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Inputs, dynamics and potential impacts of silver (Ag) from urban wastewater to a highly turbid estuary (SW France)

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HIGHLIGHTS

- Analysis of Ag along the different steps of the water treatment process at hourly, daily and weekly timescales.
- Quantification of potential NPAg inputs from personal care products (PCP).
- Evaluation of the potential fate and impacts of Ag and NPAg concentrations and fluxes on a highly turbid fluvial estuary.
- Comparison of Ag inputs from urban wastewater with non-urban sources.

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ABSTRACT

Although silver (Ag) has been listed as a priority pollutant for the aquatic environment by the European Union (Directive 2006/11/EC), the use of Ag-based products with antimicrobial effects is increasing in Europe, as well as North America and Asia. This study investigates personal care products (PCP) as a potential source of Ag in wastewater, as well as the dynamics and fate of Ag in the influent and effluent of a major urban wastewater treatment plant (WWTP) located on the fluvial part of the Gironde Estuary. Typical household PCPs marked as using Ag contained concentrations of up to 0.4 mg kg^{-1} making them likely contributors to urban Ag released into the aquatic environment. Silver concentrations in influent wastewater generally occurred during mid-week working hours and decreased during the night and on weekends clearly indicating the dominance of urban sources. Up to 90% of the total Ag in wastewater was bound to particles and efficiently (>80%) removed by the treatment process, whereas 20% of Ag was released into the fluvial estuary. Silver concentrations in wastewater effluents clearly exceeded estuarine concentrations and may strongly amplify the local Ag concentrations and fluxes, especially during summer rainstorms in low river discharge conditions. Further work should focus on environmental effects and fate of urban Ag release due to immediate localized outfall and/or the adsorption on estuarine particles and subsequent release as dissolved Ag chloro-complexes within the estuarine salinity gradient.

1. Introduction

Silver (Ag) is an element of worldwide environmental concern because of its potential toxicity to aquatic microorganisms, with sub lethal effects on the reproduction and the early life stage of marine and estuarine invertebrates and algae (Bryan and Langston, 1992; Luoma and Ho, 1995; Flegal et al., 2007; Directive 2006/11/EC; Lanceleur et al., 2011a). Due to its low toxicity to humans and its large spectra biocidal properties to microorganisms, Ag is used in a wide range of new and established medical/pharmaceutical and industrial applications including building, medicine, plastics, textile, and other consumer's goods such as personal care products (PCP).

The production of Ag on the world scale has increased by nearly 100% in the past 25 years (Eisler, 1996; GFMS, 2013) at 30 kT in 2012 with a small but rapidly growing portion of the global annual Ag production dedicated to manufacture biocidal Ag bearing products (GFMS, 2013; Mueller and Nowak, 2008). Historical records in environmental archives, such as a 30 year record of Ag accumulation in wild oysters from the Gironde Estuary, clearly show

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evidence of the transfer from continental sources to the aquatic environment and may highlight the emergence of new sources (Lanceleur et al., 2011b).

Worldwide urban populations are mostly located in coastal areas (Small and Nicholls, 2003; McGranahan et al., 2006) and are projected to increase from approximately 7.3 to 9.7 billion in 2050 (UN, 2015). Therefore, the contribution of urban households to Ag fluxes from wastewater to aquatic systems is expected to drastically increase in future years. Furthermore, when considering the steep increasing trend in global production of nanoparticle Ag (NPAg) biocidal products, growing discharge of a variety of new forms of NPAg into the environment from wastewater is likely (The Pew Charitable Trusts, 2011). This is of concern as (i) nano-sized metals are generally considered more reactive than their macroscopic homologues and (ii) toxicity studies have indicated that Ag can have possible effects on an ecosystem even after the inputs of Ag pollution are alleviated (Rozan and Hunter, 2001; Flegal et al., 2007; Levard et al., 2013; Cukrov et al., 2013; Edge et al., 2014). Anthropic-sourced Ag released into estuarine environments will most likely show high mobility because the salinity gradient favors relatively stable dissolved Ag chloride complexes that can be dispersed along the coast (Luoma and Ho, 1995; Lanceleur et al., 2012; Barriada et al., 2007). Treated wastewater is also high in easily degradable organic matter (Garnier et al., 2006; Deycard et al., 2014) influencing physical, chemical and biological processes (e.g. microbial respiration, redox oscillation, mixing, sorption processes). Although previous studies have shown an overall decrease in many metal loads to estuaries draining urban agglomerations due to improved water treatment facilities (Buzier et al., 2006; Vink and Meeussen, 2007; Rodriguez-Garcia et al., 2011; Deycard et al., 2014), information on sources, concentrations, fluxes and impact of wastewater Ag is still very limited.

This study aims to understand the spatial and temporal dynamics of Ag along the different steps of the water treatment process in an urban wastewater treatment plant (WWTP) at hourly, daily and weekly timescales under dry and wet conditions prior to discharge into the estuarine environment. We studied the total (Ag_T), particulate (Ag_P) and dissolved (Ag_D) Ag concentrations, phase repartition, input/output fluxes, and removal efficiency in a WWTP that receives and treats wastewater from the urban agglomeration of Bordeaux (Bordeaux Métropole; BXM) prior to discharge into the fluvial Gironde Estuary. This research also examined Ag concentrations in various common household personal care products (PCP) to better understand the potential contribution from this source. Finally, we compared urban Ag fluxes discharged into the Gironde Estuary to those entering into the estuary via its main tributary the Garonne River to evaluate the potential fate and impact of urban Ag outputs in the estuarine turbidity and salinity gradients.

2. Materials and methods

2.1. Study sites

2.1.1. The Gironde Estuary

The Gironde Estuary with a freshwater discharge of 800–1100 $m^3\ s^{-1}$ (HYDRO, 2011) is one of the largest meso-to macrotidal and highly turbid estuaries in Western Europe (~635 km^2 in area) draining the Garonne, Dordogne and Isle River watersheds (~80,000 km^2, southwest of France; Fig. 1). The BXM is located in the fluvial reaches (Garonne Branch) of the Gironde Estuary. On the European scale, the Gironde Estuary drains a watershed considered as not highly industrialized/urbanized, with only two major agglomerations, Bordeaux and Toulouse, each with approximately one million inhabitant equivalents (Deycard et al., 2014, Fig. 1). In addition to urban inputs, intense wine production (Fig. 1) and historical multi-metal contamination from metal refining activities near Decazeville (Lot Watershed: Fig. 1) affect the quality of this coastal-aquatic system (Audry et al., 2004; Coynel et al., 2007; Strady et al., 2011a) and contribute to the strong Ag contamination (up to 65 mg kg^{-1}) observed in wild oysters at the mouth of the Gironde Estuary (Chiffoleau et al., 2005; Lanceleur et al., 2011a,b). In the estuary, transport of dissolved and particulate matter is controlled by the complex interactions between hydrodynamics, sedimentation and geochemical gradients that create temporary retentions, reactivity and exportations related to spatial and temporal changes (Schäfer and Blanc, 2002; Audry et al., 2004). Depending on seasonal river flow variations, a strong maximum turbidity zone (MTZ) with high suspended particulate matter (SPM) concentrations (>1 g L^{-1} in surface water) migrates up and down the estuary, as a function of tidal currents, transporting estuarine particles upstream (Sottolichio and Castaing, 1999). The limit of tidal dynamics in the Garonne Branch is located near La Réole, ~70 km upstream from Bordeaux, where no change in flow direction nor brackish water intrusion occurs (Fig. 1). Because the La Réole site is the main fluvial entry to the Gironde Estuary, it serves as a long-term monitoring site for studying fluvial metal and metalloid transport along the metal contaminated Lot-Garonne River continuum (e.g. Schäfer et al., 2002; Lanceleur et al., 2011a).

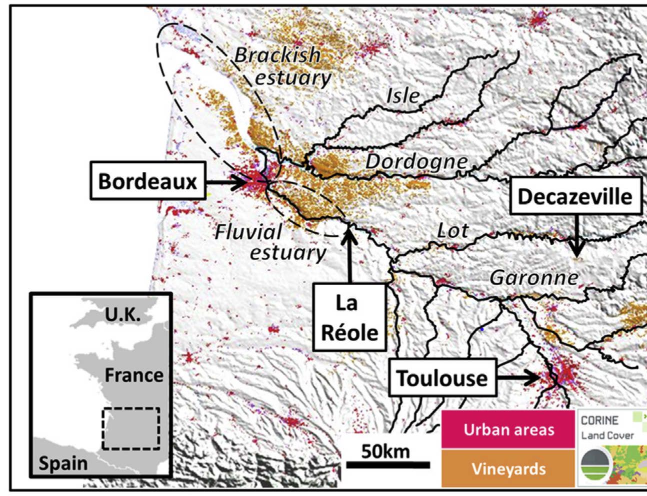

Fig. 1. Map of studied sites including the Gironde Estuary with the Garonne, Dordogne and Isle River systems including Bordeaux, La Réole, Decazeville, and Toulouse. Vineyard and urban use land cover are denoted by pink and orange representation, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In the salinity gradient of the brackish estuary (Fig. 1), the geochemical behavior of Ag is strongly non-conservative typically showing bell-shaped Ag_D concentration profiles with a mid-salinity maximum, reflecting the balance between chloride-induced desorption/complexation and dilution with seawater (Lanceleur et al., 2012).

2.1.2. Wastewater treatment plant

The WWTP Louis Fargue is one of six in the BXM treating over 70% of the wastewater coming from the city of Bordeaux and the north-western area of the BXM, covering a watershed of 38.2 km^2. The WWTP Louis Fargue treats wastewater influent that corresponds to a population equivalent of ~287,000 with a maximum capacity of ~300,000 population equivalent and discharges an average of ~100,000 $m^3\ d^{-1}$ (~55,000 to 200,000 $m^3\ d^{-1}$; Lyonnaise des Eaux, 2008) of treated effluent into the Garonne Branch. During