

**Final Report to  
Massachusetts Bays Program Research and Planning Grants**

**TRACKING THE PRESENCE AND PERSISTENCE OF PHARMACEUTICALS IN  
CAPE COD BAY**

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**Introduction**

Since the population explosion on Cape Cod in the 1980s, the health of Cape Cod Bay and its numerous coastal embayments and estuaries has become a concern. With the increasing residential and commercial development of Cape Cod come associated impacts on the surrounding waters. Initial concerns focused on the detrimental impacts of nitrogen on water quality, and numerous studies have demonstrated ecological degradation caused by eutrophication at many levels ranging from ground water to kettle ponds, estuaries and coastal waters. On Cape Cod the major cause of coastal eutrophication is excess nitrogen from septic systems discharging into groundwater, which then flows into coastal waters; septic systems serve more than 85 percent of commercial and residential developments. Unfortunately, there are other potentially harmful contaminants associated with wastewater discharges, specifically pharmaceutically active compounds (PhACs).

PhACs encompass a variety of manmade contaminants including pharmaceuticals, personal care products, household cleansers and detergents. These types of contaminants are introduced into the environment through various pathways but are predominantly associated with wastewater. A study conducted during 2000 and 2001 by the U.S. Geological Survey analyzed water from 139 streams in 30 states, including Massachusetts, specifically for the presence of pharmaceuticals, hormones, and other wastewater contaminants. An astounding 80 percent of these 139 streams contained at least one or more of the contaminants included in the study (Barnes et al., 2002).

Many Americans use over-the-counter and prescription drugs on a daily basis. According to the U.S. Department of Health and Human Services, almost half of all people took at least one prescription drug, and one in six took three or more medications in 2004 (Health, United States 2004). Excess pharmaceuticals that are not used by the human body are discharged into the wastewater stream. Also, people may dispose of leftover pharmaceuticals by flushing them down the toilet, pouring them down the sink, or throwing them away as solid waste. These discharged pharmaceutical compounds enter the environment principally in groundwater. Other PhACs such as personal care products, cleaners and detergents also enter groundwater through such pathways.

Several studies have identified a variety of contaminants that fall under the classification of PhACs in groundwater on Cape Cod (e.g., Rudel *et al.*, 1998; Swartz *et al.*, 2006). More recently, a study by Standley *et al.* (2008) documented the presence of several of these compounds (endogenous hormones and pharmaceuticals) in selected aquifer-fed ponds on the Cape.

Like the ponds in Standley *et al.*'s (2008) study, groundwater is the primary source of freshwater to

Cape Cod Bay. In fact, much of the groundwater on the Cape discharges not to bodies of fresh surface water, as is common in other watersheds in Massachusetts, but rather directly to coastal waters and embayments (USGS, 1999). Therefore, this suggests that levels of PhACs in the surface coastal waters of the Cape could be significant or potentially higher than those measured by Standley *et al.* (2008).

The potential dangers posed by pharmaceuticals in the marine environment, though not completely understood, are wide-ranging. Potential impacts include abnormal physiological effects, impaired reproduction, and increased cancer rates (Boyd and Furlong, 2002). In several species of marine organisms, negative effects on fertility, gonadal development and reproductive rates, all of which directly affect population levels, have been related to concentrations of PhACs in the environment. Also of concern are the unknown effects of exposure to low concentrations of multiple types of contaminants and whether they have synergistic, additive or antagonistic effects. Some of these interactions have been documented in controlled experiments in several species of fish (Brian *et al.*, 2005; Thorpe *et al.*, 2001).

The potential reproductive effects of pharmaceuticals on marine organisms are of particular concern for Cape Cod Bay and its embayments because these coastal waters provide nursery habitat for numerous commercially and recreationally important species of finfish and shellfish. Many of these species are threatened by other stressors such as excess nutrients, habitat loss and overfishing. If pharmaceutically active compounds are present in Cape Cod Bay waters, the implications for physiological and ecological impacts could be serious.

Given all the unknowns associated with pharmaceutical compounds in the marine environment, this study was conducted as the first step in characterizing the occurrence of these contaminants in the Cape Cod Bay ecosystem.

Specific goals of this project were to:

- Determine baseline levels of selected PhACs in Cape Cod Bay and several of its embayments through water quality monitoring;
- Track spatial and temporal changes in concentrations and types of PhACs at selected monitoring stations;
- Identify potential sources of PhACs
- Provide information to organizations and agencies to help manage PhACs and prevent the contamination of our coastal waters.

## **Methods**

Selection of PhACs: Thousands of chemical compounds have been detected in the environment including prescription and over the counter drugs, antimicrobials, veterinary medicines, and agrochemicals. Some of these enter the environment virtually unchanged, while others are partially metabolized. Once in the environment different processes (microbial degradation, sorption) can partially remove or transform some of these substances. Others persist indefinitely (Benotti and Brownawell 2009). Testing for all of these compounds would be cost-prohibitive. Therefore, 3 prescription drugs and 2 non-prescription drugs were chosen based on the following criteria:

1. Persistence in the environment. Some compounds are more resistant than others to processes such as microbial degradation and sorption to sediments. These compounds are more likely to end up in our coastal waters and so included in this study.
2. Environmental toxicity. Numerous studies have examined the toxicity of different types of PhACs to organisms ranging from bacteria to algae to invertebrates to fish. Based on the results of these studies, compounds that were determined to have noticeable detrimental effects on aquatic organisms were selected for this study.
3. Presence in coastal waters. Compounds were also selected based on a review of studies conducted in the coastal waters of the northeastern United States.
4. Presence on Cape Cod. The Silent Spring Institute has analyzed public and private wells and freshwater ponds on Cape Cod. Under the assumption that groundwater is a possible source of the contamination to not only wells and ponds, but also coastal waters, the list of compounds detected in these studies was used as a reference (Schneider 2011).

Table 1. Selected pharmaceutically active compounds (PhACs)

### Prescription Drugs

sulfamethoxazole	Antibiotic, commonly used to treat urinary tract infections and pneumonia. Often used in combination with trimethoprim.
trimethoprim	Antibiotic, commonly used to treat urinary tract infections and pneumonia. Often used in combination with sulfamethoxazole.
carbamazepine	Anti-convulsant medications used to treat epilepsy and bipolar disorder

### Non-Prescription Drugs

acetaminophen	analgesic (pain reliever) and antipyretic (fever reducer)
caffeine	stimulant, world's most widely consumed psychoactive drug

Selection of Sampling Locations: Monitoring stations for PhACs were selected based on the hypothesis that target PhACs are entering Cape Cod Bay via groundwater and surface water discharges that contain wastewater effluent from septic systems and wastewater treatment facilities. Water quality data collected by PCCS's on-going Cape Cod Bay Monitoring Program (salinity, dissolved oxygen, pH, nitrate/nitrite, ammonia, silicate, ortho-phosphate, total nitrogen, total phosphorus, refined and crude oil, colored dissolved organic matter (CDOM), chlorophyll, and turbidity) were used to assess the potential locations of sampling sites. These monitoring data, widely accepted indicators of water quality degradation due to wastewater, helped to target areas to sample for PhACs. In addition to water quality conditions, geographic diversity and the presence of potential sources of PhACs in the vicinity (e.g. wastewater treatment facilities, community health centers, and long term care residences) were used to select the five creeks targeted in this study. Two offshore sites were included for analyses of PhACs to document the persistence in offshore waters.

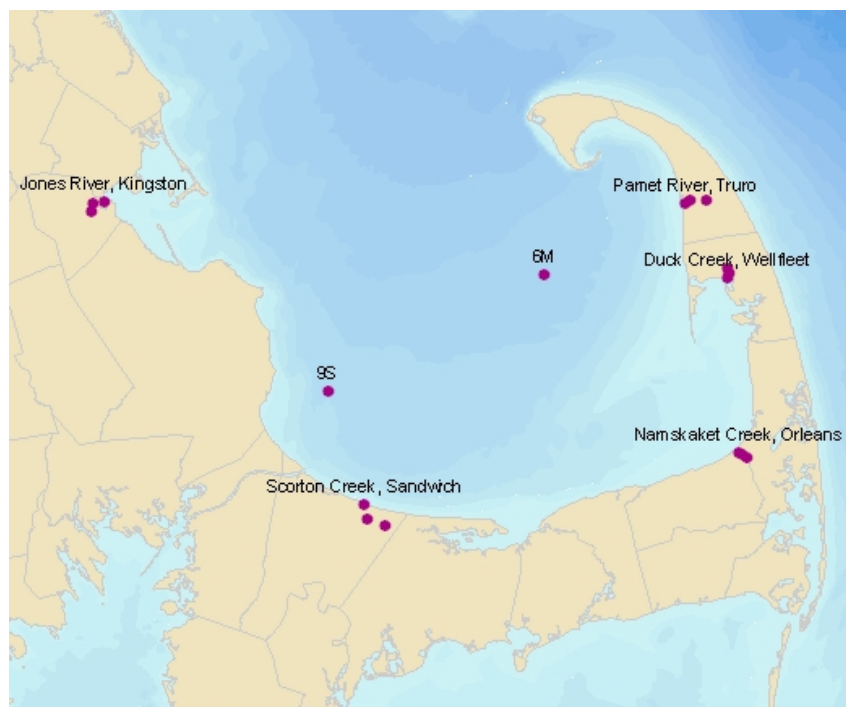


Figure 1. Map of the locations of stations sampled for PhACs.

Sampling Methods: Water samples for analyses of PhACs and select water quality parameters were collected from two offshore stations at two depths (surface and near bottom) and from the surface waters of five creeks that drain into Cape Cod Bay at three sites located along each creek. Each site was sampled three times during the study period (May, July and September). Sampling of offshore stations was done by boat. Sampling of the sites along the selected creeks was done by boat when possible and from shore at the station locations that were inaccessible by boat. Sampling of the creeks was done during the ebb tide. Sampling of the offshore stations was not dependent on the tidal cycle. Sample collection for PhACs was done following EPA Method 1694: Pharmaceuticals and Personal Care Products in Water, Soil, Sediment and Biosolids by HPLC/MS/MS (2007). Water samples were also collected for laboratory analysis of nitrate and ortho-phosphate (inorganic wastewater contaminants) and salinity (effluent tracer). The methods for sample collection for laboratory measurement of nitrate, ortho-phosphate, and salinity are discussed in detail in the PCCS Quality Assurance Project Plan (QAPP) (Costa 2012).

Laboratory Methods: Initial processing of samples for analysis of PhACs was done at the PCCS laboratory. Samples were filtered through GF/F Whatman glass fiber filters to remove particulates, acidified to pH 2.0 (+/- 0.5) and buffered with 500 mg of EDTA. Samples were then filtered through SPE HLB cartridges. The cartridge was eluted with 12 ml of methanol. This eluted sample was delivered to GeoMed Analytical for analysis. GeoMed Analytical processed the samples according to EPA method 1694. The general steps in this method are summarized as follows in the PCCS QAPP (Costa 2012). A change in analytical methods occurred for the final round of samples. For the samples collected in September, a photodiode array detector was used. This detector was able to detect caffeine and acetaminophen much better than the detector used in May and July. Therefore results for these 2 PhACs are not comparable among sampling events. All other analytes of interest (nitrate+nitrite, ortho-phosphate, salinity) were analyzed at the PCCS laboratory following the methods detailed in the PCCS QAPP (Costa 2012).

## Results and Discussion

A total of 57 samples were collected and analyzed for PhACs, nitrate and ortho-phosphate (inorganic wastewater contaminants) and salinity (effluent tracer) (Table 2).

Table 2. Completed Sampling Plan: Number of samples and analytes

Month	Station	Depths/ Station	Sites / Station	Number of Samples / Station			
				PhACs	Nitrate	Ortho- Phosphate	Salinity
May	Offshore 1 (6M)	2	1	2	2	2	2
	Offshore 2 (9S)	2	1	2	2	2	2
	Pamet River, Truro	1	3	3	3	3	3
	Duck Creek, Wellfleet	1	3	3	3	3	3
	Namskaket Creek, Eastham and Orleans	1	3	3	3	3	3
	Scorton Creek, Sandwich	1	3	3	3	3	3
	Jones River, Kingston	1	3	3	3	3	3
July	Offshore 1 (6M)	2	1	2	2	2	2
	Offshore 2 (9S)	2	1	2	2	2	2
	Pamet River, Truro	1	3	3	3	3	3
	Duck Creek, Wellfleet	1	3	3	3	3	3
	Namskaket Creek, Eastham and Orleans	1	3	3	3	3	3
	Scorton Creek, Sandwich	1	3	3	3	3	3
	Jones River, Kingston	1	3	3	3	3	3
September	Offshore 1 (CCB1)	2	1	2	2	2	2
	Offshore 2 (CCB2)	2	1	2	2	2	2
	Pamet River, Truro	1	3	3	3	3	3
	Duck Creek, Wellfleet	1	3	3	3	3	3
	Namskaket Creek, Eastham and Orleans	1	3	3	3	3	3
	Scorton Creek, Sandwich	1	3	3	3	3	3
	Jones River, Kingston	1	3	3	3	3	3
<b>Total Number of Samples</b>				<b>57</b>	<b>57</b>	<b>57</b>	<b>57</b>

Of these 57 samples, 30 samples (53%) tested positive for at least on PhAC. Of the 3 prescription PhACs tested for, carbamazepine was detected in 23 samples (40%), sulfamethoxazole in 11 samples (19%), and trimethoprim was not detected in any of the samples. Caffeine was detected in 14 samples (25%), and acetaminophen was detected in 10 samples (18%). With the photodiode array used for the September samples 12 of the 19 samples (63%) tested positive for caffeine and 10 of the 19 samples tested positive for acetaminophen (53%). The 3 prescription PhACs were reported as concentrations (ng/L). The 2 non-prescription PhACs were measured for presence/absence only. Appendix A gives detailed information about concentrations of the PhACs in each sample.

## *Carbamazepine*

Of the 3 quantifiable PhACs, carbamazepine was detected the most frequently. Therefore the concentration of this compound was analyzed in relation to other variables measured in this study.

Temporal Variation: Highest concentrations occurred during the July sampling event (Figure 2). The water quality of the nearshore and inshore areas of Cape Cod Bay tends to deteriorate during the summer months (Costa & Hughes 2012). This could be due in part to the population increase on Cape Cod during the summer (CCC 2012).

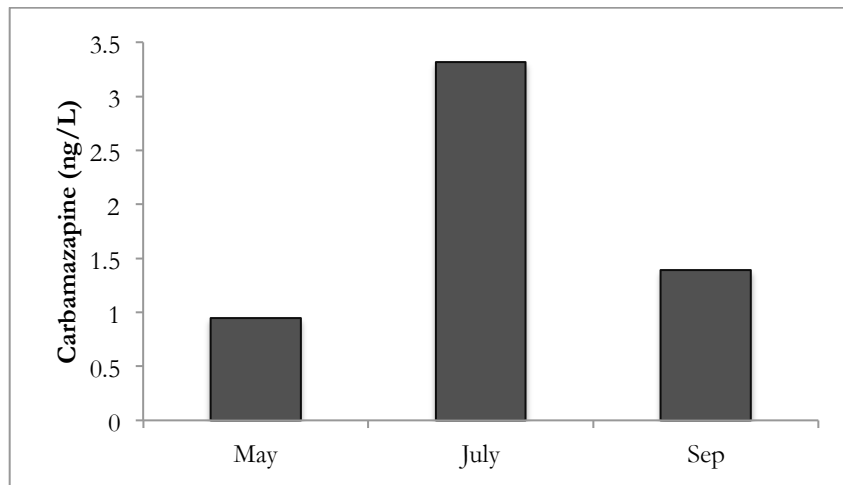


Figure 2. Average concentrations of carbamazepine.

Spatial Variation: Of the 5 inshore areas sampled, highest concentrations of carbamazepine were detected in Jones River (Figure 3).

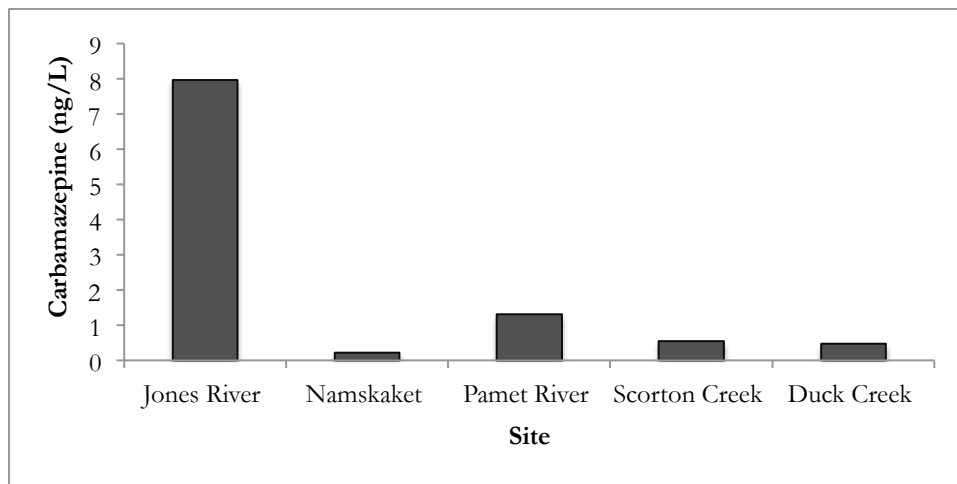


Figure 3. Average concentrations of carbamazepine detected at each of the 5 sites.

The Jones River Watershed encompasses the greatest area (Figure 4). This watershed is also more developed than the other watersheds examined in this study, including portions of the towns of Kingston, Pembroke, Halifax, Plympton, Duxbury and Plymouth.

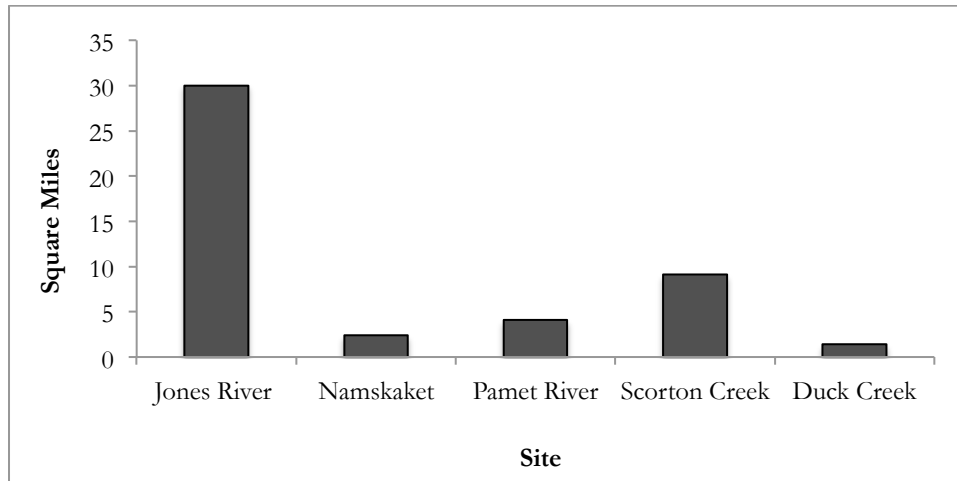


Figure 4. The area (square miles) of each watershed.

Along each creek, 3 sites were sampled, one in the upper creek, one mid-way, and one near the mouth. Overall concentrations of carbamazepine were highest in the upper section and decreased towards the mouth (Figure 5). These lower concentrations found further downstream could be due to both tidal flushing and to microbial degradation or sorption to sediments as they are carried downstream.

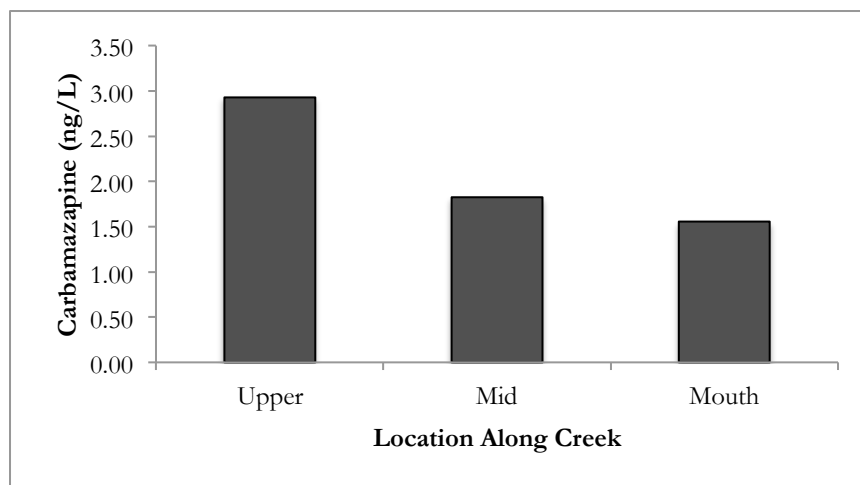


Figure 5. Average concentrations of carbamazepine measured in each region of the creeks.

Associated Water Quality Parameters: Water samples were also collected for analysis of nitrate and ortho-phosphate which could be indicators of inorganic wastewater contaminants, and salinity which could be either an effluent tracer in areas of wastewater discharge or an indicator of tidal flushing. These three parameters were tested for correlations with concentrations of carbamazepine.

There was a strong positive correlation between nitrate and carbamazepine ( $R=0.49$ , Figure 6a), and a moderately strong negative correlation between salinity and carbamazepine ( $R=-0.35$ , Figure 6b). A weak negative correlation was seen between ortho-phosphate and carbamazepine ( $R=-0.20$ , Figure 6c). Relationships between nitrogen and pharmaceutical compounds have been documented in previous studies (Standley et al 2008). Because high concentrations of nitrate often indicate areas influenced by wastewater inputs, it is not surprising that concentrations of PhACs would be detectable in these areas. The negative correlation between salinity and carbamazepine is likely related to tidal flushing. As indicated in Figure 4, the samples taken further from the mouth of the creek typically had higher concentrations of carbamazepine. These areas further upstream from the mouth of the creek likely have less influence from flushing from the bay (high salinity water) and more influence from groundwater and surface runoff (fresh water). The observed slight negative correlation between ortho-phosphate and carbamazepine will have to be investigated further to determine if there is any environmental significance to this relationship.

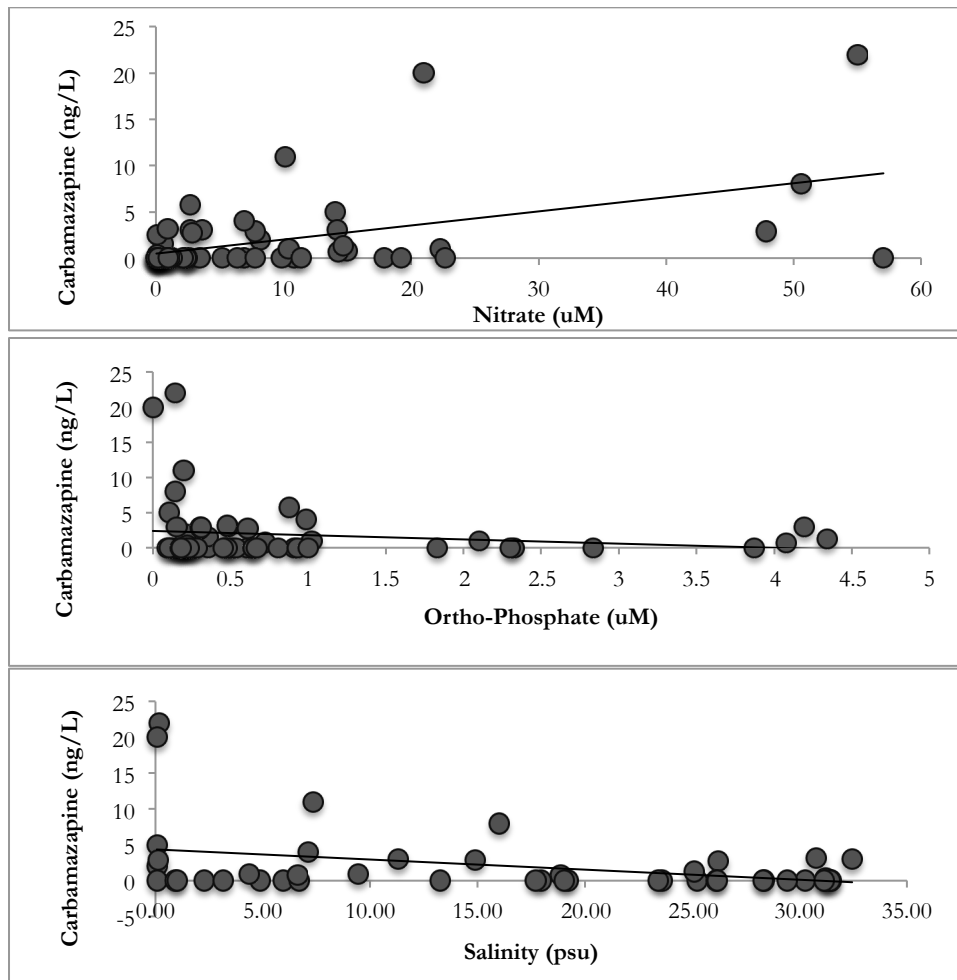


Figure 6. The relationship between concentrations of carbamazepine and (a) nitrate, (b) salinity, and (c) ortho-phosphate.



## Source Identification: Comparison of PhACs and Land Use

ArcView software was used to investigate patterns of land use within each of the watersheds. GIS data was obtained from MassGIS, the Cape Cod Commission, the Town of Wellfleet, and the Town of Kingston. Data layers included watersheds, assessors parcels, rivers, sewer systems, and locations of potential hot spots (long-term care residences, community health centers, and wastewater treatment facilities). Information on individual septic systems was not available. Therefore the assumption was made that, for all unsewered areas, there is a septic system associated with every developed parcel.

Both the Jones River watershed and the Duck Creek watershed have areas that are sewerred. These 2 watersheds will be analyzed in a separate report. The remainder of this report will address PhACs and land use for Pamet River watershed (PRW), Namskaket Creek watershed (DCW), and Scorton Creek watershed (SCW). MassGIS data ([www.mass.gov](http://www.mass.gov)) for each town (Level 3 Assessors' Parcels) were used to identify land use. For the purpose of this report, parcels are classified as either residential, commercial, or other. For a detailed list of property types see Appendix B.

The PRW encompasses an area of approximately 4.1 square miles. The entire watershed lies within the Town of Truro. MassGIS identifies 836 parcels that lie within this watershed, 553 are residential, 18 are commercial, and 265 are other. The SCW encompasses an area of approximately 9.1 square miles. It is the largest of these 3 watersheds. There are no parcels classified as commercial within this watershed. There are 2760 parcels (2222 residential and 538 other) in the Town of Sandwich that fall within the SCW, and 49 parcels (29 residential 20 other) in the Town of Barnstable that fall within the SCW for a total of 2809 parcels (2251 residential and 558 other) in the SCW. The NCW is the smallest of the 3 watersheds, encompassing an area of approximately 2.4 square miles. This watershed falls within the towns of Orleans and Brewster. There are a total of 219 parcels (149 residential, 24 commercial, and 46 other) in Orleans that fall within the NCW and 562 parcels (417 residential, 34 commercial, and 181 other) in Brewster that fall within the NCW for a total of 781 parcels (566 residential, 34 commercial, and 181 other) (Table 3).

Table 3. The number (and percentage) of parcels of each category within each watershed.

	<b>Residential</b>	<b>Commercial</b>	<b>Other</b>	<b>Total</b>
<b>Namskaket Creek</b>	566 (72%)	34 (4%)	181 (23%)	781
<b>Pamet River</b>	553 (66%)	18 (2%)	265 (32%)	836
<b>Scorton Creek</b>	2251 (80%)	0	558 (20%)	2809

To account for differences in areas of the watersheds, the number of parcels were standardized per square mile (Table 4, Figure 7).

Table 4. The density of parcels of each category (number per square mile) within each watershed.

	Residential	Commercial	Other	Total
Namskaket Creek	236	14	75	325
Pamet River	135	4	65	204
Scorton Creek	247	0	61	309

Neither the number of parcels nor the density of parcels explained the difference in average concentration of carbamazepine. Therefore, to further investigate the influence of land use on contamination from PhACs, the number of parcels were also examined by analyzing the number of each category within a set distance of the creek. Using ArcView, buffer zones were created around the creek, and the number of parcels that fell within each buffer zone was calculated. The buffer zones were 10 m, 50 m, 100 m, 500 m, 1000 m, and 2000 m (Figure 7). Maps of each watershed with information on parcels and buffer zones can be found in Appendix C.

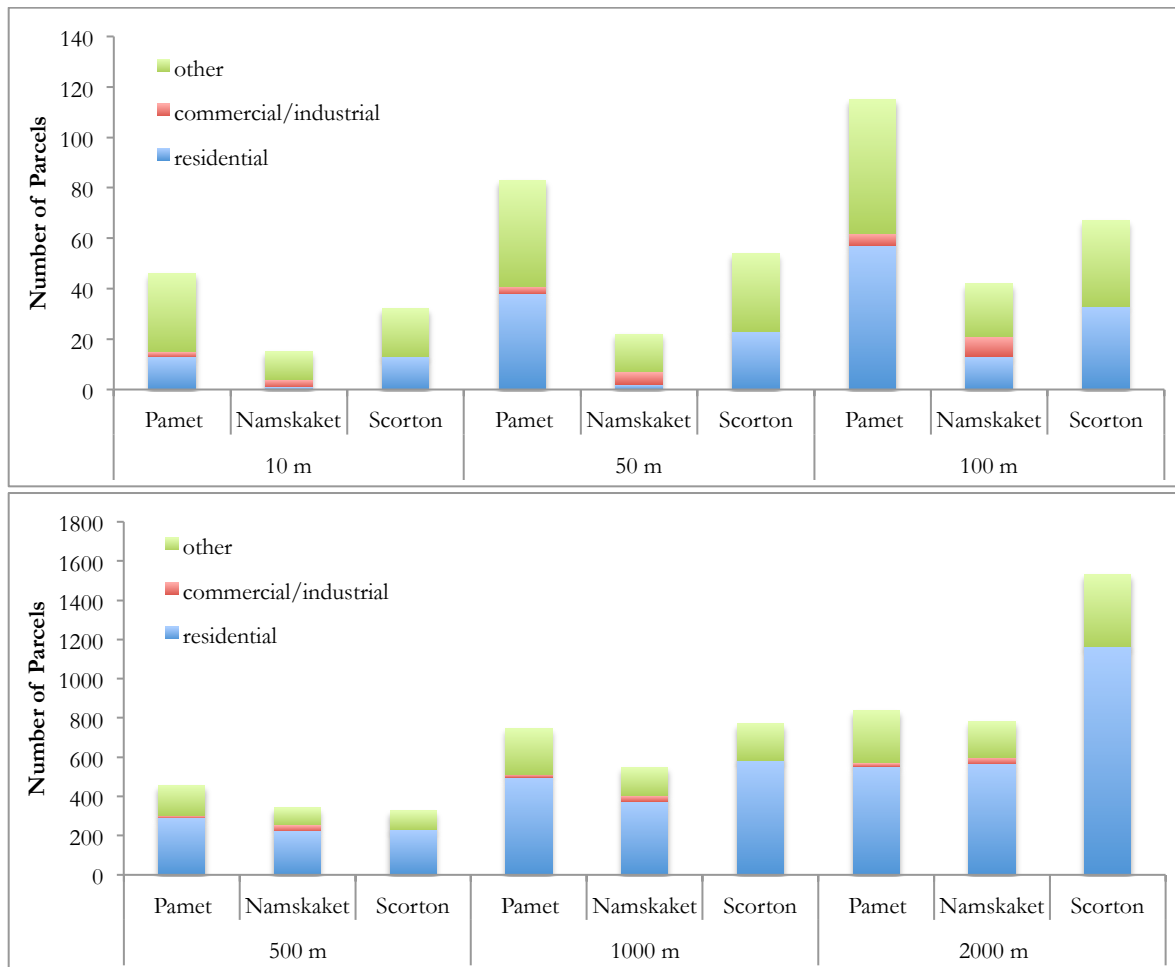


Figure 7. The number of parcels of each category within each of the buffer zones (a) 10 m, 50 m, and 100 m. (b) 500 m, 1000 m, 2000 m.

PRW has the greatest number of parcels within 100 m of the creek, and NCW has the fewest number of parcels within 100 m of the creek (Figure 7a). Figure 3 indicates that, of these 3 watersheds, PRW has the highest average concentration of carbamazepine and NCW has the lowest. At distances greater than 100 m, this pattern does not continue. These data therefore suggest that the amount of developed land within 100 m of the creek could influence the level of contamination by PhACs.

## **Conclusions and Recommendations**

Other than the preliminary sampling conducted by PCCS in 2010, this study is the first to systematically document the presence of PhACs in the Cape Cod Bay ecosystem. Four of the five selected PhACs tested for were found, and 53% of the samples tested were contaminated with at least one of these four PhACs. Because humans are the only source of these types of contaminants, these data are a clear indication that our coastal waters are impacted by wastewater, contaminated groundwater, and other anthropogenic means that introduce these types of contaminants into the ecosystem.

Not only does the presence of these contaminants implicate humans as a source of pollution to our coastal waters, but the spatial and temporal analysis of the concentration of one of the PhACs, carbamazepine, indicates that the concentrations of these contaminants are linked to the degree of human use. For example, areas that were more developed, such as the Jones River watershed, had higher concentrations of PhACs. Also, within the tested watersheds, the stations located further upstream had higher concentrations. Additionally, the samples taken in July, when human activity on the Cape peaks, had higher concentrations than those taken during May or September.

The strong correlation observed in this study between concentrations of nitrate and carbamazepine supports the conclusion that PhACs are primarily associated with wastewater, and, correspondingly, that wastewater is a key source of nitrogen to the coastal waters of Cape Cod. Therefore addressing the problems associated with wastewater, as is currently being done Cape-wide, should also lessen the potential impacts of PhACs. This study also suggests that areas within 100 m of the creek have the most influence on the level of contamination, and therefore, should be the most closely managed.

Unfortunately the results of this study do not provide enough information to evaluate potential sources or transport pathways. More compounds need to be analyzed for and more sites within each watershed need to be sampled before any conclusions can be drawn. This study has successfully built the foundation for future monitoring, and the results have indicated that additional monitoring for PhACs should be a critical part of water quality research on Cape Cod.

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## **Appendices**

Appendix A: Data on PhAC and associated water quality parameters

Appendix B: Number of parcels of each category within the designated buffer zones for each watershed.

Appendix C: Maps of each watershed showing land use by parcel and designated buffer zones.