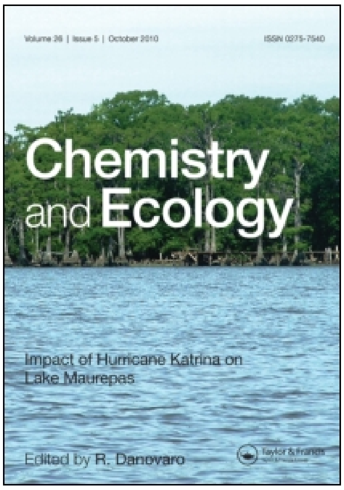

Chemistry and Ecology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455114

Mercury in surface waters of a macrotidal urban estuary (River Adour, south-west France)

T. Stoichev[a b]; D. Amouroux[a]; M. Monperrus[a]; D. Point[a]; E. Tessier[a]; G. Bareille[a]; O. F. X. Donard[a]
[a] Laboratoire de Chimie Analytique Bio-Inorganique et Environnement, France [b] Department of Food Chemistry, National Centre for Public Health Protection, Sofia, Bulgaria

To cite this Article Stoichev, T. , Amouroux, D. , Monperrus, M. , Point, D. , Tessier, E. , Bareille, G. and Donard, O. F. X.(2006) 'Mercury in surface waters of a macrotidal urban estuary (River Adour, south-west France)', Chemistry and Ecology, 22: 2, 137 — 148

To link to this Article: DOI: 10.1080/02757540500526450

URL: http://dx.doi.org/10.1080/02757540500526450

Chemistry and Ecology
Vol. 22, No. 2, April 2006, 137–148

Mercury in surface waters of a macrotidal urban estuary (River Adour, south-west France)

T. STOICHEV†‡, D. AMOUROUX*†, M. MONPERRUS†, D. POINT†, E. TESSIER†,
G. BAREILLE† and O. F. X. DONARD†

†Laboratoire de Chimie Analytique Bio-Inorganique et Environnement, CNRS UMR 5034, UPPA,
Hélioparc Pau Pyrénées, 64053 Pau Cedex 9, France
‡Department of Food Chemistry, National Centre for Public Health Protection, 15 Ivan Geshov Blvd,
Sofia 1431, Bulgaria

(Received 3 October 2005; in final form 14 December 2005)

Surface waters were collected in the River Adour estuary (south-western France) during different sampling periods from 1998 to 2001 in order to investigate the phase distribution and speciation of methylmercury ($MeHg^+$). Although a high variability is observed, significant higher average concentrations of total $MeHg^+$ (dissolved and particulate) are measured during the warm seasons, at 4.40 ± 8.18 pM and 3.90 ± 1.87 pM for July 1998 and September 1999, compared with the winter seasons, with concentrations at 0.99 ± 2.85 pM and 1.00 ± 1.75 pM for February 1998 and February 2001, respectively (one-tailed t-test, $P = 0.01$). The seasonal variations are explained with enhanced bacterial activity during summer and sedimentation/resuspension phenomena. Additionally, significant longitudinal variations of the $MeHg^+$ concentrations are observed. The highest levels in both dissolved and particulate fractions are found within the downstream urban estuarine area. This can be explained by the high methylation potential of the sediments, but direct anthropogenic inputs of $MeHg^+$ from specific discharge points cannot be neglected. Biogeochemical factors like phytoplankton biomass and salinity also show a relationship with $MeHg^+$ partitioning in the surface waters of the Adour estuary.

Keywords: Mercury; Methylmercury; Surface water; Adour River estuary

1. Introduction

After the industrial accident that occurred in the Minamata Bay in Japan [1], the biogeochemistry of mercury (Hg) in the coastal environment has been increasingly investigated in many countries. Although the Minamata disease was generated by the direct release of an extremely poisonous mercury compound, methylmercury ($MeHg^+$), most investigations to date are focused on diffuse contamination by inorganic mercury (Hg^{2+}) from various anthropogenic sources [2]. Attention is thus focused on the possibility of mercury undergoing natural transformations, some of which lead to the in situ production of $MeHg^+$ [3]. $MeHg^+$ usually

---

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

Chemistry and Ecology
ISSN 0275-7540 print/ISSN 1029-0370 online
http://www.tandf.co.uk/journals
DOI: 10.1080/02757540500526450

does not represent a large fraction of the total mercury in the aquatic environments, but the toxic effects of this compound can be significant due to its tendency towards bioaccumulation and biomagnification within the aquatic food chain [3].

Estuaries are specific aquatic ecosystems including many trophic levels often exposed to important anthropogenic discharges due to extensive urban development in their downstream section. Consequently, understanding the behaviour of mercury in estuaries undergoing important anthropogenic pressure is to date a primary preoccupation. Although mercury cycling has been intensively investigated in various estuaries, the significance of direct anthropogenic inputs in urbanized estuaries on mercury speciation and distribution has not been studied to any great extent [4, 5].

Previous investigations have shown that mercury cycling in estuarine waters is mainly related to both Hg^{2+} and $MeHg^{+}$ phase distribution between the aqueous phase (i.e. truly dissolved and colloidal) and suspended particles [4–7]. In these processes, the role of the dissolved or colloidal and particulate organic matter on the distribution of Hg^{2+} and $MeHg^{+}$ is significant, especially for mercury addition to or removal from the filter-passing fraction below *c*. 0.4–0.7 μm [5, 8–10].

The Adour estuary (south Gulf of Biscay) is an important French macrotidal dynamic estuary. According to a 'mussel-watch' monitoring programme on trace pollutants in oyster and mussel tissue samples [11], the Adour estuary might be significantly polluted with mercury. In this work, the mercury contamination levels in the Adour estuarine waters, collected during four sampling campaigns, are investigated through Hg^{2+} and $MeHg^{+}$ concentrations and phase distributions. Special emphasis is given to the seasonal and space variations of $MeHg^{+}$ levels measured in surface waters. The results are discussed in terms of direct anthropogenic $MeHg^{+}$ inputs or natural biogeochemical processes like methylation, sedimentation/resuspension, and uptake/release phenomena, which explain, at least partly, the $MeHg^{+}$ cycling in an urbanized macrotidal estuary.

2. Materials and methods

2.1 *Study area*

The Adour River is 310 km long, and the drainage area is 6189 km^2. Its estuary is situated in south-west France and flows into the Gulf of Biscay (Atlantic Ocean). The map of the study area is presented in figure 1. The investigated area is 39 km long and is set to be located between the kilometre points (KP) 101 and 140. Most of it corresponds to the estuarine mixing zone between the mouth of the estuary (KP 135) and upstream to the maximum salinity intrusion (KP 110). The tidal amplitude ranges between 2 and 5 m, and its influence can be observed up to 70 km upstream in the river. The mean annual water discharge is about 300 m^3 s^{-1}. The Adour estuary has been drastically modified and canalized in the last century. The upstream part of the estuary flows through agricultural areas, while the downstream part is within the Bayonne urban district. The detailed description of the study area is published elsewhere [12, 13].

2.2 *Sampling activities*

Surface water samples were collected from the main channel of the Adour estuary during four cruises (10–13 February 1998, 5–10 July 1998, 17–22 September 1999, 19–22 February 2001) on board the research vessels (INSU-CNRS, CQEL 64). About 11–24 samples along the salinity gradient were collected during each cruise. For all campaigns, various

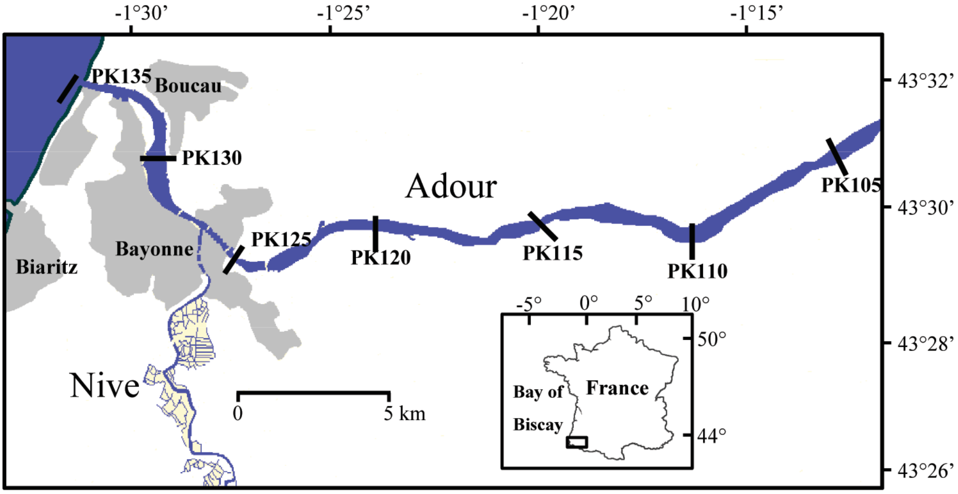

Figure 1. Map of the Adour River estuary (south-west France, Bay of Biscay).

hydrological and biogeochemical parameters were determined for each sampling station, such as pH, temperature, dissolved oxygen, and salinity, using calibrated in situ probes (WTW).

2.3 *Sample collection and filtration*

Water samples were collected using an acid-cleaned 5 l Teflon lined Go-Flo bottle (General oceanic, USA) and processed in situ following ultra-clean protocols [14]. The collected samples were transferred into polypropylene (PP) containers and subsequently filtered (0.45 µm polyvinylidone fluoride or Nylon filters) under a portable laminar flow hood (ADS Laminaire) to avoid in situ contamination. Between 0.2 and 4 l of water sample was filtered depending on the amount of suspended particles. Between 0.2 and 0.5 l of filtered water was poured into the Pyrex bottles and immediately acidified with 65% HNO_3 (Ultrapure, Baker) to 1% v/v. The water samples were stored at 4 °C in the dark until analysis. The filters were dried under a laminar flow hood and stored at −20 °C.

Collected water samples were also filtered through pre-combusted GF/F glass fibre filters (0.7 µm, Whatman) for dissolved organic carbon (DOC) measurements. Using the same filters, suspended particulate matter (SPM) was sampled for particulate organic carbon (POC) and phytoplankton pigment measurements.

2.4 *Analysis*

All analytical methods for both dissolved and particulate mercury species determinations have been described, validated, and discussed in detail in various publications [15–19].

2.4.1 Dissolved mercury species. Dissolved mercury species are identified as follows for both truly dissolved and colloidal forms: inorganic ionic mercury (Hg_D^{2+}) and methylmercury ($MeHg_D^+$). Simultaneous dissolved mercury species analyses were undertaken with sodium borohydride ($NaBH_4$) derivatization, on-line purge and cryogenic trapping (CT), gas chromatography (GC), and atomic absorption (QFAAS) detection (for the February 1998 and July 1998 campaigns) or atomic fluorescence spectrometry (AFS) (for the September 1999 and February 2001 campaigns). The precision is about 12% for Hg_D^{2+} (50 pM) and 8% for $MeHg_D^+$ (25 pM). The method detection limits for HG–CT–GC–AFS are 0.1 pM for $MeHg_D^+$ and 2.5 pM for Hg_D^{2+}. For HG–CT–GC–QFAAS, the method detection limits are higher: 3.5 pM for $MeHg_D^+$ and 13 pM for Hg_D^{2+}.

2.4.2 Particulate mercury species. The mercury species in the particulate fraction are denoted as Hg_P^{2+} and $MeHg_P^+$. Particulate mercury species were simultaneously determined after a 6 M HNO_3 extraction in open focused microwave field, subsequent on-line analysis by ethylation with sodium tetraethylborate ($NaBEt_4$) and CT-GC-QFAAS (for February 1998 and July 1998) or CT-GC-AFS (for September 1999 and February 2001). The precision of the method is 1.2% for $MeHg_P^+$ (0.08 nmol g^{-1}) and 4.3% for Hg_P^{2+} (65 nmol g^{-1}). The method detection limits for the Eth–CT–GC–AFS are 0.017 nmol g^{-1} for $MeHg_P^+$ and 0.06 nmol g^{-1} for Hg_P^{2+}. For the Eth–CT–GC–AAS system, the detection limits are higher: 0.28 nmol g^{-1} for $MeHg_P^+$ and 0.8 nmol g^{-1} for Hg_P^{2+}. The sum of the mercury species concentrations in the whole sample is referred to here as total mercury (Hg_{TOT}) and methylmercury ($MeHg_{TOT}^+$).

2.4.3 Biogeochemical parameters. POC was measured using a LECO CS-125™ analyser after removing carbonate. DOC was measured with high-temperature catalytic oxidation analyser (Shimadzu TOC 5000) [20]. Phytoplankton pigments (chlorophyll *a* (Chl) and phaeophytin *a* (Pha)) were analysed by high-performance liquid chromatography [21].

3. Results

3.1 *Hydrodynamic and biogeochemical conditions*

The four sampling campaigns (February 1998, July 1998, September 1999, and February 2001) were performed at relatively low river discharge (171.9 ± 6.3 $m^3\,s^{-1}$, 163.9 ± 22.3 $m^3\,s^{-1}$, 172.6 ± 24.7 $m^3\,s^{-1}$, and 238 $m^3\,s^{-1}$, respectively) and intermediate tide coefficients (50.8 ± 14.5, 62.5 ± 10.1, 83.3 ± 3.3, and 64.8 ± 11.3, respectively). Since these hydrodynamic conditions were similar, it is thus assumed that between-campaign changes in mercury species concentration and/or distribution should be mainly driven by the strength of anthropogenic inputs and the seasonal biogeochemical processes.

Major biogeochemical parameters of the water samples collected in the main channel of the Adour estuary are summarized in table 1. The estuary is loading a relatively low content

Table 1. Biogeochemical parameters for the Adour estuary (average values ± SD with the range in parentheses).

	T (°C)	pH	SPM (mg l^{-1})	DOC (mg l^{-1})	POC (%)	Chl (μg l^{-1})	Pha (μg l^{-1})
February 1998 (*n* = 15)	11.4 ± 1.8 (7.9–14.6)	8.06 ± 0.11 (7.84–8.30)	22.0 ± 14.1 (10.5–66.5)	4.72 ± 1.73 (1.45–8.63)	3.95 ± 1.00 (1.47–5.48)	3.4 ± 3.6 (0.2–11.1)	1.4 ± 1.1 (0–3.5)
July 1998 (*n* = 12)	21.0 ± 0.8 (20.1–22.8)	7.92 ± 0.17 (7.62–8.14)	12.2 ± 9.5 (0.7–31.9)	4.96 ± 2.03 (2.80–10.05)	7.32 ± 5.73 (3.35–21.00)	1.5 ± 0.6 (1.0–2.6)	2.2 ± 0.8 (0.9–4.1)
September 1999 (*n* = 24)	19.6 ± 1.3 (17.6–21.7)	7.76 ± 0.24 (7.26–8.22)	11.6 ± 10.4 (3.0–40.0)	2.57 ± 0.92 (1.18–5.75)	5.59 ± 2.08 (1.75–11.55)	1.0 ± 0.4 (0.4–1.9)	1.6 ± 0.6 (0.9–3.0)
February 2001 (*n* = 11)	8.7 ± 0.5 (7.6–9.3)	7.36 ± 0.25 (7.01–7.86)	13.0 ± 23.2 (1.2 –82.1)	2.01 ± 0.66 (0.80–2.90)	7.60 ± 3.34 (3.60–14.95)	–	–

of organic-rich suspended particles. The average Chl and Pha contents on the particles were found to be higher in summer than for the other seasons investigated.

3.2 *Total mercury*

The longitudinal distribution of Hg_{TOT} along the estuarine channel (as KP) is presented in figure 2. This plot indicates that no significant differences for Hg_{TOT} concentrations can be observed between the upstream and downstream samples. In contrast, high concentrations are obtained for samples collected between KP 124 and 134, which are located within the downstream urban area.

3.3 *Methylmercury distribution*

The geometric mean and concentration range for both dissolved and particulate Hg^{2+} and $MeHg^{+}$ in surface waters of the main channel of the Adour estuary are presented in table 2. Since many of the results for the mercury species, and especially for $MeHg^{+}$, are close to the detection limit, geometric means are used throughout the paper to assess better the environmental levels. For that calculation, when the mercury species are not detected, half of the value of the detection limits was used for their concentrations.

In the surface waters, $MeHg^{+}$ shows a clear seasonal trend. Significantly higher concentrations of total $MeHg^{+}$ were measured during the warm seasons (July 1998 and September 1999) compared with the winter seasons (February 1998 and February 2001; one-tailed t-test, $P = 0.01$). The ratio between total $MeHg^{+}$ and Hg_{TOT} is also higher for warm seasons than for colder seasons (one-tailed t test, $P = 0.01$).

Total $MeHg^{+}$ concentrations as a function of salinity for the Adour estuary are presented in figure 3. The maximum concentrations of $MeHg^{+}$ in the estuary are obtained both at a low salinity (0.2–1.3 psu) and at salinities greater than 20 psu. In September 1999, $MeHg^{+}$ was detectable in most samples, and a clear decrease in total $MeHg^{+}$ concentration was observed from salinity 1 to 20.

Along the estuarine channel, the longitudinal distribution of total $MeHg^{+}$ is presented in figure 4a. Concentrations measured within the downstream urban zone are up to five times

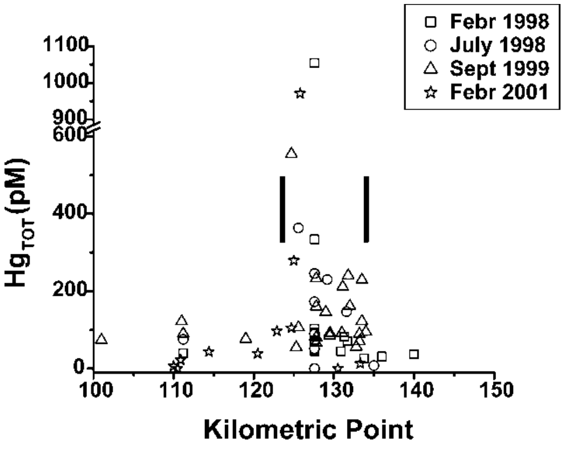

Figure 2. Total mercury concentrations as a function of the kilometre point (KP) for the four sampling campaigns. KP = 135 corresponds to the estuarine mouth. The straight lines delimit the location of the urban area between KP 124 and KP 134.

Table 2. Summary of the results for dissolved and particulate mercury species in the Adour estuary.

Sampling dates	Hg^{2+}_D (pM)	$MeHg^+_D$ (pM)	Hg^{2+}_P (nmol g^{-1})	$MeHg^+_P$ (nmol g^{-1})	$\Sigma MeHg^+$ (pM)	ΣHg (pM)	$\Sigma MeHg^+ / \Sigma Hg$ (%)
February 1998	8.2	<3.5	3.4	0.16	2.3	72	0.8
($n = 15$)	(<13–20.9)		(0.7–47.8)	(<0.28–0.48)	(<3.8–10.4)	(26–1054)	(0.0–11.1)
July 1998	23.2	3.2	4.9	<0.28	3.4	68	1.7
($n = 12$)	(<13–114.3)	(<3.5 –24.34)	(<0.8–69.4)		(<3.8–24.3)	(<18–365)	(0.0–9.9)
September 1999	5.5	0.17	20.1	0.6	3.4	115	3.7
($n = 24$)	(<2.5–37.6)	(<0.1–4.60)	(7.2–59.6)	(0.12–3.01)	(1.1–7.4)	(55–554)	(0.6–11.7)
February 2001	1.4	0.15	1.9	0.02	0.3	30	0.9
($n = 11$)	(<2.5–4.7)	(<0.1–1.53)	(<0.1–35.4)	(<0.02–0.18)	(<0.1–5.9)	(<2.7–971)	(0.0–3.2)

Note: To calculate the geometric mean, half of the detection limits stands for mercury species concentrations in all cases when they are not detected. The concentrations are given as geometric mean. The percentage of methylmercury is given as the average value.

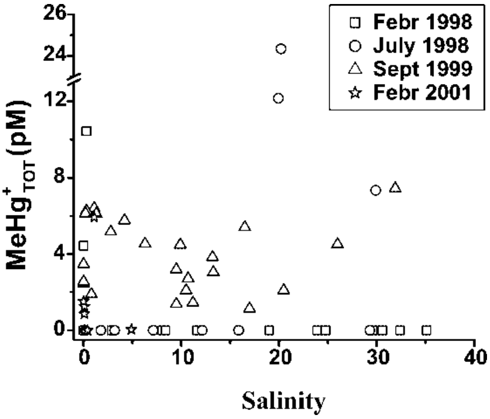

Figure 3. Total MeHg$^+$ concentrations as a function of salinity for the four sampling campaigns.

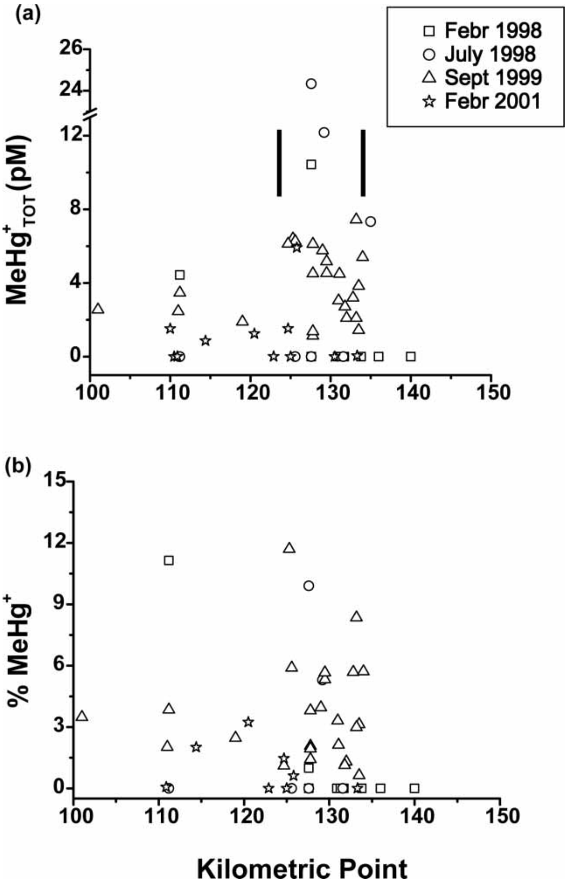

Figure 4. (a) Total MeHg$^+$ concentrations and (b) percentage of MeHg$^+$ with respect to the total mercury as a function of the kilometre point (KP) for the four sampling campaigns. KP = 135 corresponds to the estuarine mouth. The straight lines delimit the location of the urban area between KP 124 and KP 134.

higher than for other locations in the estuarine mixing zone. Irrespective of the sampling campaign, a large maximum in total $MeHg^+$ concentration is observed between KP127 and KP128. The percentage of $MeHg^+$ with respect to the Hg_{TOT} (figure 4b) has no particular longitudinal distribution and reflects the fact that in the urban area, there is also a large maximum of the Hg_{TOT} (see figure 2). This cannot be used to assess any specific signature of the highly contaminated samples downstream.

4. Discussion

The Adour estuary exhibits relatively high concentrations of $MeHg^+$, which increase in the downstream urban area (figure 4a). The concentrations of $MeHg^+$ for both dissolved and particulate phases in the Adour estuary (table 2) are also higher than for other major macrotidal estuaries [9, 17, 22]. As reported by Tseng [17], the higher residence time of water and particles in a macrotidal estuary seems to result in higher total $MeHg^+$ concentrations. However, mostly due to canalization in the downstream part, the water/particles residence time in the Adour estuary is short [23]. A higher methylation potential, compared with other coastal zones, could then be responsible for the relatively high concentrations of $MeHg^+$. Another possibility is the existence of anthropogenic point sources of $MeHg^+$ within the estuary.

4.1 *Direct anthropogenic influence*

One possibility to explain the longitudinal distribution of $MeHg^+$ in the Adour estuary (figure 4a) is to consider the possible anthropogenic impact in the urban downstream part. Most of the $MeHg^+$ coming from the wastewaters is in particulate form (82%) with concentrations up to 6.5 nmol g^{-1} [13]. Higher concentrations of $MeHg^+$ were found in effluents from the aquatic food industry [14], garbage dumps, and some sewage treatment plants [13]. The first source is probably provided by biogenic material potentially enriched in $MeHg^+$ [3]. The other two sources might be connected to the high methylation potential, especially when anoxic conditions develop [24]. A non-negligible amount of the $MeHg^+$ (*c*. 9% from the total $MeHg^+$ input) at a low river discharge enters the estuary by anthropogenic activities in the downstream part [13]. However, the estimated fluxes of $MeHg^+$ indicate that most of it is carried to the estuary by the Adour upstream waters. Thus, high values of $MeHg^+$ concentrations in the downstream estuarine part could correspond to polluted plume, poorly mixed with the water column.

4.2 *Methylation pathways*

Another possibility to explain the longitudinal variations is to consider enhanced methylation and uptake processes in the downstream part of the estuary.

4.2.1 Sediments. Surface sediment monitoring in the Adour estuary has found a strong relation between sediment biogeochemistry and $MeHg^+$ concentrations [12]. This could mean that the natural methylation processes in the sediments are important sources of $MeHg^+$ in the Adour estuary. Additionally, the specific methylation potential in the Adour fine-grained sediments [25] is higher than usual values found for other coastal areas [4, 26]. Therefore, sediments from the Adour estuary should be considered as an important source of $MeHg^+$ to the water column.

4.2.2 Phytoplankton. Since the production and transfer of MeHg$^+$ are driven mostly by biological pathways, the potential influence of phytoplankton biomass has also been examined. For September 1999, total MeHg$^+$ concentrations in the surface waters have been plotted against the concentration of Chl, as shown in figure 5a. A clear trend of increasing MeHg$^+$ concentration with increasing chlorophyll concentration is observed. This relationship indicates that a potential affinity is occurring between phytoplankton biomass and the amount of MeHg$^+$ in the water column. In contrast, no dependence was observed between Hg$_{TOT}$ and chlorophyll pigments. In figure 5b, the percentage of MeHg$^+$ (vs. Hg$_{TOT}$) exhibits an increase with the potentially active biomass, as indicated by the pigment ratio. This observed trend might indicate the preferential uptake or sorption of MeHg$^+$ by living phytoplankton species compared with Hg^{2+}. Similar interactions have already been described for the Gironde and Scheldt estuaries [17]. Although MeHg$^+$ is usually produced at the oxic/anoxic interface in sediments, methylation in the water column is another possible explanation for the high concentrations of MeHg$^+$ observed in the Adour estuarine waters. Biologically mediated methylation in waters was demonstrated for the Florida everglades [27], the Thau lagoon [28], and the Pettaquamscutt estuary [29]. Direct in vivo methylation of the Hg^{2+} by phytoplankton [22] and algae [30] has been established.

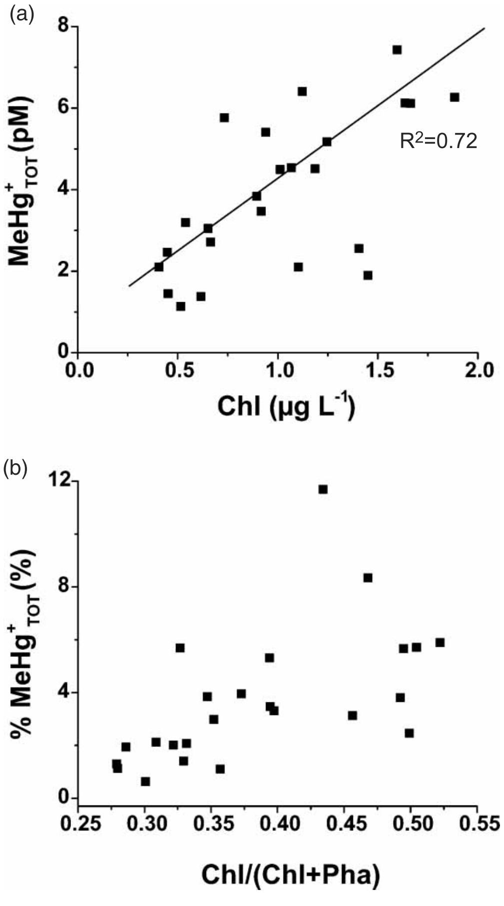

Figure 5. Relationship between (a) the total MeHg$^+$ and chlorophyll *a* (Chl) concentrations, Sept 1999 and (b) the percentage of the total MeHg$^+$ with respect to total mercury (%MeHg$_{TOT}$) and Chl/(Chl + Pha) ratio (fraction of the active Chl), September 1999.

4.3 *Methylmercury partitioning*

Using dissolved and particulate $\mathrm{MeHg^+}$ concentrations, it is possible to calculate the logarithmic distribution coefficient ($\log K_\mathrm{d}(\mathrm{MeHg^+})$) which exhibited average values of $5.2 \pm 0.4\,\mathrm{l\,kg^{-1}}$ for February 2001 and $6.1 \pm 0.8\,\mathrm{l\,kg^{-1}}$ for September 1999. A similar range of $\log K_\mathrm{d}$ is reported for the River Adour (upstream) and for wastewaters discharged into the estuary [13]. The obtained K_d values are higher than usually reported for other coastal areas [6, 8, 17]. Therefore, there is a higher affinity of $\mathrm{MeHg^+}$ for suspended particles in the Adour estuary when compared with other estuaries. One of the possible reasons could be the higher content of POC in the Adour estuary. Smaller particles, enriched in organic matter, are known to be efficient scavengers of mercury species [31]. The distribution coefficient is also relatively similar to the values found in Rhine and Scheldt estuaries, both having suspended particles exhibiting similar organic carbon enrichment [17].

The highest concentrations of $\mathrm{MeHg^+}$ in the Adour estuarine waters are measured at low and high salinity (figure 3). Irrespectively of the sampling campaign, the $\mathrm{MeHg^+}$ at low salinity is associated with the suspended particles, while at a high salinity it is in the filter-passing phase. A complete set of data for both $\mathrm{MeHg_D^+}$ and $\mathrm{MeHg_P^+}$ along the salinity gradient is available for September 99 (figure 6) and allows a better characterization of $\mathrm{MeHg^+}$ phase distribution. Particulate $\mathrm{MeHg^+}$ concentrations were higher at a low salinity (*c*. 1 psu), while higher concentrations of dissolved $\mathrm{MeHg^+}$ were observed at a high salinity. Similar investigations for other macrotidal estuaries, such as Scheldt [4, 22] and Patuxent [6], also exhibited a higher content of $\mathrm{MeHg^+}$ in the particles and in the aqueous phase, respectively, at a low and high salinity range. This behaviour can be a result of possible salinity-induced leaching of $\mathrm{MeHg^+}$ from particles along the estuarine mixing gradient. A model study has demonstrated that complexation with chloride anions can lead to desorption of the particulate $\mathrm{MeHg^+}$ during estuarine mixing [32].

4.4 *Seasonal variability*

The total $\mathrm{MeHg^+}$ concentrations and the percentage of $\mathrm{MeHg^+}$ exhibit a clear seasonal trend, appearing higher during warm seasons. Similar trends have been observed for the Wisconsin rivers [33] and the Scheldt estuary [4]. The higher concentrations of $\mathrm{MeHg^+}$ during warm seasons can be explained by the influence of temperature on sulphate-reducing rates and thus

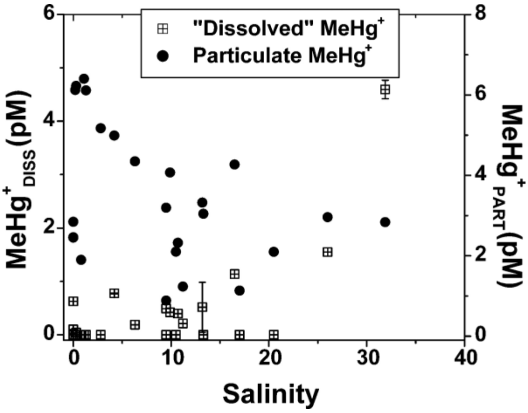

Figure 6. Dissolved and particulate $\mathrm{MeHg^+}$ concentrations vs salinity, September 1999.

Hg^{2+} methylation in the sediments [26]. The highest $MeHg^+$ concentrations in the particulate phase of the surface waters occur at the beginning of autumn, while dissolved phase $MeHg^+$ concentrations are at a maximum during the summer. Like suspended particles, the surface sediments from the Adour estuary also present a higher $MeHg^+$ content at the beginning of autumn [12]. It is important to note that the suspended particles of the Adour estuary present both higher $MeHg^+$ concentrations and the ratios $MeHg^+$ to Hg_{TOT} compared with the underlying sediments. Therefore, the cycling of sedimentation/resuspension processes, taking place in the estuary, could account for the seasonal variability of $MeHg^+$ concentrations in the water samples. However, active biogeochemical phenomena, like preferential uptake/release of $MeHg^+$ by suspended particles (phytoplankton), are involved in its cycling at the sediment/water interface.

5. Conclusions

Even if the main source of $MeHg^+$ to the Adour estuary is the upstream flow, there is an increase in $MeHg^+$ concentration in surface waters from the downstream urban area of the Adour estuary. This increase can be explained by the high methylation potential of the sediments but direct anthropogenic inputs of $MeHg^+$ from specific discharge points cannot be neglected. The sedimentation and resuspension of the sediment can explain the observed seasonal changes in $MeHg^+$ concentration in the surface waters. Biogeochemical factors like phytoplankton biomass and salinity have been shown to influence $MeHg^+$ concentrations and partitioning in the surface waters of the Adour estuary.

Acknowledgements

T. Stoichev acknowledges the French Government for his Ph.D. grant. This work is supported by the Aquitaine Region and CNRS in the Framework of the projects ECOMAN and GIS-ECOBAG. The Captain and crews of INSU-CNRS research vessels (Côte d'Aquitaine, Côte de la Manche) and A. Soulier (CQEL 64) are acknowledged for their technical assistance during the sampling campaigns. We also thank H. Etcheber (CNRS—U. Bordeaux 1) for the organic carbon and pigments measurements and T. Church (University of Delaware, USA) for improving the quality of this manuscript.

References

[1] A. Kudo, S. Miyahara. A case history; Minamata mercury pollution in Japan–from loss of human lives to decontamination. *Water Sci. Technol.*, **23**, 283 (1991).

[2] A. Picot, N. Proust. Le mercure et ses composés: de la spéciation à la toxicité. *L'actualité Chimique*, **4**, 16 (1998).

[3] E.D. Stein, Y. Cohen, A.M. Winer. Environmental distribution and speciation of mercury compounds. *Crit. Rev. Environ. Sci. Technol.*, **26**, 1 (1996).

[4] W. Baeyens, C. Meuleman, B. Muhaya, M. Leermakers. Behaviour and speciation of mercury in the Scheldt estuary (water, sediments and benthic organisms). *Hydrobiologia*, **366**, 63 (1998).

[5] R.P. Mason, N.M. Lawson, A.L. Lawrence, J.L. Leaner, J.G. Lee, G.R. Sheu. Mercury in the Chesapeake Bay. *Mar. Chem.*, **65**, 77 (1999).

[6] J.M. Benoit, C.C. Gilmour, R.P. Mason, G.S. Riedel, G.F. Riedel. Behaviour of mercury in the Patuxent River estuary. *Biogeochemistry*, **40**, 249 (1998).

[7] C.M. Tseng, D. Amouroux, G. Abril, E. Tessier, H. Etcheber, O.F.X. Donard. Speciation of mercury in a fluid mud profile of a highly turbid macrotidal estuary (Gironde, France). *Environ. Sci. Technol.*, **35**, 2627 (2001).

[8] N.M. Lawson, R.P. Mason, J.M. Laporte. The fate and transport of mercury, methylmercury and other trace metals in Chesapeake Bay tributaries. *Water Res.*, **35**, 501 (2001).

[9] M. Coquery, D. Cossa, J. Sanjuan. Speciation and sorption of mercury in two macrotidal estuaries. *Mar. Chem.*, **58**, 213 (1997).

[10] K.-Y. Choe, G.A. Gill. Distribution of particulate, colloidal and dissolved mercury in San Francisco Bay estuary. 2. Monomethylmercury. *Limnol. Oceanogr.*, **48**, 1547 (2003).

[11] D. Cossa, D. Claisse. Le methylmercure dans les mollusques du littoral français. Surveillance du milieu marin, Travaux du RNO Rapport annuel, IFREMER–MATE (1999).

[12] T. Stoichev, D. Amouroux, J. Wasserman, D. Point, A. De Diego, G. Bareille, O.F.X. Donard. Mercury speciation in surface sediments from the Adour estuary and other bays of the Basque coast (Gulf of Biscay). *Estuar. Coast. Shelf Sci.*, **59**, 511 (2004).

[13] Point D. Speciation and biogeochemistry of trace metals in the Adour estuary. Ph.D. thesis, Université de Pau et des Pays de l'Adour (2004).

[14] T. Stoichev. Spéciation et devenir du mercure inorganique et du méthylmercure dans les environnements côtiers–le cas de l'estuaire de l'Adour. Ph.D. thesis, Université de Pau et des Pays de l'Adour (2002).

[15] C.M. Tseng, A. De Diego, F.M. Martin, O.F.X. Donard. Rapid and quantitative microwave-assisted recovery of methylmercury from standard reference sediments. *J. Anal. At. Spectrom.*, **12**, 629 (1997).

[16] C.M. Tseng, A. De Diego, H. Pinaly, D. Amouroux, O.F.X. Donard. Cryofocusing coupled to atomic absorption spectrometry for rapid and simple mercury speciation in environmental matrices. *J. Anal. At. Spectrom.*, **13**, 755 (1998).

[17] C.M. Tseng. Cycle biogeochimique du mercure dans l'environnement: Développement analytique et spéciation en milieu estuarien. Ph.D. thesis, Université de Pau et des Pays de l'Adour (2000).

[18] T. Stoichev, R.C. Rodriguez Martin-Doimeadios, D. Amouroux, N. Molenat, O.F.X. Donard. Application of cryofocusing hydride generation and atomic fluorescence detection for dissolved mercury species determination in natural water samples. *J. Environ. Monit.*, **4**, 517 (2002).

[19] T. Stoichev, R.C. Rodriguez Martin-Doimeadios, E. Tessier, D. Amouroux, O.F.X. Donard. Improvements of mercury species determination in environmental matrices by cryofocusing atomic fluorescence spectrometry. *Talanta*, **62**, 433 (2004)

[20] G. Cauwet. HTCO method for dissolved organic carbon analysis in seawater: Influence of catalyst on blank estimation. *Mar. Chem.*, **47**, 55 (1994).

[21] S.W. Wright, S.W. Jeffrey, R.F.C. Mantoura, C.A. Llewellyn, T. Bjornland, D. Repeta, N. Welschmeyer. Improved HPLC method for the analysis of chlorophylls and carotenoids from marine phytoplankton. *Mar. Ecol. Prog. Ser.*, **77**, 287 (1991).

[22] M. Leermakers, S. Galletti, S. De Galan, N. Brion, W. Baeyens. Mercury in the southern North sea and Scheldt estuary. *Mar. Chem.*, **75** 229 (2001).

[23] F. Sanchez, P. Prouzet, P. Lazure, M. Amara, D. Capatina, D. Trujillo, P. Puiseux. Modele hydrodinamique de l'estuaire de l'Adour. In *Proceedings of the VIIth International Symposium on Oceanography of the Bay of Biscay*, Ifremer, pp. 250–255 (2001).

[24] R.A. Bodaly, J.W.M. Rudd, R.J. Flett. Effect of urban sewage treatment on total and methylmercury concentrations in effluents. *Biogeochemistry*, **40**, 279 (1998).

[25] R.C. Rodriguez Martin Doimeadios, E. Tessier, D. Amouroux, R. Guyoneaud, R. Duran, P. Caumette, O.F.X. Donard. Mercury methylation/demethylation and volatilization pathways in estuarine sediment slurries using species specific enriched stable isotopes. *Mar. Chem.*, **90**, 107 (2004).

[26] C.C. Gilmour, E.A. Henry. Mercury methylation in aquatic systems affected by acid deposition. *Environ. Pollut.*, **71**, 131 (1991).

[27] L.B. Cleckner, C.C. Gilmour, J.P. Hurley, D.P. Krabbenhoft. Mercury methylation in periphyton of the Florida Everglades. *Limnol. Oceanogr.*, **44**, 1815 (1999).

[28] M. Monperrus. Utilisations de traceurs isotopiques stables pour la spéciation du mercure et des butylétains: application à l'étude de la biométhylation du mercure dans les environnements aquatiques. Ph.D. thesis, Université de Pau et des Pays de l'Adour (2004).

[29] R.P. Mason, W.F. Fitzgerald, J. Hurley, A.K. Hanson Jr, P.L. Donaghay, J.M. Sieburth. Mercury biogeochemical cycling in a stratified estuary. *Limnol. Oceanogr.*, **38**, 1227 (1993).

[30] R. Pongratz, K.G. Heumann. Production of methylated mercury and lead by polar macroalgae–a significant natural source for atmospheric heavy metals in clean room compartments. *Chemosphere*, **36**, 1935 (1998).

[31] M. Roulet, M. Lucotte, R. Canuel, I. Rheault, S. Tran, Y.G. De Freitos Gog, N. Farella, R. Souza Do Vale, C.J. Soussa Passos, E. De Jesus Da Silva, D. Mergler, M. Amorim. Distribution and partition of total mercury in waters of the Tapajos River basin, Brazilian Amazon. *Sci. Tot. Environ.*, **213**, 203 (1998).

[32] A. De Diego, C.M. Tseng, N. Dimov, D. Amouroux, O.F.X. Donard. Adsorption of aqueous inorganic mercury and methylmercury on suspended kaolin: influence of sodium chloride, fulvic acid and particle content. *Appl. Organometal. Chem.*, **15**, 490 (2001).

[33] J.P. Hurley, J.M. Benoit, C.L. Babiarz, M.M. Shafer, A.W. Andren, J.R. Sullivan, R. Hammond, D.A. Webb. Influences of watershed characteristics on mercury levels in Wisconsin rivers. *Environ. Sci. Technol.*, **29**, 1867 (1995).