EMERGING CONTAMINANTS

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1. OVERVIEW

The term "chemical contaminants of emerging concern" defines chemicals that have been identified recently in natural waters that have no regulatory standards associated with them and can potentially cause adverse effects to aquatic life at environmentally relevant concentrations. Contaminants of emerging concern, known as CECs, are not necessarily new and include pollutants that have often been present in the environment, but whose ecological significance and risk are only now starting to be evaluated. They include but are not limited to non-prescription and prescription pharmaceuticals, personal care products, and industrial chemicals used in a wide range of consumer, commercial, and industrial products. The appearance and magnitude of CECs in Narragansett Bay are a result of relatively recent anthropogenic activities, as opposed to the well-documented long-term presence and persistence of legacy contaminants such as PCBs.

Historical trends of contaminants measured in sediment cores from Narragansett Bay show the recent appearance of CECs such as flame retardants, contrasting with legacy contaminants such as PCBs that show sustained decline due to enactment of strict environmental regulatory standards. Spatially, many pollutants exhibit a north-to-south gradient in Narragansett Bay due to the high density of human population and wastewater treatment facilities in the upper Bay. This trend appears to be the same for a number of CECs, since they originate from the same point source inputs. Future research needs include identifying key CECs in coastal waters such as Narragansett Bay and assessing their behavior, fate, and potential to impart adverse effects.

2. INTRODUCTION

The behavior and fate of CECs in aquatic systems are not well understood; consequently, the knowledge about the exposure risk from CECs to aquatic life and human populations is limited. This is especially true for most CECs in coastal ecosystems such as Narragansett Bay. There are numerous classes of CECs, which include but are not limited to personal care products, pharmaceuticals, and industrial chemicals. Commonly encountered CECs are found in personal care products such as soaps, cosmetics, and detergents containing various additives: antimicrobials such as Triclosan; UV blockers in sunscreens such as oxybenzone; DEET, a pesticide which is applied to human skin; and fragrances such as synthetic musks.

Pharmaceuticals (both over-the-counter and prescribed formulations) span a broad range of classes, including but not limited to: antidepressants, antihypertensives, antibiotics, painkillers, and synthetic hormones. Specifically, there are concerns about pharmaceuticals remaining biologically active after entering the environment, since they are designed to impart therapeutic effects to humans and animals at low levels (Daughton and Ternes 1999). Finally, industrial CECs likely comprise the largest and most diverse assemblage of chemicals. These include but are not limited to flame retardants like polybrominated diphenyl ethers, additives to plastics and synthetic materials such as bisphenol A (commonly referred to as BPA), benzotriazoles, and per/poly fluorinated compounds.

Many of the CECs associated with industrial usage, such as flame retardants and plastic additives, are non-polar and highly hydrophobic with low aqueous solubility, which are important factors controlling their environmental behavior. This results in their partitioning to organic particles during

the wastewater treatment process and sorption to particle-rich receiving waters in Narragansett Bay. This generally results in rapid and relatively efficient removal from the water column and sequestration in sediments. In contrast, other CECs such as pharmaceuticals and many personal care products are polar and more soluble in water, and thus they remain largely in the dissolved phase of the water column upon entering Narragansett Bay. Although CECs have also been detected in tissues and their potential to cause adverse effects is well known, studies on the presence of such CECs in estuarine biota and their organismal effects are severely lacking (Prichard and Granek 2016).

Sources of CECs entering Narragansett Bay vary both in magnitude and type of releases. Point source inputs such as sanitary wastewater treatment facility effluents are the primary contributor due to their continuous and high volume (approximately 830,000 cubic meters or 1,086,000 cubic yards per day) discharge to Narragansett Bay (Cantwell et al. 2016a). These facilities were never designed or intended to treat or remove CECs from the wastewater. Influent streams to these facilities are diverse and originate from residential dwellings, commercial businesses, industrial operations, and health care facilities and, when combined, account for many of the CECs present in Narragansett Bay and other urban estuaries. In Narragansett Bay, most wastewater treatment facility effluent is discharged (approximately 70 percent) to the Providence River with the remainder (approximately 30 percent) discharged to mid and lower Bay locations (Cantwell et al. 2017; see "Nutrient Loading" and "Wastewater Infrastructure" chapters). Non-point sources of CECs may include surface runoff and residential wastewater treatment systems, as evidenced by several recent studies (James et al. 2016, Oppenheimer et al. 2012, Phillips et al. 2015, Subedi et al. 2015), but likely contribute a very small portion of the overall total of CECs.

The quantity and detail of information available on CECs in Narragansett Bay, like most other estuaries, is limited. Potential ecological effects of many of these compounds are either unknown or not well documented in Narragansett Bay. Some of the earliest research on CECs in estuaries was conducted in Narragansett Bay on CECs such as benzotriazoles and Triclosan. Consequently, they have received more attention and have more data on their potential for adverse effects. Jungclaus and colleagues (1978) and Lopez-Avila and Hites (1980) identified numerous chemicals entering the Bay via industrial discharge to the Pawtuxet River in Cranston, Rhode Island. Some of these compounds were benzotriazoles, which comprise a broad class of chemicals used as a UV stabilizer in plastics and as a corrosion inhibitor for metals. Due to their long-term discharge, high concentrations, and local high-volume production, benzotriazoles are arguably one of the first studied CECs in Narragansett Bay. Subsequent research in Narragansett Bay focused mainly on benzotriazoles and examined their bioaccumulation in clams (Pruell et al. 1984), sediment-binding mechanisms (Reddy et al. 2000), and depositional history (Hartmann et al. 2005). Recently, Cantwell and colleagues (2015) identified long-term trends and persistence of individual benzotriazoles and confirmed the presence of several anti-corrosive benzotriazoles not previously reported in Narragansett Bay.

Lopez-Avila and Hites' (1980) research also identified Triclosan, a highly used antimicrobial CEC added to many personal care products such as soaps, detergents, and cosmetics. Cantwell and colleagues (2010) measured Triclosan in Narragansett Bay and other urban estuaries, documenting its accumulation and persistence in sediments. Sacks and Lohmann (2012) and Perron and colleagues (2013) measured Triclosan and methyl-Triclosan using passive sampling technology. Finally, Katz and colleagues (2013) identified sources and modeled the spatial distribution of Triclosan in the surface water and sediments of Greenwich Bay.

There is also limited research detailing water column concentrations of other CECs in Narragansett Bay. Polybrominated diphenyl ethers (PBDEs) are a class of highly produced flame retardants used in many products such as furniture, foam, and plastics, and they were measured in the water column of Narragansett Bay by both Sacks and Lohmann (2011) and Perron and colleagues (2013). Both studies reported very low concentrations of Triclosan and flame retardants in the waters of Narragansett Bay. Conversely, historical trends of contaminants measured in sediment cores from Narragansett Bay show the recent appearance of PBDEs, contrasting with legacy contaminants such as PCBs that show sustained decline due to enactment of strict environmental regulatory standards (Figure 1; see "Legacy Contaminants" chapter).

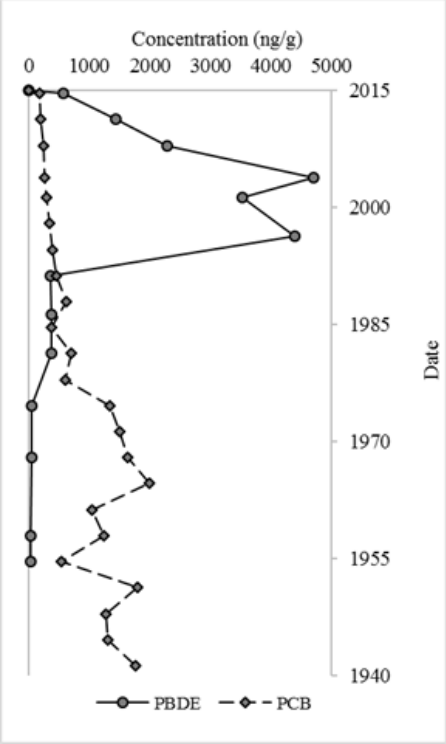

Figure 1. Concentration of PBDEs (polybrominated diphenyl ethers, flame retardants) and PCBs (polychlorinated biphenyls) from a sediment core in Field's Point, Narragansett Bay. (Source: Cantwell, unpublished data)

Other CECs measured by Sacks and Lohmann (2011) included alkylphenols, which are components of many personal care products such as soaps, detergents, and pesticides. Pharmaceutical compounds have only recently come under investigation for their presence and potential for effects in estuaries such as Narragansett Bay. Pharmaceuticals enter wastewater streams following consumer use and enter the environment following wastewater treatment processing. Removal efficiency of pharmaceuticals by these facilities is highly variable due to their mainly being present in the dissolved phase. Cantwell and colleagues (2016a) reported dissolved and particulate pharmaceutical concentrations along with partitioning coefficients for a number of highly prescribed drugs entering Narragansett Bay from riverine inputs. There is also recent research showing the spatial distribution of numerous classes of pharmaceuticals throughout Narragansett Bay during a year-long investigation (Cantwell et al., 2017).

3. STATUS, TRENDS, AND DISCUSSION

Emerging contaminants is not a true indicator because of the limited amount of data available for analysis. We are presenting what data are currently available and seek to continue measuring concentrations of emerging contaminants throughout Narragansett Bay. Efforts are presently underway to refine and validate indicators that will be effective in identifying wastewater associated contaminants in urban estuaries such as Narragansett Bay (Cantwell et al. 2016b).

The paucity of research conducted to date on CECs in Narragansett Bay limits an accurate and comprehensive examination of the magnitude and extent of contamination over time and space. In an attempt to address this lack of information, one approach is to use a suitable representative proxy or CEC itself as a marker to elucidate the behavior, fate, and transport of CECs within Narragansett Bay. However, interpretation and transferability of this type of approach is limited to CECs that have the same sources and similar physico-chemical characteristics.

An example of this approach is demonstrated with the spatial and temporal trends of Triclosan, for which there is the greatest amount of recent sediment data among CECs in Narragansett Bay. In Figure 2, a sediment core from the upper Providence River shows Triclosan concentrations from its inception point when it was patented and first produced (1963) to the surface of the core (2007) (Cantwell et al. 2010). The influences of local production and use are clear, showing high levels well into the 1980s. Trends show the impact of termination of local production in 1985, as well as the continued presence due to its widespread use in personal care products. Data from a Greenwich Bay core shows lower levels, reflecting releases from the local wastewater treatment facility, which discharges approximately 4,100 cubic meters (5,400 cubic yards) per day of effluent (Katz et al. 2013). Finally, a core in the Taunton River is data limited but shows that discharges from wastewater treatment facilities in the Taunton watershed are a continuous source for low levels of Triclosan to this sub-embayment of Narragansett Bay (Cantwell, unpublished data).

Spatial distributions of Triclosan from 2010 to 2013 illustrate the importance of point source discharges and transport processes throughout Narragansett Bay and their influence on contaminant concentrations baywide in contrast to levels observed in isolated embayments and the coastal salt ponds. Proximity and magnitude of wastewater treatment facility discharges are important factors regarding CEC distribution. Areas in the upper Bay, such as the Providence River embayment, where wastewater treatment facilities heavily impact the receiving waters, have relatively high levels of Triclosan. In contrast, levels are lower in areas of the mid to lower Bay, such as Greenwich Bay and Mount Hope Bay, due to lower wastewater treatment discharges. Locations such as the Narrow River, Point Judith Pond, and Ninigret Pond have very little in the way of measurable Triclosan present in the surficial sediments. (A draft ArcGIS map of Triclosan data produced by the Estuary Program is available here). This is due to the absence of point source inputs such as wastewater treatment facilities. The residual levels observed are suspected to be from submarine groundwater inputs, emanating from residential waste treatment systems. However, there are no local studies to date that confirm this.

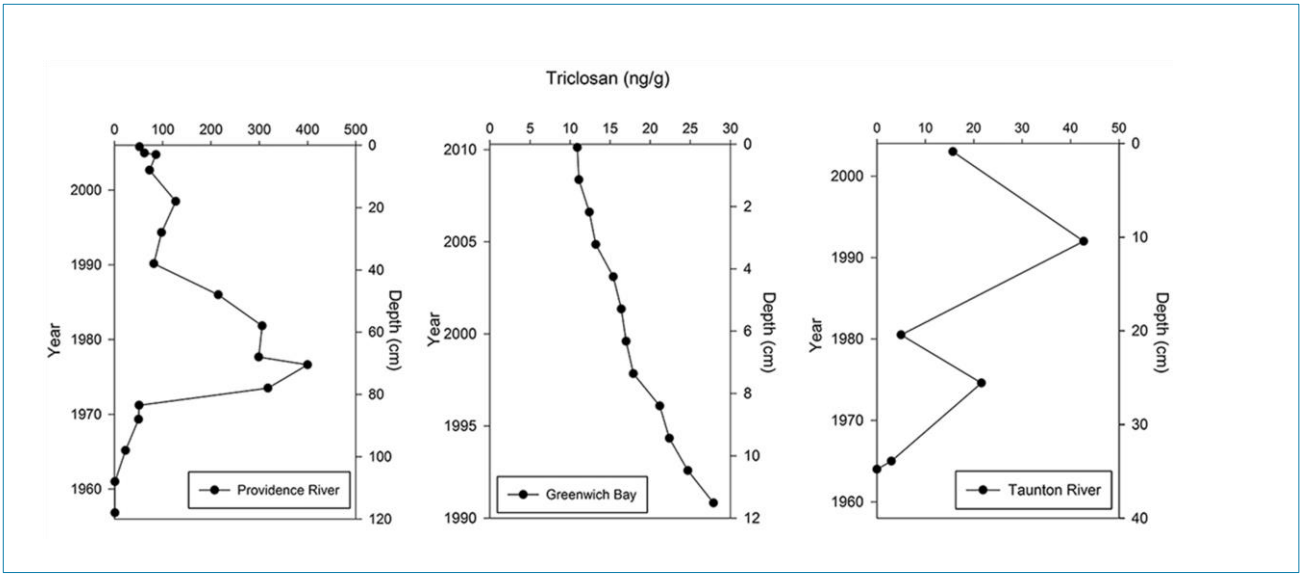

Figure 2. Triclosan concentrations in sediment cores from the Providence River and Greenwich Bay (Cantwell et al. 2010), and the Taunton River (Cantwell, unpublished data).

Pharmaceutical compounds in Narragansett Bay originate from the same point source inputs as many other CECs: wastewater treatment facilities. The pharmaceuticals present in aquatic systems are residues that enter sanitary wastewater treatment systems following therapeutic use. They are assumed to remain bioactive and consequently have the potential to affect aquatic organisms. Their physico-chemical characteristics are quite different from most other CECs by design, in order to provide their intended therapeutic effects efficiently. Their sorption to particles is limited by characteristics such as high solubility, resulting in little of their total mass discharged being removed to sediments (Cantwell et al. 2016a). Several highly prescribed pharmaceuticals measured in a sediment core taken from the Providence River show that, overall, the concentrations in the sediments are very low (Figure 3). In the case of metoprolol, a beta-blocking antihypertensive drug, levels in the sediment remain below 10 nanograms per gram. In contrast, dissolved water column concentrations on average are an order of magnitude greater, confirming their partitioning behavior in estuarine waters (Cantwell et al. 2016a). Another drug, carbamazepine, which is used to treat seizures and other disorders, exhibits similar behavior (Figure 3).

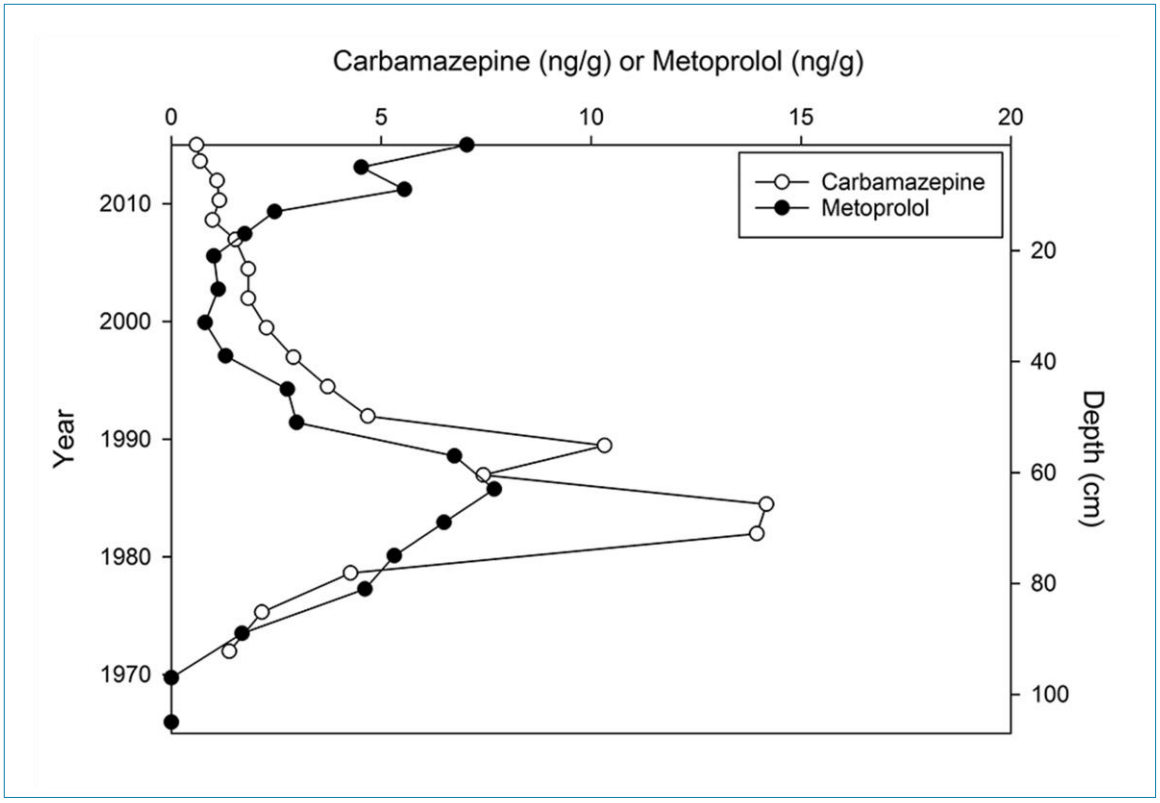

Figure 3. Pharmaceutical concentrations of carbamazepine and metoprolol in core from Field's Point, Narragansett Bay. (Source: Cantwell, unpublished data)

One result of the behavior, such as high aqueous solubility, of most pharmaceuticals is that in Narragansett Bay they remain largely in the dissolved phase and are still bioactive and likely bioavailable. If so, this exposure raises the concern that some organisms may be bioaccumulating some of these compounds. In locations such as the upper Providence River where large volumes of wastewater treatment effluents continuously enter Narragansett Bay waters, many of these pharmaceuticals may pose a risk due to the sustained, elevated levels present in the receiving waters.

A recent study (Cantwell et al. 2017) conducted over the course of a year showed elevated levels of numerous pharmaceuticals in the water column of Narragansett Bay. Various pharmaceuticals, such as metoprolol, were present at all sites and sampling periods, confirming their widespread spatial and temporal distribution (Figure 4). The study also showed many pharmaceuticals (e.g., sulfamethoxazole, an antibiotic) exhibiting a strong negative correlation with salinity, indicating that they are entering at the head of the Bay from freshwater sources such as wastewater treatment facilities (Figure 5).

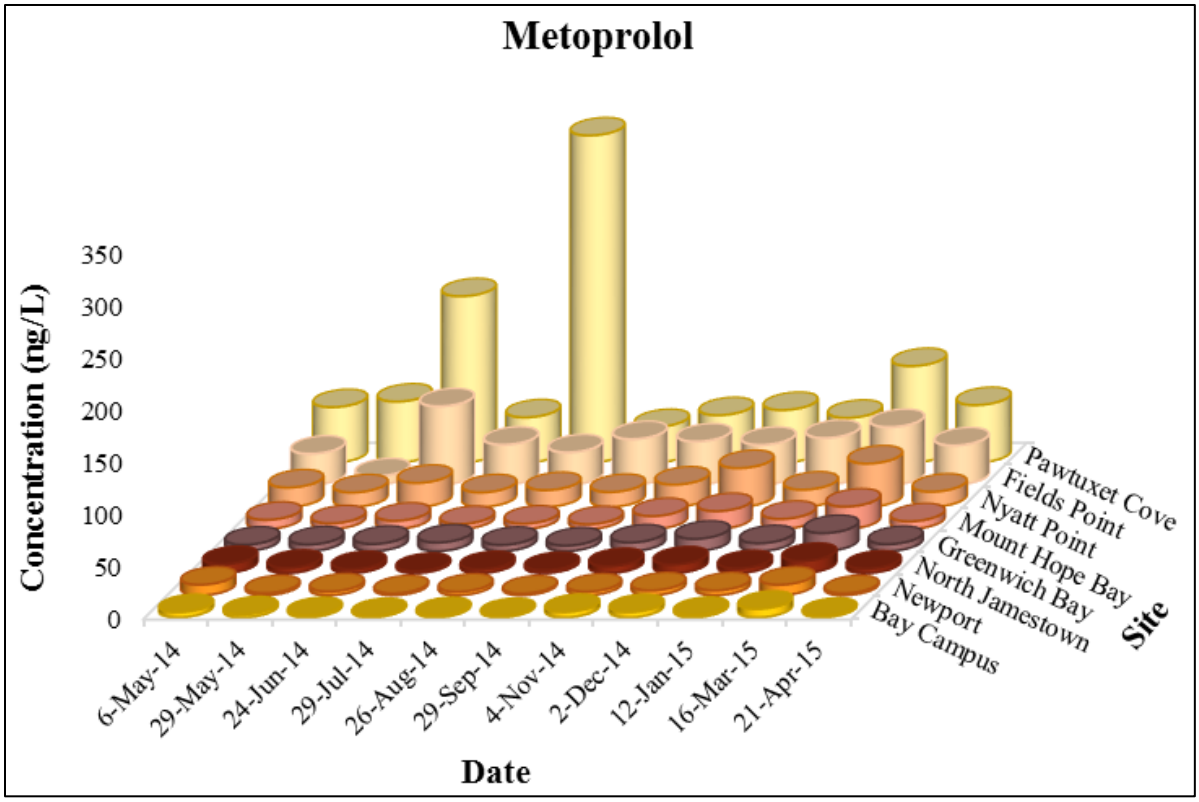

Figure 4. Spatial and temporal concentrations of metoprolol throughout Narragansett Bay. (Source: Cantwell et al. 2017)

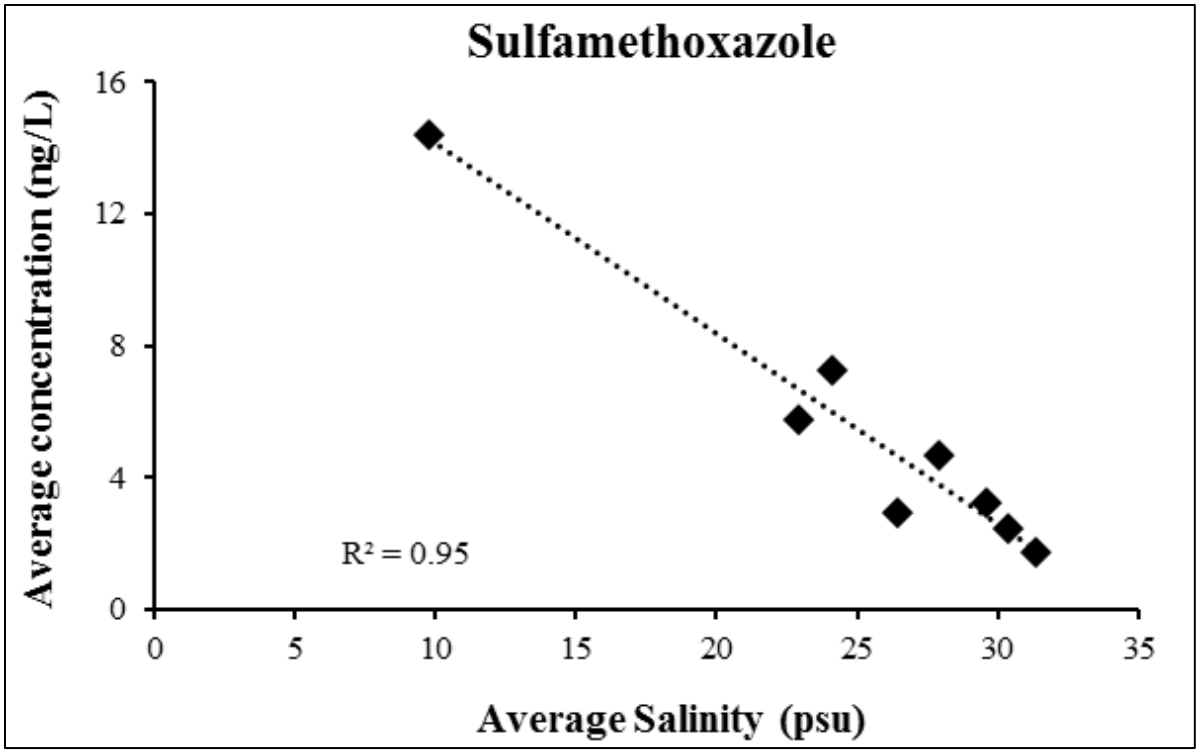

Figure 5. Correlation between sulfamethoxazole concentrations and salinity in Narragansett Bay. (Source: Cantwell et al. 2017)

4. DATA GAPS AND RESEARCH NEEDS

Continued research and field measurements are needed to better understand the potential exposure and assess the likelihood of ecological and human health risks resulting from existing and newly identified CECs entering Narragansett Bay. This is especially true for locations within Narragansett Bay that are heavily impacted by wastewater treatment discharges and contain elevated levels of CECs in the water column. The Providence River, in particular, is an area of concern due to the daily volume of wastewater effluent entering this sub-embayment. This is also critical for other locations in Narragansett Bay, particularly where commercial, wild seafood harvesting, aquaculture activities, and human recreation are occurring. More research that focuses on the effects of environmentally relevant concentrations of CECs on estuarine biota is also necessary.

Based on common point source inputs such as wastewater treatment facilities, estuaries across the United States are likely to have effluents with highly similar CEC profiles entering and residing in their waters. Each estuary is unique, however, and Narragansett Bay has its own properties due to differences in estuarine processes, morphology, and other variables such as climate and population density. For CECs that are highly soluble and remain in the dissolved phase of the water column for extended periods of time, such as pharmaceuticals and personal care products, it would be beneficial to have an improved understanding of the hydrodynamic processes within Narragansett Bay. This information along with eco-toxicity and bioaccumulation data, the direct measurement of CECs, and the use of spatial models will help to identify potential locations of concern as well as ascertain the transport, behavior, and ultimately the fate of CECs within Narragansett Bay.

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