State of Narragansett Bay and Its Watershed
2017 Technical Report

Chemical Stressor Indicators

CHAPTER 10: EMERGING CONTAMINANTS

Please use the following citation: Narragansett Bay Estuary Program. 2017. State of Narragansett Bay and Its Watershed (Chapter 10, Emerging Contaminants, pages 211-218). Technical Report. Providence, RI.

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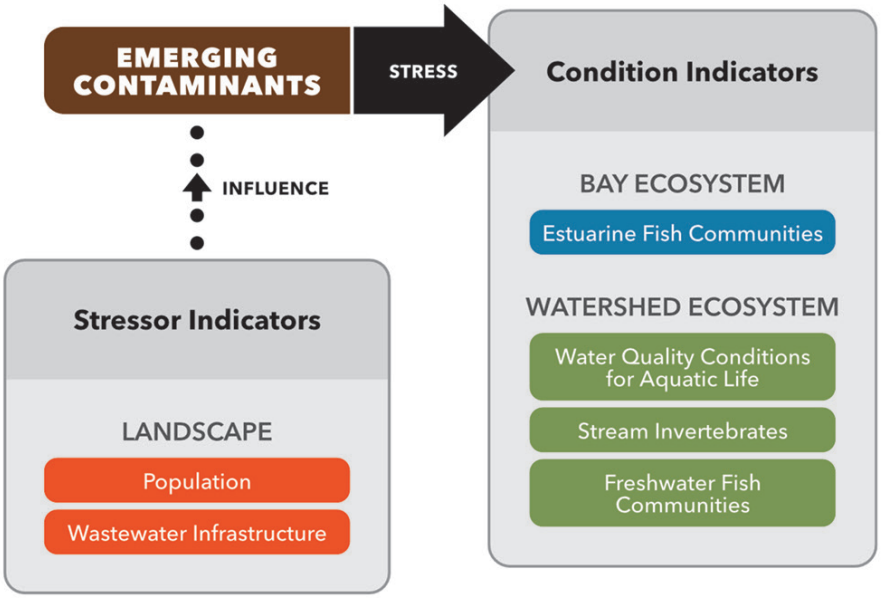
NARRAGANSETT BAY ESTUARY PROGRAM

Overview



BACKGROUND

- The term "chemical contaminants of emerging concern" (CECs) refers to chemicals with unknown ecological effects and no associated regulatory standards. Many CECs are associated with personal care products, pharmaceuticals or industrial chemicals and have been identified as being present at low levels in natural waters such as Narragansett Bay. CECs are usually found in highest concentrations near the outfalls of wastewater treatment facilities.

KEY FINDINGS

- ***Trends:*** Sediment cores from Narragansett Bay show the recent appearance of CECs, contrasting with legacy contaminants that have declined following enactment of strict regulatory standards. CECs and many other pollutants generally decrease from north to south in Narragansett Bay because the human population and wastewater treatment facilities are concentrated in the Upper Bay.
- ***Indicator in development:*** More research is needed to identify the key CECs in Narragansett Bay and to assess their behavior, fate, and potential to impart adverse effects.

Introduction

The behavior and fate of chemical contaminants of emerging concern (CECs) in aquatic systems are not well understood. The term "chemical contaminants of emerging concern" refers to chemicals that have been identified as being present in natural waters, have no regulatory standards associated with them, and are only now starting to be evaluated for their ecological significance and risks for public health or aquatic life (e.g. estuarine and freshwater fish communities, stream invertebrates) and water quality. CECs tend to be from personal care products, pharmaceuticals, and industrial chemicals. With hundreds of new chemicals entering the commercial marketplace annually, it is likely that there are numerous CECs in the environment that have not yet been identified as such. Since new chemicals are entering the environment faster than they can be thoroughly evaluated, detailed chemical assessments often focus on highly produced compounds with properties that exhibit potential for persistence, bioaccumulation, and toxicity. Thus, many chemicals enter commercial use with limited information, resulting in their unregulated and unmonitored presence in the environment.

Many CECs are present at extremely low concentrations, making detection and assessment of their effects challenging. Consequently, knowledge about the exposure risk and their potential impacts on aquatic life and human health is limited. This is especially true for most CECs in coastal ecosystems such as Narragansett Bay.

There are numerous classes of CECs. 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 for human use; 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 such as organophosphate esters, synthetic additives to plastics such as phthalates, bisphenol A (commonly referred to as BPA), benzotriazoles, and poly- and perfluoroalkyl substances (PFASs).

Many of the CECs associated with industrial usage, such as plastic additives, are non-polar and highly hydrophobic with low aqueous solubility–important factors controlling their environmental behavior. This results in their partitioning to organic particles during the wastewater treatment process and sorption to particles present in the waters of 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 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 wastewater treatment facility effluents are the primary contributor due to their continuous and high-volume discharge to Narragansett Bay–approximately 200 million gallons per day (Cantwell et al. 2016a; see "Wastewater Infrastructure" chapter). 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, approximately 90 percent, is discharged directly into upper portions of Narragansett Bay including Greenwich Bay, Mount Hope Bay, the Providence River Estuary, and the major rivers feeding the Bay, while the remainder (approximately ten percent) is 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 or onsite wastewater treatment systems, as evidenced by several recent studies (Oppenheimer et al. 2012, Phillips et al. 2015, Subedi et al. 2015, James et al. 2016), but those sources likely contribute a very small portion of the total loading of CECs to the Bay.

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. 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 there is 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 those compounds were benzotriazoles, which comprise a broad class of chemicals used as UV stabilizers in plastics and as corrosion inhibitors 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 occurrence 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.

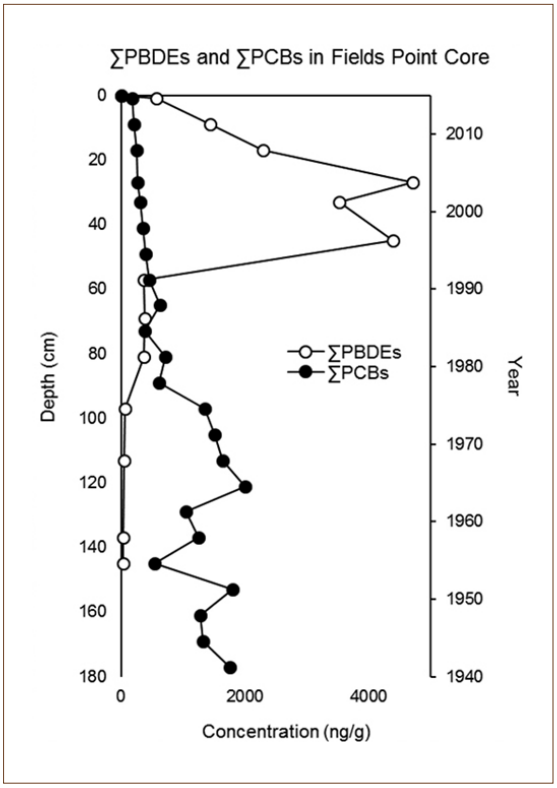


Figure 1. Concentration of PBDEs (polybrominated diphenyl ethers, flame retardants) and PCBs (polychlorinated biphenyls) from a sediment core at Field's Point, Narragansett Bay. Source: Cantwell (unpublished data)

Lopez-Avila and Hites (1980) 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 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. 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).

Other CECs measured include alkylphenols (Sacks and Lohmann 2011), which are components of many personal care products such as soaps, detergents, and pesticides. Recently, numerous PFASs have been found at sites throughout the Narragansett Bay Watershed (Zhang et al. 2016). Pharmaceutical compounds have also come under investigation for their presence and potential for effects in estuaries. 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 elevated concentrations of dissolved and particulate pharmaceuticals along with partitioning coefficients for a number of highly prescribed drugs entering Narragansett Bay from riverine inputs. A recent yearlong study showed the spatial distribution of numerous classes of pharmaceuticals present throughout Narragansett Bay (Cantwell et al. 2017).

In this chapter, the Narragansett Bay Estuary Program reports on the available data concerning emerging contaminants in Narragansett Bay. While a number of CECs have been detected, the existing information is

not sufficient to develop specific metrics for ongoing indicator reporting. Rather, this chapter identifies the need to prioritize and continue measuring concentrations of emerging contaminants throughout Narragansett Bay. Efforts are presently under way 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).

Status, Trends, and Discussion

The paucity of research to date on CECs in Narragansett Bay means that it is not yet possible to conduct an accurate and comprehensive examination of the magnitude and extent of contamination over time and space. In an attempt to address the 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. 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 Estuary shows concentrations of triclosan from its inception point in 1963–when it was patented and first produced–to the surface of the core in 2007 (Cantwell et al. 2010). The influences of local production and use are clear, showing high levels well into the 1980s. Trends show the response to 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 show lower levels, reflecting releases from the local wastewater treatment facility, which discharges approximately one million gallons 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 River 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 Estuary, where wastewater treatment facilities heavily impact the receiving waters, have relatively high levels of triclosan. Locations such as the Narrow River, with no wastewater treatment facilities, have very little measurable triclosan present in the surficial sediments. Residual levels observed are suspected to be from submarine groundwater inputs, emanating from on-site residential waste treatment systems. However, there are no local studies to confirm this.

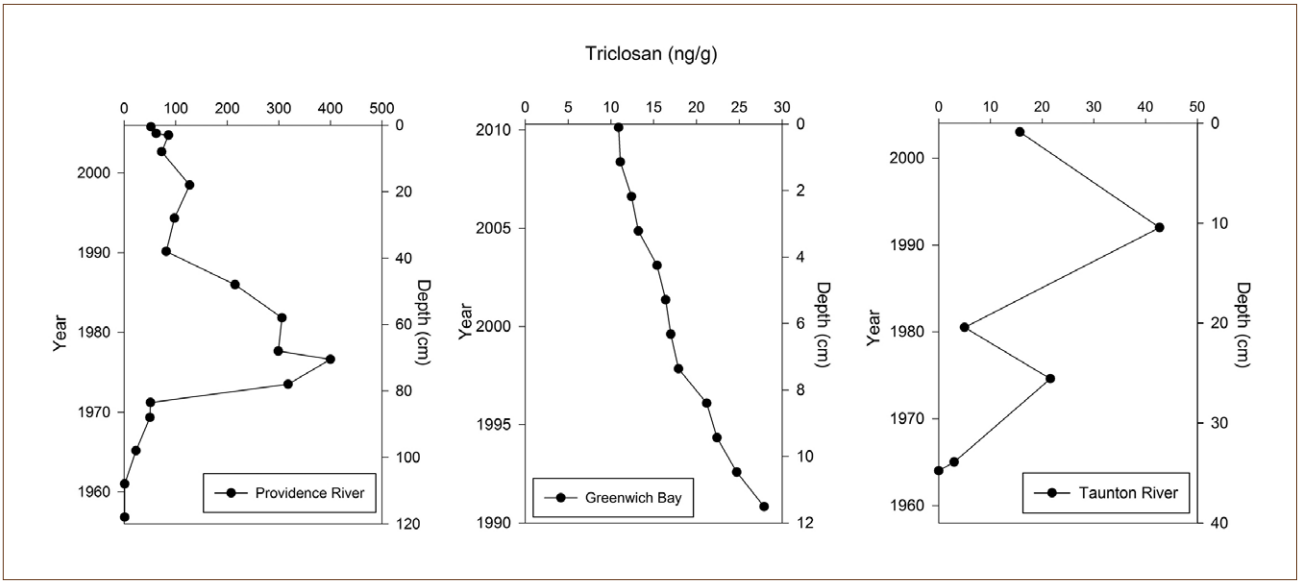


Figure 2. Triclosan concentrations in sediment cores from the Providence River and Greenwich Bay (Cantwell et al. 2010), and the Taunton River (Cantwell, unpublished data).

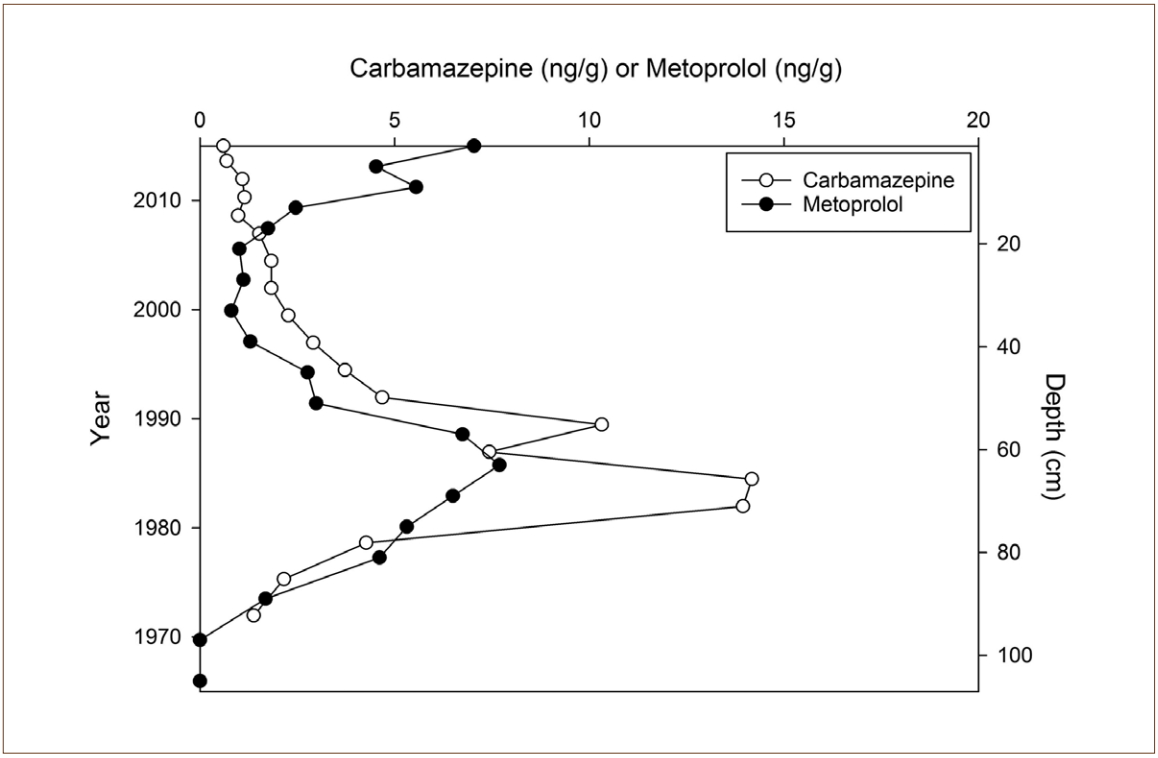


Figure 3. Concentrations of the pharmaceuticals carbamazepine and metoprolol in a sediment core from Field's Point, Narragansett Bay. Source: Cantwell (unpublished data)

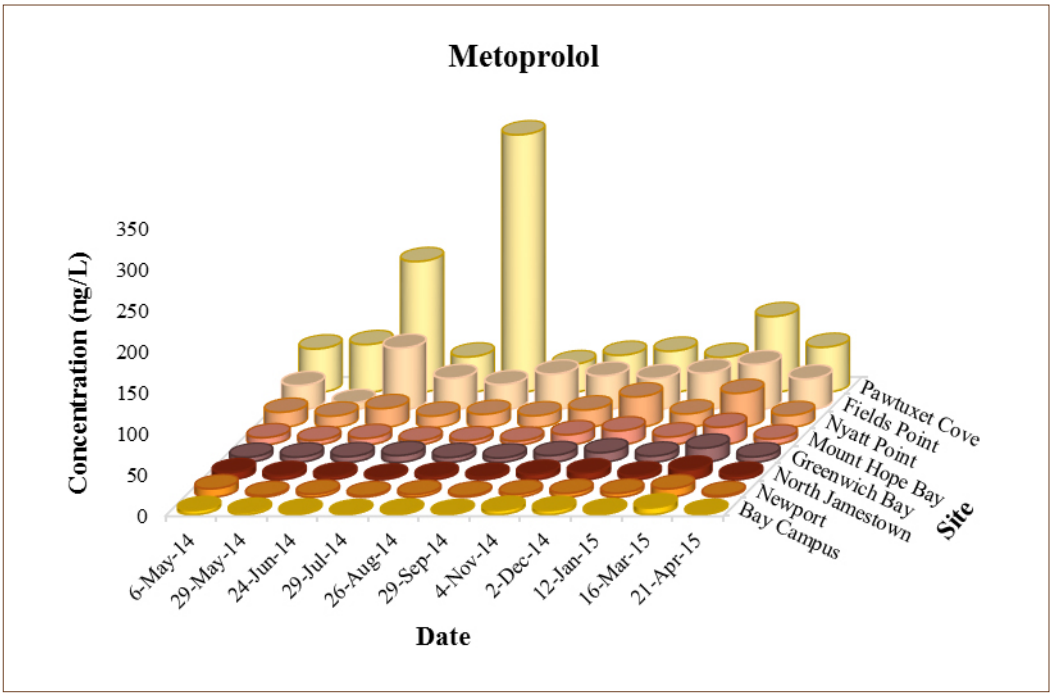


Figure 4. Spatial and temporal concentrations of metoprolol throughout Narragansett Bay. Source: Cantwell et al. (2017)

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 or disposal via toilet flushing. They are assumed to remain bioactive and consequently have the potential to affect aquatic organisms. This may also be the case for metabolites of numerous pharmaceuticals. The physico-chemical characteristics of pharmaceuticals 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). Measurements of several highly prescribed pharmaceuticals in a sediment core taken from the Providence River Estuary 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 ten 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).

A consequence of pharmaceuticals with high aqueous solubility is that they remain largely in the dissolved phase and are still bioactive and likely bioavailable. If so, this exposure raises the potential concern that some organisms may be bioaccumulating some of these compounds. In locations such as the upper Providence River Estuary 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.

In fact, 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).

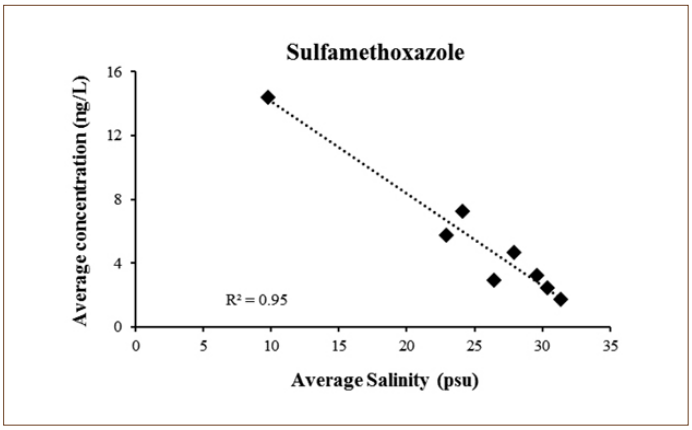


Figure 5. Correlation between sulfamethoxazole concentrations and salinity in Narragansett Bay. Source: Cantwell et al. (2017)

Data Gaps and Research Needs

- Continued research is needed to better understand the potential exposure and assess the likelihood of ecological and human health risks resulting from existing and newly identified contaminants of emerging concern (CECs). This includes research into the fate and transport of CECs in the environment.
- An assessment should be performed to identify key CECs prior to further investment in initiating a monitoring program. Any monitoring program will need to adapt to changes in the use of CECs. For example, as compounds are banned or phased out from use, compounds that may replace them should be considered for inclusion in monitoring.
- For CECs that are highly soluble and remain in the dissolved phase in the water column for extended periods of time, 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.

Acknowledgments

This chapter was written by Mark Cantwell from the USEPA Office of Research and Development, who led the development of this chapter and provided the data reported within it, with assistance from Courtney Schmidt, Staff Scientist at the Narragansett Bay Estuary Program.

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