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Limnol. Oceanogr., 52(1), 2007, 470–475
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Enhanced methane oxidation in an estuarine turbidity maximum

Abstract—Methane and suspended particulate matter (SPM) concentrations, monitored bimonthly during one hydrological year (2003–2004) along 70 km transects in the tidal regions of the Garonne and Dordogne rivers (SW France), showed a significant negative correlation, both spatially and temporally. During spring in clear waters ($\text{SPM} < 50 \text{ mg L}^{-1}$), methane production was first evidenced by a net increase in methane concentrations, in parallel with temperature and a decrease in river flow. In summer, as soon as the estuarine turbidity maximum (ETM) appeared and SPM concentrations exceeded 100 mg L^{-1} , methane concentrations decreased from ~ 600 to $\sim 30 \text{ nmol L}^{-1}$ in one month. More downstream in the turbid Gironde estuary, methane concentrations were occasionally below atmospheric equilibrium. In dark microcosms, high methane consumption was observed in samples from the ETM with SPM concentrations $> 2,000 \text{ mg L}^{-1}$, but not after removing the SPM by settling ($\text{SPM} = 16 \text{ mg L}^{-1}$), nor in a sample collected few kilometers upstream, with $\text{SPM} = 3 \text{ mg L}^{-1}$. Methane oxidation was also able to draw down methane concentrations below half the atmospheric equilibrium value in an ETM sample. Suspended clays in the ETM enhance methane oxidation and strongly reduce methane fluxes to the atmosphere.

In aquatic systems, aerobic methane oxidation significantly reduces the methane flux to the atmosphere. Methane diffusing from sediments or anoxic water bodies generally meets oxygen before reaching the atmosphere and is partly oxidized to CO_2 by methanotrophs, which use methane as the sole carbon source (Hanson and Hanson 1996). In stratified systems like lakes, pelagic methane oxidation can consume up to 90% of the methane diffusing from the sediments (Utsumi et al. 1998; Kankaala et al. 2006). In well-mixed rivers and estuaries, methane oxidation is believed to be much less efficient in limiting the degassing to the atmosphere. Indeed, contributions of oxidation to the total methane loss can vary from less than 5% in turbulent rivers (Lilley et al. 1996) to more than 50% in some estuaries (De Angelis and Scranton 1993; Abril and Iversen 2002). Environmental factors controlling the activity of methanotrophs in aquatic systems are poorly documented in general. In wetlands, King (1990) showed that light strongly controls oxidation via photosynthesis, which produces oxygen and extends the region of methanotrophic activity. In rice paddies soils, Bodelier et al. (2000) demonstrated a limitation of methanotrophs by ammonium availability as a nutrient. In epilimnia of lakes, oxidation is strongly inhibited by light, a hitherto un-

recognized process (Dumestre et al. 1999; Murase and Sugimoto 2005). In the present paper, we demonstrate the occurrence in an estuary of a major control of methane oxidation by the particles suspended in the water. Methane oxidation is particularly enhanced in the estuarine turbidity maximum (ETM), where surface suspended particulate matter (SPM) exceeds 100 mg L^{-1} .

Material and methods—During a complete hydrological cycle (November 2003–November 2004), we have monitored the surface methane and SPM concentrations in the Garonne and Dordogne tidal rivers, at the entrance of the Gironde estuary (Fig. 1), where salinity was always below 0.5. The ETM is generally present in this area during summer and low river discharge, but not during winter, when it moves downstream in the Gironde estuary. A more detailed description of the ETM dynamics and associated SPM concentrations in the Gironde estuary can be found in Abril et al. (1999). Seven stations (four stations along 70 km, noted G0 to G70 in the Garonne and three stations along 60 km, noted D0 to D60 in the Dordogne) were visited bimonthly by car, always at the same stage of the tidal cycle. The Garonne River was sampled during ebb, starting at Sta. G70 at high tide +3 h and ending at the nontidal Sta. G0 ~ 3 h later. The Dordogne River was sampled during the following flood, starting at the nontidal Sta. D0 and ending at Sta. D60, at approximately low tide +3 h. Such a constant sampling strategy, in the opposite direction as the tidal current, extends the spatial coverage of water masses and also allows a comparison of sampling dates at individual stations. Fast-moving surface waters were sampled from small domestic boats moored along the quay. Surface water was sampled with a custom sampler that limits gas exchange. The sampler is a polyethylene bottle, the bottom of which has been removed. A hole has been made in the cap, which is connected to a Tygon tube. The sampler is gently submerged and maintained few seconds below the water surface with the open part facing in the direction of the water current. When the sampler is retrieved, water flows through the Tygon tube and can be transferred to serum glass bottles with an overflow. Only the water that had no contact with air is retained in the bottles and bubbles are excluded. We filled duplicate 160-mL serum bottles that were poisoned with HgCl_2 and sealed. Samples for SPM determination were filtered through $0.7\text{-}\mu\text{m}$ preweighed filters.

CH_4 concentrations were determined by gas chromatography (GC) with flame ionization detection, after creating a 30-mL headspace with N_2 , as described in Abril and Iversen (2002). Certified $\text{CH}_4:\text{N}_2$ mixtures at 10 and 500

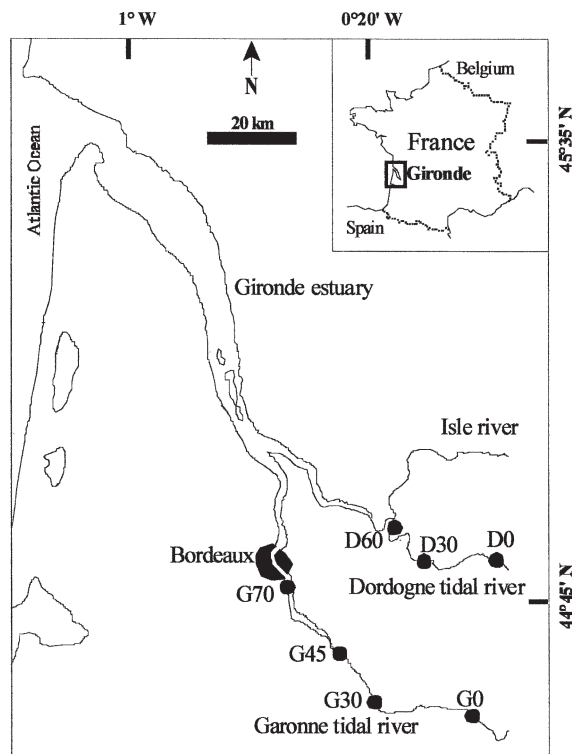


Fig. 1. Map of the Gironde estuary showing the sampling stations in the Garonne and Dordogne tidal rivers (the Isle River contributes to less than 5% of the water discharge). Stas. D0 and G0 correspond to the limit of the tidal influence.

parts per million by volume (ppmv) CH_4 were used as standards (Air Liquide). Dissolved methane concentration was calculated with the solubility coefficient of Yamamoto et al. (1976). Repeatability was generally better than 5%.

In addition to these field data, we conducted two laboratory experiments in order to investigate the impact of SPM on methane oxidation. First, in April 2005, we sampled 10 liters of water at Sta. G70 in the ETM and 5 liters of water at Sta. G30, approximately 10 km upstream of the ETM. Back in the laboratory, the two 5-liter glass bottles of turbid water from the ETM and the bottle of clear water from the river were left to settle at ambient temperature, 5°C higher than in situ, and in contact with air. After 2.5 d, one bottle from the ETM was homogenized and used for further incubations at the in situ SPM concentration ($2,020 \text{ mg L}^{-1}$, called “ETM in situ”). The second and unshaken bottle from the ETM was used to create two artificial subsamples: a first one very clear (16 mg L^{-1} , called “ETM clarified”) by siphoning the top ~ 4 liters of water; a second one very turbid ($8,720 \text{ mg L}^{-1}$, called “ETM concentrated”), after homogenizing the remaining ~ 1 liter of water with the particles settled at the bottom. Finally, the river sample was also homogenized and had a SPM concentration of 3.2 mg L^{-1} . Four aliquots of 80 mL of each sample were then transferred into clean 160 mL serum bottles that were sealed with butyl stoppers. Exact water and headspace volumes were quantified gravimetrically. For each sample, two aliquots were incubated at initial dissolved methane concentrations

close to ambient ($\sim 360 \text{ nmol L}^{-1}$, i.e., ~ 240 ppmv in the headspace) and two others aliquots at enriched concentrations ($\sim 7,200 \text{ nmol L}^{-1}$, i.e., $\sim 5,000$ ppmv in the headspace). We injected into the ~ 80 -mL headspace an adequate volume of pure methane to create these concentrations, as well as 8 mL of air, in order to create a slight overpressure and avoid problems of underpressure in the vial while injecting gas aliquots into the GC throughout the experiment. The 16 bottles were incubated in the laboratory at 22°C , in the dark to avoid light inhibition, and continuously shaken to maintain the gas equilibrium between the headspace and the sample and the particles suspended in the water. The second experiment was conducted in May 2005, at methane concentrations close to the atmospheric equilibrium. We incubated a fresh sample from the ETM ($1,730 \text{ mg L}^{-1}$) with the same procedure but with an initial methane concentration in the headspace of about twice the atmospheric concentration.

Results—At the beginning of the sampling period, in November 2003, the ETM (defined here as surface SPM $> 100 \text{ mg L}^{-1}$) was present at the more downstream stations of the Garonne (G30 to G70) and Dordogne (D60) tidal rivers (Fig. 2E,F). The two floods in December 2003 and January 2004 (Fig. 2A,B) pushed the ETM downstream in the estuary, SPM in the tidal rivers being lower than 30 mg L^{-1} in February 2004 (Fig. 2E,F). This low turbidity situation remained until June, with the exception of a third flood in the Garonne in early May (Fig. 2A), which created a temporary increase in SPM at $\sim 70 \text{ mg L}^{-1}$. Later in the year, as the rivers discharges decreased, the ETM moved upstream, reached Sta. D60 on the Dordogne, and Stas. G70, G45, and G30 on the Garonne, and remained there until November 2004 (Fig. 2A,B).

Methane concentrations in the Garonne and Dordogne tidal rivers varied over more than two orders of magnitude (Fig. 2E,F), from 5 nmol L^{-1} in October 2004 at Sta. G45 to 765 nmol L^{-1} in July 2004 at Sta. D30, within the range of previous reports in temperate rivers and estuaries (e.g., Lilley et al. 1996; Middelburg et al. 2002). From January to June, methane concentrations progressively increased in both tidal rivers and reached a maximum at Sta. G70 and D30 in the Garonne and Dordogne Rivers, respectively (Fig. 2E,F), concomitant with a raise in temperature (Fig. 2C,D) and a decrease in river flow (Fig. 2A,B). In July, as soon as the ETM moved upstream and reached the sampling stations, methane concentrations were reduced by more than one order of magnitude in about one month (Fig. 2E,F). From June to September 2004, lower methane concentrations (down to 5 nmol L^{-1}) in the two tidal rivers were related, both in time and space, to higher SPM concentrations. A statistical analysis on the whole seasonal dataset showed a significant negative linear correlation ($R = -0.33$, $p < 0.01$, $n = 160$) between methane and SPM concentrations. In Table 1, in order to extend our observations more downstream in the Gironde estuary, we refer to the Biogest methane data set from October 1996, July 1997, September 1997, and February 1998 published by Middelburg et al. (2002). A Wilcoxon–Mann–Whitney

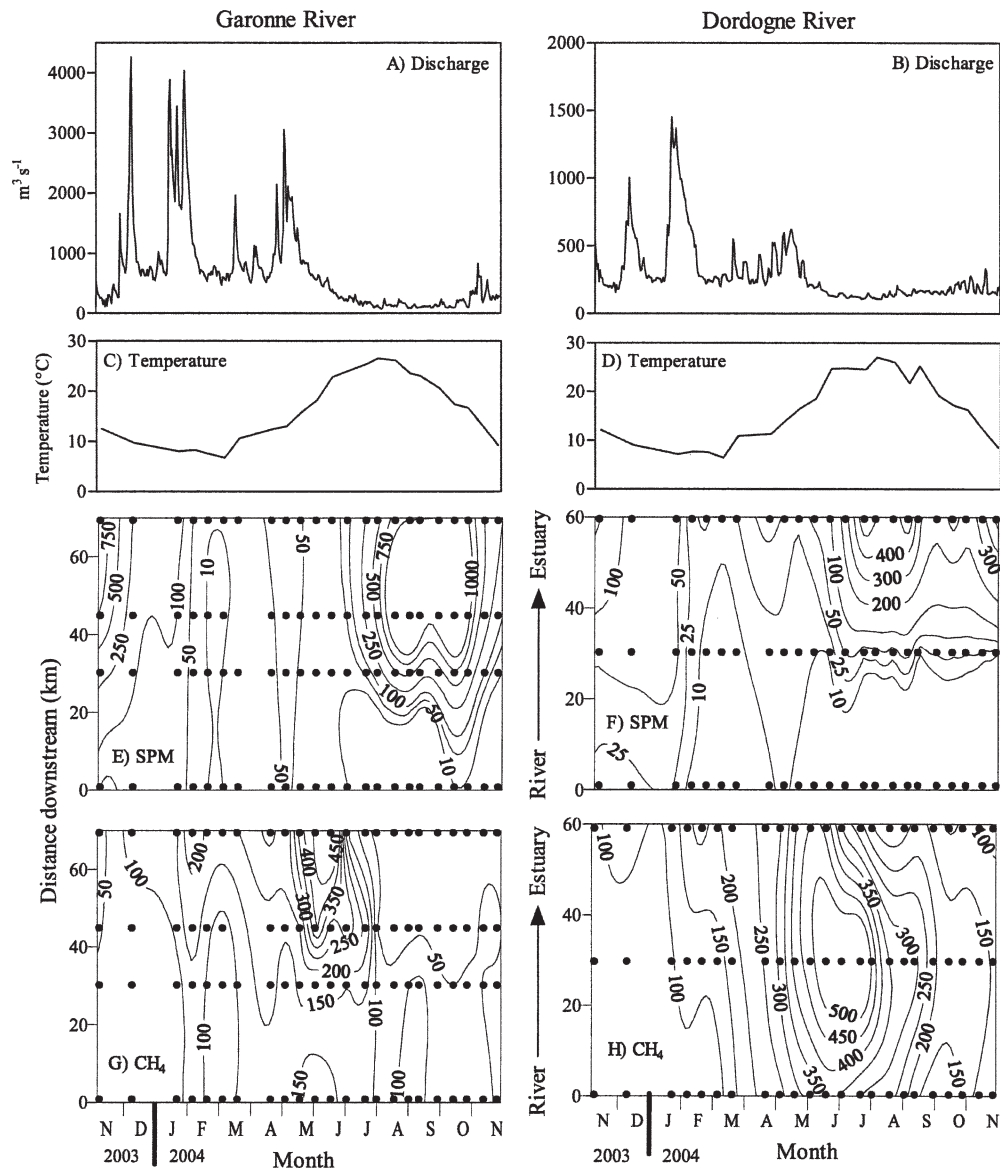


Fig. 2. Temporal changes from November 2003 to November 2004 in the Garonne and Dordogne Rivers of (A,B) water discharge and (C,D) temperature and associated distribution of (E,F) suspended particulate matter concentrations (mg L^{-1}) and (G,H) methane concentrations (nmol L^{-1}) along the studied tidal river sections. Dots indicate the sampling points.

test reveals that methane concentrations in the ETM decrease again significantly ($p < 0.01$) downstream in the estuary, with values occasionally below the atmospheric equilibrium of $\sim 2.5 \text{ nmol L}^{-1}$. At highest salinity and downstream of the ETM, methane concentrations increase slightly (Table 1), although the difference was significant only at the $p = 0.1$ level.

The time-courses of methane concentrations in the laboratory experiment (Fig. 3) showed significant methane consumption in the two samples with high turbidity, but not in the clarified ETM sample, nor in the river sample. In addition, at both methane levels, potential oxidation rates increased with SPM concentration, though not linearly. The oxidation rates in the turbid samples at the ambient concentration were in the range of $\mu\text{mol L}^{-1} \text{ d}^{-1}$, that is,

two to threefold higher than those measured in the Hudson tidal river (De Angelis and Scranton 1993). The method used here could not detect oxidation rates in the river and clarified samples, those being presumably as low as those measured by De Angelis and Scranton (1993) with the much more sensitive ^{14}C method. Last, in the ETM sample incubated at low concentration, methane in the headspace decreased down to 0.8 ppmv, that is, less than half the atmospheric average value (Fig. 4).

Discussion—The field data in the Garonne and Dordogne tidal rivers (Fig. 2) first show an increase in methane concentration in spring at Stas. G70 and D30, in the absence of the ETM. This rise in methane concentrations is likely due to large in situ methane production. A similar

Table 1. Methane concentrations (nmol L^{-1}) in the different regions of the Gironde estuarine system. Data in the Gironde estuary are from Middelburg et al. (2002), in November 1996, June 1997, September 1997, and February 1998. The ETM is defined as $\text{SPM} > 100 \text{ mg L}^{-1}$. The boundary between the tidal rivers and the estuary is defined as salinity = 1 and corresponds approximately to the junction of the Garonne and Dordogne rivers (Fig. 1). In the estuary downstream the ETM, salinity was always > 15 .

		Average \pm SD	Min	Max	<i>n</i>	<i>p</i> *
Rivers (nontidal)	Garonne	102 \pm 41	41	178	23	
	Dordogne	176 \pm 96	49	371	23	
Tidal rivers upstream ETM	Garonne	196 \pm 123	57	627	34	<0.01
	Dordogne	279 \pm 172	71	764	34	<0.01
Tidal rivers in ETM	Garonne	37 \pm 24	5	108	22	<0.01
	Dordogne	119 \pm 58	51	215	12	<0.01
Estuary in ETM	Gironde	9 \pm 7	0.3	31	23	<0.01
Estuary downstream ETM	Gironde	17 \pm 14	4.4	53	16	0.1

* The *p* value indicates how methane concentrations are significantly different from the estuarine section immediately upstream (Wilcoxon–Mann–Whitney test).

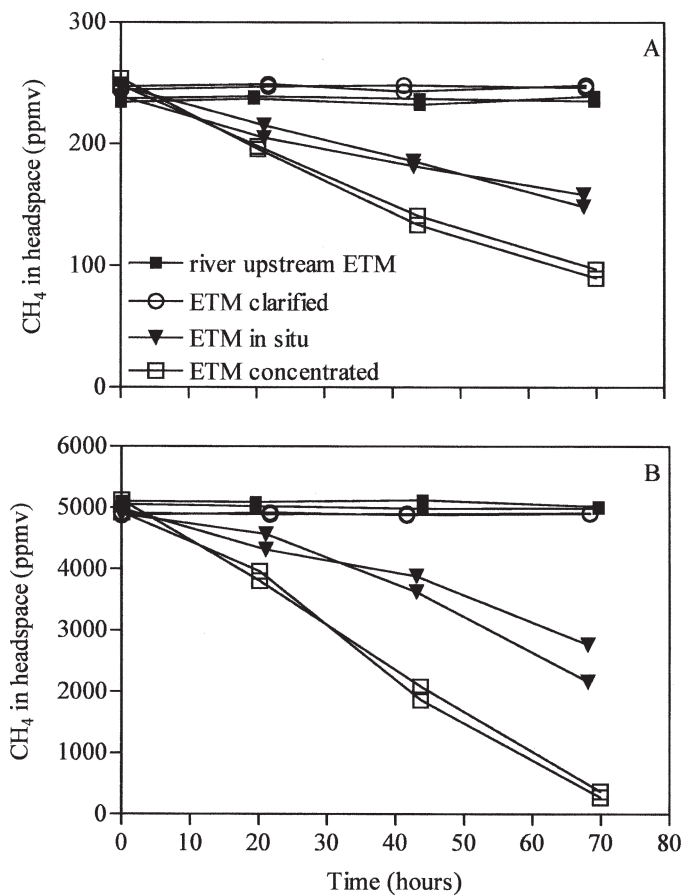


Fig. 3. Time-course of methane concentrations in headspaces of vials containing different water samples from the Garonne tidal river in April 2005. The “river upstream ETM” sample is from Sta. G30 and had a SPM concentration of 3.2 mg L^{-1} . The three ETM samples are from Sta. G70; the “ETM in situ” sample was incubated without any treatment and had a SPM concentration of $2,020 \text{ mg L}^{-1}$; in the “ETM clarified” sample, the particles were removed by settling during 54 h, and the SPM concentration was 16 mg L^{-1} ; in the “ETM concentrated” sample, SPM was increased by settling and was $8,720 \text{ mg L}^{-1}$. Headspace and sample volumes were both $\sim 80 \text{ mL}$. Incubations started at two different dissolved methane concentrations in the water: (A) 360 nmol L^{-1} and (B) $7,200 \text{ nmol L}^{-1}$.

methane maximum at low salinities has been observed in the Hudson and Humber estuaries (De Angelis and Scranton 1993; Upstill-Goddard et al. 2000). In the Hudson, the methane maxima were often related to point source sewage inputs of labile organic matter, which gets decomposed in the anoxic sediments. In the Garonne River, a similar point source can be expected near Sta. G70, at the city of Bordeaux. By contrast, in the Dordogne River there is no evidence for any important sewage input. This spring increase in methane concentrations was concomitant with an increase in temperature and a decrease in river discharges (Fig. 2A–D). In the Garonne, it occurred when chlorophyll *a* concentrations were maximal in these clear waters (Commarieu et al. unpubl. data). Inputs of labile organic matter, derived from sewage and freshwater phytoplankton, followed by trapping in anoxic sediments, due to the lower water flow and increased residence time of waters, likely favors springtime methane production in the tidal areas of the Garonne and Dordogne rivers.

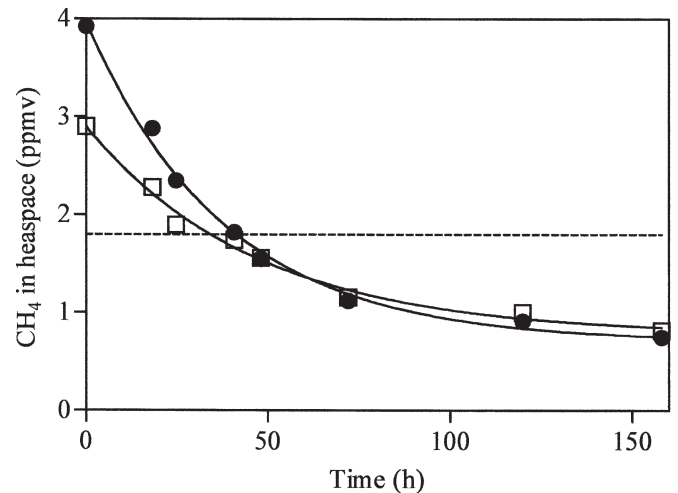


Fig. 4. Time-course of methane concentrations in headspaces of vials containing a water samples from the Garonne ETM in May 2005 (SPM concentration: $1,730 \text{ mg L}^{-1}$) performed at low methane concentrations. The dashed line shows the atmospheric methane concentration of 1.8 ppmv .

At the time of appearance of the ETM in the sampling area (June–July), the decrease in methane concentrations was very sudden (Fig. 2). The fastest methane loss occurred at Sta. G70, where concentrations decreased from 627 nmol L^{-1} in mid-June, to 55 nmol L^{-1} in mid-July. This sudden drop in methane concentrations reflects a profound change in supply and/or loss processes in the ETM, due to high SPM loads. From June to July, when the ETM appeared, the particulate organic matter concentration in the water column increased by a factor of more than 1,000, temperature continued to increase (Fig. 2C,D), and surface oxygen concentrations decreased from $\sim 105\%$ to 70% of air saturation (Commarieu et al. unpubl. data). All these factors favor methane production in aquatic systems and should have caused an increase in methane concentrations in the ETM. In parallel, an unrealistic rise in the gas transfer velocity, not supported by any change in weather conditions (wind and rain) or water current, would be required to explain the sudden methane drop in the ETM by gas evasion processes. The process that could cause such a sudden drop in methane concentration in the river waters is an enhancement of oxidation in the ETM. The first laboratory experiment (Fig. 3) demonstrates the potential for such an enhancement. The results of this experiment are also consistent with a selective filtration experiment by De Angelis and Scranton (1993) in the Hudson River, where approximately 50% of the methane oxidation activity occurred on particles greater than $11 \mu\text{m}$. In addition, Weaver and Dugan (1972) have shown *in vitro* an enhancement of methane oxidation when adding any clay minerals to a mixed culture rich in methane oxidizing bacteria. An affinity of methanotrophs for clays would also explain why most of the methane oxidation in the Randers Fjord estuary, where waters are very clear, occurs at the sediment surface and can induce water-to-sediment methane fluxes (Abril and Iversen 2002). Clays constitute the large majority of suspended solids in the Gironde, with $\sim 80\%$ of particles in the $0\text{--}25\text{-}\mu\text{m}$ grain size range (Gibbs et al. 1989). In our experiment, methane oxidation occurred associated with the particles. Our field data reveal the strength of the control of turbidity on the methane concentrations and atmospheric fluxes in the Garonne and Dordogne tidal rivers and Gironde estuary.

Another remarkable characteristic of methane oxidation in the ETM is its high affinity for methane. Our second laboratory experiment (Fig. 4) and the field data in the Gironde estuary (Table 1) consistently show that the methanotrophs present in the ETM are able to create an undersaturation in the water and generate an air-to-water methane influx. The final methane concentration in the headspace of the vials was less than half the atmospheric equilibrium of 1.8 ppmv (Fig. 4), which corresponds to $\sim 2.5 \text{ nmol L}^{-1}$ dissolved in the water. In addition, *in situ* methane concentration down to 0.3 nmol L^{-1} occurred in the Gironde ETM (Table 1). To date, thresholds for methane consumption lower than the atmospheric concentration have been observed only in oxic soils, whereas methanotrophs present in waterlogged soils or freshwater sediments are generally not able to consume methane at the atmospheric concentration (Bender and Conrad 1994). This

is due to the presence in soils of a population of unknown methanotrophs with an affinity for methane much higher than the one of common known methanotrophs (Conrad 1995). Clays in the Gironde estuary originate from the river and have been eroded from the soils on the watershed (Abril et al. 1999). Through that process, methanotrophic bacteria able to oxidize atmospheric methane could have been transported by the SPM from the soils to the ETM. However, the average residence time of particles in the Gironde ETM is about 2 yr, before reaching the Atlantic ocean. This means that, in order to maintain their activity, bacteria originating from the soils need to adapt to the estuarine conditions, including sedimentation and resuspension cycles and redox oscillations (Abril et al. 1999). Because of its low solubility in water, methane availability decreases in aquatic systems compared to soils. In estuaries, salinity can also inhibit methane oxidation (De Angelis and Scranton 1993). Methane undersaturations in the Gironde were observed at salinities as high as 21 (September 1997), when the ETM was present, which suggests that the enhancement of oxidation by suspended clays could to some extent counteract the inhibition by salinity. The ecology of the different types of methanotrophs transported by the river and found in the ETM needs a detailed investigation in order to explain this high affinity for methane. Nitrifying bacteria could also play a key role in methane consumption in ETMs, where nitrification is also enhanced (Owens 1986).

This study is the first report for a significant negative correlation between SPM and methane concentrations in an aquatic system. Very few methane studies report concomitant SPM measurements. In addition, sources and sinks are not always easy to identify only from measured concentrations. The source terms (methane production), depend on the extent of anoxia in the sediments and the supply of labile organic carbon and is not affected by the ambient methane concentration; in contrast, the two sink terms (oxidation and gas exchange) have first order-like kinetics and directly depend on the ambient methane concentrations. In addition, in rivers and estuaries, point sources like large cities (De Angelis and Scranton 1993), floodplains (Richey et al. 1988), and tidal flats (Middelburg et al. 2002) also influence the methane distributions. In temperate estuaries, the Biogest dataset (19 cruises along the salinity gradients of nine European estuaries; Middelburg et al. 2002) also reveals a significant negative correlation between surface water CH_4 and SPM (not shown, $R = -0.15$, $p < 0.01$, $n = 288$). This correlation was significant, beside the large heterogeneity of parameters others than turbidity, like the salinity of individual data points, the surface area of tidal flats, and the significance of sewage inputs in individual estuaries. In a low turbidity system like the Rhine estuary, methane concentrations occasionally exceed $1 \mu\text{mol L}^{-1}$; in contrast, highly turbid estuaries, like the Gironde, Loire, or Humber showed concentrations below 50 nM almost all along their salinity gradient (Upstill-Goddard et al. 2000; Middelburg et al. 2002). A turbid system like the Ems, however, showed intermediate methane concentrations because of the large extent of the tidal flats. It appears

that the enhancement of methane oxidation by suspended particles we demonstrated in the Gironde can be extrapolated to other estuaries. Not only estuaries exhibit high turbidity in the hydrosphere, and an enhancement of methane oxidation by suspended particles may also occur in rivers, lakes, and coastal waters. Areas of mixing waters with different SPM and methane concentrations are probably “hotspots” for methane oxidation, where methanotrophs transported with particles can encounter high dissolved methane levels. Also, short events like floods or sediment resuspensions are likely “hot-moments” (McClain et al. 2003) for methane oxidation in aquatic systems.

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Acknowledgments

We thank Henri Etcheber, Pierre Anschutz, Pascal Lecroart, and Jonathan Deborde (EPOC, Bordeaux) for their encouragement. The help of Antoine Marache (CDGA, Université Bordeaux 1) with the statistical analysis was greatly appreciated. This manuscript benefited from constructive comments provided by associate editor Mary Scranton and two anonymous reviewers. This work is part of the French GIS ECOBAG program. M.V.C. benefited from a Ph.D. grant by the Aquitaine Region and F.G. by Electricité de France.

Received: 21 March 2006
Accepted: 15 August 2006
Amended: 18 September 2006