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Gaseous mercury at the air–water interface of a highly turbid estuary (Gironde Estuary, France)

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ABSTRACT

The present work aims at better understanding dissolved gaseous Hg production and dynamics in surface water of highly turbid estuaries, where light penetration and photochemical processes in the maximum turbidity zone (MTZ) are very limited. Measurements of dissolved gaseous mercury (DGM) and total gaseous mercury (TGM) in surface water of the MTZ and at the mouth of the Gironde Estuary were carried out at different seasons. Diurnal cycles of DGM concentrations in surface water at both sites, showing variations by a factor of up to 60, may be attributed to photoreduction of Hg(II) by solar radiation. During low-turbidity situations at the estuary mouth, DGM concentrations paralleled the daily evolution of solar radiation. Under highly turbid conditions, DGM concentrations paralleled the daily evolution of the ratio between solar radiation and suspended particulate matter concentrations (rad/SPM) in surface water (~200–2000 mg L^{-1}), rather than solar radiation level alone. These results clearly suggest that high SPM levels may constitute an important factor influencing the DGM production in surface water by limiting light penetration. Despite of the generally very high SPM levels in the Gironde estuary, seasonal trends in maximum daily DGM concentrations, saturation and fluxes to the atmosphere were observed. Surface water appeared to be Hg super-saturated most of the time, especially during high radiation periods (300–1500%; May and July) resulting in Hg evasion. However, saturation levels down to 10% were observed during the night and even during the day in winter, when rad/SPM was sufficiently low. Under these conditions, Hg flux from atmosphere to the under saturated surface water may occur. Most of the year, hourly fluxes of Hg° from water to the atmosphere were positive during the day (up to 0.064 nmol m^{-2} h^{-1}; 12.8 ng m^{-2} h^{-1}) and were negative during the night, but in winter they were negative during the whole diurnal cycle (−0.01 nmol m^{-2} h^{-1}; −2 ng m^{-2} h^{-1}). Integration of the hourly fluxes over 24 h for the different campaigns, and extrapolation to the whole estuary scale suggest that the Gironde Estuary constitutes a Hg° net source to atmosphere during most of the year, with an annual Hg° net flux of ~22 mol y^{-1}. However, this net Hg° flux may probably be counterbalanced by (dry + wet) Hg deposition.

1. Introduction

The biogeochemical cycle of Hg includes an important atmospheric component, due to the high volatility of its elemental form and some of its compounds (Fitzgerald et al., 1991; Mason et al., 1994; Mason and Fitzgerald, 1996). Whereas wet deposition and particle settling are unidirectional processes, Hg gas exchange is a bidirectional process (e.g., Poissant et al., 2000; O'Driscoll et al., 2007; Andersson et al., 2008). The transfer and transport of Hg in the global environment imply exchanges between water and air, involving biogeochemical changes of its speciation (Mason et al., 1994; Mason and Fitzgerald, 1996; Fitzgerald and Mason, 1997). For example, any transformation of inorganic Hg such as reduction to Hg° and subsequent evasion, limits the formation of the bioavailable methylated Hg forms, preserving the aquatic food webs (e.g. Heyes et al., 2006; Whalin et al., 2007). Hg° is the major constituent of the dissolved gaseous mercury (DGM) forms in the open-ocean (Mason and Fitzgerald, 1996; Fitzgerald and Mason, 1997), and it is well-known that the reduction of dissolved Hg(II) to the gaseous Hg° is mostly photochemically induced in seawater and freshwater (e.g. Fitzgerald et al., 1991; Amyot et al., 1997; Canario and Vale, 2004; Rolfhus and Fitzgerald, 2004) and to a lesser extent biologically mediated by bacteria or phytoplankton (Mason et al., 1994; Rolfhus and Fitzgerald, 2004; Whalin et al., 2007; Monperrus et al., 2007). As a result, at the daily scale, a cyclic pattern of DGM concentration in relation with solar intensity is observable in both seawater and freshwater systems (e.g., Lanzillotta and Ferrara, 2001; Fantozzi et al., 2007; O'Driscoll et al., 2007).

The large majority of aquatic ecosystems studied have been found to be Hg°-supersaturated relatively to the equilibrium values predicted by Henry's law, and evasion from water bodies is a natural way for regulation of Hg burden (Poissant et al., 2000; O'Driscoll et al., 2007; Andersson et al., 2008). However, the transfer of Hg° from atmosphere to water bodies may be possible when saturation coefficient is low, and

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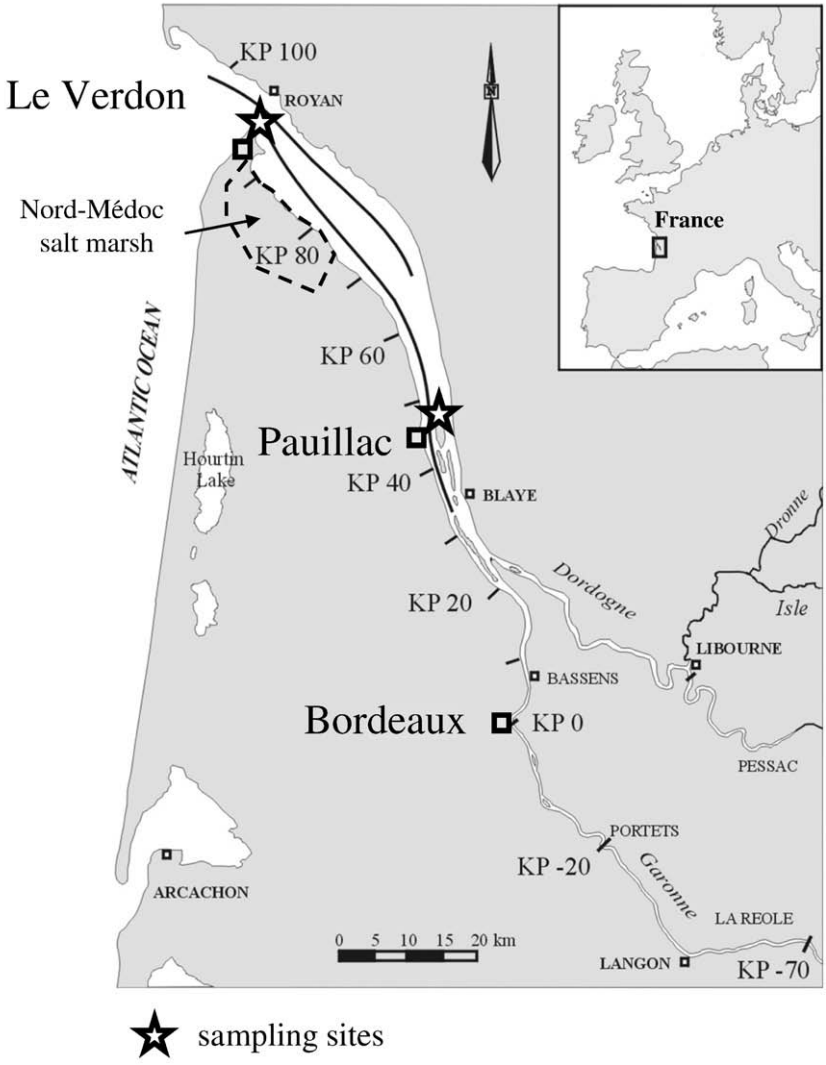

Fig. 1. Location of sampling and measurement sites (Pauillac and Verdon sites) in the Gironde Estuary.

then may be a pathway of Hg inputs into aquatic systems (Poissant et al., 2000; Andersson et al., 2008).

The Gironde Estuary is a macrotidal estuary presenting a permanent maximum turbidity zone (MTZ) with suspended particulate matter concentration (SPM) up to 10 g L^{-1} in surface water (Sottolichio and Castaing, 1999; Etcheber et al., 2007). These high SPM levels might either enhance or limit DGM production. As, particles transport more than 90% of Hg into the estuary (Schäfer et al., 2006) and sediments exposed to solar radiation may release gaseous mercury (Canario and Vale, 2004), high SPM concentrations in the Gironde Estuary might support intense Hg° formation in water. Moreover, intense particulate organic matter biodegradation in the MTZ (Abril et al., 1999; Etcheber et al., 2007), enhance dissolution of Hg (Cossa and Noël, 1987) which then may be available for photochemical or biotic reduction. However, turbidity also limits light penetration into the water column which in turn would limit the photochemically-induced Hg reduction. This work presents diurnal DGM concentrations in surface water of the Gironde Estuary for different seasons. The related Hg fluxes across the air–water interface were calculated using a two-layer model (Poissant et al., 2000), and the role of turbidity in DGM formation and exchanges between water and air was investigated in order to determine if the Gironde Estuary constitutes a sink or a source of Hg° to atmosphere.

2. Materials and methods

2.1. Study area

The Gironde Estuary (south-west France, Fig. 1) is the largest French estuary with a length of 170 km, a cover area of 625 km^2 at high tide and 442 km^2 at low tide and a mean annual freshwater discharge of ~1 100 m^3 s^{-1} (Schäfer et al., 2002). This estuary is characterized by very high turbidity, with concentrations of suspended particulate matter (SPM) exceeding 1 g L^{-1} in surface water and several hundreds of g L^{-1} in the bottom water of the MTZ. This MTZ is typically located in the low salinity region, and migrates up and down estuary with seasonal river flow variations (Sottolichio and Castaing, 1999). Roughly 50% of continental particulate organic carbon (POC) is mineralized in the estuary and this heterotrophic activity occurs mostly in the MTZ, in both oxic and anoxic conditions (Abril et al., 1999; Etcheber et al., 2007). Average residence times of water and particles, estimated from the respective average gross fluxes and the estuarine stock, are 1–3 months and 1–2 years, respectively (Jouanneau and Latouche, 1981; Etcheber et al., 2007). These commonly accepted particle residence times have recently been confirmed by radioisotope measurements (Saari et al., 2008). Several studies in this estuary are dealing with SPM dynamics and SPM concentration fluctuations, at different timescales (tidal, seasonal, interannual; Robert et al., 2004;