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Occurrence, distribution and partitioning of nonionic surfactants and pharmaceuticals in the urbanized Long Island Sound Estuary (NY)

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ABSTRACT

This work deals with the environmental distribution of nonionic surfactants (nonylphenol and alcohol ethoxylates), their metabolites (NP, nonylphenol; NPEC, nonylphenol ethoxycarboxylates; and PEG, polyethylene glycols) and a selection of 64 pharmaceuticals in the Long Island Sound (LIS) Estuary which receives important sewage discharges from New York City (NYC). Most target compounds were efficiently removed (>95%) in one wastewater treatment plant monitored, with the exception of NPEC and some specific drugs (e.g., hydrochlorothiazide). Concentrations of surfactants (1.4–4.5 μg L^{-1}) and pharmaceuticals (0.1–0.3 μg L^{-1}) in seawater were influenced by tides and sampling depth, consistent with salinity differences. Surfactants levels in suspended solids samples were higher than 1 μg g^{-1}, whereas only most hydrophobic or positively charged pharmaceuticals could be found (e.g., tamoxifen, clarithromycin). Maximum levels of target compounds in LIS sediments (PEG at highest concentrations, 2.8 μg g^{-1}) were measured nearest NYC, sharply decreasing with distance from major sewage inputs.

1. Introduction

As world population grows and concentrates in coastal areas, the number of marine systems that become exposed to the influence of both treated and untreated wastewater discharges increases. Sewage inputs may compromise the environmental quality of receiving waters as thousands of different chemicals are released this way. Among these chemicals, there has been a growing interest over the last decade on pharmaceuticals and personal care products (PPCPs), a wide group that includes therapeutic drugs, antimicrobials, surfactants, fragrances, and some polymers. Most of the wastewater is treated in developed countries, ensuring that many of these chemicals, or at least a very significant fraction of them, are eliminated before reaching the environment. As an example, typical removal percentages for surfactants, the main components in detergents and household cleaners, are often between 95% and 99% (Matthijs et al., 1999). However, there are many other compounds, especially pharmaceutically active compounds (PhACs) (e.g., carbamazepine, bezafibrate, sulfamethoxazole…) that cannot be effectively eliminated unless specific tertiary treatments such as ozonation are used (Castiglioni et al., 2006; Santos et al., 2009). Once in the water column, the presence of these biologically active chemicals may be of concern because, although acutely toxic concentrations are not approached, there has been evidence of sublethal effects in most sensitive marine species. Two very recent examples have been reported by Pinckney and co-workers (2013), who reported reduction in biomass and primary productivity in microalgae exposed to the antibiotic tylosin, and Claessens and co-workers (2013), who observed a potential chronic risk for metoprolol over marine diatoms. In this sense, the most widely studied sewage contaminants are estrogens and estrogen mimics, including nonylphenol (NP) and nonylphenol ethoxylcarboxylates (NPEC), endocrine disruptors that are formed during biodegradation of nonylphenol ethoxylates (NPEO), non-ionic surfactants still widely used in the U.S., proven to feminize selected fish species at levels of potential environmental concern (Jobling et al., 1996). Some specific pharmaceuticals such as fluoxetine can also influence the endocrine system of fish according to recent in vitro assays (Fernandes et al., 2011).

An increasing number of papers have been reporting the occurrence of PPCPs in aquatic systems around the world. Most of the information is related to freshwater systems and it is limited to the aqueous phase sampling, and has been recently reviewed by

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Hughes and co-workers (Hughes et al., 2013). Information on the concentrations and distribution of these compounds either associated with particulate matter or in marine systems is still scarce, especially for pharmaceuticals (Benotti and Brownawell, 2007; Ferreira et al., 2011; Fang et al., 2012). Additionally, the behavior and fate of PPCPs once they are released into the sea are still not fully understood. Many are expected to disappear after a relatively short period of time by means of a combination of biological and physicochemical processes, although some of them such as carbamazepine or sulfamethoxazole are slowly degraded in coastal seawater and have distribution consistent with conservative behavior (Benotti and Brownawell, 2007). Biodegradation can be a relatively fast process for surfactants in the marine environment, with half-lives below 2 days reported in laboratory studies (Perez-Carrera et al., 2010), but it can vary significantly among different pharmaceuticals (Benotti and Brownawell, 2009) and, in many occasions, photodegradation predominates (Yamamoto et al., 2009). A significant fraction of most surfactants (Lara-Martín et al., 2008), as well as some pharmaceuticals like cationic beta-blockers (Ferreira et al., 2011), may be found in sediments after sorption to suspended solids and later deposition. These compounds are often degraded much slower in sediment beds in comparison to the water column (Huber et al., 2000; Ferguson et al., 2003; Ericson, 2007), especially in the absence of oxygen. There are several studies reporting the concentration of surfactants in coastal sediments all along the world, with values that can be up to several tens of ppm in the most contaminated areas (Ferguson et al., 2001; Jonkers et al., 2003; Lara-Martín et al., 2008). Information on the concentrations and distribution of pharmaceuticals in marine sediments is presently still very limited, and only a few compounds have been detected so far (Long et al., 2013), always at very low concentrations (low ng g^{-1}).

The sampling area selected in this work was sewage impacted Long Island Sound (LIS) Estuary, NY, which receives over 4000 million of liters of sewage per day, most of which enters from the sewage treatment plants (STP) located in the East River in New York City (NYC). Multiple objectives were pursued. First, we determined the composition and efficiency of removal of wastewater contaminants in a STP. Targeted compounds included a selection of nonionic surfactants (NPEO and alcohol ethoxylates, or AEO), their metabolites (NP, NPEC and polyethylene glycols, or PEG) and 64 widely used pharmaceuticals. We compared concentrations and composition of both treated and untreated wastewater with those found in the receiving waters, measured in a site in the East River, where we also conducted a sampling campaign aimed at determining the partitioning of target compounds and the influence of tides and sampling depth. Finally, we measured levels of the same surfactants and pharmaceuticals in surface sediments from Long Island Sound along a pollution gradient at different distances from NYC.

2. Materials and methods

2.1. Sampling sites and sample collection

Water column sampling was conducted in a fixed station in the easternmost stretch of East River, which receives wastewater inputs from several of the largest STPs in NYC, as well as numerous combined sewer overflows (CSOs) that discharge largely untreated sewage during significant rainfall events (see Fig. 1). LIS is a partially mixed estuary with freshwater inputs dominated by the Hudson River as well as STP inputs in the lower Hudson Basin. Semidiurnal tides control estuarine circulation with flood tides carrying more saline and less sewage affected water from the east, and ebb tides carry more sewage affected water from metropolitan NYC. In more detail, LIS has over 44 STPs located along its shores discharging about 4000 million L^{-1} day, and a large portion of this sewage is focused in a small area of the East River and the Western LIS (WLIS) region of the sound (Sanudo-Wilhelmy and Flegal, 1992; Wolfe et al., 1991). According to Wolfe and co-workers (1991), sewage outfalls from the Bronx and Queens on the East River (excluding the very large Newtown Creek STP, whose discharge into the East River affects both LIS and NY Harbor) supplies 70% of the sewage-derived nitrogen found in LIS. More specifically, there are 4 major STPs (Tallman Island, Hunts Point, Bowery Bay, and Wards Island) located in the northern East River adjacent to WLIS that discharge a combined 1750 million L^{-1} day and represent the strongest input of sewage into the LIS watershed (68%). The remaining inputs of sewage are mostly concentrated in the watersheds of southern Connecticut (27%), with an additional 5% coming from the northern shores of Long Island.

Surface ($n = 10$) and bottom ($n = 5$) water samples were taken at station SW (Fig. 1) during a tidal cycle, from 8:00 (low tide) to 20:30 (low tide) on May 2009. Niskin bottles were used, and 2 L of water were transferred to pre-cleaned amber glass bottles. A

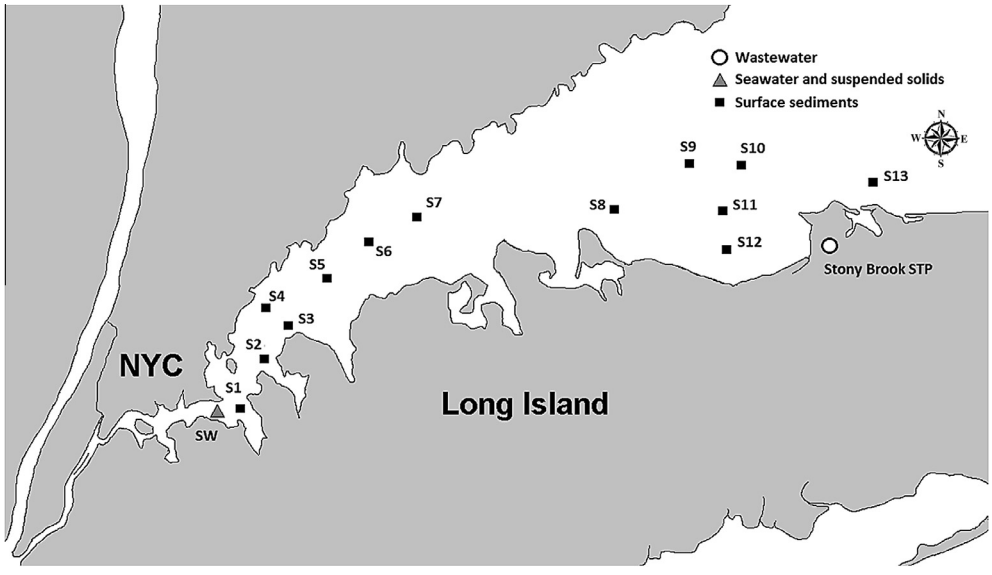

Fig. 1. Map showing the location of the sampling stations along the East River and Long Island Sound.

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