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Fate and tidal transport of butyltin and mercury compounds in the waters of the tropical Bach Dang Estuary (Haiphong, Vietnam)

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ABSTRACT

In this work, two field campaigns were performed in July 2008 (wet season) and March 2009 (dry season) to produce original data on the concentration, partition and distribution of mercury and butyltin compounds along the tropical Bach Dang Estuary located in North Vietnam (Haiphong, Red River Delta). The results demonstrate that mercury and butyltin speciation in the surface waters of this type of tropical estuary is greatly affected by the drastic changes in the seasonal conditions. During high river discharge in the wet season, there was a large estuarine input of total Hg and tributyltin, while the longer residence time of the waters during the dry season promotes increasing MMHg formation and TBT degradation. Although most of the Hg and TBT is transported into the estuary from upstream sources, tidal cycle measurements demonstrate that this estuary is a significant source of TBT and MMHg during the wet (~3 kg TBT/day) and dry (~3 g MMHg/day) seasons.

1. Introduction

Currently, the presence and pollution impact of organometallic species in the environment, especially in marine ecosystems, is well-known to be generally associated with the increase of anthropogenic activities (Amouroux et al., 2011). One of the most hazardous contaminants is mercury, which is ubiquitous and widespread; its most toxic form, monomethylmercury (MMHg), can cause severe neurological damage to humans and wildlife from even very low concentrations in water (Fitzgerald et al., 2007). There are several sources of mercury contamination in aquatic ecosystems, *e.g.*, atmospheric deposition, erosion sources, urban discharge, agricultural sources, mining discharge and combustion and industrial discharge (Wang et al., 2004).

Another organometallic pollutant present in the aquatic environment is tributyltin (TBT), and its uses, including as an antifouling agent in boat paints, in wood preservation, as an antifungal agent for textiles and in industrial water systems, have been responsible for its anthropogenic introduction into the aquatic environment (Donard et al., 2001). The TBT degradation products dibutyltin (DBT) and monobutyltin (MBT) are mainly used as heat and light stabilizers for PVC material, and DBT is also increasingly used as a binder in water-based varnishes (Antizar-Ladislao, 2008). Butyltin compounds are persistent in water and particularly in sediments, and they have extremely high toxicity and endocrine-disrupting effects at low concentration levels, *e.g.*, imposex in gastropods or deformities in oysters (Donard et al., 2001).

The toxicity, mobility and bioavailability of these compounds is closely related to their chemical form, *e.g.*, alkylmercury is more toxic than inorganic mercury (Hg (II)) and trialkyl more than di- or monoalkyltin. Therefore, the speciation of organometallic compounds is of primary interest due to their species-dependent toxicity (Leermakers et al., 2005).

Although most of the methylated species are mainly formed from the inorganic tin or mercury form via biomethylation (*e.g.*, bacteria and fungi), heavier alkylated compounds are usually of anthropogenic origin (*e.g.*, butyltin or phenylmercury). In most cases, biomethylation occurs in biofilms and at the water–sediment interface, where the microorganisms develop (Hirner, 2006; Saniewska et al., 2010). Thus, aquatic ecosystems have been found to be the most susceptible to MMHg and butyltin contamination (Amouroux et al., 2011; Donard et al., 2001; Fitzgerald et al., 2007).

Unlike the European Union, which included mercury and TBT and their degradation products in the list of priority pollutants in

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the Water Framework Directive and established limit values in water at 0.07 μg/L and 0.0015 μg/L, respectively (Directive 2008/105/EC), the Association of Southeast Asian Nations regulated total mercury (THg) in seawater (0.16 μg/L) in 1999, but the use of organotin compounds in antifouling paints is still permitted in many Asian countries. Only Japan and Hong Kong have regulated the use of TBT, and since 2000, South Korea has implemented partial restrictions on its use for small boats and fishing nets.

Many studies on methylmercury and TBT pollution have been performed in sediments, biota and fish in Asian coastal areas (Harino et al., 2009; Jiang et al., 2010; Li et al., 2009; Midorikawa et al., 2004; Nhan et al., 2005; Oh et al., 2010; Sudaryanto et al., 2002; Suehiro et al., 2006; Yawei et al., 2005), but few works dealing with water samples have been found in the literature (Bhosle et al., 2004; Cao et al., 2009; Choi et al., 2010; Garg et al., 2010; Laurier et al., 2004), and none in Vietnam. Thus, there is a need to assess the environmental impact of these pollutants in these areas through the implementation of consolidated methodologies of analysis (Monperrus et al., 2005a,b).

The Bach Dang Estuary, located on the easternmost branch of the Red River, plays an essential role in the economic development of North Vietnam. The area is subjected to increasing anthropogenic pressures on the ecosystem due to intensive agriculture, strong urbanization and the presence of one of the principal industrial ports in Vietnam. The organic pollutants used in agriculture, the organic residues and inorganic components of urban effluents, and the metals derived from urban and industrial activities are all found in the estuarine system, many of which have undergone either no or minimal treatments (Carvalho et al., 2008; Hung and Thiemann, 2002; Nhan et al., 1998, 2005). The environmental degradation resulting from these effluents can have major economic consequences through negative impacts on public health, natural resources and tourism in the affected areas, and thus these issues pose a major challenge for the sustainable economic development of the region.

The present work is a part of a multidisciplinary project on the impact of anthropogenic and hydrological constraints on the biological functioning of the Bach Dang estuarine ecosystem in North Vietnam (Torréton et al., 2009). Rochelle-Newall et al. (2011) have demonstrated that the phytoplankton and bacterioplankton diversity, distribution and productivity are not only affected by the hydrological dynamics of carbon, particles and nutrients loads but most likely by the occurrence of contaminants, such as organometallic compounds of tin (butylSn) and mercury (MeHg). Thus, the distribution and variability of both autotrophic and heterotrophic species within estuarine waters was hypothesized to potentially control the speciation, fate and transport of these organometallic contaminants (Rochelle-Newall et al., 2011). In addition, Lefebvre et al. (2012) evaluated the seasonal variability of the sediment transport, aggregation and deposition in the Bach Dang Estuary. This study demonstrated that high river discharge during the wet season induces large sedimentary particle fluxes to the coastal bay while tidal pumping during the dry season favors significant particle input from the bay and promotes sedimentation within the inner estuary (Lefebvre et al., 2012).

Thus, the objectives of this work are to provide, for the first time, a comprehensive distribution of the mercury compounds and butyltins in water samples from this estuary and to evaluate how both seasonal and tidal hydrodynamic features may affect their respective seaward transport. For this purpose, 18 sites were sampled to assess the spatial distribution of the organometallic compounds along the Bach Dang Estuary. This site is subjected to a sub-tropical humid climate with a wet season from May to October and a dryer, cooler season from November to April. The sampling was therefore performed during these two hydroclimatic seasons (wet and dry). Both the spatial distribution of the sampling stations and the seasonal characteristics were intended to evaluate the influence of the salinity and suspended matter on the concentration of the pollutants. Moreover, the tidal flux of the pollutants was evaluated in one sampling site for 24 h to determine the upstream/downstream estuarine flux contributions.

2. Materials and methods

2.1. Sampling area and sample collection

The samples were collected in the Bach Dang Estuary along three axial transects during the wet season (July 1–11, 2008) and the dry season (March 12–23, 2009), covering a wide range of salinities. During each campaign, 19 stations in 2008 and 18 stations in 2009 (see Fig. 1) were sampled from the deck of a 12 m flat-bottomed coastal vessel for the butyltin and MMHg analyses in both the aqueous and particulate fractions.

At each sampling station, a CTD profiler (SeaBird SBE 19 plus, Sea-Bird Electronics, Inc., Bellevue, WA, USA) was deployed to measure the vertical profiles of temperature, salinity, photosynthetically active radiations (PAR) and *in vivo* fluorescence in the water column. Turbidity (in Formazin Turbidity Units, FTU) was also measured using a Seapoint turbidity meter attached to the CTD package. More details on the sampling strategy and methodology are described elsewhere (Lefebvre et al., 2012; Rochelle-Newall et al., 2011).

2.1.1. Tidal cycle (24 h) at Dinh Vu station

The 24 h cycles were performed at the confluence of the Bach Dang and Cam Rivers (Site 4, Dinh Vu, see Fig. 1) to estimate the influence of the salinity and suspended particulate matter on the organometallic concentrations. For both sampling campaigns, water samples were collected every 3 h for the 24 h cycles (1 full tidal cycle) on July 5–6, 2008 for the wet season (starting at 9:30 a.m.) and on March 17–18, 2009 for the dry season (starting at 11:00 a.m.). This station in particular also allowed the concentration values obtained to be combined with the current measurements upstream and downstream of the estuary.

Instantaneous river discharge was also determined from the cross-sections of the velocity profiles measured by an acoustic Döppler current profiler (ADCP) RDI Workhorse 600 kHz (Teledyne RD Instruments, Poway, CA, USA) every 3 h in Dinh Vu (site 4) for a 24 h tidal cycle. The particle size distribution along the water column was measured by a laser diffractometer (Laser *In-Situ* Scattering and Transmissiometry, USST-100X Type-C (Sequoia Scientific, Inc., Bellevue, WA, USA)), delivering the size distribution of the suspended particles in 32 logarithmically spaced size classes between 2.5 and 500 μm. The surface and bottom water suspended particulate matter (SPM) concentration was determined by filtration through Nuclepore 0.4 μm membranes, followed by weighing. The total net flow was calculated from the riverine outflow and marine inflow as calculated from the transversal current measurements (from bank to bank across the channel during the diurnal tidal cycle) conducted for a 24 h cycle on the river. A positive value was inferred from the net seaward flux of estuarine or riverine inputs, whereas a net negative value corresponded to an upstream flux of marine or estuarine inputs.

2.1.2. Water and sediment collection and pre-treatment

The samples were directly collected by hand at the sub-surface (0.5 m depth) in clean Teflon vials while using large polyethylene gloves to avoid any contamination from any sampling device or the surface microlayer.

To analyze the particulate and dissolved concentrations, each water sample (0.3–1.5 L) was filtered through a pre-cleaned, preweighted and labeled Durapore® PVDF filter membrane (0.45 μm,