ($MM^{201}Hg$ and $^{199}Hg(II)$, ISC) (Rodriguez Martin-Doimeadios et al., 2004). The detection limit of the method was 0.03 ng Hg g^{-1}. The analytical results were continuously quality-checked by analysing reference materials certified for Hg speciation (IAEA-405 Estuarine Sediment). Relative standard deviation of MeHg concentration has been evaluated to 1.7%, from triplicate preparations and analyses of the reference material.

2.3.3. Dissolved compounds

The sediment water content was determined from the weight difference between wet and dry sediments. Dissolved iron (Fe^{2+}) was analysed using the colorimetric method by adding a ferrozine solution in an aliquot (Stookey, 1970). Dissolved manganese (Mn^{2+} and Mn^{3+}) was determined colorimetrically using a Cd–TCPP complex according to Madison et al. (2011). Dissolved Fe and Mn were determined with ± 5% precision. Dissolved sulphate was analysed by a nephelometric method based on $BaSO_4$ precipitation using $BaCl_2$ (Rodier, 1976). The detection limit was 10 µM, and the precision of replicate samples was better than 8%.

3. Results

3.1. Mercury in fish

We observed the highest average total Hg concentrations in carnivorous fish from Lake Carcans-Hourtin (Table 2), with a maximum value of 6.238 mg kg^{-1} dw. Total Hg concentrations were two to five times lower in fish collected from Lake Parentis-Biscarrosse. We measured intermediate values in fish from Lake Lacanau and Lake Cazaux-Sanguinet. Therefore, the data revealed a decreasing gradient from north to south for total Hg in piscivorous species.

3.2. Sedimentary cover of lakes

3.2.1. Sediment mapping

Sediment type was strongly influenced by bathymetry. Therefore, we used bathymetry to draw the sediment map from the grab and core observations (Fig. 2). Deep areas in the western parts of the lakes presented muddy deposits. These deposits had a homogeneous appearance and a very soft consistency. The water content of this substrate was greater than 95%, making the sediment texture very fluffy. These sediments were highly organic deposits. Organic deposits were found below 5 m depth in lakes Carcans-Hourtin and Lacanau, below 7 m in Lake Cazaux-Sanguinet, and below 10 m in Lake Parentis-Biscarrosse. For these two last lakes, deep areas also presented a mixture of these organic deposits with sand, called sandy organic deposits or organic sands, depending on the proportion of sand and organic carbon (Fig. 2). Organic sands were present in sub-lacustrine channels. These channels are the paleo-valley of the rivers that flowed to the ocean before the formation of lakes through the development of coastal dunes in the last thousand years (Buquet et al., 2017). Shallow zones presented sands with shades of green, yellow, black, or grey depending on the content of iron oxides or organic matter. The water content of sands was 20% in weight.

Vegetated areas of lakes Lacanau and Parentis-Biscarrosse consisted of sandy sediments. In sheltered areas, 2 to 10 cm of muddy sediment covered the sand.

3.2.2. Grain size

Sand grain size after organic matter removal with H_2O_2 was very homogeneous, with a median size of 362 µm, a standard deviation (SD) of 49 µm, and a standard error of the mean (s.e.) of 7 µm. The sand was the same as the soils of the lake catchment (Fig. 3). The grain size of the mineral

fraction of organic deposits was centred between 10 and 20 µm (Fig. 3). X-ray diffraction indicated that the mineral fraction consisted of quartz, clay minerals (illite and kaolinite), and feldspars. Carbonate minerals were not detected.

3.2.3. Total carbon and total sulphur

Particulate organic carbon (POC) and total carbon (TC) measurements on grab and core sediments gave the same concentration, indicating that TC consisted exclusively of POC and that inorganic carbonate was absent or very scarce. TC concentration ranged from 10% to 30% in organic deposits. Averaged TC concentrations (± SD) in organic sediments were 15.8% (± 3.1), 17% (± 1.4), 15.5% (± 1.7), and 15.2% (± 0.9) for lakes Carcans-Hourtin, Lacanau, Cazaux-Sanguinet, and Parentis-Biscarrosse, respectively (Fig. 4). Concentrations ranged from 3% to 10% in sandy organic deposits, and from 1% to 3% in organic sands. TC was below 1% in sands.

Total sulphur (TS) content was also dependent on the type of sediment. TS ranged from 1% to 4% in organic deposits (Fig. 4). The mean concentrations were close to 2.5% (± 0.8% SD) except for organic sediments of Lake Parentis-Biscarrosse, in which the value was 1.2%. TS ranged from 0.1% to 1% in sandy organic deposits and organic sands. TS was below 0.1% in sands.

3.2.4. Particulate total mercury (HgTp)

HgTp concentrations were closely related to the nature of sediment and the organic carbon concentrations. Classes of mercury concentration fitted classes of TC content (Fig. 2). HgTp concentrations ranged from 100 to 420 µg kg^{-1} in organic deposits (means of 230 (± 82 SD), 203 (± 60 SD) 206 (± 68 SD), and 142 µg kg^{-1} (± 53 SD) for lakes Carcans-Hourtin, Lacanau, Cazaux-Sanguinet, and Parentis-Biscarrosse, respectively). HgTp concentrations in Lake Parentis-Biscarrosse were significantly lower (ANOVA test) than in other lakes (Fig. 4). HgTp concentrations ranged from 20 to 100 µg kg^{-1} in sandy organic deposits. HgTp concentrations ranged from 4 to 20 µg kg^{-1} in organic sands. Finally, HgTp concentrations ranged from below the detection limit to 10 µg kg^{-1} in sands (Fig. 2).

3.2.5. Geochemical background levels

Sand samples from forest soil east of Lake Cazaux-Sanguinet had the same particle size distribution as the sandy sediments from lakes (Fig. 3). HgTp concentrations ranged from 0.5 to 21 µg kg^{-1}. Highest values were associated with soil samples enriched in organic carbon. However, HgTp values were not significantly different (ANOVA test) in lake sands and in drainage basin soils (Fig. 2). Fine sediments collected from the beds of streams that feed Lake Carcans-Hourtin and Lake Lacanau had a mean HgTp concentration of 2.3 ± 1.8 µg kg^{-1}, which was much lower than values measured in lake organic sediments.

3.3. Lake sedimentary column

Cores of organic deposits had a TC concentration between 10% and 30% (Fig. 1S, Supplementary Material), like sediment grabs. TC decreased slightly with depth, except for Lake Carcans-Hourtin, which showed a sharp decrease in TC below 10 cm depth from 30% to 15%. TS concentrations were similar to values measured in grabs. Concentrations increased with depth, except in organic muds of Lake Carcans-Hourtin, where sediments below 25 cm depth were less enriched in sulphur than those above. Iron and manganese oxide concentrations extracted by leaching with ascorbate decreased with depth. Ascorbate-extracted iron was two- to three-fold higher in muddy sediments of Lake Parentis-Biscarrosse than in other lakes. HgTp concentrations were between 100 and 300 µg kg^{-1} in organic sediments. Shallow vegetated sediment from Lake Parentis-Biscarrosse contained up to 80 µg kg^{-1} HgTp in the muddy layer of the superficial sediment. This muddy layer of vegetated sediment contained about 10% TC.

Methylmercury concentrations of organic sediments were maximal in the first centimetres below the water–sediment interface (Fig. 1S, Supplementary Material). There was an increasing gradient in MeHg from the southern lakes to the northern lakes: average vertical concentrations in the top 10 cm below the sediment–water interface were 4.61 (± 2.6 SD) µg kg^{-1} for Lake Carcans-Hourtin, 5.14 (± 2.8 SD) µg kg^{-1} for Lake Lacanau, 1.56 (± 0.14 SD) µg kg^{-1} for Lake Cazaux-Sanguinet, and 1.1 (± 0.32 SD) µg kg^{-1} for Lake Parentis-Biscarrosse, which represented 2.53% (± 1.0), 1.69% (± 0.7), 0.55% (± 0.1), and 0.53% (± 0.1) of HgTp, respectively.

Concentrations of TC, mercury, Fe and Mn oxyhydroxides, and sulphides were lower by a factor of 10 to 100 in sandy sediment cores compared to muddy sediments. Contrary to observations for organic sediments, mercury decreased with depth. MeHg concentrations were often below the detection limit of the GC-ICPMS method (i.e. 0.03 µg Hg kg^{-1}).

3.4. Lake water and pore waters

Sandy sediment depleted in organic carbon (e.g, Fig. 1S-A and 1S-G, Supplementary Material) did not show a pronounced gradient of dissolved redox compounds below the sediment surface, except a small sulphate decrease with depth. Pore water dissolved Fe and Mn remained at concentrations similar to those measured in lake waters. Sandy sediments with an organic carbon content above 0.5% showed more pronounced redox gradients, with appearance of reduced dissolved species and rapid loss of sulphate in the first centimetres below the interface (Fig. 1S-H and 1S-J, Supplementary Material). Dissolved iron and manganese concentrations were present from the first centimetre of the sedimentary pore water column in cores that were collected in muddy sediments. Dissolved sulphate concentrations decreased below the sediment surface in organic sediment pore water to reach the detection limit a few centimetres below the interface. Dissolved sulphate concentrations of overlying water differed depending on the lake. Mean water sulphate concentrations were 328 (± 28 SD), 221 (± 26 SD), 100 (± 19 SD), and 82 (± 17 SD) µM for lakes Carcans-Hourtin, Lacanau, Cazaux-Sanguinet, and Parentis-Biscarrosse, respectively (N > 50 for each lake). Therefore, there was a decreasing north–south gradient of sulphate concentrations. Mean dissolved sulphate concentration of the stream waters that feed the lakes was lower than 150 µM, except for the Lake Carcans-Hourtin catchment, where streams contained up to 600 µM sulphate (Fig. 5). For this lake, sulphate concentrations were the highest in head waters close to agricultural areas. Values above 1000 µM were measured in upstream waters of the Caillava river, which drain large maize fields (Fig. 5). Head waters that drain maize fields of the Cazaux-Sanguinet catchment were also enriched in dissolved sulphate, with mean concentrations of 300 µM.

4. Discussion

4.1. Mercury distribution, diagenetic processes, and mercury mobility in sediments

4.1.1. Mercury distribution and background concentrations

The concentration of HgTp was close to 200 µg kg^{-1} in organic muds and below 20 µg kg^{-1} in sandy sediments. Concentrations were below 2 µg kg^{-1} in sands poor in organic carbon. Sandy sediments had concentrations identical to those measured in forest sandy soil from the lake drainage basin. Sands were deposited before the formation of Aquitaine lakes, whereas the fine particles present in organic deposits were autochthonous sediments. Higher HgTp values in organic muds may result from a grain-size effect: deep parts of lakes accumulate fine-grained particles that consist of fine quartz and clay minerals, which are probably enriched in Hg relative to sandy sediments (Bloom and Crecelius, 1987). However, grain size alone cannot explain the difference, because mercury has a strong affinity with organic carbon, sulphur, and Fe/Mn oxides (Feyte et al., 2010), which are highly enriched in muddy sediment. The difference in HgTp content between sands, sands enriched in organic matter, and muds is most likely explained by the organic matter content (Fig. 2), suggesting that organic matter is the initial carrier phase of Hg that accumulates in the sediment.

4.1.2. Diagenetic processes

Mercury has affinity with organic matter, iron/manganese oxyhydroxides, and sulphides. Therefore, it is strongly influenced by diagenetic processes (Matty and Long, 1995). These processes are directly linked to benthic organic matter mineralization. Mineralization of organic matter is the result of its oxidation, carried out in presence of microorganisms, and is accompanied by reduction of electron acceptors according to a sequence of reactions where O_2 is used preferentially, then nitrate when the sediment becomes depleted in dissolved oxygen. In anoxic sediments, mineralization consumes oxides and oxyhydroxides of manganese (MnO_2, MnO(OH)) and iron ($Fe(OH)_3$) present in the solid fraction of sediments, and dissolved sulphate (SO_4^{2-}) and CO_2, which generally represent both the main electron acceptors in anoxic environments (Stumm and Morgan, 1996). Anoxic sediment is generally enriched in particulate sulphur because of the precipitation of sulphide minerals as a result of sulphate reduction.

372 Redox species profiles in the cores (Fig. 1S, Supplementary Material) agreed with a typical
373 diagenetic sequence. Iron and manganese oxides extracted with an ascorbate solution have the highest
374 concentrations at the sediment surface and decrease with depth. Dissolved reduced iron and
375 manganese appear in the top core samples. This indicates that sediments are anoxic from the first
376 centimetre of the sediment column. Sulphate concentration decreases rapidly and reaches a value
377 below the detection limit a few centimetres below the sediment surface, which means that the sulphate
378 reduction process occurs effectively. Sulphide precipitate is produced as FeS, as suggested by the high
379 particulate S content in organic deposits and the decreasing pore water iron concentration with depth.
380 It must be noted that the concentration gradients in organic sediments are stronger than gradients in
381 sandy sediments, suggesting that diagenetic processes are more intense in muddy sediments. However,
382 the decrease and disappearance of sulphate in sandy cores suggest that the small amount of organic
383 matter present in sands is labile.

384 *4.1.3. Mercury diagenesis*

385 Mercury transformation in sediments depends on many biogeochemical processes, which may
386 affect the ability of mercury to be methylated, or to migrate from sediment to the water column
387 (Schäfer et al., 2010). Mercury mobility depends on its speciation between solid and dissolved phases.
388 This distribution is intimately coupled to organic matter mineralization as Hg distribution is influenced
389 by the presence of Mn/Fe oxyhydroxides and sulphide minerals. In oxic sediment layers, Hg mobility
390 is generally low because it is essentially associated with the solid phase by adsorption or precipitation
391 with Fe/Mn oxyhydroxides (Feyte et al., 2010). During the organic matter mineralization process,
392 Fe/Mn oxyhydroxides may be reduced, and associated Hg is released (Matty and Long, 1995). In the
393 sediment cores studied, the decrease in Fe/Mn oxyhydroxide concentrations with depth in lakes
394 Carcans-Hourtin, Lacanau, and Cazaux-Sanguinet can be interpreted as metal oxide reduction. In Lake
395 Parentis-Biscarrosse, the oxide concentration remains high in all organic cores, suggesting that Hg
396 mobility is limited in this lake. In anoxic sediments, sulphate reduction leads to sulphide production,
397 for which Hg has a strong affinity. Mercury precipitates as HgS or it is absorbed on FeS and included
398 in pyrite (Fitzgerald and Lamborg, 2003). Grab samples show that the Hg concentration increases

399 when total S concentration increases as well (Fig. 6). This trend also occurs in organic sediment cores.
400 Sulphur is associated with organic matter either as an initial compound or as a result of the
401 sulphurization by sulphide of organic matter during diagenesis (Urban et al., 1999). Therefore, high
402 organic matter concentrations correspond to high sulphur concentrations. Urban et al. (1999) found an
403 averaged C:S ratio of organic matter between 167 and 198 based on sediment cores from 50 lakes. For
404 lake sediments with the highest concentrations of organic carbon they found a maximum organic
405 sulphur concentration of 260 µmol g^{-1} (0.83%), which is below the concentration of sulphur measured
406 in muddy sediments (Fig. 6). This indicates that most of the sedimentary sulphur occurs as particulate
407 sulphide, and that particulate sulphides are major carrier phases of Hg in organic sediments. Organic
408 matter itself presents many adsorption sites for Hg, which plays a role in Hg mobility (Benoit et al.,
409 1998). This probably explains why organic sediments are enriched in Hg relative to organic-poor
410 sandy sediments (Fig. 2). Organic matter is mineralized in sediments through early diagenesis
411 processes. In anoxic lake sediments, Hg initially trapped in the fraction of organic matter that is
412 consumed is most likely released into the interstitial waters and then quickly trapped by sulphides
413 when sulphate reduction occurs (Benoit et al., 1999).

414 ## 4.2. Methylation

415 ### *4.2.1. Vertical distribution*

416 Organic sediments of Lake Carcans-Hourtin and Lake Lacanau show the highest
417 concentrations of MeHg at the depth where the decreasing gradient of dissolved sulphate occurs.
418 Inorganic Hg methylation takes place during Hg(II) absorption by some anaerobic microorganisms
419 which methylate Hg in their cytoplasm (Benoit et al., 1999; Gilmour et al., 1998). Microbial sulphate
420 reduction (MSR) is recognized to be the most common pathway leading to mercury methylation in
421 sediments (Barkay and Wagner-Döbler, 2005; Compeau and Bartha, 1985). Other anaerobic
422 microorganisms such as iron-reducing bacteria are able to methylate Hg (Podar et al., 2015).
423 Diagenetic profiles of organic cores show that anaerobic processes occur at the depth of the maximum
424 MeHg concentrations (Fig. 1S, Supplementary Material). This suggests that the predominant process
425 of mercury methylation is carried out by a consortium of anaerobic microorganisms, including those

involved in MSR. Communities of Fe- and sulphate-reducing bacteria are also involved in MeHg demethylation processes (Oremland et al., 1991; Bouchet et al., 2013). It is the balance between methylation and demethylation in sediment that dictates the standing pool of MeHg (Rodríguez Martín-Doimeadios et al., 2004). The progressive decrease in MeHg with depth of the sedimentary column could be related to the dominance of demethylation processes in the deep sediment, when sulphate becomes depleted (Pak and Bartha 1998).

4.2.2. Spatial distribution

Organic sediments of the four lakes have different MeHg concentrations. The fraction of total Hg present as MeHg (%MeHg) describes a positive south–north gradient from 0.5% in Lake Parentis-Biscarrosse to 2.5% in Lake Carcans-Hourtin (Fig. 7). The proportions between 0.5% and 0.6% obtained in the southernmost lakes are consistent with those found in the literature for lacustrine or coastal systems (Table 3). Generally, MeHg concentration in sediment is less than 1% of HgTp (Morel et al., 1998). MeHg proportions in northern lake sediments are high (especially Lake Carcans-Hourtin), which means that the methylation potential is high in these lake sediments.

Main factors that are known to influence the methylation rate are Hg(II) availability and bacteria activity within the sedimentary column. Sulphate inputs stimulate MSR activity. As sulphate concentrations differ between lakes, the high proportion of MeHg in northern lakes, more particularly in Lake Carcans-Hourtin, can be related to high methylation potential as sulphate concentrations are the highest (Fig. 7). Previous studies have found that sulphate addition stimulates net methylation rates in fresh water sediments (e.g, Gilmour et al. 1992; Åkerblom et al. 2013). Sulphide from sulphate reduction is known to have two effects on the availability of Hg(II). At low concentrations, sulphide promotes methylation. By contrast, for higher concentrations, as may be the case in marine sediments, sulphide limits the bioavailability of Hg(II) to be methylated (Benoit et al., 1998; Hsu-Kim et al., 2013; Johnson et al., 2016). This suggests that there is a range of sulphate concentration which is optimal for Hg methylation, above which methylation is inhibited. A broad range in the sulphate concentration associated with maximum efficiency of Hg methylation has been observed. For example, Orem et al. (2014) observed maximum MeHg concentrations at sulphate concentrations of 2

453 and 10–15 mg L^{-1}in the Everglades Protection Area. Peak MeHg was observed in wetland mesocosms
454 with a sulphate concentration of 59 and 93 mg L^{-1} (Myrbo et al., 2017). In the case of Aquitaine lake
455 muddy sediments, MeHg concentrations increase with sulphate, suggesting that MSR is not limited,
456 and that produced sulphide does not inhibit Hg availability. The availability of dissolved sulphide
457 produced by MSR will depend on iron oxide availability. The reactive fraction of iron oxides
458 determined by the ascorbate reagent is above 100 µmol g^{-1} in the surface sediments of the four lakes,
459 which represents at least, when considering sediment water content, 4000 µmol L^{-1}, suggesting that
460 the sulphide produced is efficiently trapped as Fe sulphide phases with this abundant available reactive
461 Fe.

462 Temperature is an important control factor for methylation process. Low temperatures will
463 slow down methylation(Hintelmann and Wilken, 1995; Ramlal et al., 1993). The cores studied were
464 sampled in different seasons, but MeHg was measured only in cores collected in winter and early
465 spring. Higher concentrations of MeHg in summer may be expected, although the effect of
466 temperature on biotic demethylation is not well known. Gradients of dissolved sulphate between the
467 water column and the sediment were sharper when the water temperature was the highest at a given
468 station sampled in two seasons, suggesting that the sulphate reduction rate, and the related
469 methylation, was more efficient in summer and autumn.

470 The gradient of mercury contamination in carnivorous fish muscles between the four lakes
471 (Table 2) fits well with sediment MeHg concentrations, since the highest levels were measured in fish
472 from northern lakes. Therefore, the muddy sediment compartment may be one of the main sources of
473 MeHg which accumulates in the trophic chain (e.g. Hammerschmidt et al., 2004). Periphyton
474 microbial communities of aquatic macrophytes of Lake Cazaux-Sanguinet have also been recognized
475 to potentially methylate Hg (Gentès et al., 2013). This study was based on experimental batches placed
476 under high environmental Hg concentrations and anoxic conditions. Hence, through dietary
477 bioaccumulation, the MeHg in higher trophic levels within Aquitaine lakes may be attributed to MeHg
478 produced in anoxic muds, as observed in the present study and in the periphyton (Gentès et al., 2013),
479 both being limited by sulphate.

480 Sulphate from lake waters may originate from several sources: atmospheric inputs from rain
481 and ocean spray, rocks from the drainage area, and anthropogenic inputs. The distance from lake to
482 ocean is the same for the four lakes studied, suggesting that the atmospheric sources by spray are
483 similar. The lake catchment geology is also the same for the four lakes. The major difference between
484 lake catchments is the land use. The drainage area of Lake Carcans-Hourtin has the highest proportion
485 of agriculture areas (Fig. 1). Tributaries of this lake are enriched in dissolved sulphate, with a
486 concentration as high as 1200 µM in ditches located upstream, in the cultivated areas (Fig. 6). Head
487 waters collected in ditches close to agriculture surfaces of the Lake Cazaux-Sanguinet catchment are
488 enriched in dissolved sulphate compared to waters collected downstream, but the concentrations
489 remain below 300 µM. Thus, agricultural activity is the main source of sulphate. Discussions with
490 farmers informed us of the fact that sulphate was supplied indirectly to croplands through liming,
491 which allows control of soil pH. Lime comes from limestone or dolomite quarries, and in some cases
492 in the recent past from neighbouring paper mill plants that produce lime sludge as a by-product.
493 Depending on lime origin, the sulphate content can be high, and lime can become a source of sulphate
494 for lakes.

495 *4.2.3. MeHg diffusion and bioavailability*

496 Our study points out that MeHg concentration is related to sulphate concentration. Methyl
497 mercury produced in the sediment can be transferred to the water column through molecular diffusion
498 and resuspension of surface sediments. Hence, the amount of MeHg diffusing into the water column
499 and thus the amount bioavailable to pelagic organisms depends, among other things, on the proportion
500 of lake floor carpeted with organic sediments. Organic deposits account for 21%, 20%, 19%, and 18%
501 of the surface area of lakes Carcans-Hourtin, Lacanau, Cazaux-Sanguinet, and Parentis-Biscarrosse,
502 respectively. These proportions are close and suggest that the proportion of organic sediment is not the
503 variable that explains the gradient of fish contamination. Bioturbation and bioirrigation may affect the
504 transport of Hg from sediment to water (Benoit et al., 2006). We observed the presence of chironomid
505 larvae in some grabs from the four lakes. The density of these organisms was low, with zero to three
506 individuals per grab. Even if the density of benthic organisms was low, burrowing organisms may

assimilate MeHg directly from underlying anoxic sediments and become vectors of MeHg to pelagic predators (Gagnon et al., 1996). Finally, despite the occurrence of episodic bottom-water anoxia during the summer in Lake Parentis-Biscarrosse, this lake remains the one in which the fish are less contaminated with Hg. The methylation of Hg in a polymictic lake can be shifted from the sediment to the anoxic water column, because sulphate reduction is shifted in the same way to the water column (Ramlal et al., 1993; Wartras et al., 1995). This suggests that sulphate availability remains a key environmental parameter for Hg methylation, wherever sulphate reduction occurs, in the water column or at the sediment surface.

4.3. Sources of Hg

Land use is not impacted by activities that may represent point sources of Hg. HgTp concentrations are similar in lake sandy sediments and in watershed sandy soils, with values below 20 µg kg^{-1}, suggesting that the geological background level is low. Moreover, we measured HgTp concentrations of between 1 and 7 µg kg^{-1} in fine sediments of river beds, which is low compared to the 200 µg kg^{-1} measured in lakes muds, suggesting that the contribution of Hg from lake catchment is negligible. Hg distribution in lakes depends exclusively on sediment type, not on geography: there is no zone that presents a peak of HgTp concentration. This suggests the absence of a point source in lakes. Several lines of evidence suggest that Hg that accumulates in muddy sediment is mainly of atmospheric origin. Considering that the superposition principle applies to organic sediment deposits, the decrease in Hg concentrations when approaching the water–sediment interface (Fig. 1S, Supplementary Material) may be explained by the decrease in atmospheric emission in European countries in recent decades (UNEP, 2013).

South-western France is not a hot spot for atmospheric Hg emissions (Colette et al., 2016). In the light of the concentrations measured in lake sediments, Hg fluxes are not alarming. Average atmospheric Hg flux on the Aquitaine coast is estimated by modelling as 10 µg m^{-2} yr^{-1} for the year 2001 (Roustan et al., 2006). Such a flux represents 620, 200, 580, and 350 g yr^{-1} for lakes Carcans-Hourtin, Lacanau, Cazaux-Sanguinet, and Parentis-Biscarrosse, respectively. Considering that all Hg that reaches the lake surface is trapped in organic matter that accumulates in organic sediments,

534 considering also the mean HgTp of each lake and the particle content of organic sediment (40 g L^{-1}),
535 we found that 1 cm of deposit contains between 1 and 1.8 years of Hg deposition. This suggests that
536 the mean sedimentation rate is between 0.6 and 1.0 cm yr^{-1}. A very similar value was found for lakes
537 Lacanau and Carcans-Hourtin using a mass balance based on dissolved inorganic nitrogen retention
538 (Buquet et al., 2017). The higher sedimentation rate found here (1 cm yr^{-1}) is for Lake Parentis-
539 Biscarrosse. This lake has a higher phosphorus content than the other lakes (Cellamare et al., 2011),
540 which results in higher primary production. Eutrophication of the lake may explain a higher
541 sedimentation rate of organic matter. As a consequence, the concentration of HgTp is lower in the
542 muds of Lake Parentis-Biscarrosse than that of other lakes, even if the atmospheric flux is the same,
543 due to a dilution effect.

544 ## *5. Conclusion*

545 Our study presents new results from Aquitaine lake sediments. We have established the first
546 map of sediment distribution and we have determined several physicochemical properties of these
547 sediments. More particularly, we showed that the bottom of the four lakes consists of sands. Sandy
548 sediments are covered with organic muds, which accumulate only in the deepest parts of lakes and in
549 shallow densely vegetated areas. The highest Hg concentrations are encountered in these organic
550 deposits. However, they do not exceed reference thresholds for sediments (1100 µg kg^{-1} for the
551 probable effect concentration; MacDonald et al., 2000). Organic sediment traps Hg in the four lakes,
552 which is most likely of background diffusive atmospheric origin. These sediments are hot spots for Hg
553 methylation, due to sulphate reduction processes.

554 The mercury concentration gradient in the muscles of carnivorous fish is the same as the
555 methyl mercury concentration gradient of lake sediment. This suggests that the sedimentary
556 compartment could be a MeHg source for the water column, resulting in its accumulation along the
557 trophic chain. Methylation rate depends on sulphate reduction activity. This activity is limited by
558 sulphate availability. Lake Carcans-Hourtin is the most concentrated in sulphate. Lake Lacanau, whose
559 waters come partly from Lake Carcans-Hourtin, is enriched in sulphate by this very fact. Agricultural
560 activity is the main source of sulphate in the Lake Carcans-Hourtin drainage basin. This excess

sulphate that is leached from soils instead of being absorbed and exported by plants originates likely from liming. Therefore, the use of sulphate-rich lime in the headwater drainage area has an indirect consequence on carnivorous fish Hg content in lakes located at the outlet of the catchment, because sulphate favours methylation of the background flux of atmospheric Hg in anoxic environments of lakes, such as autochthonous organic sediments, as seen in this study, or in other compartments, such as aquatic plant periphyton (e.g. Gentès et al., 2013). One question that remains unresolved focuses on the pathway that transmits MeHg produced from the sediment to fish. For that the distribution of Hg in fish and in the food web is presently conducted in Aquitaine lakes.

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Figure captions

Fig 1 Location map of Aquitaine coastal lakes and drainage basin land use. Small rings: Location of river sampling for sulphate measurements; black star: location of soil sampling.

Fig 2 Sediment mapping of Aquitaine lakes. Black dots and stars show the location of grab and core samples in which Hg has been measured, respectively. Red dots are additional grabs that have been collected to validate the sediment mapping based on bathymetry. The range of total carbon (TC) concentrations and particulate total mercury (HgTp) levels for each sediment class is indicated in the legend.

Fig 3 Average grain size distribution of lake sandy sediment and catchment soils (right panel), and of lake organic deposits after organic matter removal with H_2O_2 (left panel).

Fig 4 Mean concentration of total carbon (TC), total sulphur (TS) and total Hg (HgTp) in organic deposits (white bars) and in sandy sediments and catchment soils (grey bars) from the four Aquitaine lakes. Error bars are standard deviations. Number of samples is indicated.

Fig 5 Mean sulphate concentrations in streams that feed the lakes. Error bars are standard deviations. Number of samples indicated in brackets. See Figure 1 for sampling location.

Fig 6 Total Hg (HgTp) concentrations vs total sulphur (TS) concentrations in sediment grabs collected in Aquitaine lakes.

Fig 7 Relationship between the proportion (%) of MeHg relative to HgTp in organic sediments and average sulphate concentrations in lake water column. Error bars are standard deviations (N=5 for %MeHg, and N=15 for sulphate)

Table 1 Morpho-dynamics characteristics of Aquitaine lake.

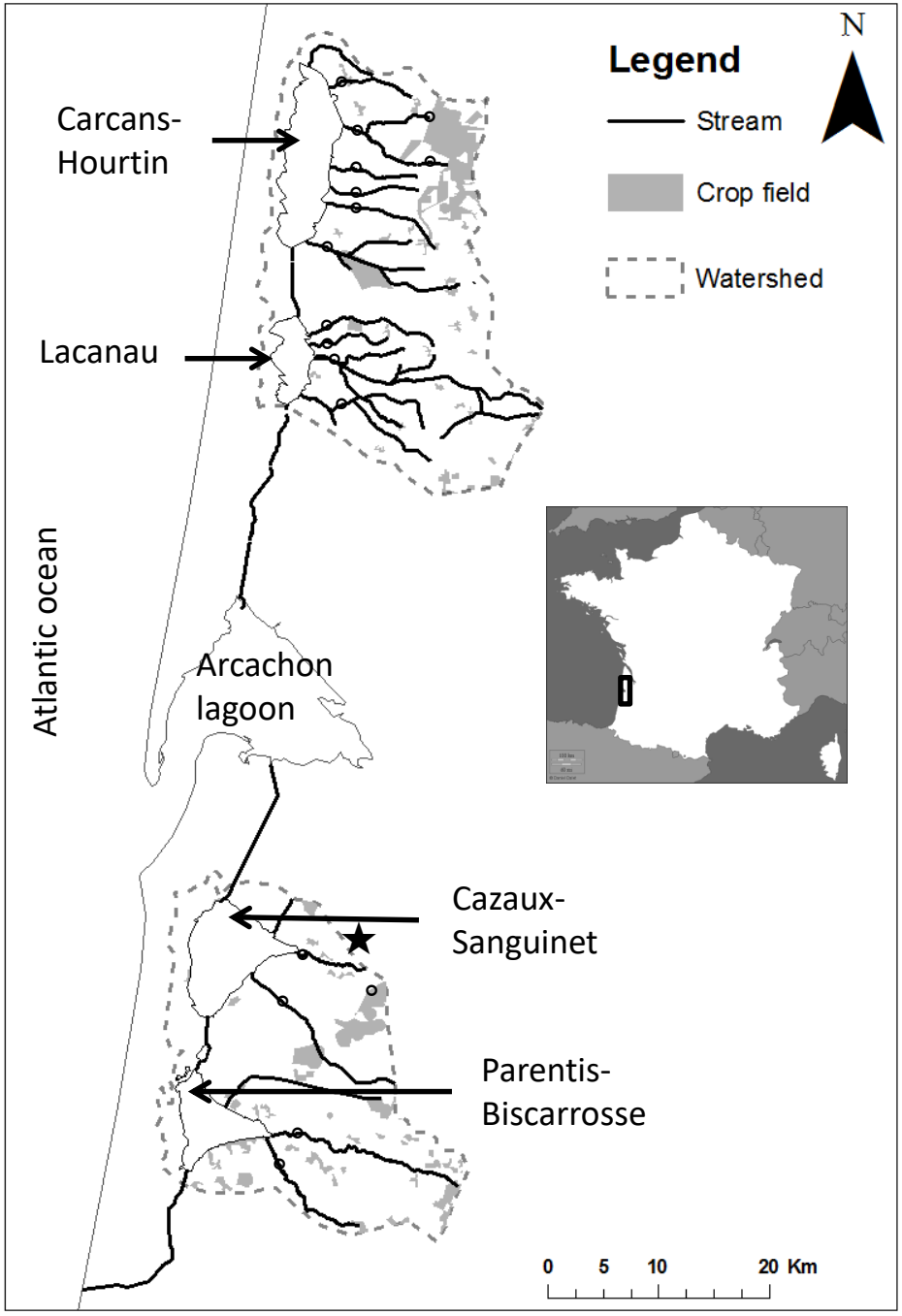
Lake	Area (km^2)	Maximum depth (m)	Volume (10^6 m^3)	Water residence time (year)	Elevation (m)	Catchment area (km^2)
Carcans-Hourtin	62	9	210	1.8	15	302
Lacanau	20	7	53	0.4	14	310
Cazaux-Sanguinet	58	23	498	4.3	21	200
Parentis-Biscarrosse	35	20.5	252	1	20	303

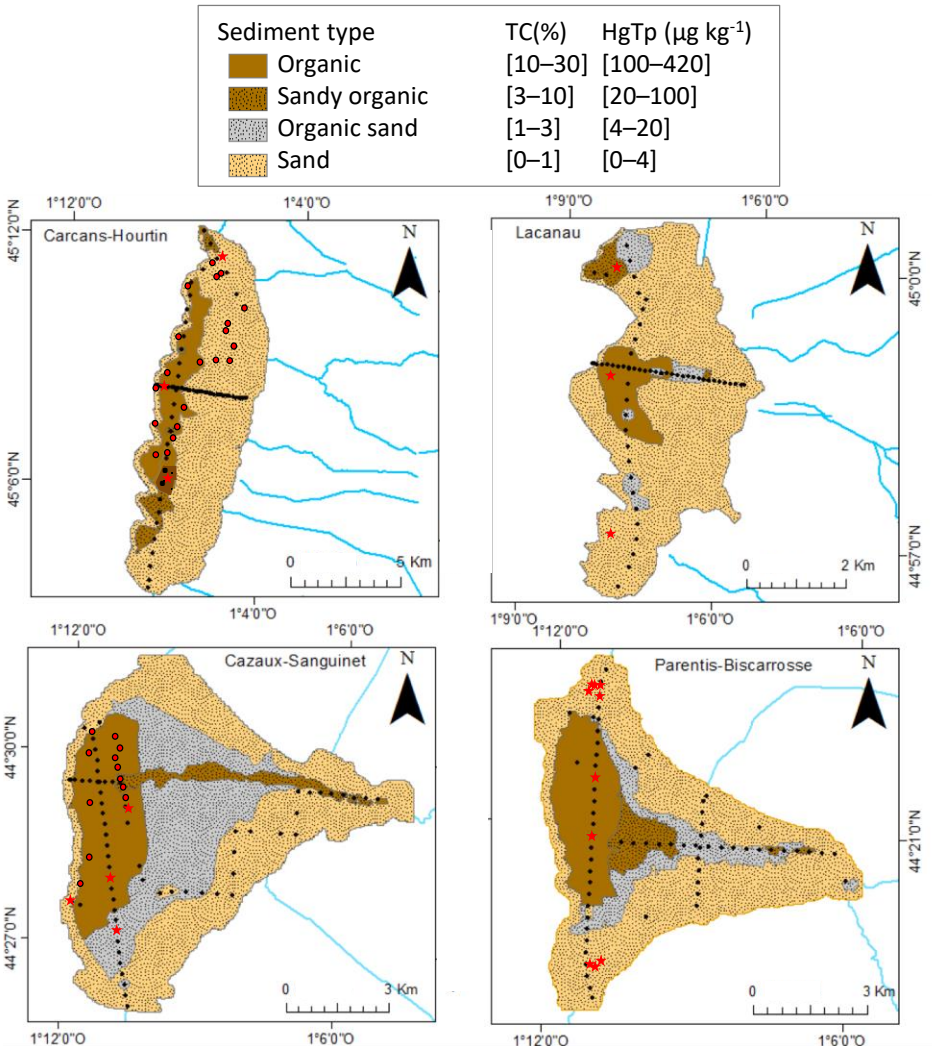
Table 2 Average mercury concentrations (mean total Hg, µg kg^{-1} dry weight) in muscle of adult Perch (length 18-23 cm), Pike (>50 cm), and Zander (>50 cm) in the four lakes. Value ± standard deviation; N: number of samples for different analysis.

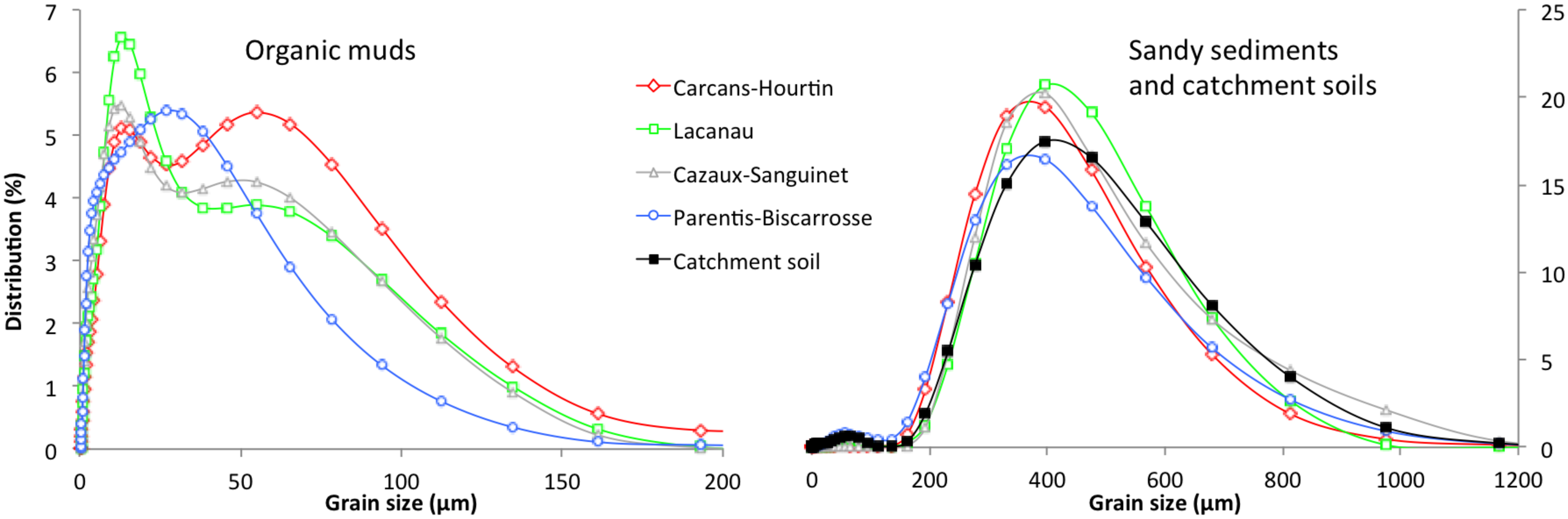
	Carcans-Hourtin	Lacanau	Cazaux-Sanguinet	Parentis-Biscarrosse
Perch (*Perca fluviatilis*)	1811±281 (N=6)	876±217 (N=7)	379±75 (N=16)	337±209 (N=4)
Pike (*Esox spp.*)	3151±1207 (N=8)	1608±752 (N=12)	1725±544 (N=7)	1459±333 (N=5)
Zander (*Sander lucioperca*)	6238 (N=1)	4809 (N=1)	3563±913 (N=6)	1642±485 (N=3)

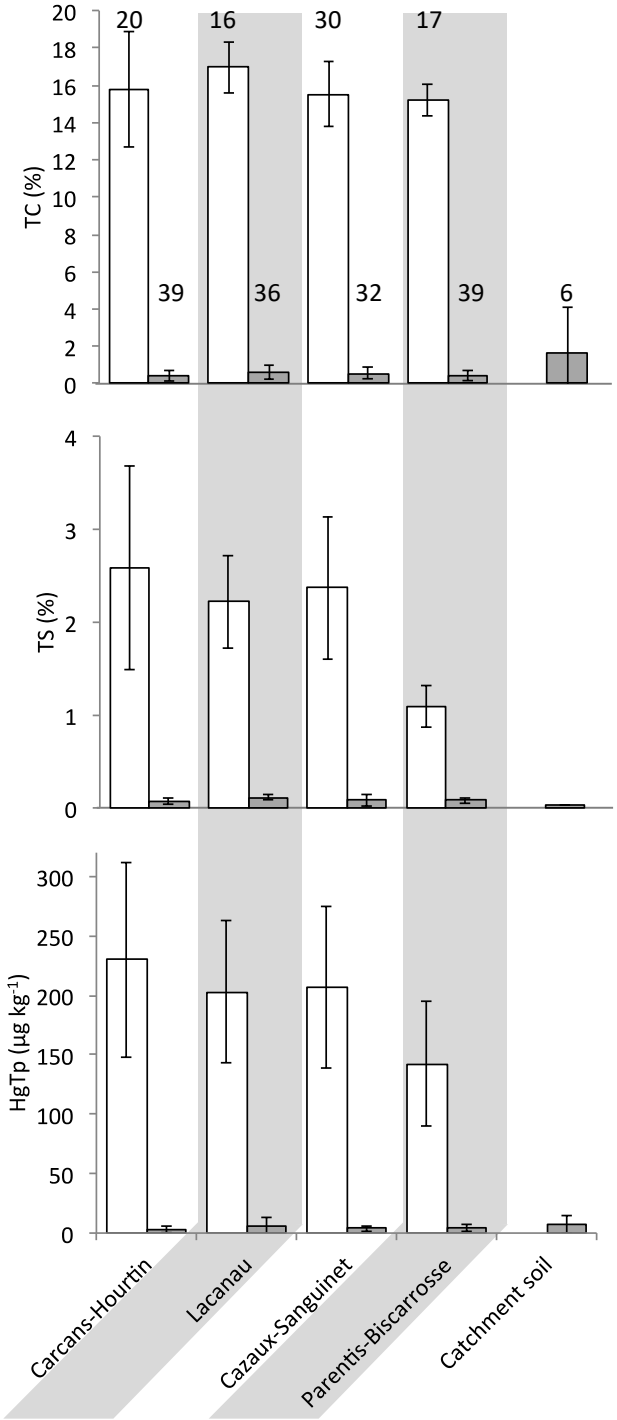
Table 3 Total mercury (HgTp) and methyl mercury concentrations and methyl mercury fraction relative to HgTp of lake sediments and of SW France coastal sediments, and values reported in the literature.

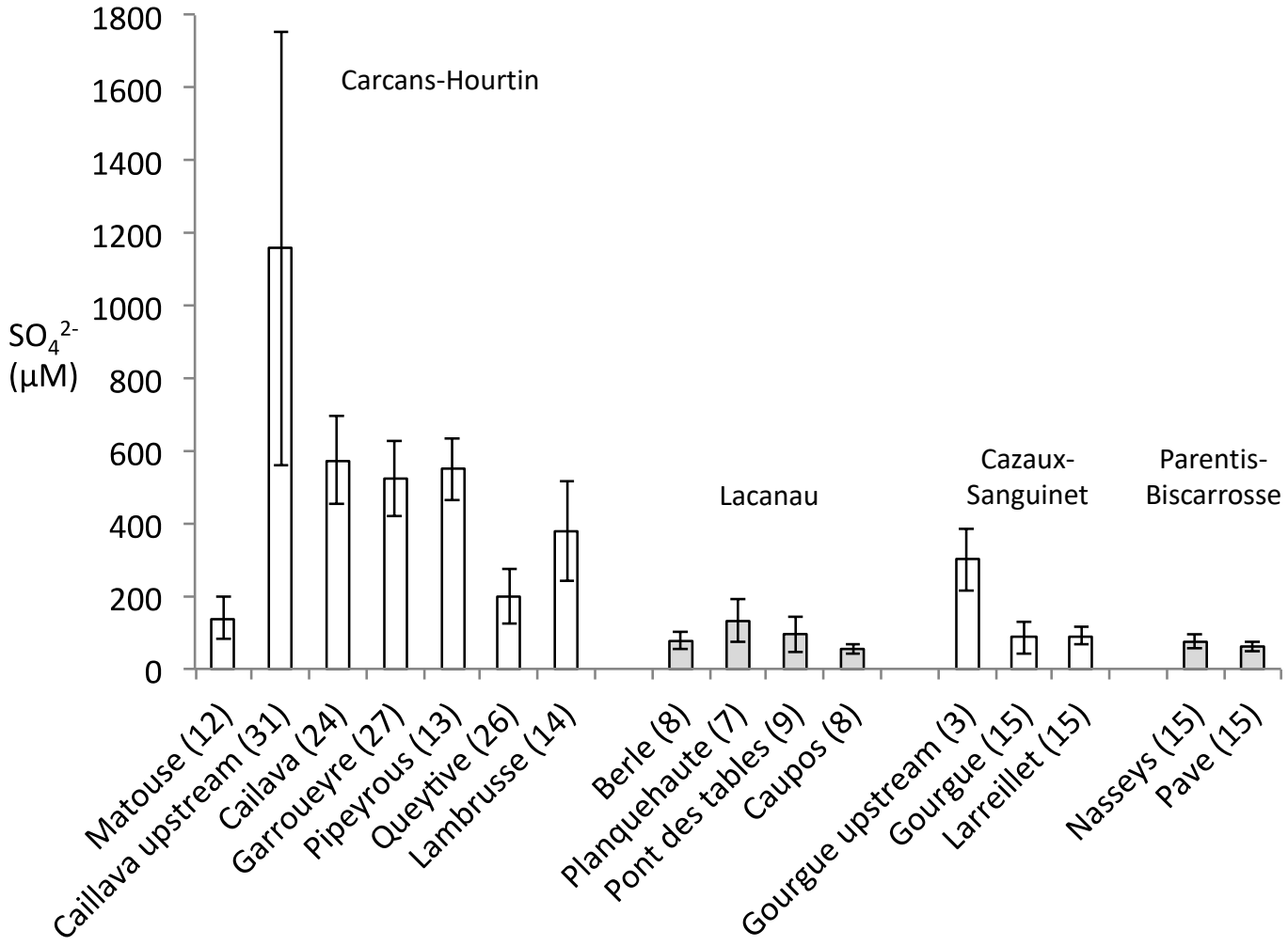
Sediments	$[HgT_p]$ (µg kg^{-1})	$[MMHg_p]$ (µg kg^{-1})	$MMHg/HgT_p$ (%)	References
Aquitaine lakes	100-420	1.1-5.1	0.5-2.5	This study
Arcachon Lagoon (SW France)	~ 200	~ 1	0.5	Bouchet et al., 2013
Gironde estuary (SW France)	~ 216	~ 0.7	0.3	Castelle, 2008
Everglades lakes (Florida)	50-400	<0.1-5	<0.2-2	Gilmour et al., 1998
Murray Lake (Papoua-New Guinea)	~ 111	~ 0.9	0.8	Bowles et al., 2001
St Lawrence River	~ 1500	~ 2.5	0.2	Avramescu et al., 2011
Lake Superior	83 ±12	0.21 ± 0.03	<1	Rolfhus et al., 2003
Lake Titicaca	45-114	0.51-1.36	1.8±1.5	Guedron et al., 2017
Western North America lakes data base	29.3±6.5	0.55±0.05	0.9±0.1	Fleck et al., 2016

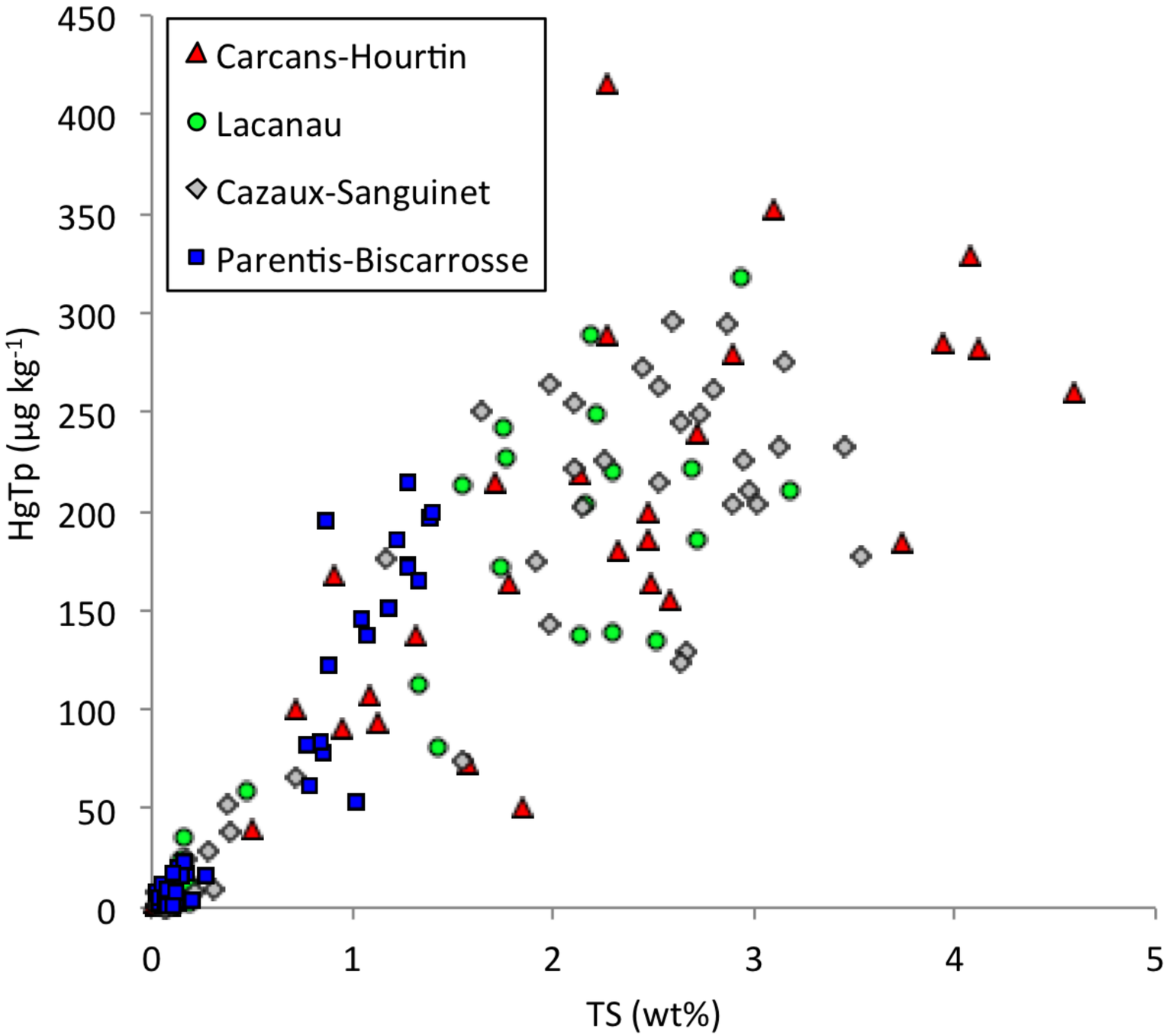

N
Legend
Stream
Crop field
Watershed
Carcans-
Hourtin
Lacanau
Atlantic ocean
Arcachon
lagoon
Cazaux-
Sanguinet
Parentis-
Biscarrosse
0 5 10 20 Km

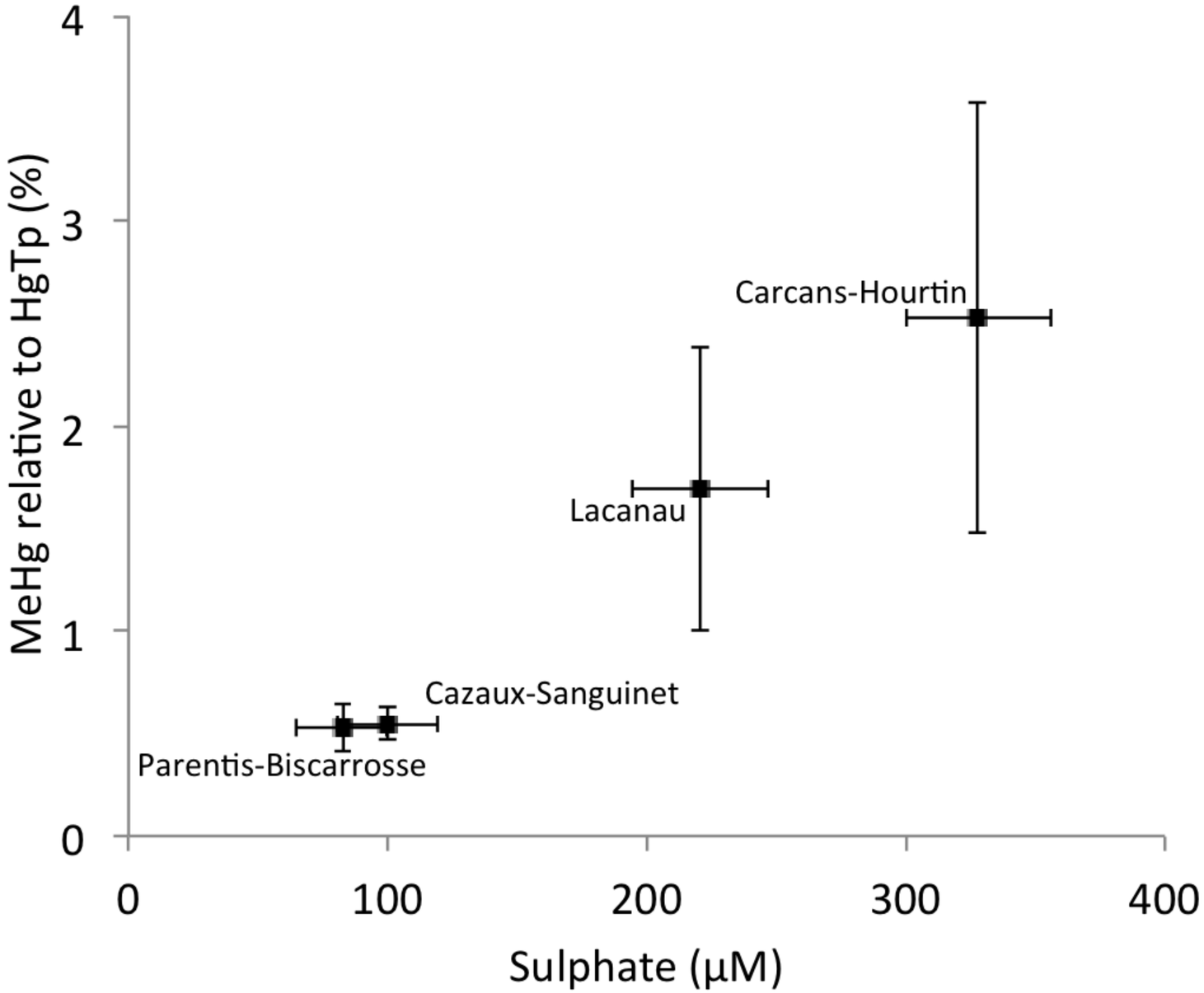

Sediment type
TC(%)
HgTp (µg kg-1)
Organic
[10–30]
[100–420]
Sandy organic
[3–10]
[20–100]
Organic sand
[1–3]
[4–20]
Sand
[0–1]
[0–4]
Carcans-Hourtin
Lacanau
Cazaux-Sanguinet
Parentis-Biscarrosse
N
0
5 Km
2 Km
3 Km
1°12'0"O
1°4'0"O
1°9'0"O
1°6'0"O
45°12'0"N
45°6'0"N
45°0'0"N
44°57'0"N
44°30'0"N
44°27'0"N
44°21'0"N

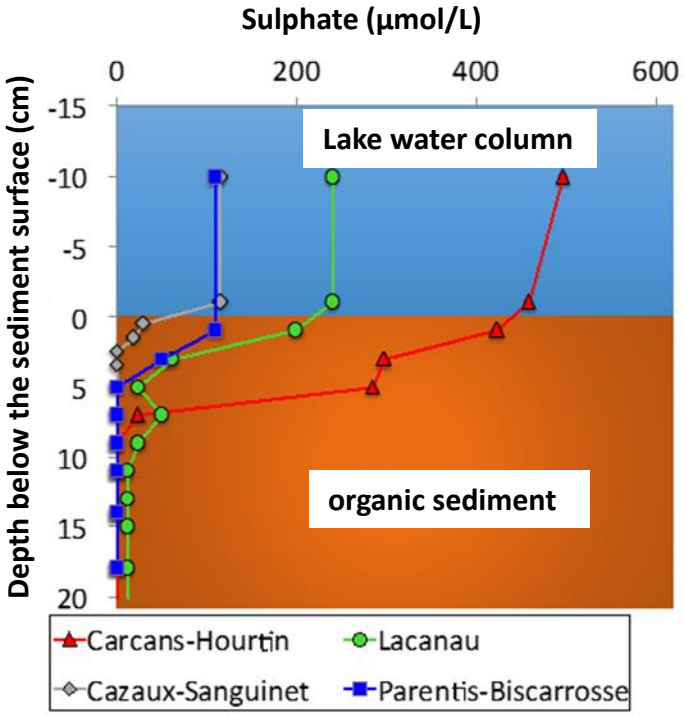

Organic muds
Sandy sediments
and catchment soils
Carcans-Hourtin
Lacanau
Cazaux-Sanguinet
Parentis-Biscarrosse
Catchment soil
Distribution (%)
Grain size (µm)
Grain size (µm)
0
1
2
3
4
5
6
7
0
50
100
150
200
0
5
10
15
20
25
0
200
400
600
800
1000
1200

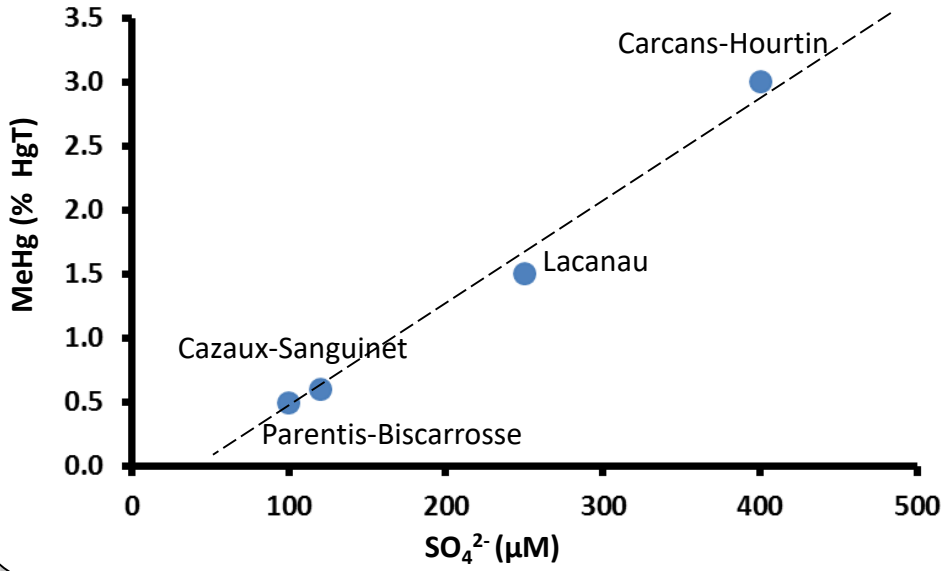

20
16
30
17
39
36
32
39
6
TC (%)
TS (%)
HgTp (µg kg-1)
Carcans-Hourtin
Lacanau
Cazaux-Sanguinet
Parentis-Biscarrosse
Catchment soil


1800
1600
1400
1200
1000
800
600
400
200
0
SO_4^{2-} (µM)
Carcans-Hourtin
Lacanau
Cazaux-Sanguinet
Parentis-Biscarrosse
Matouse (12)
Caillava upstream (31)
Cailava (24)
Garroueyre (27)
Pipeyrous (13)
Queytive (26)
Lambrusse (14)
Berle (8)
Planquehaute (7)
Pont des tables (9)
Caupos (8)
Gourgue upstream (3)
Gourgue (15)
Larreillet (15)
Nasseys (15)
Pave (15)


Carcans-Hourtin
Lacanau
Cazaux-Sanguinet
Parentis-Biscarrosse
HgTp (µg kg-1)
TS (wt%)
0
50
100
150
200
250
300
350
400
450
0
1
2
3
4
5


MeHg relative to HgTp (%)
4
3
2
1
0
Carcans-Hourtin
Lacanau
Cazaux-Sanguinet
Parentis-Biscarrosse
0
100
200
300
400
Sulphate (µM)


Sulphate (µmol/L)
0
200
400
600
Depth below the sediment surface (cm)
-15
-10
-5
0
5
10
15
20
Lake water column
organic sediment
Carcans-Hourtin
Lacanau
Cazaux-Sanguinet
Parentis-Biscarrosse


MeHg (% HgT)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500
SO4 2- (µM)
Carcans-Hourtin
Lacanau
Cazaux-Sanguinet
Parentis-Biscarrosse